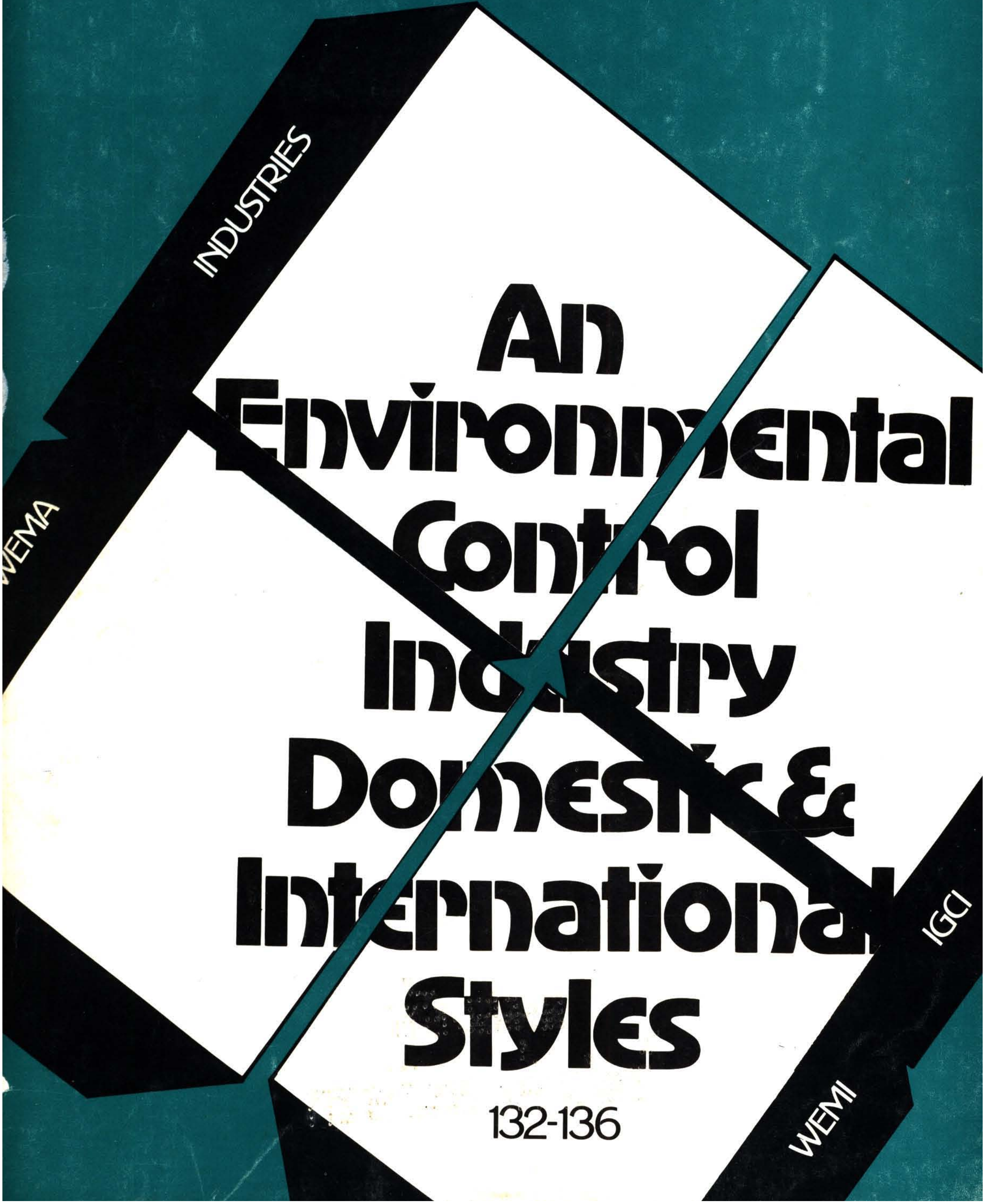
Environmental
Science & Technology

FEBRUARY 1977



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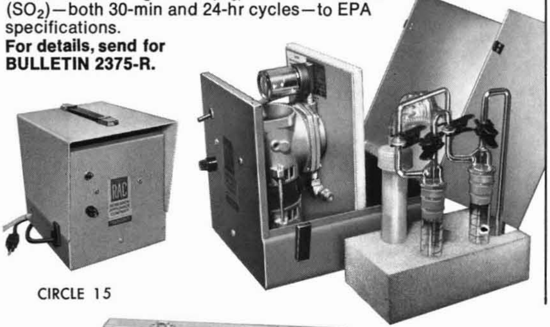

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For details, send for BULLETIN 2441.

CIRCLE 16

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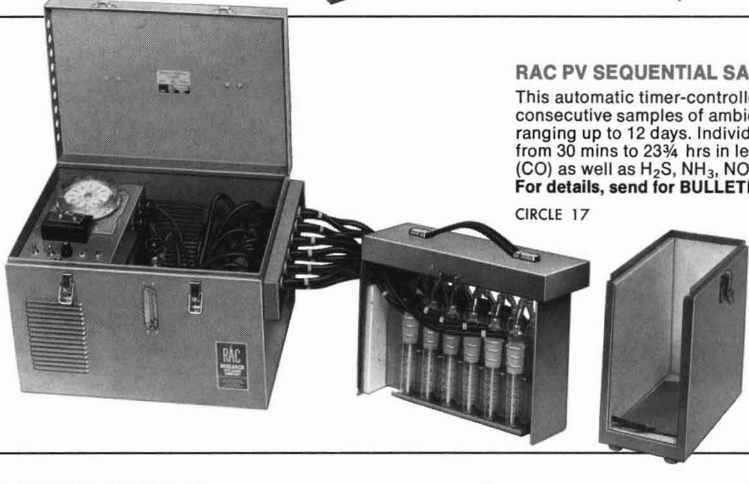
CIRCLE 17



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CIRCLE 18

RAC MIDGET SAMPLER

A lightweight dual-purpose design, this is an ideal instrument for spot checking ambient air to comply with OSHA requirements. It can sample airborne particulate matter in addition to CHO, H_2S, NH_3 and NO_2. An optional battery-powered model also is available.
For details, send for BULLETIN 2312AB-R.

CIRCLE 19

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Environmental
Science & Technology

Volume 11, Number 2, February 1977

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Chi-Hung Shen, George S. Springer*, and Donald H. Stedman

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Michael W. Holdren and Reinhold A. Rasmussen
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* To whom correspondence should be addressed.

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

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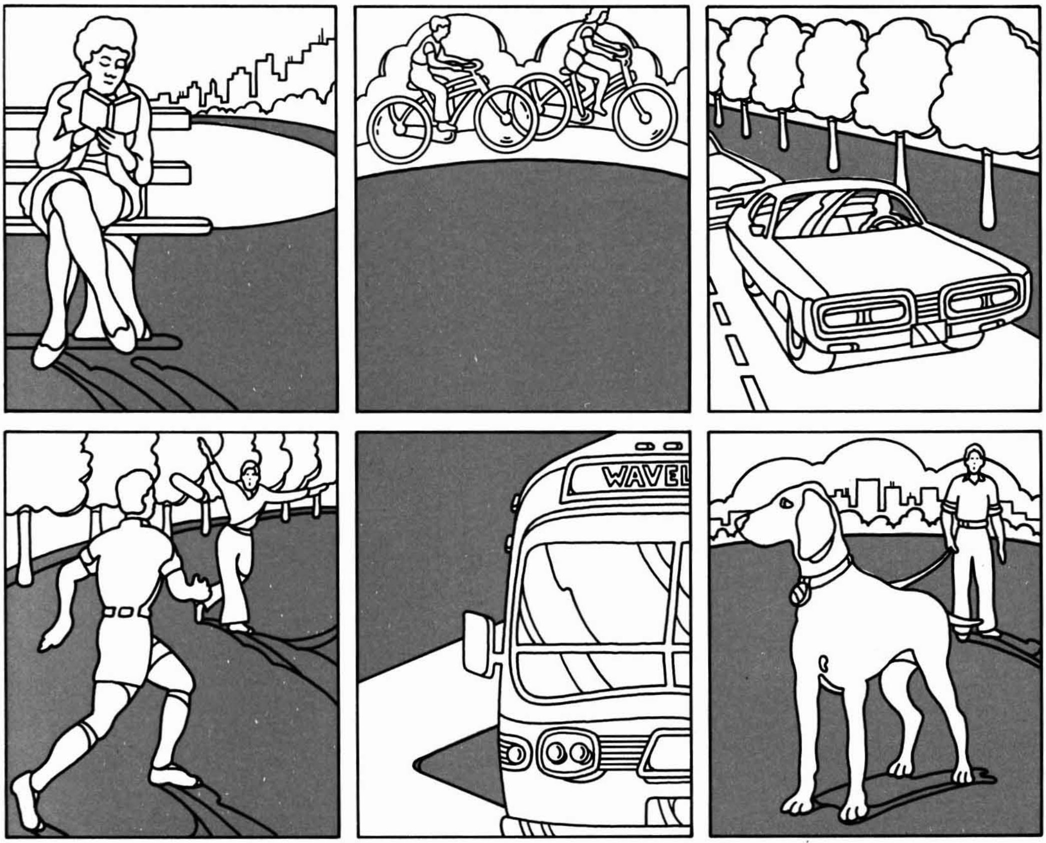
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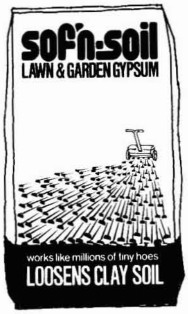
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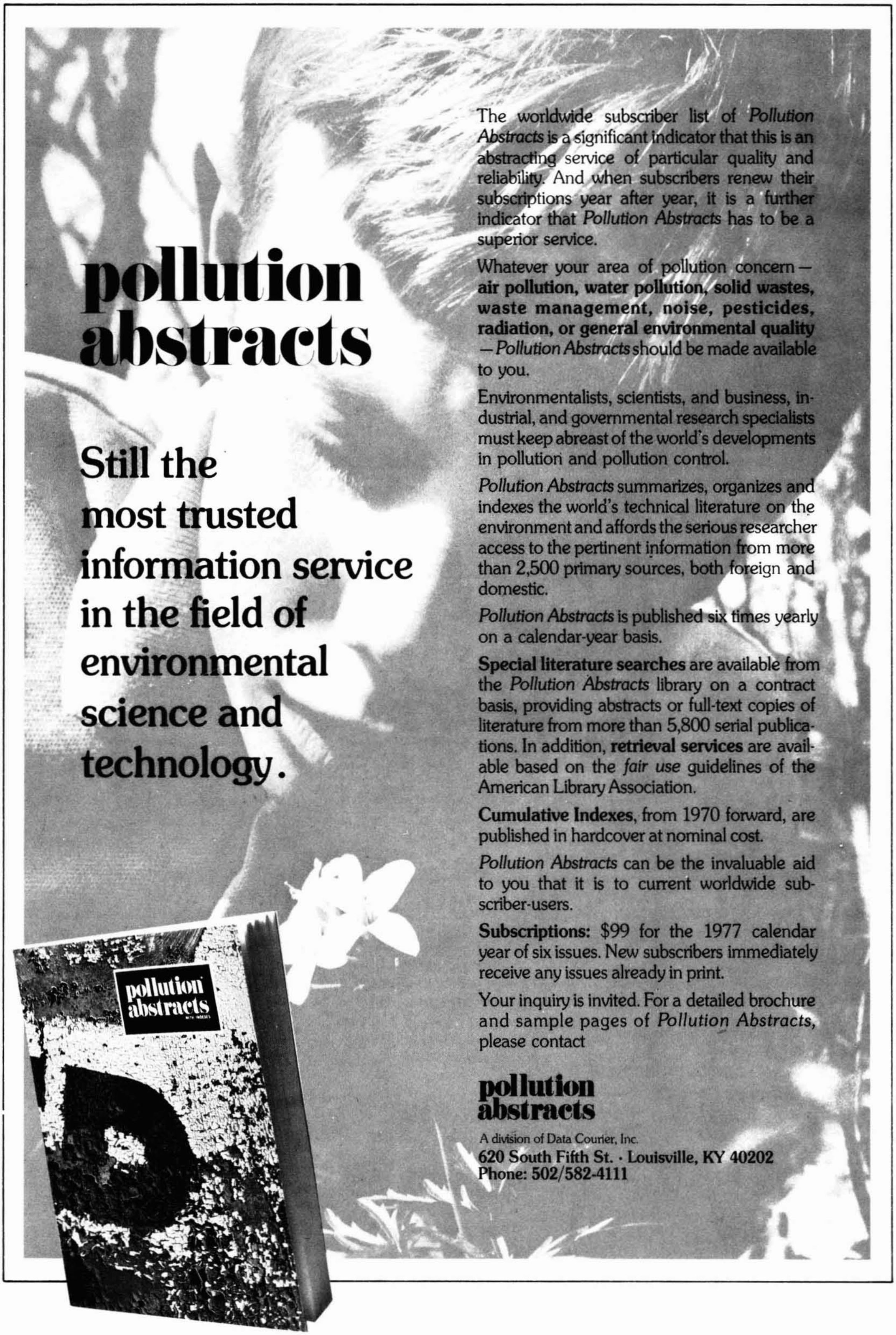
pollution
abstracts
WITH INDEXES

EDITORIAL

Environment as industry

Little more than two decades ago the environmental issue was more or less the domain of conservationists, the elite, and sophisticated. Pesticide production was reaching record levels, secondary sewage treatment was rare, drinking water quality was largely unregulated, and no one had ever heard of an impact statement, to cite just a few presently incredible facts. No one foresaw the magnitude of the social reform that has transpired; not even those who proudly trace their environmental origins back into antiquity. The transformation from leisure activity, to fad, to national commitment was rapid, and its ramifications have been detectable in the pulse of the industrial economy.

The environmental industry has come of age. Last year we will have spent over $34 billion on pollution control, over half of which is a direct result of Federal environmental legislation. The supply of environmental equipment and services is currently totaling $15 billion a year and if our clean water, air, and land goals are to be met, the grand total of public and private expenditures will surpass $250 billion in 1984.

Employment figures are equally impressive. Approximately 1.5 million persons are employed in private environmental industry, and an additional 100 000 run various public environmental agencies, mostly at the Federal level. University graduate-training programs designed to supply science and engineering sectors of this job market are strong, numerous, and are developing all the trademarks of independent professional disciplines, i.e., they maintain national professional societies and support accreditation mechanisms and specialty research journals. Many other specialists are finding new career opportunities in this industry. For instance, the number of lawyers engaged in environmental practice has increased manyfold since 1969, although the allegations pertaining to air, water, solid waste, pesticide, radiation, and noise pollution in the U.S. judicial system accounted for less than 1.0% of the 1975 case load.

In this issue's Outlook and International sections an *ES&T* staff member reports on other signs of this industry's growth; the new Environmental Industry Council that pulls together air, water, and solid waste trade associations and the triennial Düsseldorf conference and exposition.

R F Christman

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For author's guide and editorial policy, see June 1976 issue, page 553, or write Katherine I. Biggs, Manuscript Reviewing Office *ES&T*

1. Physiological Responses of Marine Biota to Pollutants

Edited by F. JOHN VERNBERG, ANTHONY CALABRESE, FREDERICK P. THURBERG, and WINONA B. VERNBERG

From the Preface:

Since the publication in 1974 of the papers presented at a symposium entitled "Pollution and Physiology of Marine Organisms," a significant scientific surge has taken place in this subject area. As a result of this continuing interest, the editors of this volume felt the need both to have a second symposium and to have the papers published. The symposium was sponsored jointly by the Middle Atlantic Coastal Fisheries Center, National Marine Fisheries Service, and the Belle W. Baruch Institute for Marine Biology and Coastal Research, University of South Carolina.

. . . In comparison with the 1974 book, the papers included in this volume reflect continuing concern about the influence of petroleum products, heavy metals, and pesticides and PCBs on the physiology of marine organisms.

1977, 482 pp., $21.50/£15.25 ISBN: 0-12-718240-3

2. Water Renovation and Reuse

Edited by HILLEL I. SHUVAL

A Volume in the WATER POLLUTION Series

Editors-in-Chief: K. S. Spiegler and J. I. Bregman

CONTENTS: PART I: GENERAL AND TECHNOLOGICAL ASPECTS: *F. M. Middleton*, Advanced Wastewater Treatment Technology in Water Reuse. *H. I. Shuval*, Health Considerations in Water Renovation and Reuse. *J. Noy with A. Feinmesser*, The Use of Wastewater for Agricultural Irrigation. *L. K. Cecil*, Water Reuse in Industry *G. J. Stander*, Reuse of Water for Municipal Purposes. *G. Belfort*, Pressure-Driven Membrane Processes and Wastewater Renovation. *L. Duckstein and C. C. Kisiel*, Alternative Water Reuse Systems: A Cost-Effectiveness Approach. PART II: EXPERIENCE AND PRACTICE AROUND THE WORLD: *H. J. Ongerth and W. F. Jopling*, Water Reuse in California. *W. J. Müller*, Water Reuse in the Federal Republic of Germany. *S. J. Arceivala*, Water Reuse in India. *G. Shelef,* Water Reuse in Israel. *T. Kubo and A. Sugiki*, Wastewater Reuse in Japan. *O. O. Hart and L. R. J.* van *Vuuren*, Water Reuse in South Africa. *G. E. Eden et al.*, Water Reuse in the United Kingdom. *D. F. Bishop*, The EPA-DC Pilot Plant at Washington, D.C.

1976, 488 pp., $29.50/£20.95 ISBN: 0-12-641250-2

3. Atmospheric Chemistry

By JULIAN HEICKLEN

This marks one of the first major summaries of atmospheric chemistry since Philip Leighton's highly acclaimed "Photochemistry of Air Pollution." Although recent books have appeared on various aspects of upper atmospheric chemistry, ATMOSPHERIC CHEMISTRY represents one of the first books to discuss both upper and lower atmospheres, unifying them in such a way that obtains a comprehensive picture of the atmospheric chemical cycles. Topics covered in this discussion include: the structure and chemistry of the atmosphere; pollutants in urban areas; emission rates, concentrations, effects and influence on the chemistry of urban atmospheres; control methods.

1976, $38.00/£27.00 ISBN: 0-12-336740-9

4. Stormwater Modeling

By DONALD E. OVERTON and MICHAEL E. MEADOWS

From the Preface:

This book presents the fundamentals of deterministic, parametric, and stochastic stormwater modeling. . . .

Land use activities are continuing with an increasing world-wide intensity. Assessment of the environmental impact of these activities is of great concern both before and after the fact. Urbanization, agricultural practices, coal strip mining, and logging operations are examples of land use activities that have allegedly contributed to flooding and stream water quality degradation. In order to develop defensible environmental impact statements associated with these activities, it is essential that the most scientifically based methodology be applied to the problems. Since little hydrologic data are available on smaller watersheds, it is becoming widely accepted that mathematical modeling is the only available means of making reliable predictions of the effects of land use changes on stream flow quantity and quality. The intent of the authors is to give a view of present methodology with illustrative examples.

1976, 376 pp., $22.50/£15.95 ISBN: 0-12-531550-3

5. Introduction to Wastewater Treatment Processes

By R. S. RAMALHO

This book introduces fundamental processes of wastewater treatment. The author's objective is to train the reader to evaluate any wastewater treatment problem so that he may properly select the processes and the design of the required equipment. To this end the author presents a three step treatment involving: a summary of the theory for each process; definition of important design parameters for the process and determination of such parameters from laboratory-scale or pilot-plant equipment; development of a systematic design procedure. The author illustrates this sequence at every step by clear numerical examples.

1977, about 415 pp., in preparation ISBN: 0-12-576550-6

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CURRENTS

INTERNATIONAL

The monitoring and long-range transport of air pollutants in Europe is under investigation by a task force of the Economic Commission for Europe. ECE, an agency of the United Nations, will perform this program in close cooperation with the World Meteorological Organization and the United Nations Environment Program; the monitoring program stems from a Norwegian proposal that was adopted by the Conference on Security and Cooperation in Europe in 1975. In the period 1910–1950, the emissions of SO_2 in Europe seem to have been fairly constant at about 25 million tons annually. However, in recent decades there has been a large increase in such emissions. In 1973, the SO_2 emissions in Europe have been estimated at 60 million tons (*ES&T*, February 1976, p 124).

WASHINGTON

According to the CEQ and the EPA, pollution control expenditures will have a "noticeable but modest" effect on the U.S.'s overall economic growth, unemployment and prices over the period 1970–1983. This conclusion was reached in a recent study entitled "Macroeconomic Impacts of Federal Pollution Control Programs," prepared by Chase Econometric Associates for the two federal agencies. By 1983, real GNP is projected to be 2.2% below the baseline forecast, while unemployment will rise gradually to a level of 0.2% above the baseline forecast. By 1983, the Wholesale Price Index will have increased by 5.8%, the Consumer Price Index by 4.7%, and the GNP deflator by 3.6% more than they would have in the absence of pollution control expenditures.

Tertiary wastewater treatment plants might not be the way to go, especially since less expensive alternative methods might suffice to remove the last 15% of pollutants remaining after secondary treatment. The U.S. General Accounting Office suggested that low dams to aerate stream water and storage of water to augment flows during dry periods might be sufficient in many cases to prevent algal growth. Consideration and, if feasible, implementation of these pollution control alternative methods could reduce the $18 billion authorized for grants to aid local governments build advanced wastewater treatment plants.

ERDA's Atmospheric Release Advisory Capability (ARAC) began limited operation recently. This computerized system, the first of its kind in the U.S., calculates the potential exposure of the population at risk in the event of an accidental atmospheric release of toxic material from an ERDA facility. The central facility is located at the Lawrence Livermore Laboratory and provides limited service to three ERDA sites. The present system has the capacity to handle 75 sites or facilities; the projected date for full operational capability is 1978. The National Cancer Institute has released its second atlas **The Atlas of Cancer Mortality Among U.S. Nonwhites: 1950–1969.** Cancer death rate patterns were found to be similar for nonwhites and whites. For example, cancers of the breast, colon, rectum and esophagus were strikingly similar, being more prevalent in the northern U.S.

The U.S. Navy Project Seafarer's weak-field biological effects program should not be cause for concern, according to a preliminary statement issued by the National Research Council's Committee on Biosphere Effects of Extremely Low Frequency Radiation, chaired by J. Woodland Hastings of Harvard University. The committee's final report is to be released in the spring. This preliminary statement was delivered to the Navy, who plans to build a system to provide communication with submarines and other military installations from a single transmitting location in the U.S. The Northern Peninsula of Michigan has been one suggested location.

NRC committee chairman Hastings

The Dept. of the Interior is now mapping the wetlands of the U.S. Conducted by the department's Fish and Wildlife Service, the National Wetland Inventory project will classify and map all coastal wetlands of the U.S. This inventory is expected to be completed by the end of 1979. The last inventory was completed in 1954. This latest inventory will maintain a data base in map and computer form that can be continuously updated. In a related matter, the EPA has just released a report that documents the adverse impact of construction activities on the nation's wetlands. It is estimated that more than a third of the nation's wetlands have been lost and that more than half of the remainder has been adversely affected.

STATES

The Alaska Pipeline Commission has commissioned a study of the reasons for cost overruns in the construction of the Trans Alaska Pipeline. This study may affect the cost of oil sold within Alaska. A separate study conducted by the Interstate Commerce Commission will affect the price per barrel of oil shipped out of the state. In 1969, the first estimate of the cost of construction was set at $1 billion. By the summer of 1974 a more realistic estimate of almost $6 billion was made. Latest official estimates set direct costs at $7.7 billion; interest costs to the oil companies could hike the cost to $10 billion.

The Ohio EPA found that $31.6 million will be needed to bring 64 state facilities into compliance with air and water pollution control regulations. According to Director Ned E. Williams, these funds will be needed over the next two years to purchase and install the requisite control equipment. The Youth Commission, the Dept. of Natural Resources, the Dept. of Mental Health and Mental Retardation as well as the

Ohio EPA director Williams

Ohio Board of Reagents will request that this money be appropriated in their budgets for the next two years. In a separate study performed for the Ohio EPA, resource recovery was found to be a viable alternative to sanitary landfills. The state's municipal solid waste has the energy value of 65 trillion Btu's/y, which would replace 2.4 million tons of coal, 9.5 million barrels of fuel oil and 53 million cu ft of natural gas.

Berwick, Me., now has a water pollution control plant designed to treat domestic and tannery wastewaters. The secondary treatment facility, built at a cost of $3.9 million, was designed to remove more than 85% of the BOD suspended solids, and more than 98% of the chromium that originates from the tanning process. Yarmouth, Mass., has filed a grant application with the EPA and the Mass. Dept. of Environmental Quality for the construction of a $1.1 million, 30 000 gpd septic waste treatment facility. This facility will use the Purifax superchlorination process, and when funded, will be the first of its kind to treat septic wastes separately. The process will eventually be used as a sludge processing system. The San Antonio, (Tex.) City Water Board has opened what may be the world's only museum entirely devoted to water.

Under Va.'s new Toxic Substances Information Act, people manufacturing or emitting toxic substances were required to report the uses to which the material will be put and the quantity to be produced or emitted to the Va. Board of Health last month. These people are required to file a more detailed report, including such information as adverse health effects and detoxification methods, by July 1, 1977.

American Motors Corp. will pay California $1.1 million for selling cars with faulty emissions controls and for falsifying test reports. However, the fine will be paid in five installments of $220 000 beginning in May and ending in May 1981. This is the largest fine ever collected by the Calif. Air Resources Board. The special payment arrangements were arranged because of AMC's dire financial losses—$46.3 million for the fiscal year that ended September 30. Air Resources Board Chairman, Tom Quinn, stated that "We are determined to enforce California's smog laws, but we intend to do it in a manner that will avoid adverse economic consequences."

"More than 92% of Michigan's inland lakes are affected solely by non-point sources of pollution, such as rain, soil runoff and septic tank seepage," according to a recent report from the Dept. of Natural Resources. The report is entitled "Industrial and Municipal Point Source Discharge to Michigan Inland Lakes." Almost 2000 lakes and impoundments were surveyed.

The Fairfax County, Va., Water Authority (FCWA) has had a virus monitoring program since November 1974. There has been no recovery of viruses in the county's finished water, according to FCWA records, since the start of this program. FCWA's program consists of a portable field virus concentrator that, by the process of adsorption, concentrates small amounts of viruses from large volumes of water, both untreated and treated The 1-liter collected samples are shipped to the University of New Hampshire where they are further concentrated (to 30 ml) and analyzed. In June, July and August 1975, contractors for the U.S. EPA sampled water in the county's distribution system and, of 12 samples, found 4 that contained Polio I virus. These findings are now being confirmed. Findings from another EPA-sponsored study conducted in 1976 are not yet available.

By May 1977, Willard, N.Mex., will have the first U.S. solar-powered irrigation system. The pilot project is designed to replace natural gas-powered irrigation pumps. When completed, the solar-powered system will pump enough water to irrigate about 100 acres of crop land. During the nongrowing season, the system will be used to heat farm houses and fish ponds used for fish farming. This project is funded by ERDA, New Mexico and the Four Corners Regional Commission.

MONITORING

Satellites can be used to monitor distribution and flow of water as well as seepage and evapo-transpiration, and protect endangered species. For example, they are excellent for covering ecologically fragile areas such as Florida's 3600-km^2 Everglades, according to the National Space Institute (NSI, Arlington, Va.). Information relayed to the Landsat 2 satellite in its 900-km high polar orbit, and then to the Miami, Fla., office of the U.S. Geological Survey, is not garbled by the Everglades' frequent electrical storms. Landsat 1 is also used. The NSI said that the improved monitoring efficiency is hoped for with the GOES geostationary satellite poised 35 800 km above the earth. The satellite data also helped to uncover a land sales fraud by showing that homesites were actually under water.

TECHNOLOGY

One way to remove heavy metals from water could be with sphagnum peat moss. The peat moss is used in the Couplan process patented by Hussong-Walker-Davis Co. The metals to be removed are adjusted as oxides, hydroxides, or sulfides. Then use is made of the fact that the peat moss' lignin and cellulose contain polar constituents that can bond chemically to the metals. Also, peat offers a cellular structure with high porosity. For example, at 50 gph/ft^2, and with peat 0.5–0.75 in. thick, metal hydroxides or sulfides were adsorbed. Remaining ions were removed by peat's chemisorption action. With a special technique even hexavalent chromium could be handled, and is, at a Nashua, N.H., firm. The company says that EPA norms are met and exceeded.

Nature also contributes to stratospheric ozone layer destruction, Richard Thorne of the University of California (Los Angeles) told the American Geophysical Union. One natural ozone consumer is nitrous oxide released from the earth's surface, and converted to nitric oxide (NO) aloft. Another NO spreader is galactic cosmic rays. A third way nature makes NO, especially near the poles, is through energetic protons emitted during solar flare activity. Thorne says that a fourth mechanism is scattering of electrons, normally trapped in radiation belts, into the atmosphere by magnetic substorms, mainly in subauroral latitudes. These electrons appear to promote NO formation. NO is a voracious ozone "eater."

Work on the largest coal liquefaction plant ever planned in the U.S. started with groundbreaking at Catlettsburg, Ky. The plant will use the "H-Coal" process, and is being funded to the tune of $178 million by ERDA, the Commonwealth of Kentucky, Ashland Oil, Inc. (Ashland, Ky.), and others. ERDA's share is $142 million. To make liquids, coal is mixed with a process

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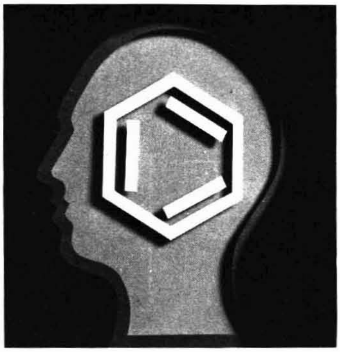

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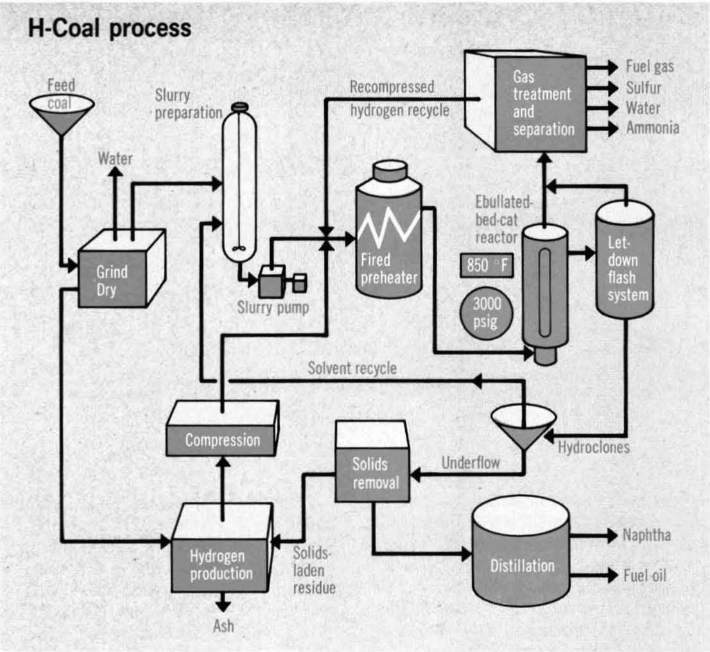

H-Coal process

liquid, then catalytically reacted with hydrogen. Products are depressurized and fractionated. No char is made. About 3 bbl of oil/t of coal are produced. In the commercial process, the H-Coal plant would make its own hydrogen. Bituminous, subbituminous, and brown coal, and lignite are suitable process feedstocks.

Also in Kentucky, a $150 million solvent refined coal (SRC) facility is to be constructed. Its design and engineering will be done under a $5 million contract that the Kentucky Center for Energy Research signed with Wheelabrator-Frye, Inc. (W-F, Hampton, N.H.). SRC is an essentially de-ashed, desulfurized fuel that can be made in solid or liquid form. Initially, the plant is to process 2000 tpd of coal. Previously, a W-F subsidiary, The Rust Engineering Co. (Birmingham, Ala.), built a 50-tpd demonstration SRC plant at Fort Lewis, Wash.; another operating plant is run by Southern Services, Inc., also of Birmingham (*ES&T*, June 1974, p 510).

What is a fast, efficient way of extracting coal liquids? One way might be supercritical gas extraction, being looked at by Catalytic, Inc., and Britain's National Coal Board. The gas that is to extract the coal liquids is chosen so that its critical temperature is slightly below the extraction temperature. The liquids' volatility then increases up to 10 000 times, and they are easily converted to hydrocarbons and chemicals. The gas (toluene) is easily recoverable. Hydrogen is not needed, nor is filtration to separate the char, which lends itself to gasification or fluidized-bed combustion. Catalytic says that the process appears to be cost-competitive.

INDUSTRY

It will cost the U.S. petroleum industry $10–17 billion/y to comply with environmental regulations by 1985, says a study undertaken by Battelle Columbus (Ohio) Laboratories for the American Petroleum Institute (API, Washington, D.C.). This study covered out-of-pocket costs for pollution control and nonpolluting fuel manufacture. It did not deal with delays caused by impact statements, land-use laws, siting problems, the toxic substances act, resource recovery legislation, and the like. The $10–17 billion figure compares with $4 billion in 1975. Probably the most costly regulation will cover sulfur in fuel oil ($2 billion) with effluent problems as a close runner-up ($1.9 billion).

The Manufacturing Chemists Association (MCA, Washington, D.C.) is approaching the Toxic Substances Control Act (P.L. 94-469) by establishing a 21-member Chemical Regulations Advisory Committee. George Dominguez of Ciba-Geigy Corp. (*ES&T*, April 1975, p 302) will chair the committee. The MCA will hold seminars concerning toxicology testing, analysis of the law's requirements, mechanisms of compliance, management and uses of new products, and other pertinent topics. The MCA is also preparing a layman's summary of P.L. 92-469. For further information concerning the summary and seminars, contact George Ingle, MCA, 1825 Connecticut Ave., N.W., Washington, D.C. 20009.

Three firms have mothballed the first privately-owned uranium enrichment plant in the U.S., Bechtel Corp. (San Francisco, Calif.), manager of the 3-company Uranium Enrichment Associates (UEA), confirmed. One reason for this move may be that the Nuclear Fuel Assurance Bill which would, if passed, have allowed private participation in uranium enrichment, with government technology and assurances against failure of the venture, died in Congress. UEA will continue to exist, but its activity stands suspended pending any possible legislative mandate to proceed. Ironically, the UEA idea was generated by a 1972 government plea for such a plant to be built by industry, as was the legislation.

Environeering, Inc. (Skokie, Ill.) has a test program that can predict energy needed for any wet scrubber, and predict pressure-drop performance. The key is a patented "Dust Difficulty Determinator" (DDD) which is, in effect, a miniature wet scrubber that can take into account influence of process variables on energy demand. This can determine proper full-scale equipment sizing without reliance on particle size analysis. Environeering president N. Balakrishnan says that the DDD can also precisely estimate energy needs "imposed by the introduction of future codes." He noted that the device has assessed condensation effects, optimized pressure-drop design, evaluated process change effects, verified laboratory data, and performed many other useful predictive tests.


Environeering's Balakrishnan

Upgrading biological sewage treatment plants today

Church & Dwight, the largest U. S. producer of sodium bicarbonate for the last 100 years, tells how this old chemical works in both aerobic and anaerobic systems in wastewater plants

The approaching 1977 secondary treatment standards have encouraged municipal sewage plant operators and municipal consulting engineers to closely examine the efficiency of their biological waste treatment plants. For many, the options of tightening monitoring procedures and fine tuning aerobic and anaerobic processes are far more attractive than investing in expensive in-ground equipment to meet the new standards.

"In the era of EPA effluent guidelines, sodium bicarbonate is quickly becoming a viable treatment chemical alternative," says Nicholas Barber, Church & Dwight's application development manager. "Laboratory and field studies, conducted by Church & Dwight Co., Inc., over the past year indicate that sodium bicarbonate is an ideal chemical for adjusting pH, providing reserve alkalinity and contributing to increased efficiency of both aerobic and anaerobic processes."

Buffering is the key

Sodium bicarbonate is a naturally occurring pH buffer in all aqueous systems. It is found in all living organisms and is a major constituent of blood plasma and tears; it is found in most all metabolic processes. In the water treatment plant sodium bicarbonate can be added any place where there is accessibility to the system. In a secondary treatment plant, this chemical can be added to the aerobic system at the influent inlet, at the primary setting tanks, or at the vacuum break of a digester.

Ideally, sewage treatment plants that could use sodium bicarbonate are those with flows less than five million gallons/day (mgd) or those plants with predominantly low pH or acidic wastes. The 5-mgd flow is an economic break-point based upon metering equipment, storage space, and manpower considerations. Plants with less than 5 mgd flow usually cannot afford the sophisticated metering equipment or the engineering expertise to handle dangerous chemicals such as lime. The safe-handling characteristics of sodium bicarbonate make it the ideal treatment chemical for these smaller plants. Sodium bicarbonate is a natural buffer and cannot be overdosed; thus, its use does not require precise measurements. Sodium bicarbonate, regardless of the amount added to an aerobic system, cannot raise the pH higher than 8.1–8.3.

Anaerobic systems

pH is the predominant factor in stabilizing the environment of anaerobic micro-organisms. In anaerobic systems, microbial action is a balanced process involving two groups of bacteria, methane formers and acid formers. Methane formers are far more sensitive to their physical and chemical environment; shock increases in the concentration of toxic substances or changes in pH or temperature inhibit their metabolism, resulting in an accumulation of short-chain fatty acids that are the products of acid fermentation.

An excess of fatty acids causes an imbalance in the digestion process because fatty acids lower the pH less than 6.6–7.2, the optimum for methane fermentation. At pH values lower than 6.5, methane formers may not grow at all. Raising pH to appropriate levels requires reserve alkalinity and increased buffering capacity.

As for the interaction between alkalinity and volatile acids during digestion, it is generally accepted that the value of alkalinity to the system is embodied in its acid-neutralizing ability.

This balance between alkalinity and volatile acids during normal digestion is extremely important. Because alkalinity is the measurement of acid-neutralizing power, the volatile acids present, which also react with acid, actually appear as part of the alkalinity. This portion of the alkalinity is subtracted from the total alkalinity to obtain the bicarbonate alkalinity, which represents the potential capacity for neutralizing volatile acids.

An increase in volatile acids, over and above the available acid neutralizing capacity of the solution, could result in the production of free volatile acids and a destruction of the buffering potential of the system with a resultant decrease in methane gas production and pH. Similarly, the digestion process, as affected by the suffering potential, will not be disrupted as long as the bicarbonate alkalinity is significantly greater than the total volatile acids concentration on an equivalent basis.

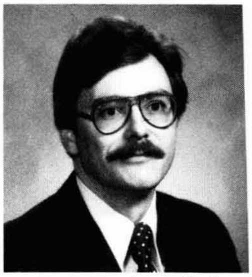
Aerobic systems

The impact of pH and alkalinity on aerobic systems is best demonstrated in terms of the nitrification process. During nitrification, the biological oxidation of ammonia to nitrate, alkalinity is destroyed. When wastewaters are low in alkalinity, this results in a pH drop that proves inhibitory to the nitrifying bacteria, causing reduced efficiency of ammonia oxidation.

During nitrification, alkalinity is destroyed with the conversion of bicarbonate to carbon dioxide (H_2CO_3 in the aqueous phase). Two equivalents of alkalinity are destroyed for each molecule of ammonia oxide or 7.14 milligrams (mg) of calcium carbonate are destroyed/mg NH_4N oxidized.

The pH of an aerobic system is determined from the ratio of the molecular concentrations of H_2CO_3 and HCO_3^-. During nitrification the H_2CO_3 level increases through the conversion of HCO_3 and through the oxidation of organic material. However, the H_2CO_3 level may be decreased by stripping carbon dioxide from the liquid by the aeration process. Thus the pH of the system depends on the amount of alkalinity destroyed, the amount of carbon dioxide produced and the rate at which carbon dioxide is removed from the liquid.

The reduced alkalinity affects the pH, which in turn affects the rate of nitrification. The maximum rate of nitrification



Church & Dwight's Barber
"buffering is the key"

occurs in the pH range of 8–9. Substantial reduction of nitrification rate for unacclimated organisms occurs below 7.0, while pH below 6.5 is seriously inhibitory.

Despite the fact that sodium bicarbonate is fairly safe to handle, provides the necessary pH balance and reserve alkalinity, and has been cost effective, its use in municipal sewage treatment facilities has not been widespread. In fact, the first significant mention of sodium bicarbonate did not appear in the literature until 1960.

Reasons for its exclusion are a combination of technical, economic, and tradition-oriented factors. The wastewater treatment industry is conservative in nature, and, consequently, is skeptical of any chemical additions to a delicately balanced biological system. The industry's dependence on lime, alum, and other treatment chemicals is based on years of relatively successful experience.

Sodium bicarbonate can be more expensive, sometimes by as much as a factor or two. Also, the pre-EPA discharge standards and effluent monitoring requirements were not as stringent as they are today. The new secondary treatment standards and the stricter monitoring requirements are perhaps the biggest boosts to recent evaluation of sodium bicarbonate as a treatment chemical.

Evaluation has shown that not only is sodium bicarbonate capable of producing pH and reserve alkalinity required by the higher standards, but it also eliminates some of the operational difficulties caused by the current industry stalwarts.

The competition

Lime, which has historically been used for pH adjustment because of its economics, works successfully in adjusting pH up to 6.5, barely within the acceptable pH for anaerobic digestion. Lime's reaction with carbon dioxide generated by the digester is the limiting factor in the pH range.

Administering lime to either anaerobic or aerobic systems requires extreme precision. If not dosed properly to the aerobic systems, lime could raise pH levels to 13–14. Lime has also been used in aerobic treatment to facilitate settling, but it can precipitate to the point where it causes more sludge handling problems than it solves. Despite its inherent difficulties, lime is still a very viable treatment chemical. It is the chemical of choice for raising pH up to the 6.3–6.5 level. Sodium bicarbonate can then be used to raise pH above the 6.5 level.

Sodium hydroxide has been used on occasions in anaerobic digestion. Some operators feel that because of its strength (pH of 14) it will cause an immediate pH boost in the digester. Alum, like lime, is typically used to facilitate settling in aerobic treatment. However, aluminum sulfate imparts an acidic pH to the solution. Typically, in an activated sludge plant, the solids settle out in a tank and the supernatant, which is returned to the aeration tank, becomes acidic from the chemical characteristics of alum.

New alternative

While sodium bicarbonate should not be viewed as the ultimate treatment chemical (no chemical really is), it should be considered as a very viable alternative, particularly in light of the more stringent 1977 effluent quality guidelines.

In laboratory and field tests, sodium bicarbonate has proven more effective than lime in raising pH above the 6.5 level and has proven an excellent reservoir of reserve alkalinity. Furthermore, it has done what lime and other traditional treatment chemicals cannot do without endangering the integrity of the biomasses and damaging operating equipment.

Though sodium bicarbonate is an old chemical, manufactured in this country for over 100 years, it could easily prove a new solution to chemical treatment problems of the modern sewage treatment plant.

Conservation and reuse are "in"!

Pollution control with water and energy saving was featured at the fifth Ecodyne Resources Roundtable

Well, you finally bought that dream house in a nice subdivision in a semitropical setting. It's near the water, just like you wanted it. A number of years later, it's *in* the water, and you are, essentially, minus a house.

Such a scenario did take place at the Brownwood Subdivision near Baytown, Tex. A number of its homes now stand in Trinity Bay. One reason why, as Leonard Limon, vice president, marketing, of the Graver Water Division (Union, N.J.) of Ecodyne Corp. (Lincolnshire, Ill.) told the fifth Ecodyne Resources Roundtable, was that in the area of that subdivision, the land has sunken 8 ft since 1918. Most of the subsidence occurred in fairly recent years. The reason for it, Limon explained to the roundtable, held near Houston, Tex., last December, is that ground water was being removed faster than it could be recharged. Indeed, so much ground water was removed so fast that certain aquifer formations could not recharge.

Broadened emphasis

In the past, Ecodyne roundtables concerned themselves principally with problems related to water's use, reuse, and disposal. By contrast, this roundtable focused on a broader aspect of the company's business—resource utilization, particularly use of energy and water, as Graver Division president Richard Hoard pointed out. Implications of land use were also an important topic of discussion, which is why the Baytown subsidence and analogous phenomena were on the roundtable agenda.

What the Baytown episode and other sinkings in the Houston-Galveston area finally led to was the formation of the Harris-Galveston Coastal Subsidence District (HGCSD), of which Ed Wagoner is general manager. The HGCSD, created by act of the Texas Legislature, sets fees and sharply restricts ground water use (600 million gpd are presently taken from the ground in the District). The HGCSD also is forcing industry and utilities to go to surface water. Municipalities and residences will probably have to go to surface water use, as well, in the future.

As is well known, surface water is generally not as "clean" a resource as ground water. Also well known is the increasingly stringent interdiction against discharging polluted effluent to surface waters. Graver Water's Limon described to the roundtable some of what his division is doing to meet the challenges of surface water around Houston.

One approach allowed Shell Oil, together with Ethyl Corp., and Tenneco to start using surface water. This approach involves Graver's Reactivator, which handles raw water with 35 ppm of suspended solids (SS) and 120 mg/L of hardness. The Reactivator, whose main function is clarification, uses untapped residual water energy and new nozzle design to provide more efficient water contact with ferrous sulfate, lime, and sulfuric acid, but much less of these than conventional mechanical water drives call for. The nozzle design is the core of Ecodyne's "Hydro-Circ" system, which coagulates, softens, and adjusts pH to about 8. Sludge is "dropped" by gravity; water is decanted back to the system.

Next, the decantate, with about 5 ppm of SS, is filtered at 15 gpm/ft^2 through anthracite and sand—a filter medium that Ecodyne believes will meet 1983 standards. Filtrate with about 1 ppm of SS goes to the plants. Filter backwash goes through the cleaning cycle again.

About 10 mgd of filtrate can go straight to Shell's cooling towers. The rest goes through an ion-exchange demineralizer for hardness and dissolved solids removal. According to Limon, this very compact approach provides considerable savings in energy, treatment chemicals, water and space. He also noted that this pretreatment technique has made vast surface water resources "accessible and usable."

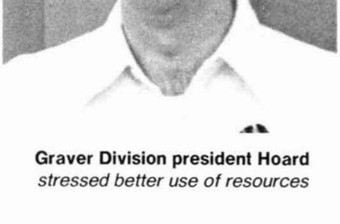
A heat stretcher

Remember when energy costs could be figured at about 3% of the cost of a finished product? Today, 15–20% is a more realistic number. Thus, processes must be designed with the highest possible degree of energy saving in mind.

Henry Lankenau, senior vice president of Ecodyne's Unitech Division (Union, N.J.), told how a Tennessee chemical company needed a quintuple-effect system to heat an evaporator/crystallizer facility aimed at meeting this year's water pollution guidelines, and recovery of sodium sulfate. The approach is vapor recompression, or, as Lankenau prefers to call it, "vapor re-energizing" (*ES&T*, August 1976, p 735).

Normally, an evaporator system receives its heat from steam; the heat is transferred through tube walls. That heat is heat released when the steam condenses. The heat-source steam is prepared in a boiler, and steam condensate is boiled again or, in a multiple-effect system, revaporized under lower pressures and temperatures. Use is still made of the steam's condensation heat loss/transfer.

Suppose, however, that instead of a boiler, there is a compressor running fast enough to maintain a desired pressure on steam piped in from a chamber. The compressor's intake receives a lower-pressure steam, but recompression, adding about 40 Btu/lb of steam, returns the steam to desired pressures and temperatures. By comparison, a reboiler system would need over 1000 Btu/lb for the same pressure range.



Graver Division president Hoard
stressed better use of resources

To be sure, the Tennessee firm had to pay an additional $375 000 in capital costs for a vapor recompression system. But its energy costs will be less than 50% of the $600 000 normally needed for steam in a plant of the type that the firm runs. The investment would thus be recouped in 1.5–2 years. Moreover, the recompression system can be made self-sustaining; the motor/compressor unit is near the evaporator units, so energy is saved even in transmission; and space and piping needs are materially curtailed. The need for condensate pumps is eliminated.

Playing it cool

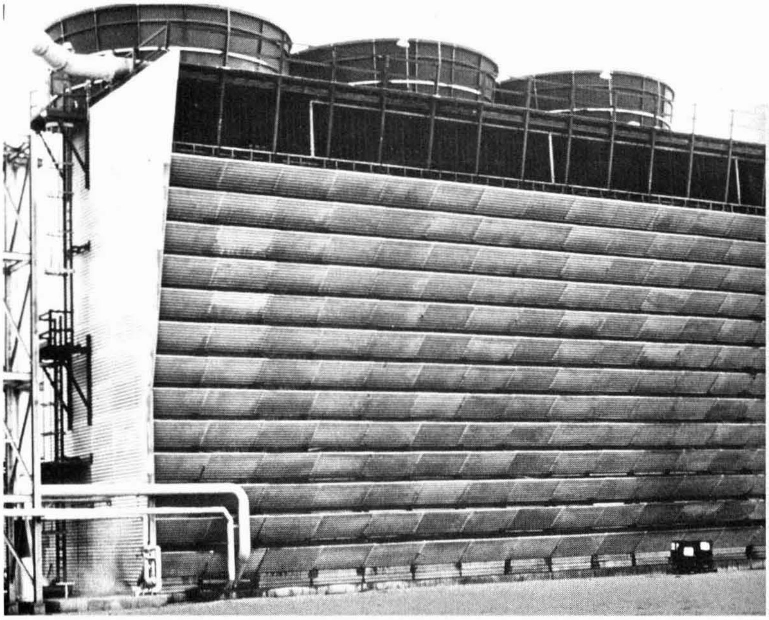
With increasing needs for cooling towers to curb thermal pollution, and conserve water, energy, and chemicals, different approaches need to be developed. H. William Brewster, vice president, marketing, of Ecodyne Cooling Products Division (Santa Rosa, Calif.), discussed one approach—that of the wet-dry cooling tower. Such a tower uses a non-evaporative air-cooled heat exchanger, such as those that Ecodyne's MRM Division makes at Conroe, Tex., to handle part or all of cooling requirements. They can be built to compensate for weather situations that could lead to fogging or formation of plumes. Special temperature controls stop condensation and tube and fin corrosion from occurring.

A further water conservation step is to use brackish, or even sea water for cooling towers, if the drift problem can be addressed. Brewster told the roundtable that his division came up with a drift suppressor that reduces drift to 0.008% of circulation water (the industry standard is 0.2%). In this way, prospects of salt pollution of surrounding land are virtually wiped out.

Brewster noted that all of these features, plus new construction techniques that Ecodyne developed together with the M. W. Kellogg Division of Pullman Corp. (Houston), lead to conservation of water and precious capital. They also allow for siting of power plants in such a manner as to optimize transmission, fuel transportation, and land availability and costs.

Don't dump it—use it!

If low energy costs were a cause for ecstasy in the good old days, the fact that water for industry was essentially a free, public resource certainly made life heavenly. Well, water generally doesn't fit into that category today, and increasingly strict pollution abatement requirements add considerably to the cost of that resource. An example of water's rising cost was given to the roundtable by Guy Mace of Ecodyne's Industrial Waste Treatment Division (Union, N.J.). He noted that in Pittsburgh, Pa., for instance, water went up from 73¢/1000 gal to 88¢/1000 gal on January 1, 1976; and that the Houston City Council is debating raising water prices by 26.7% over the present 11.5¢/1000 gal.


Wet/dry cooling towers. *They are saving water for Consumers Power*

During those days of cheap or free water, and lax or non-existent environmental regulations, few gave much thought to pollution controls, or to water conservation/recycling. With the picture so radically changed as it is today, however, Mace suggests serious efforts at water reuse. After all, recycling will not only help to control pollution, but it can save thousands of dollars in fresh water and wastewater treatment bills. As Mace puts it, "If money must be spent on a treatment system, it's worth some extra change to put in the pumps and extra piping for directing the treated water to the front end of the plant for recycling. It's then just a matter of knowing where in the plant treated water can be used."

To optimize recycling cost-effectiveness, Mace suggests a complete plant water/wastewater survey. For example, one can find where water use can be cut. Then, might a process work well with lower-quality water? If so, perhaps water less thoroughly and expensively treated can be used there. In a food plant, for instance, preliminary washings do not call for highest-quality water; nor do rinse tanks at metal finishing shops; nor, for that matter, do many non-potable uses.

An example of the water conservation ethic could be found at Armco Steel's Houston plant where 25 000 t/mo of wide-flange beams are made for building construction. Here, water is treated in a 4-compartment dual-media horizontal filter, with SS reduced to 10 ppm from 75–100 ppm. This water, supplied at 3300 gpm, can then be used for roll cooling, descaling, washdown, and cleanup. The use of recycled water saves Armco 3.8 mgd.

In some cases, what would otherwise be pollutants might become recoverable resources that could save money, or even bring income. This concept has good prospects of becoming economical with today's climbing material costs, particularly if only one, or a few easily separable pollutants are to be handled. Examples Mace gave include vanadium from power plant ash; valuable metal hydroxides from metal finishing; and metals recovery from mining or smelting wastes. He considers evaporation a very sound method for metals recovery, especially where vapor recompression can be used as a heat supply.

From burden to benefit

Probably the principal idea that the roundtable was to impart was the notion that if pollution control is regarded as an economic burden, perhaps certain changes in the way this effort is looked at, plus the expenditure of not excessively more dollars, can turn the effort into a money-saver, or even a money-maker. Also, as Ecodyne's spokesmen and others at the roundtable pointed out, water, land, energy, and material resources can no longer be considered separately; what conserves and recovers one does the same for the others. And with mounting costs of water, land, energy, and materials, maximum conservation and recovery makes increasingly good economic, engineering, and environmental sense. JJ

Britain was the first to go on-line;
the U.S. is celebrating its silver anniversary;
and Sweden leads the world in electricity produced from . . .

Nuclear energy: how bright a future?

The energy appetite of industrialized nations was never so poignantly demonstrated as when the Arabs abruptly inserted the plug in the barrel of oil more than three years ago. The embargo, followed by gargantuan price increases, sent these dependent countries scurrying for solutions to their energy problems, solutions that would render them immune to future Arab actions. One option available was nuclear energy.

The ability to release awesome power by cracking the atomic nucleus was frighteningly demonstrated over Hiroshima and Nagasaki more than 30 years ago. This technological advance ended World War II and was soon—at least by the few countries that jealously harbored the proper materials and technical know-how—transformed to more peaceful purposes. One use was the harnessing of nuclear energy for the generation of electrical power.

The proliferation of nuclear power reactors worldwide has proceeded with deliberate speed; long-term projections show a continued, steady growth pattern. But the stage for a "go/no-go" decision on a nuclear future is rapidly approaching, and the debates, worldwide, are heating up.

Proponents view nuclear power expansion as inevitable (and the technical problems solvable) if the world is to meet its future energy needs. Opponents fear its growth as a dangerous step for the future of mankind, one that would bestow a legacy of risk and responsibility on future generations.

In fact, had it not been for the various weapons programs, nuclear generation of electricity—at present the most viable alternative to fossil fuels—might be at the same immature state of development as the next most viable alternative—solar generation. Because of the long lead times required to develop a new energy technology, those countries choosing to pursue the nuclear option must begin putting the machinery in place now.

The technical and institutional problems associated with the control of nuclear development and the protection of the environment are being intensely addressed, but the more sticky political, social and ethical underpinnings of these issues need more careful consideration.

The case for expansion

The bombing of Japan permanently set an emotional/moralistic coloration to the topic of nuclear energy, even for peaceful purposes. Arguing for continued expansion of nuclear power for electrical generation, proponents state that technological solutions can be found to reduce the risks from serious accidents to acceptable and negligible limits. Nevertheless, opponents fear that the greatest hazards will stem from human error, and that safeguards against all possible failure mechanisms are impossible. Since a blanket guarantee of safety cannot be made, opponents query: Does the present generation have the right to impose a legacy of risk on its future descendants?

On economic grounds, proponents argue that nuclear energy is the only viable prospect for meeting the galloping energy needs required to support high-living standards. Without a nuclear future, the world would experience economic stagnation and societal decline. Nuclear-generated electricity, at least in some countries, is purported to be significantly cheaper than fossil-fuel-generated power. And according to proponents, nuclear power plants use less fuel than do fossil-fueled plants.

On environmental grounds, proponents state that degradation is less with nuclear than with fossil-fuel electrical generation. Radioactive discharges to air and water are radiologically insignificant, and nuclear power plants do not release the particulate matter and gases (SO_2 and CO_2) associated with fossil-fuel plants.

The case against expansion

Arguments against expansion center on safety, proliferation and diversion issues.

Despite the nuclear industry's excellent safety record, with its diligent attention to design, construction and operation safety, opponents note that it is impossible to anticipate all possible failure mechanisms that could result in reactor accidents and, therefore, appropriate safeguards cannot be built in. Further, as time passes, complacency is likely to creep in and the industry's present diligence may soften.

Barring accidental releases of radioactivity, the very real possibility exists that in time of war reactors will be the targets of attack. This vulnerability negates against the concentration of reactors in "nuclear parks" and argues for the construction of underground installations.

One strong point against the proliferation of nuclear installations is the present technological inability to safely handle the highly radioactive waste materials. These wastes must be isolated from the biosphere for extended periods of time, sometimes thousands of years.

Storage of liquid wastes in tanks is not suitable as a long-term solution. Processes are under development to convert these liquid wastes to insoluble, solid forms, but the problem of isolation of this solid matter remains. Storage in deep geological formations or under ocean beds are suggestions that have been put forward, but which need further study.

Another source of concern is that the logical progression in thermal reactor development is the construction of fast-breeder reactors. These plants produce more plutonium than they consume and this excess plutonium could be diverted for use in an explosive weapon that could be used for illicit purposes.

The development of the fast breeder would rapidly steer society toward a "plutonium economy" which, in addition to the diversion problem, would impose added environmental risks, especially during the transportation of this toxic material between nuclear installations. The increased opportunity for theft during transportation might also necessitate the institution of security measures that, in a democracy, could infringe on individual freedoms.

The options available

Careful calculations that consider all foreseeable technical, economic and environmental questions indicate that nuclear capacity, even under the most auspicious conditions, would be able to fill only about one-sixth of the envisioned energy gap in the early part of the next century. Oil and gas reserves are diminishing; hydroelectric power and firewood are inconsequential energy sources. Small but local contributions could come from geothermal and tidal power.

Solar energy and its indirect forms—wind and wave power—can potentially make a significant contribution to plugging this energy gap. Unfortunately, in the presence of an oil and gas glut, the technology to exploit solar energy has not been sufficiently developed. Nevertheless, of all existing alternatives to fossil fuels, nuclear and solar generation along with a strict conservation program appear to be the most viable.

A British response

Last September, after a 2.5-y study, the Royal Commission on Environmental Pollution, chaired by Sir Brian Flowers, released its sixth report "Nuclear Power and the Environment." In this report, the commission recommended a prudent, "go-slow" course for nuclear energy development in the United Kingdom (U.K.). Adding significance to the report is the fact that Britain was the first nation to build a nuclear reactor for the generation of electricity.

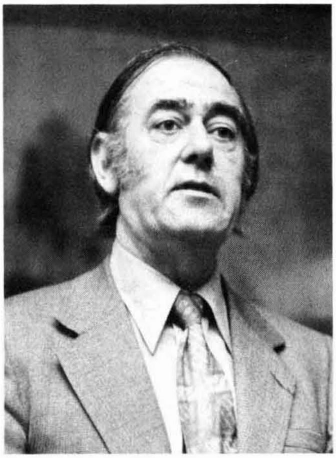
In general, the commission stated that hazards to humans and the environment from accidents at existing reactors are not "unique in scale and of such a kind as to suggest that nuclear power . . . be abandoned for this reason alone." However, the commission did stress that as nuclear installed capacity increases worldwide, so will the risks. While the commission felt that "The abandonment of nuclear fission power would be neither wise nor justified," it cautioned that "a major commitment to fission power and a plutonium economy should be postponed as long as possible."

The report was optimistic that, despite prevalent projections, other energy sources could be developed. It called for increased research into the development of solar energy and its indirect forms, fusion power, combined heat and power systems and energy conservation measures.

On the matter of waste storage and disposal, the report stated: "There should be no commitment to a large programme of nuclear fission power until it has been demonstrated beyond reasonable doubt that a method exists to ensure the safe containment of long-lived highly radioactive waste for the indefinite future." The commission was certain that an acceptable solution would be found, but that intensified efforts for this search were needed.

Energy in any form ultimately appears as heat in the environment. Increased numbers of nuclear power plants would result in increased waste heat that could have significant impact on weather patterns and climate, especially in localized areas. For England, new power plants would be sited along the coast to obtain the needed cooling water. Besides the possible adverse ecological effects, coastal sitings would present esthetic problems.

While the commission found no fault with current methods for deriving standards for allowable exposure to radiation or with the machinery in place to protect the public against discharges from nuclear plants, it feared the implications, including the possible loss of personal freedoms, of a plutonium economy.


Britain's Sir Brian Flowers
postpone a major commitment


Sweden's Prime Minister Fälldin
a halt to nuclear reactors?

For Britain, the commission recommended the appointment of a high-level advisory board on energy policy, an increased effort to develop a method to safely dispose of nuclear wastes, and the serious consideration of alternative energy options.

In responding to this report, the U.K. Atomic Energy Authority (AEA) welcomed the commission's finding of a more than respectable record of safety, security and environmental protection. But the AEA strongly disagreed with the commission's fears of the potential effects of expanded nuclear power on the environment and on the very fabric of society.

In short the AEA felt that no alternative source to nuclear could make a major contribution to Britain's energy needs in the near term. Further, "the uncertainty of future energy demand and supply make it essential that development of the fast breeder should proceed uninterrupted, with the building of one full-scale fast reactor to demonstrate the efficiency, environmental acceptability and safety . . . in the time-scale required." The AEA did not go so far as advocating an immediate commitment to a large-scale fast-breeder program, however.

Parliament's response to the commission's report can be summed up in one word . . . silence.

U.S. initiatives

The British report, released more than a month before nuclear initiatives appeared on the ballots of six states in the November presidential election, appears to have had little effect on U.S. decisions.

The propositions on the ballots in Arizona, Colorado, Montana, Ohio, Oregon and Washington, as well as the earlier June initiative in California, which would have halted nuclear development, were resoundingly rejected by the voters. And despite the claims of the nuclear power industry, the rejections were not unconditional votes to proceed with nuclear power expansion. What the voters rejected in June and November were the constraints—construction would have been subject to legislative certification of reactor core safety systems and waste disposal systems—proposed to condition future expansion. Citizen action will probably surface again. Ballot initiatives are being readied for Maine and Michigan.

While approval of the seven initiatives would have placed restraints on the number of nuclear plants planned, prevailing and ever-increasing construction costs may be having the same effect. In 1975, 11 construction projects were announced, and 13 were canceled.

Although the nuclear power industry appears to have won several victories in November, that election also witnessed Jimmy Carter's ascension to the presidency. Carter appears to favor reducing the dominance nuclear energy enjoys in current U.S. energy programs; he has been quoted as saying that he would have voted for the Oregon initiative. Most importantly, Carter has promised to develop a comprehensive national energy policy—one in which alternative energy sources are likely to be stressed.

The Swedish turnabout

Another significant event occurred last September: Olof Palme's Social Democrats were swept out of office after a reign of 44 years. Palme claimed that the election turned on the issue of nuclear power expansion. At that time, Sweden

had five reactors in operation, one at the start-up stage and plans to make the country the world leader in nuclear energy generated per capita by 1990. Today, nuclear power supplies 20% of the country's electricity; this contrasts with 10% in the U.K., and 8% in the U.S.

Leader of the opposition Center Party, Thorbjörn Fälldin, now head of the new coalition government, vowed to halt Sweden's nuclear programs and shut down all existing plants. However, Fälldin's two coalition partners, the Liberal and Moderate parties, favor nuclear expansion, and since the election Fälldin appears to have altered his stance, although he claims otherwise.

The Swedish Parliament now has a bill before it that favors the continued operation of existing plants and approves construction of eight more plants, half of which are in the planning stage. The bill also provides for government-guaranteed loans for the stations now under construction.

This legislation also requires that private nuclear industry or the State Power Board provide acceptable plans for fuel reprocessing and waste management before the plants now under construction begin operation. The bill is expected to be passed and implementation of its provisions to begin next month.

Fälldin's new government plans to set up a select parliamentary commission to assess the safety and environmental effects of nuclear energy. This commission will, by 1978, submit a proposal to parliament detailing alternative strategies as a basis for a new energy policy. In the event that safety problems are found to be insoluble, the commission will draw up an emergency option for the abandonment of nuclear power.

With deliberate caution

Sweden is on a straight-line course in the pursuit of fission power, yet it has no plans to build a fast-breeder reactor; all existing and planned plants are of the thermal type. On the contrary, Britain, while expanding its fission base is scaling up to a prototype (equivalent to the U.S. demonstration stage) fast breeder. Britain built its first fast-breeder model in 1959, and intends to proceed to a commercial plant in due course.

The U.S. is not quite so far along in its fast-breeder program as is Britain, but in ERDA's budget, fast-breeder and fusion programs receive heavy funding while solar energy programs, relatively speaking, receive the short shrift. Neither Britain nor Sweden have solar energy programs, but both are watching international developments closely.

Recognizing all the safety and environmental pitfalls of the only viable energy source opened to them at the present, these western countries are charting a nuclear course deliberately, but with much caution. LRE

Almost "instant book"

Noyes Data tells how it can put out a title 3.5 months after receipt of manuscript

"It's not how hard you work; it's how smart you work that counts," a Washington, D.C. business man once told *ES&T*. This adage, in turn, prompted the question, "What if one works both hard *and* smart?" One answer to that question was given by Robert Noyes, president of Noyes Data Corp. (NDC, Park Ridge, N.J.), publisher of many state-of-the-art technical books, who said, "Business couldn't be better!" Noyes ascribes the success of his company to hard, smart, super-efficient work and performance on the part of his staff and contributing authors; excellent in-house harmony; and presence of most writers and all services needed in the New York City metropolitan area, with one exception. Another factor in NDC's success is the ability to foresee book needs, and to get books from the author to the readership fast.

How fast?

Noyes said that with his company's way of doing things, and with efficient work by qualified authors who work to tight deadlines on a royalty or fee basis, a book can be prepared in two months, on the average. Another 4–6 weeks are added for production. Ten highly trained editors—all of whom are women with at least a master's degree in chemistry—make all substantive, technical corrections in-house. All told, it takes about 3½ months from start to availability.

Also done in-house are all necessary illustration and composition. All mechanical errors are ironed out at that point; thus, the company has close control over what goes into the book's master sheets. No galleys need be made; the material goes straight to paper with cold type. In this way, with a total part- and full-time salaried staff of about 40, plus free-lance editors and authors, NDC can and does turn out about 45 technical books/year, all with virtually up-to-the-minute information. "Nobody else works this way," Noyes told *ES&T*.

NDC was formed in 1959, and moved to its present quarters about six years later. Its books were at first concerned with the chemical manufacturing industry. Later, the firm branched out to food technology, and to the paper and textile industries. In 1972, environmental titles began to appear; and in 1974, energy books were introduced. Now, typically, of all the technical works published annually, about eight are on environmental matters, and a half dozen are concerned with energy. If corrosion, petroleum, and the like are classed as "environment," one could then say that at least a dozen environmental titles are published by NDC each year.

Who's in charge

Robert Noyes is the man at NDC's helm. The editor-in-chief is Gloria Weiss, who has a background in chemistry. The editorial director is Paul Stecher who was in charge of putting out the Merck index for many years before joining NDC, and who is conversant in 13 languages. As for technical staff, the reason why there are so many editors is that some books are actually written in-house when there is an urgent need for a book, and no outside author to do it. An example of such a book is one on solar energy—now in its third printing. Nevertheless, the company does have 15 authors with appropriate specialties on tap. Also NDC has two subsidiaries, Noyes Press and Noyes Art Books (New York, N.Y.), which publish 6 books/year on art, archaeology, and classics.

A relentless search

The way the company is run, nothing except final printing and binding is contracted out for preparation of technical books. This not only allows for on-the-spot correction, but cuts out error and delay factors that cannot be controlled in-house. Efficiency is further increased by the way the books come out—all are 6 in. by 9 in., designed in a standard format. Even packing and shipping goes like clockwork.

Management selects authors not only on the basis of qualifications, but also on the basis of how fast they can move. The work of these authors is supplemented by the work of a free-lancer in Washington, D.C.—the only one associated with NDC who is not in or near New York—who furnishes latest patent and other government information, as instructed. Noyes told *ES&T* that all of these factors, plus "a relentless, unceasing search, and knowledge of where to look and what to look for, ensures the proper timing and timeliness of books."

Yet another efficiency factor is the versatility of staff people in editorial and production positions. They are well acquainted with each other's needs, and business needs as well; thus, all "mesh" well together. Finally, the goal-oriented nature of NDC—which is still always open to new ideas as to how to turn out even better, more timely products faster—might be the "lowest common denominator" that explains why the company's titles move from the author to "hitting the street" as quickly as they do. JJ

L to r: Weiss, Noyes, and Stecher. *"Nobody else works as we do"*

Economic growth with environmental quality

Environmental control equipment makers and their industrial users are winding up for a new ball game

There is a new political persuasion in Washington, D. C. There is also a new organization—an Environmental Industry Council (EIC)—for producers of environmental control equipment—makers of air, water, solid wastes, noise, and heat and resources recovery equipment—and its industrial users.

At press time, 16 members had joined the group. Formed last July, this council comprises 13 industrial corporations and three trade associations—IGCI (the air cleaning people), WWEMA (the water and wastewater equipment makers), and MECA (the automobile control retrofit makers). John Blizard is the chairman of the EIC.

Initially, the organization seeks better information and, in a sense, will serve as a referral service. But the main reason for forming the new group was to give the membership a voice in the Washington legislative machinery. The council is interested in changes in tax policy, and in publicizing case histories where environmental controls have led to industrial savings.

The council will be presenting its National Environmental Industry Awards at a meeting later this month (February 23–25) in Washington, D.C. The function of the awards program is to give public recognition to firms that have demonstrated outstanding technological achievement and leadership in pollution abatement and protection of the environment.

Automobile, steel, paper, chemical, and others companies will compete in the awards program. These awards will honor outstanding achievements by individual companies in all areas of pollution control:

- air pollution control
- water and wastewater pollution control
- solid waste management
- noise pollution control.

More importantly, the meeting will set the theme for the new administration and its aspirations and goals for environmental protection.

Preview of the EIC meeting, color it new

- *new environmental priorities at the White House*
- *environmental priorities of the new Congress, the 95th*
- *the new CEQ chairman on policies of the new administration*
- *the new EPA administrator's view of the next four years*
- *views from state officials and the first EPA administrator*
- *economists' views on economic growth with environmental quality*
- *economics of the new environmental control technology*
- *implementation incentives for environmental quality management*
- *industry's role in the global environmental control challenge*
- *balancing short-term need and long-term benefits*
- *analyses of trends in public concern over pollution*

The new thrusts

New priorities at the White House will be elaborated by the new CEQ chairman, unannounced at press time. The new EPA administrator will preview the next four years of the federal regulatory agency for environmental protection. An address from the first EPA administrator should serve to put the whole environmental regulatory program of this nation in perspective. In addition, prominent economic and industrial spokesmen, and federal and state officials, will highlight tax policy considerations and other economic incentives to ease heavy capital burdens on industry.

Lester Lave, an economist at Carnegie-Mellon, heads a panel that will discuss what pollution is costing the public. He and Eugene Seskin are authors of a new book, whose tentative title is "Air Pollution and Human Mortality," which will be available this Spring from The Johns Hopkins University Press. The book develops some careful models which depict the association between air pollution and mortality. Lave says that it is a careful epidemiologic study (1960–1970) that estimates the effects of sulfates and particulates on mortality in more than 100 large cities in the U.S.

With regard to mobile sources, automobiles and the like, the evidence suggests that the most stringent emission controls mandated by the Congress are probably somewhat too stringent from the cost/benefit viewpoint. The National Academy of Sciences had estimated that for the late 1970's the control cost would be about $10 billion: benefits would be somewhat less than $5 billion and maybe as low as $2 billion, according to Lave.

The budget of EPA for estimating benefits of environmental improvement has decreased over the past years and is now at an inadequate funding level. Lave says, "Particularly since billions of dollars are being spent annually on environmental cleanup as mandated by the EPA regulations."

Further, outstanding Harvard economists of the Carter persuasion including Otto Eckstein and distinguished futurist Herman Kahn of the Hudson Institute will discuss "economic growth with environmental quality," a theme attributable to Russell Train.

Building bridges

Associations have built bridges to legislative committees in the past and will do so more this year, at least with regard to the environmental industry council, its trade associations, and the Chamber of Commerce of the U.S.

John Thomas of the Chamber identifies 83 issues of concern of the business, including an environmental share, that may be considered by the 95th Congress. The need for bridges is clear when one realizes that the majority of Congressmen simply have not been involved in business-oriented activities. In the previous Congress, the 94th, only 152 of the total 535 members classified themselves as businessmen or bankers. Then, 261 members of the new House of Representatives were endorsed by unions! The Environmental Industry Council (EIC) has a message to get across. Truly, business cannot rely on the presidential veto.

The biggest game in town

The wastewater construction grants program is the biggest game in Washington, D.C. Of the $18 billion for the construction of treatment plants, at this late hour, $6.5 billion remains to be obligated, which must be done before this September 30. At a WWEMA forum late last year (Washington, D.C.), it was acknowledged that although P.L. 92-500 was passed in December 1972, the flow diagram for getting through the construction grants program was made available three years later. It's still complicated.

Some legislative watchers remind current meeting goers that in past legislative hearings many proposed that EPA be a regulatory agency modeled after the highway construction program. The highway construction grants program involved 5000 people with 50 grantees to construct the interstate highway system. In contrast, EPA has only 907 staffers, of which only 300–350 are engineers, on the construction grants program—the $18 billion package.

Playing ball

Obviously, it will be a whole new ball game in the 95th Congress. The clean air and clean water bills will be taken up again. The money items, at least with regard to water, may be taken up as early as this month. Controversial air and water items will be discussed in the Fall.

Players. Jim Wright of the House Public Works Committee is moving up; the new man has not been announced at press time. Sen. Edmund Muskie (D-Me.), of course was reelected but he has indicated that it will be his last term.

Congress will have to bite into the environmental legislation; the earlier the better. Some states have run out of money, others have money in jeopardy—all of which slows down the construction program.

Unresolved, for example, is the key item on dredging (section 404), which tied up the whole bill last session. Extension of the 1977 water deadline is not the question; it is how to do it—administratively or legislatively. Another moot point is whether the EPA can exercise any judgments over a state's priority list for wastewater plant construction.

No one bit the bullet on the NWQC recommendations. It all adds up to the fact that the 1983 data will most likely be postponed; there will be more delegation of authority to the state on construction activities, and constant funding will enter the wastewater construction picture.

Don't drink the water?

Two years ago, Congress enacted and former President Ford signed the nation's Safe Drinking Water Act. On December 24, 1975, EPA promulgated interim drinking water regulations, which become effective July 24, 1977. State officials are watching. If the state doesn't sample and analyze its water supplies—anything with more than 24 users and 15 service connections—then it is in violation of the law. Some 250 systems serve more than half of the U.S. population, but there are 90 million other systems including 40 000 community systems.

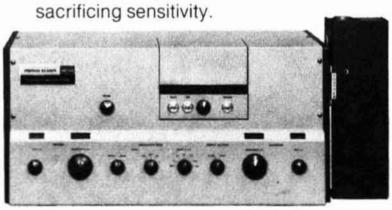
But no one is too excited. The options are open. A state can be given up to five years to come into compliance. In addition, another year, making it six, is possible if a state goes into a regionalization plan.

For drinking water watchers, the NAS study on organics is due next month. By April 1, the report to the Congress is due on the cost of implementing this act. It has been estimated that over the 5-year period, an estimated $1.5–1.8 billion could be spent for water supply facilities.

Expenditures last year

Dr. Edwin Clark, economist from the CEQ, presented facts on environmental control expenditures for last year. They totaled $34.7 billion, about half of which ($17.7 billion) was traced to federal environmental legislation, some eight major thrusts. The water expenditure came to $13.9 billion, up $6.5 billion from the previous year. A further breakdown of the $13.9 billion showed that some $7.7 billion went for the construction of wastewater treatment plants.

Macro-economic projection of the CEQ revealed that $50 billion might be spent in the next ten years (1975–1984). Of course, this estimate included a number of assumptions, including perhaps the biggest—whether or not the environmental legislation will be enforced. SSM



German pollution control

Düsseldorf fair and exposition pulls together all aspects of environmental control technologies and monitoring instruments for air, water, wastes, noise, and heat

This month, all international environmental roads lead once again to Düsseldorf for a second Umweltschutz (pollution control show). ENVITEC 77 (for *env*ironmental *tec*hnology) is sponsored by VDMA (the Association of German Machinery Manufacturers) in cooperation with seven trade associations, three technical associations, and an association of German cities. The organizer was Düsseldorfer Messegesellschaft mbH (NOWEA). It is important to note that ENVITEC 77 is being held since the enactment in West Germany of important environmental legislation.

At first glance, environmental protection fairs appear to be new, at least to the untrained environmental watcher. No so. Both in 1965 and 1969 there were congresses in Düsseldorf on the subject of clean air preservation. In Munich, the subject of wastewater has been handled in a separate event since the end of the fifties.

Until 1973, there was no combination of the most important fields of activity. ENVITEC 73 attracted 363 exhibitors from 14 countries and about 25 000 visitors. This year's show will attract a similar audience.

Dr. Arnold F. Lahrem, of the coordinating office of the Association of German machinery manufacturers (VDMA), reminded the congress that "it is today very difficult for one person to attain a digestive comprehension even in any one of the main fields of environmental activities—science, economics, politics, and technological production. But the one who tries to deal with the subject of environmental protection shall be confronted with exactly the same problem."

Lahrem summed up what environmental technology is all about. "The environmental consciousness has opened a new branch of technology; there are numerous technical possibilities and new ones are added continuously by the running researches," he says. "The task of environmental technology is to reduce the contamination caused by technical progress and communal change in the modern social life, thus ensuring that the human life on this earth may not be exposed to environmental dangers."

In conclusion, Lahrem said that the trend for the coming years goes clearly to growing expenditures for the field of water contamination. Air pollution takes the second place. But one should not forget that "broadly speaking the future of the human race depends upon the future of the environment."

On drinking water

In general, with increased pollution, water supplies for drinking purposes are threatened. In Europe, 20 million people use drinking water obtained from the Rhine River—one of the largest wastewater discharge outlets in the world. Although more than 10 million people in West Germany get their drinking water from the highly polluted Rhine, authorities have to date been very hesitant about supplementing advanced treatment processes. When the new Water Resources Act was drafted, their legislation did not exert pressure in the direction of advanced wastewater treatment.

It is true that the condition of water supplies has been improved in individual sectors in recent years through the installation of large effluent treatment works by industry and with the aid of various clarification plants installed by local authorities. Nevertheless, in general, the quality of the water has declined. For example, in 1974 the salt content of the Rhine, at the German-Dutch frontier, was 53 million kg/day. In the first of 1975 the salt content had risen to 56 kg/day. In this respect, the Netherlands is not without its problems. And by the year 2000 at the latest, it has been estimated that drinking water is likely to be in such short supply that it will constitute a threat to the existence of all mankind. Even today, 130 million people in 75 countries have insufficient water supplies of adequate quality, free from severe pollution.

On water pollution

In West Germany, the basic Water Resources Act was enacted July 27, 1957. Stringent regulations are being drafted at the national and international levels. Among them is a Bill to impose a levy on industries discharging effluents into surface waters, similar in concept to the U.S. EPA regulations on industrial effluent discharges.

But the German legislation is somewhat inconsistent. At present there is no national standard for the quality of surface waters. Nevertheless its federal government can enact regulations establishing standards for effluent discharges. Thus, in the next few years, all branches of German industry will be compelled to install considerably more and effective effluent treatment systems. Such systems require plant equipment, construction firms, and related controls. But, of course, this is true not only in Europe but in the U.S. also.

Industrial, association and local backers for ENVITEC 77

- ***The Association of German Machinery Manufacturers (VDMA) with its 7 trade associations***

Air technical equipment
Plant machinery for the chemical and allied industries
Valves and fittings
Construction of complete plants
Industrial furnaces, oil and gas firings
Turbines, engines and other prime movers
Pumps and compressors

- ***Three technical associations***

General Association of the Electrotechnical Industry (ZVEI)
The Association of German Precision Engineering and Optical Industries
The Association of the Chemical Industry

- ***The Association of German Cities***

Meeting goers. *Attendees hustle about updating their information*

On sewage

In West Germany, as elsewhere, the process of sewage treatment has consisted, and still consists, of the mechanical removal of suspended solids and the oxidizing of dissolved solids, with the aid of bacteria and other organisms. This will not meet the requirements of the quality standards laid down in the latest environmental protection legislation.

At present, 50% of all wastewaters is inadequately treated or subjected to no form of purification. Only an estimated 30% of the effluents are given full biological treatment. By 1985, West Germany plans to have 90% of all households connected to biological treatment plants.

A Battelle study of last year revealed that the major part of DM 100 000 million ($42 billion) was needed for investment in environmental protection in the 5-year period 1975–1979, to clean up discharges from households. Budget estimates of the federal and regional authorities call for an investment of DM 16 300 million ($6.8 billion) for water pollution controls in that 5-year period.

On sewage sludges

In West Germany approximately 6000 treatment works, operated by local authorities, generate almost 23 million m^3 of sludge in a year. These plants account for more than 40% of the population. In 10 years, the sewage of 90% of the population will be treated by public works, and it has been estimated that these plants will have to dispose of 38–40 million m^3 annually.

Dewatering, drying, and incineration are some of the ways to treat sewage sludges. For example, thermal drying of a dry solid material for application to topsoil and irradiation of sewage are attracting considerable attention. Pyrolysis is another method that is gaining in significance for sludge disposal.

One must remember that sludges from public sewage treatment works are rich in organic matter. Apart from the 50–70% dry substance, they contain 2–3% nitrogen, 2–3% phosphorus (P_2O_5), 6–12% lime, magnesium and sulfur compounds, and 0.2–0.5% potash.

On industrial effluents

The Germans realize that it will be essential to pay greater attention to the treatment of industrial effluents if adequate supplies of water are to be provided for all branches of industry in the future. To date, this has been achieved only by using increasing amounts of surface waters!

One understands that the biological oxidation stage can only remove a small part of any eutrophicating and toxic substance. Also, many organic materials are difficult to degrade.

Local authorities are having to incorporate advanced processes, which may include physical-chemical treatment schemes and combinations of these with the biological process, to eliminate toxic, nondegradable substances of high concentrations of oxygen-consuming matter. Often, this advanced treatment is accomplished by passing the effluent from the secondary (biological) treatment through a fine sand filter.

On air

It is a good two years since the West German government enacted federal legislation for the abatement of air immissions. An important aspect of the Act was the creation of uniform legislation for the whole of the country. As in the U.S., tax incentives for investing in pollution abatement are evident. The willingness to sink capital in pollution abatement schemes would be considerably stimulated if the central and regional German governments would offer suitable inducements in the form of tax concessions and better facilities for writing off the investment. In the course of time, hopefully, the discrepancies between theory and practice will disappear.

Meanwhile, in actual practice, it has been proved that some of the maximum permissible emission concentrations in the Clean Air Code, for example, with respect to fluorides, and for fuel oils of certain compositions, cannot be maintained. Another example is the desulfurization of exit gases from large power plants, another of the requirements that could be done only at prohibitive costs.

In actuality, the basic Clean Air Act has fallen short of expectations and has not come up to the mark. The organizational setup providing for the appointment of a single inspector to check the emissions of a large variety of plants is by no means satisfactory. The penalties embodied in the Act of fines ranging from DM 50 000 to DM 100 000 ($21 000–$42 000) and imprisonment for periods up to 5 years can have the desired effect only if the law is seriously and generally enforced and the real culprits penalized.

But neither can the cost aspects of air pollution control be ignored, especially in time of recession. Nobody has anything to gain from non-polluting manufacturing methods if the products cost so much that there is no longer a market for them. Nevertheless, a great deal of development work has been done to meet the requirements of the federal act for the abatement of immissions to coordinate theory and practice. Some branches of industry have pointed out that if the immission and emission threshold limit values specified in the Clean Air Cost were strictly applied, many old plants would have to be shut down. This is a familiar plea wherein lie allegedly both truth and threat which no one dares quantify for publication.

In West Germany, suspended solid matter in the air alone amounts to more than 30 million metric tons in the course of a year. Cars and lorries account for 10 million tons of CO yearly. In 1974, the emission of SO_2 from power stations and boiler plants exceeded 4 million tons; another 2 million tons of SO_2 were emitted from industrial operations (compare *ES&T,* February 1976, p 124). In 1974, power stations also emitted 2 million tons of NO_x and motor vehicles 1.5 million tons.

In Germany, as elsewhere, the construction of tall stacks for the discharge of exit gases from power plants and factories in many densely populated areas in

Europe by no means affords a completely satisfactory solution to SO_2 immissions (*ES&T,* June 1975, p 522).

Some progress is being made. For example, years ago some 30% of the output of a cement plant was lost as dust. Currently, the dust discharged by one of West Germany's large cement grinding and crushing plants amounts to only 0.015% of production. In the chemical industry, too, the recovery of solvents, dyestuffs, and the like is a prerequisite to profitable production.

On air monitoring

It was noted that continuous air monitoring systems and constant measurements of emission quantities are the sole means of ensuring satisfactory abatement of air pollution. Mobile and stationary measuring equipment, national instrumentation networks, and international coordination of test results are the obvious approach to effective local and general control actions.

On recycling

In West Germany, recovery and reuse of waste have long played a significant role in a number of its manufacturing industries. For example, almost every other ton of steel used in West Germany is obtained from scrap metal and every third ton of paper is produced from repulped stock.

West Germany currently produces nearly 100 million tons of waste annually. Last year, it spent DM 2 500 million ($1.05 billion) on the disposal of household refuse alone. The household and commercial refuse contained 5 million tons of paper, 2.5 million tons of glass, 1.8 million tons of steel, and nearly 1.5 million tons of plastics. The view which emerges is that continued destruction of salvageable commodities would appear to be a suicidal anachronism.

In the past, half of the tonnage of paper consumed in West Germany ended up in the rubbish bin. Paper manufacturers are now in a position to increase the proportion of recycled material—currently about 33%—by more than 10%. The processing of derelict cars and abandoned hulks with the aid of large shredders is another rapidly growing source of scrap metal supply.

In contrast, the reclamation of quality materials from household refuse is still in its infancy, much as it is in the U.S. today. The reclamation of plastics has been practiced on a limited scale; the recovered material is used for landfill as a soil conditioner. The new processes of pyrolysis and hydrolysis warrant attention, as the recycling of plastics would lead to a reduced consumption of petroleum.

On noise

More than 30 million West Germans are exposed to unwanted sounds. The highest priority against noise has been marked to the sphere of traffic noises. It is necessary to apply measures to the vehicles as well as the travel routes for this purpose.

In 1965, 114 workers were awarded compensation for loss of hearing through exposure to industrial noise. In 1971, there were 624, and in 1974 more than 1200. Together with air pollution, noise is the most widely manifest by-product of progress in industrialized countries.

The West German Act for Protection Against Immissions, described as a weapon to fight pollution by particulate matter and noise, was enacted on March 15, 1974. To date, the central and regional authorities responsible for enforcement of the Act still have not produced maximum permissible noise levels for most areas.

Nevertheless, sound insulation and noise control engineers have come up with numerous practical means of reducing noise at the source, including silencers for engines and machinery and sound-resistant enclosures for isolating heavy vibrating systems. Much work has been done and effective measures introduced to control noise, especially in areas exposed to excessive sound levels.

German environmental policies on the books

- **federal law on protection against immissions with its seven decrees**
- **technical guidance to prevention of air pollution**
- **technical guidance to prevention against noise**
- **the law on water-household**
- **the law on soap and other washing mediums**
- **the program on water economy**
- **the law on lead content in gas**
- **the law on garbage removal**
- **the law on oil-discard**

On thermal pollution

At the present time, it is impossible to say when energy consumption will be such that thermal pollution will constitute a harmful factor for the overall climate of the earth. However, it has been estimated that thermal releases to the air and surface waters are about 7 million megawatts (MW) each year. By 1980, they are expected to be 9.5 million MW and by the year 2000, about 25–30 million MW.

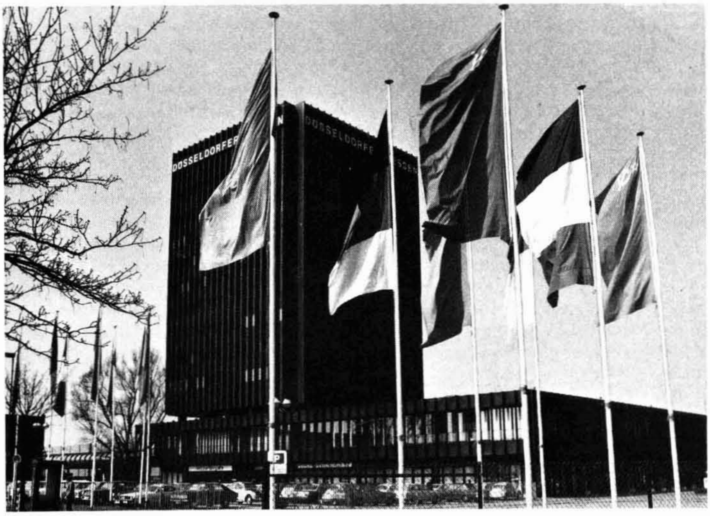
Irrespective of whether the power is generated by oil, coal, gas, or nuclear one must remember that only a given portion of the thermal energy generated can be converted into useful energy. Nuclear plants, with an efficiency of only 35%, dissipate large amounts of heat. With the commissioning of additional water-cooled nuclear power plants to be constructed in the present decade, the cooling capacity of rivers would be seriously exhausted.

The European Convention of the Protection of International Watercourses Against Pollution has recommended a maximum permissible temperature of 28 °C for inland waters. However, this cannot be generally applied since the maximum tolerable for some forms of aquatic life is 25 °C.

To minimize the economic and ecological disadvantage of existing cooling systems in power plants and in manufacturing industries, thoughts are being given to a combination of dry and wet cooling towers. In any case, the capital outlays would be considerable.

It all seems to add up to a big bill. But as Lahrem's reiterates, "broadly speaking the future of the human race depends upon the future of the environment."

SSM



Representation. *Show will draw attendees from more than 14 countries*

FEATURE

Determining TOC in waters

The instrumental method for detecting total organic carbon in water samples is rapid and reliable; yet it has its limitations and for certain applications precautions must be taken

Thomas J. Kehoe

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The acceptance of the instrumental technique to determine the organic content of potable and wastewaters has grown rapidly since its introduction over ten years ago. Van Hall, Safranko and Stenger first described the technique in 1963. Basically, their approach was to inject aqueous samples containing carbonaceous material into a combustion furnace. By virtue of the catalyst present, all carbon-bearing compounds were oxidized to carbon dioxide and swept, by means of a carrier gas, into a non-dispersive infrared analyzer (NDIR) to determine the resulting CO_2 concentration. This technique, and the various modifications that inevitably follow, has been widely discussed in the literature. The American Society for Testing and Materials (ASTM) first published this method in 1967, and the number of applications continue to grow. Some of these applications include:

- monitoring of industrial and municipal waste effluents
- municipal waste treatment plant efficiency studies
- potable water quality
- oil spill detection
- product losses into industrial waste effluents
- organics in boiler condensate
- organic contaminants in inorganic products.

Recently, interest appears to be increasing concerning the lower detection limits of the total organic carbon (TOC) method. Studies comparing TOC, BOD and COD analyses of the same samples are being made and correlations are being attempted. The question of conversion efficiency at the catalytic combustion stage continues to persist.

Detection limits

In the evolutionary cycle of most analytical instruments, the first stage generally concerns itself with the methodology involved and the practicality of the device itself. The instrument must then prove itself better than competing methods. As the instrument gains acceptance, the potential extension of its capabilities becomes a matter of interest.

Most laboratories analyzing potable water supply, treatment and delivery are pushing the TOC method to its outer extremes, requiring it to measure at the ppm or ppb level. This is because the TOC content of most drinking water is relatively low.

Many studies have attempted to establish prevailing TOC levels in rivers, lakes and underground water supplies. Various EPA, state and university laboratories have on-going programs to further identify the specific nature of the organic carbon present by use of GC/MS and other sophisticated analytical methods. These studies are aimed at establishing the prevailing levels of insecticides, herbicides, hydrocarbons from industrial wastes and naturally occurring organic contaminants. Certainly the TOC analysis provides the basic screening measurement to trigger subsequent specific analyses as high-TOC levels are encountered.

In the measurement of industrial and municipal wastes, TOC levels are typically at the 25–100 mg/L organic carbon levels. However, in the measurement of potable waters from lakes, rivers and reservoirs, TOC levels are typically at least ten times *less* than the levels of wastewaters. Table 1 summarizes the TOC levels typically found in potable water supplies.

Nelson and Lysyj also reported on the work of Birge and Juday in 1934 who found that the organic carbon in the waters from 529 lakes ranged from 1.2–28.5 mg/L, with a mean of 7.7 mg/L. Because of the early date of this work, it is assumed that the method of analysis was non-instrumental.

Thus, it becomes obvious that those concerned with the TOC concentration of potable water supplies and, particularly, the treated water prior to distribution must monitor relatively low levels of TOC, typically in the range of 1–5 mg/L. Therefore, the lower limits of detection of the TOC analyzer and the confidence level one can expect at these levels are of prime importance to those involved with potable water processing.

A practical range

Historically, the claims for repeatability of TOC analyzers have been plus or minus 5% in the 0–5 mg/L full-scale range. Usually, this level of sensitivity is more than adequate for most routine monitoring. However, there are some investigators who seek to characterize water supplies or determine treatment process efficiencies, or monitor for possible regulatory control purposes who require further extension of prevailing detectable limits and ranges. It is not uncommon to hear of minimum detectable limits being claimed in the range of 10–50 μg/L, and full-scale ranges of 0–1 mg/L and 0–5 mg/L.

TABLE 1

Typical potable water TOC levels

	Carbon found, mg/L					
Source	**Inorganic**	**Organic**			**Total**	**Reference**
		Min.	**Max.**	**Av**		
Lake Huron	17.7			3.1	20.8	3
Municipal water (unidentified)	7.0			1.6	8.6	3
River water (unidentified)	34.7			11.8	46.5	3
Municipal waters[a]		0.6	1.6	0.9		8
Municipal waters[b]		1.1	7.7	3.2		8
Canadian lake waters		1.5	3.1	2.2		9

[a] Av. of 12 cities located in Ariz., Calif., and N. Mex.

[b] Av. of 20 cities located in Ariz., Calif., Nev., N. Mex. and Ore.

Source: See Van Hall et al., Nelson and Lysyj; and Goulden and Brooksbank references.

However, certain qualifications must be attached to such claims since the success of the TOC analysis is highly dependent upon the skills of the operator, and the performance of the instrument. These qualifications involve the:

- techniques and experience of the analyst
- quality of the "organic-free" water used for glassware and standard preparation
- pre-analysis preparation and treatment of the sample to be analyzed
- quality of the carrier gas in respect to its CO_2 content
- capabilities and condition of the TOC analyzer assigned to the analysis
- sample (and standard) contamination from ambient air CO_2.

For the typical user concerned with the TOC levels of potable water supplies, a practical range of 0–5 mg/L of TOC is a reasonably attainable level of measurement. When necessary, lower ranges of measurement are attainable but only with increased care and experience on the part of the analyst. When one attempts TOC measurements at the 1 mg/L level or less, the quality of the dilution water becomes a critical factor because of its own organic (and inorganic) carbon content. Many investigators have found that the elimination of carbonaceous material to levels below 0.1–0.2 mg/L is most difficult. Such levels seem to persist despite use of deionizers, double distillations and absorbers.

TOC versus BOD and COD

This subject has been widely discussed and is of interest primarily to those concerned with municipal and industrial wastes rather than to those solely concerned with the quality of potable waters. Correlations of these indices also may be of interest to analysts in potable water treatment plants for a variety of reasons. Studies concerning the nature of suspended solids and sediments in lakes and reservoirs, early warning of oil spills and industrial waste contamination at or approaching water plant intakes, and characterizing water-filter-bed sludges are instances where the TOC analyzer offers a rapid method of analysis compared to the other more classical methods.

The EPA Handbook for Monitoring Industrial Wastewater succinctly expresses the relationship of these methods:

"In attempting to correlate BOD or COD of an industrial waste with TOC, one should recognize those factors which might constrain or discredit the correlation. These limitations include:

- A portion of the COD of many industrial wastes is attributed to the dichromate oxidation of ferrous iron, nitrogen, sulfites, sulfides, and other oxygen consuming inorganics; the TOC analysis does not include oxidation of these compounds.
- The BOD and COD tests do not include many organic compounds which are partially or totally resistant to biochemical or dichromate oxidation. However, the organic carbon in these compounds is recovered in the TOC analysis.
- The BOD test is susceptible to variables which include seed acclimation, dilution, temperature, pH and toxic substances. The COD and TOC tests are independent of these variables.

". . . In summary, it is evident that the TOC is a valid indication of biological demand and can be correlated to COD values in many applications. These tests are extremely good control parameters because of the abbreviated analysis time associated with the respective analyzers. It is less probable that TOD, TOC, or COD can be correlated to BOD unless the constituents in the

TABLE 2

Determination of carbon in solutions

Substances	Carbon[a] %	Carbon in standard solutions (mg/L)					
		Calculated	Found (av.)	Calculated	Found (av.)	Calculated	Found (av.)
Acetone	40.75	25.0	23.8	5.0	5.0	1.0	1.5
Alkyl benzene sulfonate	34.20(P)	25.0	24.5	5.0	5.5	1.0	1.0
Benzoic acid	68.80	25.0	23.8	5.0	5.3	1.0	1.5
Cellulose	41.62(P)	24.5	23.4	4.9	5.4	1.0	1.3
Condensed milk	13.80(P)	25.0	22.8	5.0	4.5	1.0	1.0
EDTA	**30.85**	**23.5**	**24.3**	**4.7**	**5.3**	**0.9**	**1.3**
Egg albumin	**45.01(P)**	**21.0**	**19.1**	**5.0**	**5.5**	**1.0**	**1.0**
Ethanol	**52.10**	**25.0**	**25.0**	**5.0**	**5.3**	**1.0**	**1.5**
Garden soil (dried)	**4.74(P)**	**25.0**	**25.5**	**5.0**	**5.6**	**1.0**	**1.5**
Glycine	**32.00**	**25.0**	**24.3**	**5.0**	**5.3**	**1.0**	**1.0**
Hydracrylonitrile	51.04(P)	25.0	26.0	5.0	5.0	1.0	1.0
Lignin	52.51(P)	22.0	22.3	4.4	4.8	0.9	1.0
Malathion	35.90(P)	25.0	25.1	5.0	5.0	1.0	1.1
Methanol	41.30	25.0	26.0	5.0	5.3	1.0	1.3
Phenol	76.60	25.0	24.8	5.0	4.8	1.0	0.8
Pyridine (HCl salt)	**49.51(P)**	**23.9**	**23.8**	**4.8**	**5.0**	**1.0**	**1.3**
Salicylic acid	**61.05(P)**	**25.0**	**24.3**	**5.0**	**5.8**	**1.0**	**1.0**
Settled clay (dried)	**4.67(P)**	**25.0**	**22.0**	**5.0**	**6.9**	**1.0**	**1.8**
Sodiumlauryl sulfate	**14.37(P)**	**25.0**	**22.5**	**5.0**	**4.6**	**1.0**	**1.0**
Sodium oleate	**68.69(P)**	**25.0**	**25.3**	**5.0**	**4.8**	**1.0**	**1.0**
Soluble starch	13.30(P)	25.0	25.8	5.0	5.5	1.0	1.0
Sucrose	42.20	25.0	25.5	5.0	5.5	1.0	1.0
2,4,6-Trichlorophenol	36.50	25.0	24.3	5.0	5.0	1.0	1.3
2,4,5-Trichlorophenoxyacetic acid	37.60(P)	25.0	25.0	5.0	4.9	1.0	1.3
Urea	19.80	25.0	24.8	5.0	4.9	1.0	1.0

Source: Schaffer et al., also see Van Hall et al. references.

[a] Calculated unless marked (P) in which case carbon was determined by Pregl combustion method.

TABLE 3

Determination of carbon in standard solutions

Substance	Carbon found, mg/L				Std. dev. (+)	Av. % recovery
	Calculated[a]	Max.	Min.	Av.		
Benzoic acid	68.8	69.0	67.4	68.2	0.66	99.1
Phenol	76.6	77.2	76.5	76.9	0.30	100.4
Sucrose	104.8	105.1	104.3	104.5	0.40	99.7
Glycine	100.7	101.2	99.5	100.3	0.69	99.6
Pyridine	105.6	104.4	103.6	104.2	0.40	98.7
Urea	100.0	100.9	99.1	99.8	0.86	99.8
Sodium cyanide	122.5	122.1	119.5	120.5	1.11	98.4
Acetanilide	75.4	76.0	75.0	75.4	0.48	100.0
p-Nitroaniline	106.2	105.8	104.9	105.4	0.52	99.2
4-Aminoanipyrine	111.5	110.6	108.9	110.2	0.85	98.8
Sulfanilic acid	89.3	90.5	88.6	89.3	0.90	100.0
Diphenylamine-sulfonate, Ba salt	87.8	87.6	86.8	87.4	0.40	99.5
dl-Methionine	103.0	102.7	101.8	102.5	0.45	99.5
2,4,6-Trichlorophenol	75.4	76.0	74.0	75.0	0.84	99.5
Sodium carbonate	99.5	100.0	99.2	99.4	0.40	99.9
Acetic acid in 20% NaCl	100.0	101.0	99.0	100.0	0.82	100.0
Acetic acid in 20% $CaCl_2$	100.0	100.0	98.1	99.1	0.78	99.1

Source: Van Hall et al. reference.

[a] Carbon determined by the Pregl method. All results based on four determinations.

wastewater remain relatively constant. The conjunctive use of these parameters in terms of BOD, COD, TOD, and TOC ratios can be helpful in properly evaluating the organic nature of a wastewater."

It is of interest to note that the ASTM Committee D-19 on Water officially withdrew the BOD method (D2329-68) in 1971 as an approved method.

Conversion efficiency

Throughout the evolution of the TOC method, questions regarding the conversion efficiency of carbonaceous material to CO_2 continue to arise. Based on the work of various investigators and the accumulated experience of TOC users over the years, it is this writer's opinion that one can assume 100% efficiency for essentially all of the samples, assuming that the sample requiring analysis are potable waters, municipal wastewaters, condensate, and cooling-tower water. The same can be said for most industrial wastes where the organic carbon compounds present come from petroleum refineries, pulp and paper plants, and food processing plants. It is possible that wastes from certain organic chemical processes may contain specific organic compounds that partially resist complete catalytic combustion conversion, although none have yet been reported in the literature to the knowledge of this writer. The work of various investigators concerned with this topic is summarized in Tables 2 and 3.

Probably of more immediate concern to most analysts is the question of potential loss of volatile organic fractions in samples where the inorganic carbon must be eliminated in order to establish the true TOC levels. The two most common techniques to determine the inorganic carbon concentration of a sample involve either the acidification of the sample to pH 2 followed by sparging with a CO_2-free inert gas, or the injection of the sample into a heated column packed with acid-coated quartz chips that decompose the carbonates (and bicarbonates). The CO_2 thus formed is swept into the NDIR analyzer and the inorganic carbon is thus determined.

It has been demonstrated that volatile organic carbon fractions, possibly existing in typical potable or wastewaters, do not convert to CO_2 in the acid-packed column maintained at 150 °C. On the other hand, the acidification/sparging technique may cause a partial loss of volatile organic carbon fractions if such compounds are present at relatively high concentrations, have relatively high-vapor pressures and are sparingly soluble in water. Some investigators, however, found no significant loss of volatile organic material in the heated-packed column from the hundreds of *natural waters* they examined even though their technique involved passing acidified samples through heated-packed columns. They did point out, however, that this lack of volatiles may not prevail in analyzing certain industrial wastes.

The TOC method is a rapid technique that can reliably characterize the organic content of an array of water and waste samples. Although its reliability has been proven, it is necessary to be aware of its limitations so as to be able to apply certain precautions and take special effort.

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Coordinated by LRE

Water management at power plants

The goal is zero pollution discharge, but TDS is a big problem. Here is one way to handle it, and save some liquid cash

Gerald Westbrook and Louis Wirth, Jr.

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Like it or not, the zero discharge concept is becoming a way of life in the steam electric industry. Now zero discharge does not necessarily mean an operating entity cannot produce a waste. But it may mean that a production facility must digest or manage its wastes within the property limits of the facility. With the zero discharge concept, sharp limits are placed on wastes of all kinds.

Regulatory bodies, and the effects of their regulations, are felt in every phase of design, construction, and operation of new facilities. They will ultimately impact heavily on the eventual fate of existing facilities. The result of all this will be higher costs to the consumer.

One very important facet of waste management is that of total dissolved solids (TDS). The many thousands of gallons of water, containing varying amounts of salt, which are generated by washing and regenerating processes, such as blowdown from cooling towers, sluicing of salt-bearing substances, to name a few, present significant problems when zero discharge is mandated. The problem is one of too much water carrying too little salt, but still having a TDS content too great for discharge to a receiving stream.

The electric power industry faces this problem today, especially in the water-short, high-TDS areas of the western U.S. The same problem will eventually extend to the midwest and other areas.

Several processes for concentrating salts or desalting water can address this problem. For example, a relatively new system of brine concentration, using electrodialysis (ED), can reduce the magnitude of the brine disposal problem. ED brine concentration has significant cost advantages when compared to other means of attacking this problem. Also, cooling water salinity, properly analyzed and optimized, will provide for efficient management of the salt disposal problem, while maintaining best possible efficiency of the power generation system under zero discharge conditions.

Side stream processing

Treating cooling tower blowdown for zero discharge requirements is expensive; hence, reducing the volume of blowdown should become a primary objective. One way to accomplish this is through the concept of side stream processing. For example, side stream treatment by lime and soda ash is an effective means of reducing scaling substances, so cooling towers can operate at higher cycles of concentration. However, high levels of TDS in the cooling water will result. This can add to capital and operating cost requirements for several of the basic steam and power generation systems.

Systems that will be affected as cooling water salinity increases include:

- cooling water pumping system
- cooling towers, fans, and drift eliminators
- condensers
- condensate polisher
- steam boiler
- turbine

Of primary importance is the impact of high-sodium content condenser water leakage at high TDS levels on ion-exchange condensate polisher operation, regeneration schedules, and quality of condensate that can be effectively maintained. In addition to problems that these operating abnormalities cause for turbine and once-through steam generators, additional wastes are generated because of more frequent regeneration of the ion-exchange polishers.

As mentioned previously, the side stream softening process is a very effective method of reducing scaling substances such as calcium and silica, thus permitting operation at high cycles of concentration. The one major drawback to this approach, however, it the very high cooling-water salinities that result, and the associated problems that operating at such salinities brings. Nevertheless, the increase in cooling-water salinity that results with use of the side stream softening process can be controlled by adding an appropriate desalting unit or water recovery/brine concentration system. At the same time, valuable water will be recovered, and waste brine would be reduced.

The most important aspect of incorporating a side stream desalting process into a cooling tower circuit is the process' ability to allow the salinity of this water to become an independent variable. A key question then becomes: "What is the optimum salinity of this recirculating cooling water?" An answer to that question, which considers capital requirements, would be in order.

Although higher cooling-circuit salinities will lead to significantly higher capital and operating costs for several key steam and power systems, the opposite is true for water recovery/brine concentration (WR/BC) systems. The reason is that in zero discharge plants, the higher the initial feed concentration to the WR/BC system, the lower the ultimate volume of water that must be finally evaporated, treated, or processed. Thus, with an evaporative cooling tower in the system, it is desirable to use this evaporator to preconcentrate the cooling system's recirculating water to a sufficiently high level to make economic sense.

The general nature of the system proposed is illustrated in Figure 1. The total system would consist of:

- chemical softening
- filtration
- water recovery/brine concentration desalting
- brine disposal

FIGURE 1

Side stream process

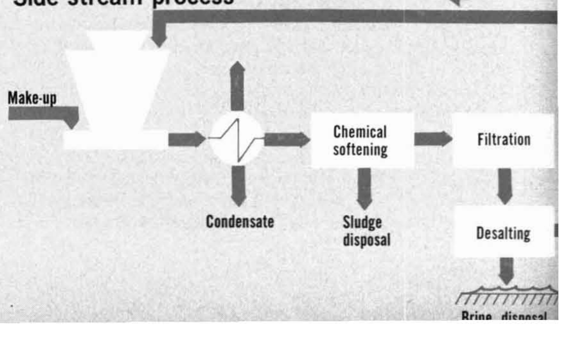
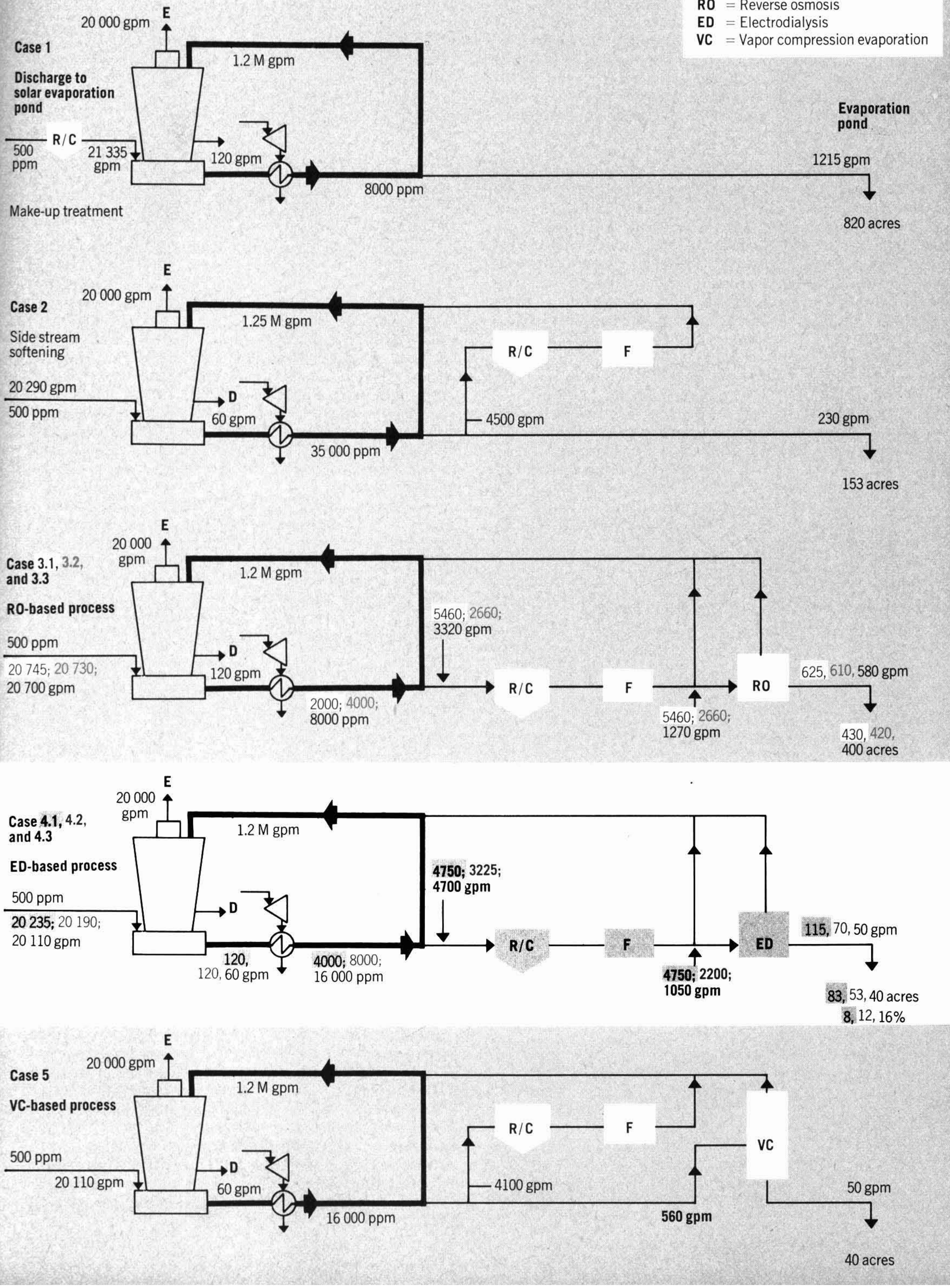


FIGURE 2

Alternative water reuse/brine concentration processes

Key

R/C = Reactor/clarifier
F = Filter
E = Evaporation loss
D = Drift loss
RO = Reverse osmosis
ED = Electrodialysis
VC = Vapor compression evaporation



Three types of desalting processes are considered for the WR/BC system: reverse osmosis (RO), electrodialysis (ED), and vapor compression evaporation (VC). These three processes would operate on a side stream from the main cooling circuit.

Chemical softening

Almost all schemes for zero discharge include the use of side stream processing with warm lime or lime-soda treatment. With either RO or ED it is first necessary to treat the blowdown water by lime soda or other suitable treatment. This treatment will provide for calcium, silica, and suspended solids control in the water returned to the circulating water. In fact in many cases it will eliminate the need for lime-soda treatment of the cooling tower makeup water. A much smaller stream of more concentrated, warm water taken from the circulating water return line will be softened by a high-density sludge unit.

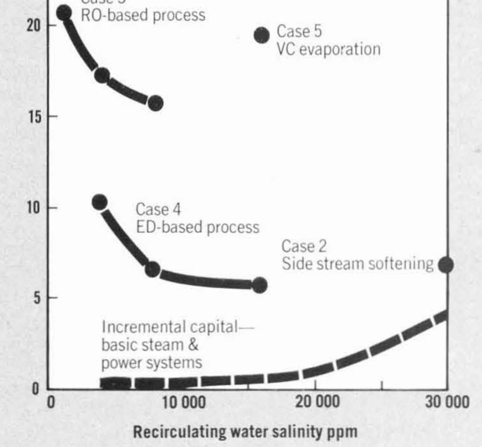
Side stream filtration by itself can be of major utility on cooling tower circuits. At an Electric Power Research Institute (EPRI) seminar, D. E. Noll said, "Dirt is the greatest enemy of recirculating cooling systems . . . the presence of dirt makes corrosion control very difficult." The same can undoubtedly be said about scale control. And at the 34th International Water Conference (October 1973), G. J. Crits noted, "As the cycles increase above five concentrations, the dirt injected by the air becomes an important limitation." Data from his work show that although 80% of these solids would settle out in the tower basin, additional removal would be desirable.

Side stream desalting

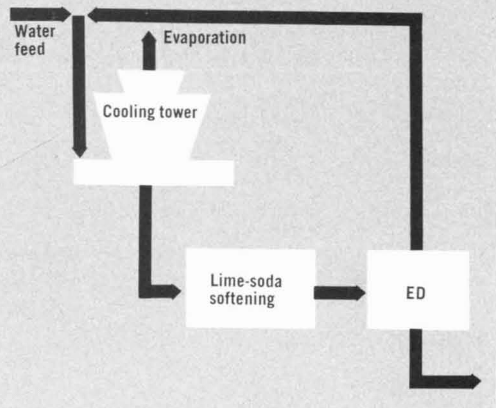
For side stream desalting, here is what RO-based process can do: As TDS mounts, RO gradually becomes a less effective brine concentrator in the sense of its ability to concentrate the recirculating water further. With today's RO technology, the maximum feed water salinity likely is below 8000 ppm, and maximum brine concentration would be roughly double that level. As RO technology is developed for desalting seawater, however, its range of application should increase.

FIGURE 3

Preliminary estimate—optimum salinity



Cooling tower operation—side stream desalting



With the ED-based process, the pretreated blowdown water can be concentrated 10 times or more within the ED system; desalted water is recovered and recycled back to the tower at one-half the original TDS concentration. To accomplish this, a volume of water is pretreated, filtered and passed through the ED system. Because of recirculation, it is possible to concentrate the salts into a small stream, while allowing for recovery back to the tower of about 90% of the water removed at one-half concentration of TDS.

In the case of the VC evaporation-based process, an evaporator is the most expensive WR/BC system to buy and operate, but is a highly effective means of handling the problem of brine concentration. In large installations, one evaporator of selected size may accomplish much of the work normally done by the makeup demineralizer. At the same time, the salts present in cooling tower blowdown are concentrated to high levels. But beyond this single unit, other means of concentrating brine would be more economical.

Detailed design studies and cost estimates for several alternative water reuse/brine concentration processes have also been completed. Five different technologies have been studied, as indicated in Figure 2. The side stream softeners are sized to provide the necessary calcium and silica bleed. The desalters are sized to provide the necessary salt bleed for the salinities indicated.

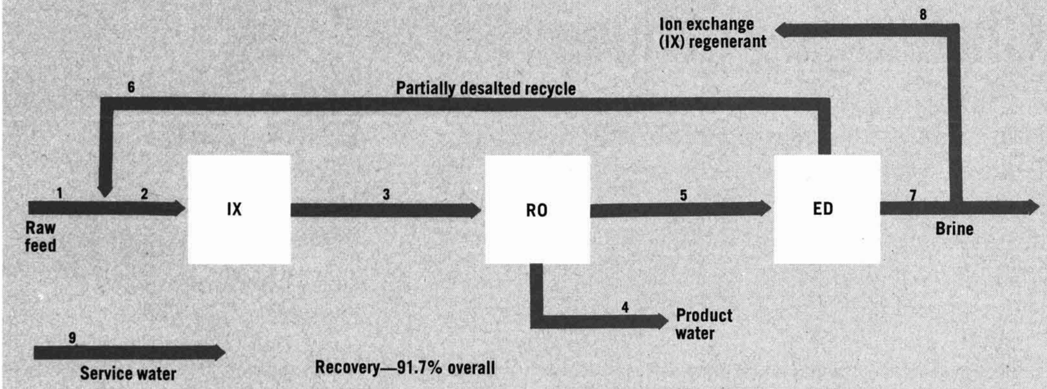
The estimated capital costs are plotted in Figure 3 as a function of recirculating water salinity. The side stream process design utilizing electrodialysis results in the lowest capital costs for the conditions specified. The cost of solar evaporation ponds, where they can be used, is the determining factor. While of necessity of a preliminary nature, and clearly not incorporating operating costs, the optimization presented in Figure 3 is believed to be of sufficient accuracy to indicate the optimum salinity range to be 10 000–16 000 ppm.

Water management considerations

With regard to management of wastewater from zero discharge plants, it is a natural and historical practice to utilize the inherent evaporator capability of the cooling tower to take the cooling waters to as high a salinity as can be achieved, in order to minimize the costs of any further concentration required. However, as the salinity of the cooling water increases, the capital, operating, and maintenance costs for several key steam-electric plant subsystems also increase. While the individual increases are not big, in total, they can add up to a substantial amount.

Hence, an optimum level for cooling water salinity exists. This

RO/ED high-recovery plant, Roswell, New Mexico



	Operating data								
	1	2	3	4	5	6	7	8	9
Flow mg/L	14.9	36.3	36.3	14.5	21.8	21.4	0.4	0.24	0.9
Na^+	1035	2060	2206	184	3550	2690	49 500	49 500	
Ca^{++}	217	102	22	2	35	25	600	600	
Mg^{++}	63	35	7	—	10	10	151	151	
Cl^-	1560	2310	2310	248	3680	2580	62 500	62 500	
SO_4^{--}	548	1500	1500	51	2465	2095	22 200	22 200	
HCO_3^-	217	98	98	6	160	160	40	40	
TDS mg/L	3640	6105	6143	491	9900	7560	134 991	134 991	

optimum will vary between types of plants, plant configuration, feed water salinity, and ultimate brine disposal method. The results from an initial evaluation of one situation indicates the optimum salinity region to be in the range of 10 000–16 000 ppm.

The process combining side stream softening plus electrodialysis had the lowest overall capital requirements for the cases studied. If the comparison were made on overall annual operating costs, it is expected that the same results would occur. In addition to lowest capital requirements, this design has attractive process features including:

- a smaller, more stable, and more easily operated chemical softening unit, with the use of warm, concentrated, circulating water rather than cold raw makeup water
- far better suspended solids removal, not only for precipitated solids but also for solids introduced to the system from the air
- less severe corrosion environment, owing to salinity and suspended solids reduction
- removal of the maximum point of gypsum scaling tendency from the condenser to the brine side of the electrodialysis unit
- reduction in capital, operating, and maintenance expenses for several key steam and power plant subsystems that would be adversely affected by operation at high salt levels; pounds/day of salt carried out in the drift would also be reduced.

While unlikely to pay for the total capital outlay for the WR/BC system, these cost reductions could recover a significant percentage. Further, improved system reliability could lead to a potential payoff for this investment. Electrodialysis with side stream softening is thus an excellent combination to operate in the proposed salinity region to achieve the necessary calcium, silica, and overall salt bleed from a cooling system.

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Coordinated by JJ

Challenging effluent limitations

Industry has filed more than 200 suits against EPA's effluent guidelines and another 90 cases have contested new source and pretreatment standards, as of July 1976

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Washington, D.C. 20036

Since the enactment of the Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500), more than 30 000 National Pollutant Discharge Elimination System (NPDES) permit applications have been filed for permission to discharge industrial wastes into the nation's waterways. NPDES permits incorporate technology-based effluent limitation standards promulgated by EPA and are issued either by the EPA or a state that has been delegated such authority by EPA.

This article will discuss:

- EPA's statutory mandate and the techniques it utilizes to set effluent standards applicable to a variety of industrial point sources
- the legal procedures for challenging EPA determinations
- the technical evidence to support or challenge EPA determinations. A chronological history of the development of the regulations delineating the effluent limitations guidelines for the inorganic chemical manufacturing industry is included to illustrate the EPA decision-making process. These regulations are presently under review by the U.S. Supreme Court.

Since many of EPA's so-called *final* regulations are being reevaluated by the Agency, important opportunities remain to confer with EPA officials and to present additional technical data relative to what limitations, consistent with P.L. 92-500, can be achieved by various industrial point-source categories. Indeed, failure by interested persons to present evidence and comments now regarding the applicable 1977, 1983 and new-source standards may preclude or limit the effectiveness of their right to appeal final regulations promulgated by EPA.

Statutory provisions

P.L. 92-500 distinguishes between existing effluent discharges and those from facilities constructed after the publication of proposed regulations applicable to such facilities. Existing dischargers must achieve effluent limitations by July 1, 1977, which require the application of the "best practicable control technology currently available" (BPCTCA) as defined by EPA. Not later than July 1, 1983, stiffer EPA regulations take effect requiring existing dischargers to apply the "best available technology economically achievable" (BATEA). To implement this mandate, P.L. 92-500 requires EPA to publish regulations providing guidelines for effluent limitations that "identify, in terms of amounts of constituents and chemical, physical and biological characteristics of pollutants, the degree of effluent reduction attainable."

In addition, EPA is required to specify factors to be considered in determining the control practices applicable to point sources within a given category or class of point sources. For BPCTCA 1977 limitations, the factors to be considered are the total cost of application of the technology in relation to the effluent reduction benefits to be achieved from such application; the age of equipment and facilities involved; the processes used; the engineering aspects of the application of various types of control techniques; process changes; nonwater quality environmental impact (including energy requirements); and other factors the Administrator deems appropriate. Similar factors are specified for the BATEA standards, but with additional emphasis on including control technologies within the manufacturing process.

For "new" effluent discharges, the Act requires EPA to establish "standards of performance" reflecting "the greatest degree of effluent reduction . . . achievable through application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants."

Although EPA has not promulgated the effluent limitations guidelines as promptly as the Act requires, it has by now proposed effluent limitations applicable to practically all the major industrial dischargers in the U.S. (see box). Many of the regulations are being revised as a result of litigation.

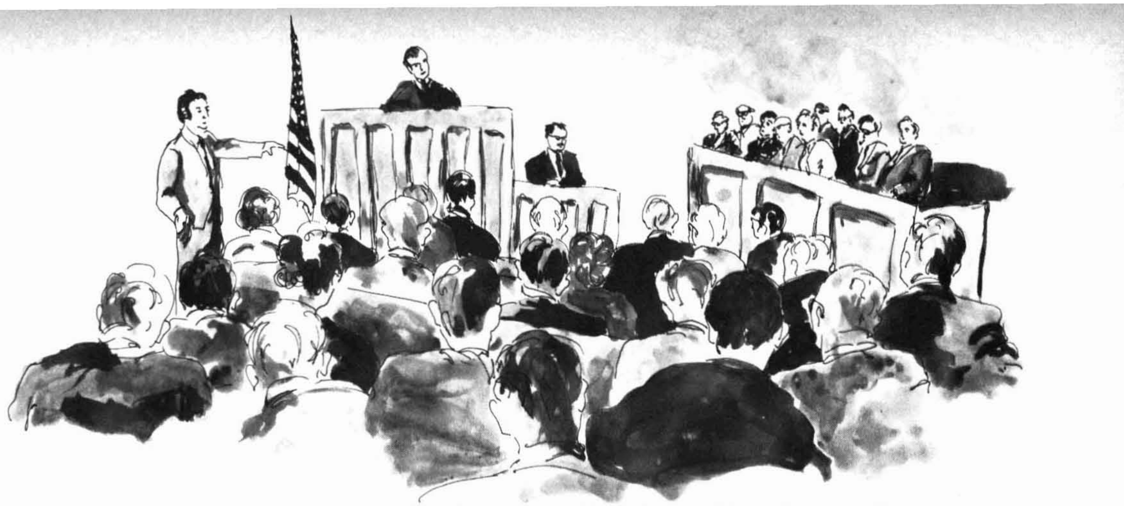
Variances

An existing discharger has several opportunities to present evidence to EPA concerning limitations it could reasonably comply with, as well as evidence showing that it is subject to a number of unusual factors that should allow it to receive special treatment. First, the discharger may present evidence to EPA prior to the promulgation of effluent limitation guidelines applicable to its industrial category. If EPA failed to give appropriate consideration to this evidence, the discharger could seek court review of those regulations.

If final regulations imposed after court review are still too strict for a particular discharger, or if the time for court review has expired, the discharger may seek a variance from the permit issuer. Although P.L. 92-500's legislative history makes clear the need for uniform national limitations to eliminate any incentive a discharger might have to re-locate in another state with more lenient requirements, EPA has come to recognize—at least for the 1977 deadline—that not all dischargers within a given category can reasonably be expected to achieve the established effluent limitations.

EPA, with the approval of several Federal appellate courts, has provided for variances from the industry-wide BPCTCA standards. If a discharger can show that its facility is subject to factors "fundamentally different" from the factors considered in the establishment of the guidelines. Specifically, almost all of the effluent limitation guidelines include the following provision:

"It is, however, possible that data which would affect these limitations have not been available and, as a result these limitations should be adjusted for certain plants in this industry. An individual discharger or other interested person may submit evidence to the Regional Administrator (or the state, if the state has authority to issue NPDES permits) that factors relating to the equipment or facilities involved, the process applied, or other such factors related to such dischargers are fundamentally dif-



ferent from the factors considered in the establishment of the guidelines. On the basis of such evidence or other available information, the Regional Administrator (or the state) will make a written finding that such factors are or are not fundamentally different for that facility compared to those specified in the Development Document. If such fundamentally different factors are found to exist, the Regional Administrator (or the state) *shall* establish for the discharger effluent limitations in the NPDES permit either *more* or *less* stringent than the limitations established herein, to the extent dictated by such fundamentally different factors. . . .'' (emphasis added)

The right to challenge

While this provision offers some relief, many industries contend that it is too narrowly drawn. It allows less stringent limitations only where the requisite fundamentally different factors are not *considered* in the establishment of the guidelines. It should also be noted that, depending on the data presented, this provision could result in the imposition of either *more* or *less* stringent limitations than the generally applicable limitations.

In response to a suit brought by the utilities' steam-electric generating thermal discharge limitations, one Court of Appeals found that the variance provision was unduly restrictive because it allows only technical and engineering factors, not the cost of control measures, to be considered in granting a variance.

If the permit-issuer (either EPA or a state that had adopted a NPDES program approved by EPA) denies the requested variance, the discharger, subsequent to an administrative appeal process within EPA, has the right to seek review of that decision in the U.S. Court of Appeals. The same right of review is available to any interested person and, thus, if a variance had been granted, an individual opposing the variance could seek to have the Court of Appeals overturn the variance grant.

In addition to these established procedures to challenge imposition of EPA's effluent limitations, a pending case before the U.S. Supreme Court may lead to further opportunities to challenge EPA's determinations. This case, *E.I. du Pont de Nemours and Company, et al* v. *Train,* was instituted by 15 of the nation's largest chemical manufacturers who, among other things, argue that P.L. 92-500 does not authorize EPA to set uniform nationwide single-number effluent limitations but rather restricts EPA to establishing "guidelines for effluent limitations" that provide each permit-issuer with a range of numbers from which the permit-issuer could choose the appropriate effluent limitation on a case-by-case basis. The Supreme Court heard oral arguments in this case in December, and a decision should be issued this spring.

With only one exception, all of the Federal appellate courts that have previously ruled on this controversy have upheld EPA's position. In the event the Supreme Court rules for the industry position, permit-issuers will have more flexibility in deciding what effluent limitations should be imposed. Furthermore, the permit-issuer will have an obligation to give more specific consideration to the age of the equipment and facilities involved, the processes employed, the engineering aspects of the application of various types of control techniques involved, process changes, nonwater quality (including energy requirements) and the cost of achieving such effluent reduction in relation to the benefits achieved in the application of the particular control techniques necessary to achieve the effluent limitations imposed for each particular discharger. On the other hand, if the EPA position is upheld, the effluent limitations will be incorporated into discharge permits without any special reference to a plant's individual circumstances, unless a variance is granted.

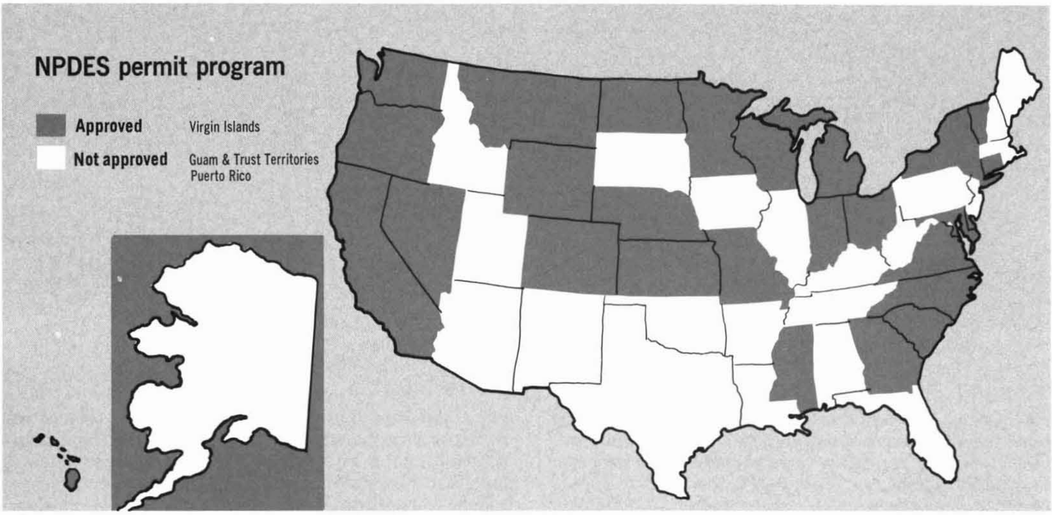
Regardless of the outcome of the Supreme Court's decision, the type of evidentiary showing required by both the regulatory agencies who may seek to impose the most stringent standards allowed by law, and the permit applicant who may seek to receive the most lenient treatment allowed by law are essentially the same. The major difference is that a discharger probably would have a greater burden of proof imposed upon it in attempting to seek a variance from the single-number effluent limitations established by EPA than it would have in obtaining the least-restrictive effluent limitation allowed if EPA were compelled to establish a range of numbers rather than a single-number limitation.

How EPA sets effluent limitations

In August 1973, approximately ten months after the enactment of the P.L. 92-500, EPA published a notice setting forth its procedures for adopting effluent limitations guidelines. EPA stated that it had initiated technical studies by independent contractors for some 30 separate point-source industrial categories for which regulations would be initially adopted. This was subsequently expanded to a much larger number of categories. Among the industrial categories was the Inorganic Chemicals Manufacturing Category. A review of the manner in which EPA promulgated regulations for this category, which ultimately led to the case presently before the Supreme Court, is illustrative of its procedures for dealing with the other categories as well.

To analyze the inorganic chemical industry, and determine the feasibility of various control technologies, and their economic costs, EPA's first step was to retain an independent contractor—General Technologies Corp. That firm was retained because it was familiar with this point-source category. In June 1973, EPA released General Technologies' *Draft Contractors Report,* setting forth technical wastewater treatment information for 22 separate products in the industry. Copies of the draft report were mailed for comment to interested parties, including other government agencies, industry, and environmental groups. Next, in August 1973, EPA made available an *Economic Analysis of Proposed Effluent Guidelines, Inorganic Chemicals, Alkali and Chlorine Industries (major products).* This report also was prepared for EPA by an independent contractor, under the Agency's supervision.

After reviewing comments from interested parties on these



reports, and upon completing its independent review of the General Technologies' technical report, EPA issued its *Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Major Inorganic Products Segment of the Inorganic Chemicals Manufacturing Point Source Category.* The standards recommended in this document were then incorporated into proposed regulations published on October 11, 1973. EPA then received and reviewed comments on the proposed regulation, and subsequently published final regulations on March 12, 1974.

Several major inorganic chemical manufacturers filed suit attacking these rules in both federal District Courts and the Court of Appeals for the Fourth Circuit. The courts then determined that, under the P.L. 92-500, only the Courts of Appeal have jurisdiction to review EPA's effluent limitations guidelines. Subsequently, in a separate opinion, the U.S. Court of Appeals for the Fourth Circuit upheld EPA's position that it has authority to impose single-number effluent limitations for the inorganic chemicals point-source category as well as other point-source categories. In so ruling, the Court noted with approval that EPA had provided for variances to its requirements for existing sources. In addition, the Court found that since neither the Act nor the regulations contained any variance provision for new sources, the EPA on remand should come forward with "some limited escape mechanism for new sources."

The Supreme Court subsequently agreed to review the Fourth Circuit's decision on the questions of whether the district courts or the court of appeals have jurisdiction for the initial review of EPA's effluent limitations guidelines, and whether EPA may impose a uniform nationwide standard for each industrial category or whether it is limited to establishing guidelines for effluent limitations. The Supreme Court's decision should be issued this spring.

Meanwhile, the Court of Appeals' analysis of the evidence and rationale supplied by EPA in support of its regulations provide substantial insight into the types of evidentiary showings that industrial dischargers will have to make in the future in order to obtain either a variance from effluent limitations standards or a less-restrictive standard.

The evidence required

With respect to the specific subcategory for sodium carbonate, EPA established regulations applicable to existing sources for both the 1977 and 1983 deadlines, specifying the permissible dischargers with reference to both total suspended solids (TSS) and pH. In its brief to the Court of Appeals, EPA admitted that it erred in its TSS requirements and stated that it would not oppose a remand of the suspended solids limitations for consideration of the appropriate flow rate and the projected economic impact on the industry. While EPA did not admit error with respect to its pH requirements, the Court agreed with the industry that the pH requirement should also be remanded. In the Court's words: *"nothing in the (administrative) record sustains the EPA conclusion that neutralization of the inherently alkaline effluent from a sodium carbonate plant is practicable or economically achievable . . . also, the cost of neutralization should be considered along with the cost of removal of suspended solids. On remand, EPA should make clear the technology which it deems available."* (emphasis added)

As to those new source standards requiring no discharge, the Court found that the EPA regulations conflicted with the Agency's own statement that "no technology is available and economically achievable for the elimination of discharge from Solvay plants." Furthermore, the Court noted that the alternatives to discharge from a new Solvay plant, if one is ever built, might have substantial nonwater environmental impacts that the Agency had failed to consider. That is, the alternative technologies on which EPA based its new source standards were found to be neither "available" nor "demonstrated" when nonwater environmental impact is considered. Accordingly, the Court set aside and remanded to the Agency for reconsideration its effluent limitations guidelines and new source performance standards for discharges of pollutants from production of sodium carbonate by the Solvay process. The Court also set aside other portions of specific subcategory regulations that had been challenged including all or part of the regulations for the production of chlorine, hydrochloric acid, sodium dichromate, sodium metal, sodium silicate, sulfuric acid, and titanium dioxide.

In addition, the Court set aside and remanded for reconsideration regulations of general applicability involving "process waste water," "process waste water pollutants," and "catastrophic rainfall." In this regard, the Court referred to EPA's brief which stated that for chlorine the Agency would amend the "process waste water" definition "to make clear it does not extend, in the context of no discharge standards, to unavoidable leaks and spills." The Court also repeated EPA's statement on nitric acid, namely that the Agency was preparing a proposed amendment to its regulations to make clear that "in the case of point sources subject to a no discharge limitation, water which has had only incidental contact with raw materials, intermediate products, finished products, by-products or waste products will not constitute process waste water." Thus, the Court's action in overruling many of EPA's regulations were prompted by the Agency's own admission of the need to revise its standards.

Another fundamental aspect of EPA methodology that the Fourth Circuit considered was EPA's selection and utilization of certain plants as "exemplary" plants for use in establishing the limitations. For example, the Court explained that it doubted the propriety of EPA's use of one company's chemical plant as "exemplary" to support the no-discharge requirements for the production of hydrochloric acid where the evidence showed that this plant had no discharge of pollutants "during normal operation," but it did discharge during "start-up of production runs." The Court found the EPA explanation "not convincing," and ordered the Agency to "clearly articulate" its position on remand.

Relevant data

It is now well established that the administrative record before the courts in water pollution cases is steeped in technological data. Despite an understandable reluctance to engage in discussions of technical data that are unfamiliar to most lawyers and jurists, the courts have nevertheless demonstrated their ability to inquire into complicated calculations and test procedures, and have frequently ordered EPA to reconsider various regulations in light of additional evidence collected by EPA.

In addition to raising legal questions about EPA's statutory authority and its procedures, practically all of the industries involved in litigation have challenged EPA's methodology, alleging, for example, that representative samples of plants were not always being used in formulating the guidelines, and that EPA either miscalculated or ignored the energy and cost factors it was required to consider. In addition, most industries have contended that the technical information and statistics upon which EPA relied were inaccurate, and that the requisite technology is not "available" or "demonstrated." Another common complaint is EPA's failure to account for the wide fluctuations in geography, water flow, processes, materials, plant operations and other characteristics that do not lend themselves to uniform nationwide effluent limitations.

Effluent limitations have been proposed or established for . . .

Asbestos manufacturing
Builders papers and board mills
Canned and preserved fruits and vegetables
Canned and preserved seafood
Carbon black manufacturing
Cement manufacturing
Coal mines and mining
Dairy products
Electroplating
Explosive manufacturing
Feedlots
Ferroally manufacturing
Fertilizer manufacturing
Glass manufacturing
Grain mills
Gum and wood chemicals manufacturing
Hospitals
Ink formulating
Inorganic chemicals
Iron and steel manufacturing
Leather tanning and finishing
Meat products
Mineral mining and processing
Nonferrous metals
Offshore oil and gas extraction
Ore mining and dressing
Organic chemicals
Paint formulating
Paving and roofing materials
Petroleum refining
Phosphate manufacturing
Plastics and synthetics
Pulp and paper and paper board
Rubber processing
Soaps and detergents
Steam electric power generating
Sugar processing
Textiles
Timber products

For example, in reviewing the effluent limitations guidelines for the plastics and synthetics point-source category, the U.S. Court of Appeals for the Fourth Circuit (Md., N.C., S.C., Va., W.Va.) made the following statement and decision about certain TSS limits set by EPA:

"EPA's conclusion is that the results attained in these municipal treatment systems and waste facilities used in the petroleum industry waste treatment operations are transferable to the plastics and synthetics industry since the raw waste loads, especially of the petroleum industry, are similar. The record, however, is devoid of any consideration by EPA of transferability and we are unable to judge the reasonableness of its conclusion. The Agency asks us to rely on its expertise. This Court, however, cannot decide such questions on blind faith. Because the Administrator has failed to establish that the technology necessitated by the new source TSS limits is presently 'available,' the new source standards of performance are remanded to the Agency for further documentation on the transferability of the designated technology. A different standard of 'availability' applies however to the 1983 limitations. They will not be put into effect for another seven years. EPA should, therefore, be given more latitude to make predictions and assumptions as to transferability. Accordingly, the 1983 limitations are not disturbed by this Court . . ."

Other courts have allowed EPA even less flexibility in establishing the 1983 limitations. Thus, in remanding the 1983 regulation of "no discharge" of process waste water for phosphorus manufacturers, the U.S. Court of Appeals for the Second Circuit (Vt., Conn., N.Y.) emphasized EPA's failure to properly consider and discuss whether recycle technology using settling ponds could be feasibly applied to plants in cold climates, and further criticized EPA's failure to take the costs of cold-weather technology into consideration. While recognizing that courts have been reluctant to set aside 1983 effluent limitations that are predicted on technology that is still in the development stage, the Court concluded:

"[b]ut the absence of any practical consideration of costs is unjustifiable, and where the record leaves those who are subject to the 1983 limitations without any suggestions or specifications as to how they may attempt to comply, the 1983 limitations must be vacated. The implementation of plans to control 1983 effluent discharge must be begun now. A record which fails to disclose a reasonable basis for belief that a new technology will be available and economically achievable is deficient."

The portions of the court decisions discussed above are only suggestive of the types of questions that have been raised concerning the validity and reasonableness of EPA's regulations. These questions will continue to surface in other cases, and it will be several years before these controversies are resolved.

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Coordinated by LRE

Aircraft, noise, and land use

Worried local planning authority has no options left
Landowners pay taxes on land they cannot reasonably use
The aircraft noise–urban development conflict is unresolved

The September issue (*ES&T*, September 1976, p 872) carried an interesting article entitled "Cities Spread to Once Remote Airports." The description of problems and circumstances surrounding airport compatibility planning as well as the author's summary of what must be done to address the issue prompts me to relate the following experience in that sphere of planning.

Fairfax County, Va. shares Dulles International Airport, noise and all, with Loudoun County, Va. Consequently, Fairfax planners have faced the issue of airport/aircraft noise and land-use compatibility planning with what seems to be the best available analytical and administrative procedures. The result, despite the hard and costly work involved, has been that the problem of aircraft noise in conflict with urban development does not seem to be nearing resolution.

Some facts

A short history of land-use planning around Dulles would list a report, put forth by citizens, professional planners, developers, and involved local and federal officials, which proposed restricting land uses in the Dulles noise impact area, objective criteria for permitted noise zone development, and a program of complementary zoning to implement a policy of planning for compatible land use. Following the adoption of the report and implementation of its provisions, a consultant was hired to reassess the probable noise impact under what seemed, in 1973, to be probable conditions with regard to future aircraft fleet size, mix, and noise emission characteristics.

Roughly 3900 acres were predicted to fall within the noise exposure forecast (NEF) zone of 30 NEF or greater; Fairfax County proceeded to plan and rezone land accordingly. Industrial and commercial zoning replaced the unsuitable single family and low density residential uses originally planned for the area. The County took these steps with some reluctance, as it was then left with approximately a 150-year supply of land for those uses classed under historical levels of demand.

Meanwhile

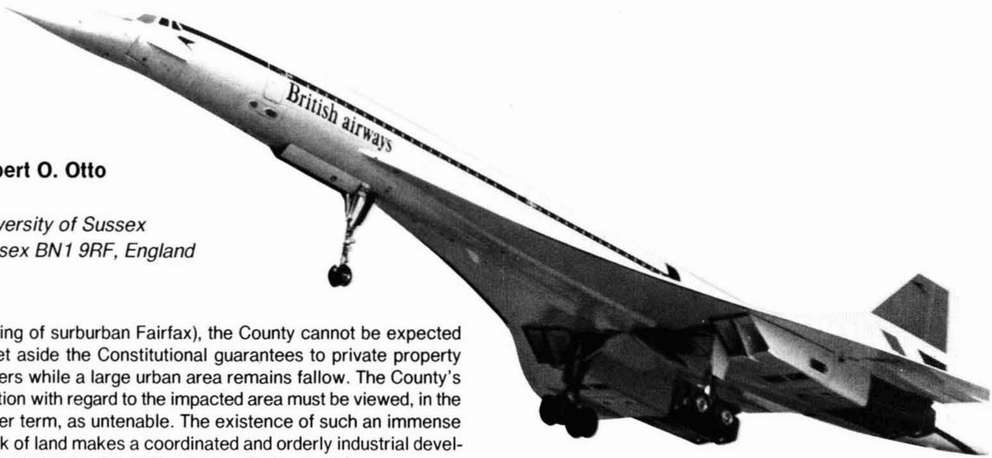
The advent of Concorde SST service to Dulles from London and Paris prompted a review of the noise exposure forecast zone. The County has determined that, in the intervening years, economic, technological, and political factors have effectively thwarted Federal programs of aircraft noise attenuation retrofit, noise impact reducing take-off and landing procedures, and aircraft fleet changeover to newer, less noisy aircraft.

New U.S. Department of Transportation noise exposure forecasts show approximately 8500 acres of Fairfax County are now included in the noise impact zone deemed by the U.S. Department of Housing and Urban Development and the Federal Aviation Agency (FAA) as being generally unsuitable for most residential uses. To date, neither the airport owner (in this case the FAA) nor the aviation regulatory agency (again the FAA) has proposed a remedy for the problem as perceived by the County and area residents and land owners.

New starts

The recent proposal for implementing noise standards within the U.S. air fleet, announced by President Ford on October 21st, 1976, does not appear to address the problem of Dulles Airport noise. It excludes provision of control over international flights—a major use of the airport. The viability of the proposed control program for the domestic fleet must be considered questionable for reasons that include funding and a possible change in policy direction brought about by a change in administration.

While the possibility of an 8500 acre industrial park is not in the future for the entire Metropolitan Washington area (to say



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nothing of surburban Fairfax), the County cannot be expected to set aside the Constitutional guarantees to private property owners while a large urban area remains fallow. The County's position with regard to the impacted area must be viewed, in the longer term, as untenable. The existence of such an immense block of land makes a coordinated and orderly industrial development plan for the Dulles area quite impossible.

The County could attempt to impose its own standards for interior noise levels as a means of addressing part of the noise problem in the impact area. However, it is quite possible that State courts will disallow the initiative until the State of Virginia reluctantly includes such standards in the state-wide mandatory building code, a move it is reluctant to make.

There are other strategies for aircraft noise impact reduction, in use at other world airports, which may be of partial benefit, and deserve consideration in the Dulles context. The strategy used at Ringway Airport, Manchester, England involves a partial rebate of landing fees for "quiet" take-offs and landings. This is contrasted with a Japanese noise abatement strategy which imposes fines for operating emissions exceeding established standards. Further, various individual air carriers have implemented company policies of using noise abatement operating procedures to some effect.

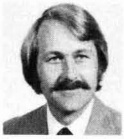
Liaison

Talks with FAA officials, which have run the gamut of urgent pleas for Federal implementation of noise abatement flight procedures to threats of legal action, have been met with the suggestion that action could not be taken at this time. While it is not desirable to oversimplify the situation with regard to Federal control of airport noise, air transport interest groups seem to command an inordinate amount of respect from the FAA, its principal regulator.

So there you have it; a number of impatient landowners who pay taxes on land they cannot reasonably use, a concerned local planning authority with no more options to exercise in the airport compatibility planning game, and a seemingly diffident FAA. Without a serious effort to implement effective emission standards for existing aircraft, and the coupling of this with noise-abating flight patterns, the best land-use planning strategies available will not suffice in the Dulles situation.

Author Major Terino is correct in stating that a "multifaceted, multilevel approach" is required for airport compatibility planning. One facet that must be seen now is the FAA's earnest effort at implementing approach and departure noise abatement strategies and a retrofit of noise abatement materials and equipment on older, noiser aircraft types.

The views expressed in this article are the author's and do not necessarily reflect those of the County of Fairfax, Va.



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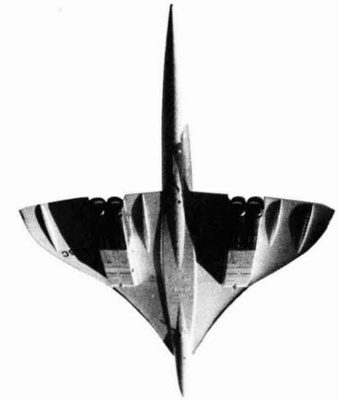
"The addition of the proposed two Concorde daily flights at Dulles would not greatly increase the number of people within either (the NEF 30 or NEF 40 contours), although four additional square miles would be included in the NEF 30 contour and less than one additional square mile in the NEF 40 contour. On the basis of the NEF data, the effect of the proposed Concorde operations at Dulles will be hardly perceptible."



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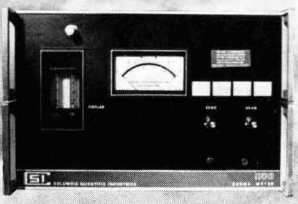

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CURRENT RESEARCH

Photochemical Ozone Formation in Cyclohexene–Nitrogen Dioxide–Air Mixtures

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■ Experiments were performed investigating the formation of ozone in cyclohexene–nitrogen dioxide–air mixtures flowing inside a 9-m long and 15-cm i.d. Pyrex tube irradiated by ultraviolet fluorescent lamps. The ozone concentration along the tunnel was measured with the initial cyclohexene concentration varying from 0.5 to 50 ppm and the initial nitrogen dioxide concentration from 0.6 to 10 ppm. Measurements were made at relative humidities of 50 and 100%; the relative humidity did not affect the ozone formation in the mixture. The data obtained were compared with data reported by previous investigators, and on the basis of the present and existing data, expressions were developed for predicting the maximum possible ozone concentration in different types of hydrocarbon–nitrogen dioxide–air mixtures.

Ozone is formed when a mixture of air, nitrogen oxides, and certain types of hydrocarbons is irradiated by sunlight. However, the mechanism by which ozone is produced in photochemical reactions is not yet clearly understood, and the influence of many important parameters on the amount of ozone generated is not yet well established. The objective of this investigation was to study the effects of mixture composition and relative humidity on ozone formation in different hydrocarbon–nitrogen dioxide–air mixtures. To this end, the amounts of ozone formed in irradiated mixtures of cyclohexene, nitrogen dioxide, and air were measured under a wide range of experimental conditions. The results were then extended to other types of hydrocarbons by combining the present data with data reported by previous investigators.

Experimental Apparatus

The experiment was performed in a flow-type apparatus which consisted of the test section, the gas supply system, and the measuring instruments (Figure 1).

The test section had three major components: the irradiation tunnel, the gas mixing chamber, and the lighting system. The photochemical reactions were generated in the irradiation tunnel made from six 1.52-m long, 15.2-cm i.d. Pyrex tubes joined together and arranged horizontally in a straight line. Two openings were made in the wall of each tube on top of the tubes for inserting the sampling probes. The first opening was 25 cm from the entrance of the tunnel. The distance between any two successive openings was 76 cm.

The sampling probes were 26 gauge (0.02 cm i.d. and 1.27 cm long) hypodermic needles connected to 9-cm long and 0.48-cm i.d. syringes (Figure 2). The syringes were mounted in ground glass joints welded to the tunnel. The needles were vertical with their openings about 4 cm deep inside the tunnel. The plungers inside the syringes were removed, and one end of a 60-cm long, 0.376-cm i.d. polyethylene intramedic tubing was inserted into each syringe. The other end of the tubing was connected directly to the ozone analyzer. The flow rate through the sampling probe was about 6 cm^3 s^{-1}. This is only ~13% of the flow rate in the tunnel which was 46 cm^3 s^{-1} (see below). For the 6 cm^3 s^{-1} sampling flow rate, the residence time in the sampling tube was 2 ms. During this period only a negligible amount of ozone (~0.1%) is expected to be lost in the sampling tube due to dark reaction of ozone and nitric oxide.

The mixing chamber, made from a 30.4-cm long, 15.2-cm i.d. stainless steel tube, was connected to the upstream end of the irradiation tunnel. The open end of the chamber was covered by a stainless steel plate connected to the gas supply

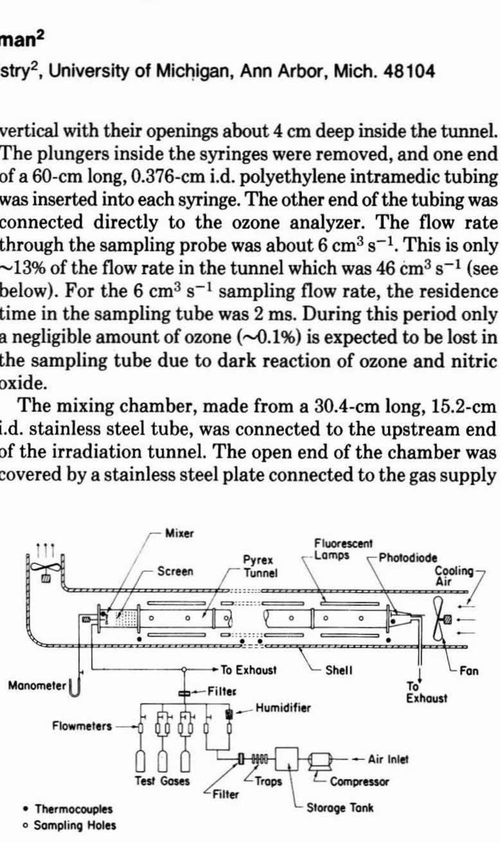

Figure 1. Schematic of experimental apparatus

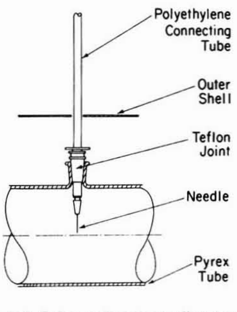

Figure 2. Schematic of sampling probe

line and a mercury manometer. The gas–air mixture inside the chamber was stirred by a fan. Six screens, made of 0.08-cm thick perforated stainless steel plates and serving as flow straighteners, were placed downstream of the fan.

The downstream end of the tunnel was connected to an exhaust vent. The temperature of the mixture was measured by thermocouples both near the exhaust vent and in the mixing chamber.

The ultraviolet radiation was produced by 48 F40BL (General Electric) fluorescent lamps arranged in six clusters along the tunnel. Each cluster contained eight lamps placed around the tunnel symmetrically on a 31.7-cm diameter circle. The lamps in each cluster were mounted on two semicircular metal shells covered on the inside with aluminum foil. To minimize the temperature rise of the gas–air mixture inside the tunnel, room air was blown through the annulus between the irradiation tunnel and the shell in the direction opposite to the flow inside the tunnel. The temperature of the cooling air was monitored by thermocouples placed inside the annulus. The maximum temperature rise of the cooling air was 7 °C. The temperature rise of the gas–air mixture in the tunnel (i.e., the temperature difference between the gas–air mixture in the mixing chamber and at the exhaust port) was always less than 4 °C.

The air used in the experiments was supplied from an air-conditioned room kept at constant temperature (20 °C) and constant relative humidity (75%). The air was compressed by an oil-free, diaphragm-type compressor and then passed through four traps connected in series: 0.45 kg of activated carbon in a Plexiglas container; 1.5-m long, 1.9-cm i.d. tygon tubing filled with anhydrous calcium chloride; 0.45 kg of "indicating" anhydrous calcium sulfate packed in a glass jar; and a Gelman-type A glass fiber filter. After these four stages of purification, the air was branched into two streams. One stream was designated as "dry air", and the other stream passed through a humidifier where it was saturated with water vapor. The two streams were then joined together. The relative humidity of the test air was controlled by adjusting the flow rates of the two streams of air.

The test gases were prediluted with pure dry nitrogen to approximately 200 ppm by the manufacturers. The flow rates of each gas were regulated by stainless steel needle valves and were measured by flow meters. Beyond the flow meters the air and gas lines were joined. The mixture then passed through a Gelman-type A glass fiber filter and entered the mixing chamber. The pressure in the mixing chamber was nearly atmospheric. The pressure drop along the tunnel was less than 0.7 mN m^{-2} so that the pressure throughout the tunnel was practically atmospheric during the tests.

The flow rate in the tunnel was kept at 46 $cm^3\,s^{-1}$. The average velocity corresponding to this flow rate is 0.26 cm s^{-1}, and the Reynolds number is approximately 24. At such low Reynolds numbers the flow was expected to be laminar in the tunnel.

The concentration of ozone in the tunnel was measured by a Thermo Electron Corp. Model 12A chemiluminescent analyzer. The total intensity of the ultraviolet light inside the irradiation tunnel was monitored by a silicon Schottky PIN-5 photodiode inserted about 30 cm deep inside the downstream end of the tunnel. The spectral distribution of the ultraviolet radiation was measured with a CGA/McPherson monochromator and an RCA photomultiplier tube 1P28-A. The outputs of the photodiode and the monochromator were not calibrated and hence did not provide directly the light intensity and the spectral distribution. These measurements were performed only to ascertain that the light intensity and spectral distribution remained constant throughout the tests. A measure of the total light intensity was obtained as described in the next section.

Experimental Procedure

Before the start of the tests the system was "cleaned" as follows. The ultraviolet lamps were turned on, and 50% relative humidity air (without any of the test gases) was fed through the tunnel continuously until the ozone meter reading was practically zero (<0.005 ppm) at every sampling station. This condition was usually reached in four to seven days. The required gas–air mixture was then introduced into the tunnel. After the ozone concentration reached a constant "steady state" value in the entire tunnel, the ozone concentration was measured along the tunnel. The system was not "cleaned" each time the initial concentration of either the nitrogen dioxide or the cyclohexene was changed. Whenever the inlet gas concentration was changed, the ozone concentration was measured after it was ascertained that the ozone concentration had stabilized along the tunnel and did not change with time. Once the system was cleaned, in subsequent experiments in a given series, the results were reproducible when changing the order of tests. This suggests that there was no appreciable effect of contamination from earlier ones.

The composition of the gas–air mixture was not measured in the tunnel. In the subsequent discussions the specified test gas concentration refers to the amount of test gas in the air–gas mixture at the entrance of the tunnel, i.e., before the mixture was exposed to the ultraviolet light. This concentration is denoted by the subscript o.

The dominant reactions at the initial state of the photochemical reactions in a nitrogen dioxide–dry air mixture are

$$NO_2 + h\nu \xrightarrow{k_1} NO + O \qquad (1)$$

$$O + O_2 + M \xrightarrow{k_2} O_3 + M \qquad (2)$$

$$O_3 + NO \xrightarrow{k_3} NO_2 + O_2 \qquad (3)$$

where k_1, k_2, and k_3 are the respective rate constants. The photolysis rate constant of nitrogen dioxide k_1 may be related to the light intensity J_λ by the expression

$$k_1 = \sum_\lambda 2.303\ \phi_\lambda \alpha_\lambda J_\lambda \qquad (4)$$

ϕ_λ is the primary quantum yield of nitrogen dioxide photolysis, and α_λ is the absorption coefficient of nitrogen dioxide. The subscript λ refers to a particular wavelength. The light intensity in a system may be specified either by the total light intensity $J = \Sigma_\lambda J_\lambda$ or by the value k_1. Generally, the light intensity is characterized by k_1, and this practice is followed here. k_1 was determined for the present apparatus in the following manner.

The rate equation for the nitrogen dioxide may be written as

$$\frac{d[NO_2]}{dt} = -k_1[NO_2] + k_3[O_3][NO] \qquad (5)$$

A nitrogen mass balance at any instant gives

$$[NO_2]_o = [NO_2] + [NO] \qquad (6)$$

where $[NO_2]_o$ is the initial nitrogen dioxide concentration (i.e., the concentration supplied to the system). Some time after the start of the photochemical reaction the "photostationary state" is reached at which the concentrations of nitrogen dioxide, nitric oxide, ozone, and atomic oxygen do not change with time:

$$\frac{d[NO_2]}{dt} = \frac{d[O_3]}{dt} = \frac{d[NO]}{dt} = \frac{d[O]}{dt} = 0 \qquad (7)$$

Depending upon the initial nitrogen dioxide concentration, this state was reached in the tunnel in 120–300 s. Equations 5 and 7 yield

$$k_3[O_3]_{pss}[NO]_{pss} = k_1[NO_2]_{pss} \tag{8}$$

The subscript *pss* denotes the photostationary state. For low initial nitrogen dioxide concentrations ($[NO_2]_o$ less than about 1 ppm), $[NO]_{pss}$ may be approximated by $[O_3]_{pss}$

$$[NO]_{pss} \simeq [O_3]_{pss} \tag{9}$$

From Equations 6, 8, and 9, we obtain

$$[O_3]^2_{pss} \simeq \frac{k_1}{k_3}\{[NO_2]_o - [O_3]_{pss}\} \tag{10}$$

In most practical situations $[O_3]_{pss}$ is negligible compared to $[NO_2]_o$ and

$$[O_3]^2_{pss} \simeq \frac{k_1}{k_3}[NO_2]_o \tag{11}$$

According to Equation 10 a plot of $[O_3]^2_{pss}$ against $[NO_2]_o - [O_3]_{pss}$ should result in a straight line, the value of k_1/k_3 being given by the slope of this line. Knowing this slope and the value of k_3, the parameter k_1 can be calculated readily. The value of k_3 has been determined by several investigators, the reported values of k_3 ranging from 0.35 to 1.23 $ppm^{-1}\ s^{-1}$. The value of $k_3 = 0.425\ ppm^{-1}\ s^{-1}$ was adopted here as recommended by Stedman and Niki (*1*).

To construct the $[O_3]^2_{pss}$ vs. $[NO_2]_o - [O_3]_{pss}$ curve, the ozone concentration was measured at different points inside the tunnel using dry air and three different initial nitrogen dioxide concentrations. The results of these measurements are given in Figure 3. The maximum value of the ozone concentration was taken as the photostationary state value since this maximum point satisfies the condition $d[O_3]/dt = 0$ (see Equation 7).

The $[O_3]^2_{pss}$ vs. $[NO_2]_o - [O_3]_{pss}$ curve is shown in Figure 4. The slope of this plot together with $k_3 = 0.425\ ppm^{-1}\ s^{-1}$ gives $k_1 = 0.0063\ s^{-1}$. For comparison, typical values of k_1 for the photodissociation of nitrogen dioxide in the lower atmosphere are presented in Table I. The k_1 values of the present experiment compare well with those which exist in the atmosphere. The k_1 values used in other experimental apparatus vary from 0.00078 to 0.0092 s^{-1}; the present $k_1 = 0.0063\ s^{-1}$ falls in this range.

The foregoing results, as well as all subsequent results, are based on the assumption that the ozone concentration is uniform across the tunnel and that the center line ozone concentration is a fair representation of the amount of ozone at each cross section. To assess the accuracy of this assumption, first, ozone concentrations were measured across the tunnel at several different sampling stations in dry air–NO_2 mixtures. There were no measurable differences in the ozone concentration across the tunnel at any sampling point. Second, the center line ozone concentration as a function of exposure time was determined by measuring the concentration at different sampling stations for a fixed flow rate in the tunnel, and at the same sampling station for different tunnel flow rates. For the same exposure times, both methods gave the same ozone concentration within the accuracy of the tests. These observations support the assumption that the concentration gradients across the tunnel were not appreciable.

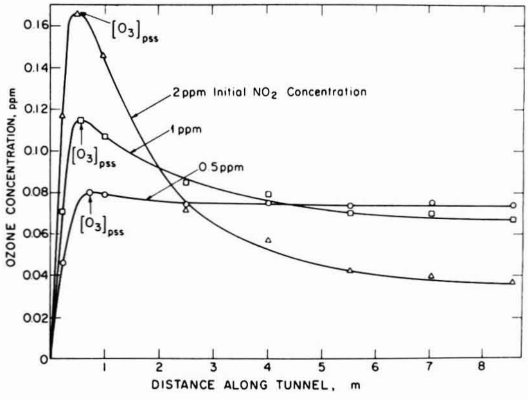

Figure 3. Ozone concentration along tunnel in various nitrogen dioxide–air mixtures

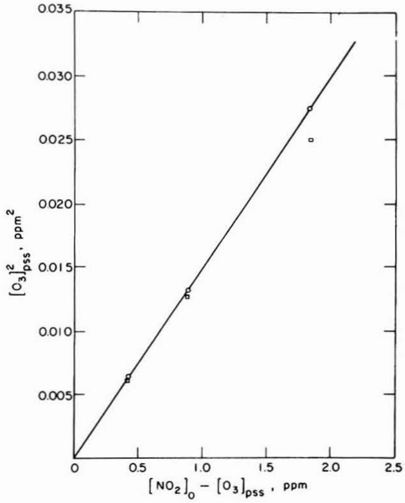

Figure 4. Relationship between photostationary concentration of ozone and initial concentration of nitrogen dioxide
○ Data, — fit to data, □ numerical solution of reaction scheme in Table II

Table I. Rates of Photodissociation of Nitrogen Dioxide in Lower Atmosphere in Wavelength Range 290–430 nm

Solar zenith angle Z, degree	Photodissociation rate[a] $k_1 = \sum_\lambda 2.303\ \phi_\lambda \alpha_\lambda J_\lambda$, s^{-1}
0	0.0095
20	0.0092
40	0.0080
60	0.0056
80	0.0017

[a] Values of ϕ_λ from Table A-II (*3*); values of α_λ from Table 14 (*20*); values of J_λ from Table 8 (*20*).

To evaluate further the performance of the apparatus, the photostationary state concentration of ozone $[O_3]_{pss}$ was calculated along the tunnel from the reaction equations listed in Table II. The calculations were performed numerically using the experimentally determined value of $k_1 = 6.3\ ks^{-1}$. The results of these calculations are also shown in Figure 4. Below an initial NO_2 concentration of about 1 ppm, the measured and the calculated $[O_3]_{pss}$ results agree within 4%. This indicates that the simple model (Equations 1–3) used in deducing k_1 from the data is reasonable at least at low NO_2

Table II. Reactions Used for Calculating Photostationary State Concentration of Ozone

Reaction		Reaction rate constants[a] k
$NO_2 + h\nu \rightarrow NO + O$	(1)	$k_1 = 6.3\ ks^{-1}$
$O + O_2 + M \rightarrow O_3 + M$	(2)	$0.33\ ppm^{-1}\ s^{-1}$
$NO + O_3 \rightarrow NO_2 + O_2$	(3)	$0.425\ ppm^{-1}\ s^{-1}$
$NO_2 + O_3 \rightarrow NO_3 + O_2$	(12)	$1.58\ ppm^{-1}\ ks^{-1}$
$O + NO_2 \rightarrow NO + O_2$	(13)	$108\ ppm^{-1}\ s^{-1}$
$O + NO_2 + M \rightarrow NO + M$	(14)	$33\ ppm^{-1}\ s^{-1}$
$NO_2 + NO_3 \rightarrow N_2O_5$	(15)	$75\ ppm^{-1}\ s^{-1}$
$N_2O_5 \rightarrow NO_2 + NO_3$	(16)	$0.23\ s^{-1}$
$NO + NO_3 \rightarrow 2NO_2$	(17)	$250\ ppm^{-1}\ s^{-1}$
$O + NO + M \rightarrow NO_2 + M$	(18)	$41.7\ ppm^{-1}\ s^{-1}$
$2NO + O_2 \rightarrow 2NO_2$	(19)	$4.67\ ppm^{-1}\ Ms^{-1}$

[a] The values of k_2–k_{19} are from Stedman and Niki (*1*).

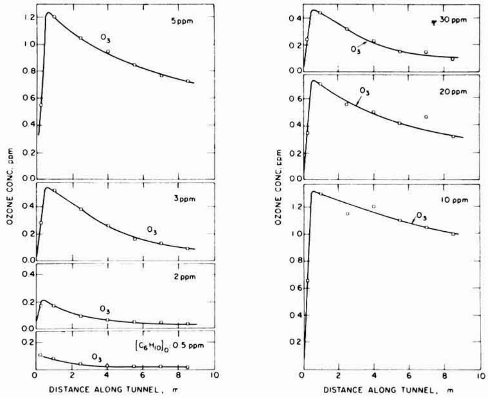

Figure 5. Typical variations of ozone concentration along tunnel in cyclohexene–nitrogen dioxide–air mixtures

Initial nitrogen dioxide concentration: 3 ppm. Relative humidity: 50%

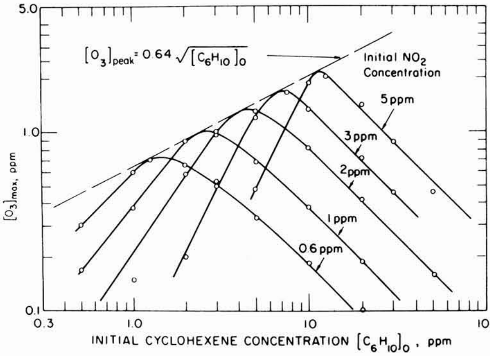

Figure 6. Maximum ozone concentration in cyclohexene–nitrogen dioxide–air mixtures

Relative humidity: 50%. Light intensity $k_1 = 0.0063\ s^{-1}$

concentrations. The agreement between the measured and calculated $[O_3]_{pss}$ values suggests further that photostationary state was approximated in the tests. Further details of the experiment may be found in Shen and Springer (*2*).

Results and Discussion

Photochemical reactions in a cyclohexene–nitrogen dioxide–air mixture depend on several parameters, including the initial concentration of cyclohexene, the initial concentration of nitrogen dioxide, the relative humidity, the ultraviolet light intensity, and the length of time the mixture is irradiated. The major goal of this study was to evaluate the first three of these effects, namely, the influence of the cyclohexene concentration, the nitrogen dioxide concentration, and the relative humidity on the formation of ozone. Therefore, throughout the tests the light intensity was kept constant ($k_1 = 0.0063$ s^{-1}), and the flow rate was maintained at 46 $cm^3\ s^{-1}$. Most of the experiments were first performed at 50% relative humidity. Measurements were also made with other relative humidities, but as will be shown subsequently, the relative humidity did not appear to affect the results.

In the first series of tests, 50% relative humidity was used while the initial concentrations of cyclohexene and nitrogen dioxide were varied in a systematic manner. Five concentrations of cyclohexene (0.5, 1, 2, 3, and 5 ppm) and five concentrations of nitrogen dioxide (0.6, 1, 2, 3, and 5 ppm) were permutated to provide 25 different mixture combinations. A few additional mixture compositions were tested to provide information in certain areas of particular interest. Typical ozone concentrations along the tunnel are illustrated in Figure 5. Although this figure represents only one set of data, similar trends were observed with other initial concentrations of cyclohexene and nitrogen dioxide. For all mixture combinations the ozone concentration along the tunnel first increased, reached a maximum, and then decreased. Qualitative explanations for this behavior were given by Demerjian et al. (*3*) and Niki et al. (*4*). Here we shall not investigate in detail the rate of formation and depletion of ozone along the tunnel but shall be concerned only with the maximum ozone concentration in the tunnel $[O_3]_{max}$. These maximum concentrations were determined by plotting all the data in a manner similar to those shown in Figure 5 and by estimating the maximums from these plots.

The variations of $[O_3]_{max}$ with the initial concentrations of cyclohexene ($[C_6H_{10}]_o$) and nitrogen dioxide ($[NO_2]_o$) are shown in Figures 6 and 7. For a given initial nitrogen dioxide concentration, $[O_3]_{max}$ first increased with increasing cyclohexene concentration. An increase in the cyclohexene concentration beyond a certain value resulted in a decrease in $[O_3]_{max}$ (Figure 6). Similar behavior was observed when the initial cyclohexene concentration was kept constant, and the concentration of nitrogen dioxide was varied (Figure 7). Such an interrelation between $[O_3]_{max}$ and the initial concentrations of the hydrocarbon and the nitrogen oxides has also been noticed by other investigators, and plausible qualitative explanations of these phenomena have been offered by Glasson and Tuesday (*5*) and Seinfeld et al. (*6*). Using similar logic, a brief explanation of these phenomena is given here by referring to the reaction mechanism in Table III. Equation 8 can be rewritten as ($[O_3]_{pss} = [O_3]_{max}$, see Figure 3)

$$[O_3]_{max} = \frac{k_1[NO_2]}{k_3[NO]} \tag{8}$$

From this expression, an initial increase in NO_2 concentration increases $[O_3]_{max}$. The effect of increase in the hydrocarbon concentration is to build up oxidizing radicals which convert NO to NO_2 (Equation 27) without consuming O_3. Thus, an initial increase of hydrocarbon concentration also causes an increase in $[O_3]_{max}$. As the hydrocarbon concentration is increased further, the loss of O_3 via Reaction 26 can no longer be compensated by Reactions 1, 2, and 27. This results in a decrease in $[O_3]_{max}$. In the case of high NO_2 concentrations, $[O_3]_{max}$ also decreases due to the reaction $O + NO_2 \rightarrow O_2 +$

NO. This reaction, however, can be neglected in typical photochemical smog systems (*1*).

The results presented in Figures 6 and 7 apply only to the formation of ozone in cyclohexene–nitrogen dioxide–air mixtures. An attempt is now made to generalize these results to gain additional information regarding ozone production by other types of hydrocarbons. In a reaction described by N reaction equations, $[O_3]_{\max}$ depends on the initial concentration of nitrogen dioxide $[NO_2]_o$, the initial concentration of the hydrocarbon $[HC]_o$, and the rate constants k_i ($i = 1$ to N)

$$[O_3]_{\max} = f([NO_2]_o, [HC]_o, k_1, k_2, \ldots k_N) \tag{29}$$

Equation 29 may be rewritten in a dimensionless form. The dimensionless groups appearing in this expression may be selected arbitrarily as long as all the parameters in Equation 29 are included in the result. Here we rewrite Equation 29 in the following dimensionless form

$$\frac{[O_3]_{\max}}{\sqrt{\frac{k_1}{k_3}[NO_2]_o}} = g\left(\frac{[HC]_o}{[NO_2]_o}, k_1^*, k_2^* \ldots k_{N-1}^*\right) \tag{30}$$

where $k_1^*, k_2^*, \ldots k_{N-1}^*$ represent $N - 1$ dimensionless groups formed from the different rate constants in the mixture. For a hydrocarbon–nitrogen dioxide–air mixture which contains just one type of hydrocarbon, the values of the $k_1, k_2 \ldots$ are constants, and $[O_3]_{\max}/\sqrt{k_1/k_3[NO_2]_o}$ depends only on the ratio of the initial concentrations of the hydrocarbon and the nitrogen dioxide, i.e.,

$$\frac{[O_3]_{\max}}{\sqrt{\frac{k_1}{k_3}[NO_2]_o}} = g\left(\frac{[HC]_o}{[NO_2]_o}\right) \tag{31}$$

The left-hand sides of Equations 30 and 31 were normalized with respect to $[O_3]_{pss} = \sqrt{k_1/k_3[NO_2]_o}$ (Equation 11). By choosing this normalizing factor, we ensure that these equations remain applicable even in the limit when there is no hydrocarbon present in the mixture ($[HC]_o \rightarrow 0$).

We must evaluate now the validity of our choice of dimensionless groups in Equation 31. This can be done by plotting the data on a $[O_3]_{\max}/\sqrt{k_1/k_3[NO_2]_o}$ vs. $[HC]_o/[NO_2]_o$ plot. According to Equation 31, for a given type of hydrocarbon the data points should fall on a common curve on a $[O_3]_{\max}/\sqrt{k_1/k_3[NO_2]_o}$ vs. $[HC]_o/[NO_2]_o$ plot. Such a plot for the present data is given in Figure 8. Within experimental error, the data follow a single curve. This lends support to the validity of Equation 31. It would be desirable to test further the validity of this equation by plotting the data reported by other investigators in a graph similar to Figure 8. This, however, is difficult for the following reasons. In many of the previous experiments, instead of nitrogen dioxide, nitric oxide was used in the initial gas-air mixture; instead of ozone, the amount of "oxidant" was reported; instead of the rate constant k_1, the photodissociation rate of NO_2 k_d was used to characterize the light intensity; the data points are so scattered that it is difficult to ascertain the maximum amount of ozone formed in the tests; and the reported value of the oxidant or ozone concentration may not have been the maximum value.

To overcome the above difficulties and to be able to include here the available results, the following approximations have been made. It was assumed that nitric oxide and nitrogen dioxide produce the same amount of ozone. The reason for this assumption is based on the observation that usually both nitric oxide and nitrogen dioxide result roughly in the same amount of ozone, even though the time required to reach the maximum ozone concentration is different with nitric oxide

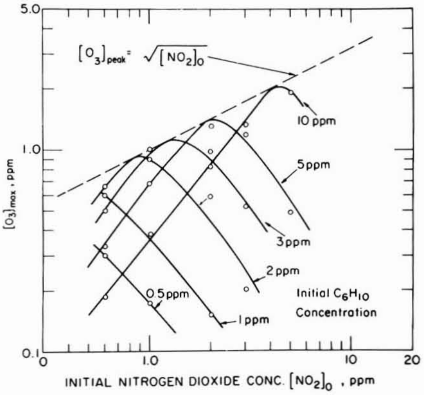

Figure 7. Maximum ozone concentration in cyclohexene–nitrogen dioxide–air mixtures
Relative humidity: 50%. Light intensity $k_1 = 0.0063\ s^{-1}$

Table III. Reaction Mechanism Proposed by Eschenroeder and Martinez (*21*)

$$NO_2 + h\nu \xrightarrow{k_1} NO + O \tag{1}$$

$$O + O_2 + M \xrightarrow{k_2} O_3 + M \tag{2}$$

$$O_3 + NO \xrightarrow{k_3} NO_2 + O_2 \tag{3}$$

$$OH + NO_2 + M \xrightarrow{k_{20}} HNO_3 + M \tag{20}$$

$$NO + NO_2 \xrightarrow[H_2O]{k_{21}} 2HNO_2 \tag{21}$$

$$HNO_2 + h\nu \xrightarrow{k_{22}} OH + NO \tag{22}$$

$$OH + NO + M \xrightarrow{k_{23}} HNO_2 + M \tag{23}$$

$$O + HC \xrightarrow{k_{24}} b_1(RO_2) \tag{24}$$

$$OH + HC \xrightarrow{k_{25}} b_2(RO_2) \tag{25}$$

$$O_3 + HC \xrightarrow{k_{26}} b_3(RO_2) \tag{26}$$

$$RO_2 + NO \xrightarrow{k_{27}} NO_2 + d(OH) \tag{27}$$

$$RO_2 + NO_2 \xrightarrow{k_{28}} c(PAN) \tag{28}$$

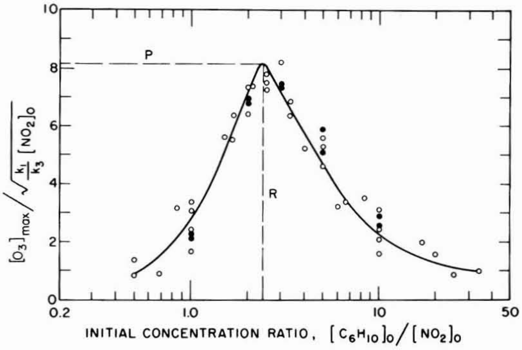

Figure 8. Normalized maximum ozone concentration in cyclohexene–nitrogen dioxide–air mixtures
○ 50% relative humidity, ● 100% relative humidity, — fit to data. Light intensity $k_1 = 0.0063\ s^{-1}$

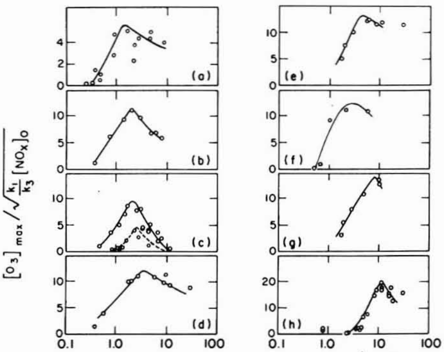

Figure 9. Normalized maximum ozone concentration in hydrocarbon–nitrogen oxide–air mixture

(a) Ethylene (*8*), (b) 3-methylheptane (*9*), (c) *cis*-2-butene (*10*), — $[NO]_o = 0.05$ and 0.125 ppm, - - - $[NO]_o = 0.25$ and 0.50 ppm, (d) propionaldehyde (*11*), (e) acetaldehyde (*11*), (f) propylene (*12*), (g) formaldehyde (*11*), (h) *n*-butane (*13*)

and nitrogen dioxide. It was assumed that the amounts of "oxidants" are the same as the amounts of ozone in the mixture and that the value reported in the literature was the maximum value. Although the oxidant measured includes other chemical compounds besides ozone (e.g., peroxyacyl nitrates), ozone is generally the largest amount (by volume) present in the measured oxidant (*7*). The k_d values reported previously were converted to k_1 using the relationship $k_1 = 0.64\ k_d$ (*1*). "Best fit" curve was drawn through the available data, and an estimate was made of the maximum ozone concentration.

With these approximations the data of Altshuller and Cohen (*8*), Scott (*9*), Stephens and Price (*10*), Kopczynski et al. (*11*), and Altshuller et al. (*12, 13*) could be estimated as shown in Figure 9. From Figure 9, all the data reported by the above investigations collapse onto one curve with one exception. For *cis*-2-butene (Figure 9c) there appear to be two curves, one for initial nitric oxide concentrations of 0.05 and 0.125 ppm and one for initial concentrations of 0.25 and 0.50 ppm. The reason for this is not clear. However, each curve includes data for one high and one low initial nitric oxide concentration suggesting inconsistency in the data.

Note that the limit of $[O_3]_{max}/\sqrt{k_1/k_3[NO_2]_o}$ is unity as $[C_6H_{10}]_o/[NO_2]_o \rightarrow 0$. Thus, the normalized maximum ozone concentrations plotted in Figure 8 cannot be less than unity. In Figure 9 the vertical axis is $[O_3]_{max}/\sqrt{k_1/k_3[NO_x]_o}$, i.e., it is normalized with respect to NO_x (instead of NO_2). Thus, the value of this parameter may be below unity.

The ozone (or oxidant) measurements reported by Altshuller et al. (*14*), Bufalini and Altshuller (*15*), Glasson and Tuesday (*5*), Harton and Bolze (*16*), Rogers (*9*), and Romanovsky et al. (*17*) could not be included in Figure 9 because either there was not enough information given to plot the graph, or the amount of ozone (or oxidant) measured was not specified directly.

We can further test the validity of Equation 31 by observing that, according to Equation 31, for a given type of hydrocarbon and for fixed initial hydrocarbon and nitrogen dioxide concentrations, the ratio $[O_3]_{max}/\sqrt{k_1}$ should be a constant. Consequently, $[O_3]_{max}$ should vary directly with $\sqrt{k_1}$

$$[O_3]_{max} \sim \sqrt{k_1} \qquad (32)$$

or since k_1 is proportional to the light intensity (Equation 4), with the square root of the light intensity. The measurements of Altshuller et al. (*12*), Groblicki and Nebel (*18*), and Harton and Bolze (*16*) confirm this result. The numerical computations of Niki et al. (*4*) for photochemical reactions in a propylene–nitrogen oxide–air mixture also support this conclusion.

$[O_3]_{max}$ is the maximum ozone concentration produced for a given initial concentration of cyclohexene and nitrogen dioxide. However, $[O_3]_{max}$ is not necessarily the highest ozone concentration that can be obtained for a given initial cyclohexene concentration or for a given initial nitrogen dioxide concentration. For each initial cyclohexene concentration there is a "highest" or "peak" ozone concentration $[O_3]_{peak}$ which occurs at a certain initial nitrogen dioxide concentration, as illustrated in Figure 7. Conversely, for each initial nitrogen dioxide concentration there is a "peak" ozone concentration, this peak being reached at a certain initial cyclohexene concentration (Figure 6). For example, for $[C_6H_{10}]_o = 2$ ppm and $[NO_2]_o = 3$ ppm, the maximum ozone concentration $[O_3]_{max}$ is 0.2 ppm (Figure 5). On the other hand, for $[C_6H_{10}]_o = 2$ ppm the highest possible ozone concentration $[O_3]_{peak}$ is 0.9 ppm, and this occurs when $[NO_2]_o \sim 0.8$ ppm (Figure 7), while for $[NO_2]_o = 3$ ppm, $[O_3]_{peak} = 1.7$ ppm at $[C_6H_{10}]_o = 7.2$ ppm (Figure 6).

The peak ozone concentrations ($[O_3]_{peak}$) are represented in Figures 6 and 7 by the envelopes of the $[O_3]_{max}$ vs. $[C_6H_{10}]_o$ and the $[O_3]_{max}$ vs. $[NO_2]_o$ curves (dotted lines in Figures 6 and 7). From Figures 6 and 7, the equations of these curves (envelopes) may be determined and are

$$[O_3]_{peak} = 0.64\sqrt{[C_6H_{10}]_o} \qquad (33)$$

and

$$[O_3]_{peak} = \sqrt{[NO_2]_o} \qquad (34)$$

It would be desirable to be able to predict the peak ozone concentration $[O_3]_{peak}$ for different types of hydrocarbon–nitrogen oxide–air mixtures and the initial concentrations of the hydrocarbon and the nitrogen oxide at which this peak occurs. An estimate can be made of the value of the $[O_3]_{peak}$ and the $[HC]_o/[NO_x]_o$ ratio at which the peak occurs by observing that for cyclohexene as well as for the other hydrocarbons shown in Figure 9, the data normalized with respect to $\sqrt{k_1/k_3[NO_x]_o}$ and $[NO_x]_o$ reduce to a single curve. We denote by P the highest value of the $[O_3]_{max}/\sqrt{k_1/k_3[NO_x]_o}$ vs. the concentration ratio curve, and by R the concentration ratio corresponding to this point P (Figure 8)

$$P = \left(\frac{[O_3]_{max}}{\sqrt{\dfrac{k_1}{k_3}[NO_x]_o}}\right)_{\substack{\text{highest}\\ \text{value}}} \quad \text{when } \frac{[HC]_o}{[NO_x]_o} = R \qquad (35)$$

These equations may be rearranged to yield the highest possible value of the ozone concentration

$$([O_3]_{max})_{highest} = [O_3]_{peak} = P\sqrt{\frac{k_1}{k_3}[NO_x]_o} \qquad (36)$$

$$([O_3]_{max})_{highest} = [O_3]_{peak} = \frac{P}{\sqrt{R}}\sqrt{\frac{k_1}{k_3}[HC]_o} \qquad (37)$$

The above equations provide $[O_3]_{peak}$ for any type of hydrocarbon provided the initial concentrations of the hydrocarbon and the nitrogen oxide as well as the parameters P and R are known. It remains to evaluate P and R. In principle, the values of P and R could be obtained from the appropriate reaction equations (e.g., equations in Table III). In practice, this is a formidable, if not an impossible task owing to the complexity of the equations. The data summarized here, however, provide some information about P and R.

For cyclohexene the present data (Equations 33 and 37) and $\sqrt{k_1/k_3} = 0.122\ ppm^{1/2}$) give the relationship

$$P = 5.3\sqrt{R} \tag{38}$$

To estimate the relationship between P and R for other types of hydrocarbons, P was plotted as a function of R for the nine different hydrocarbons for which values of P and R could be estimated (Figures 8 and 9). The results, given in Figure 10, show that in all cases P varies approximately with the square root of R with the proportionality constant being ~5.3. Therefore, the relationship given by Equation 38 appears to be valid not only for cyclohexene but for other types of hydrocarbons as well. Substituting Equation 38 into Equation 37 and recalling that $k_3 = 0.425$ ppm^{-1} s^{-1}, Equation 37 becomes

$$\frac{[O_3]_{\text{peak}}}{\sqrt{k_1}} = 8.13\sqrt{[\text{HC}]_o} \tag{39}$$

According to this result, the peak ozone concentration depends only on the initial concentration of the hydrocarbon but not on its type, at least for the hydrocarbons investigated thus far.

The peak ozone concentration that can be formed for a given concentration of nitrogen dioxide depends on P (Equation 36). Since it is easier to determine R than P, Equation 36 is rewritten as (see Equations 36 and 38)

$$\frac{[O_3]_{\text{peak}}}{\sqrt{k_1 R}} = 8.13\sqrt{[\text{NO}_x]_o} \tag{40}$$

Therefore, the peak ozone concentration depends both on $[\text{NO}_x]_o$ and on R, the latter being different for different types of hydrocarbons. However, the ratio $[O_3]_{\text{peak}}/\sqrt{k_1R}$ is independent of the type of the hydrocarbon and depends only on the initial concentration of the nitrogen oxide.

Table IV. Reactivities of Different Hydrocarbons ($\hat{k} = k/k_{C_3H_6}$)

Hydrocarbon	Initial concn ratio, R[a]	Reactivity $\hat{k}_{24}$	$\hat{k}_{25}$	$\hat{k}_{26}$[b]	$\hat{k}_{\text{NO}}$[c]
n-Butane	10.5	0.008[d]	0.24[d]	...	0.2[d]
Formaldehyde	8	0.05[d]	0.9[d]	...	0.7[d]
Propylene	5	1.0	1.0	1.0	1.0
Acetaldehyde	4	0.15[d]	0.9[d]	...	0.7[d]
Propionaldehyde	3.5	0.2[d]	1.8[d]	...	2.0[d]
Cyclohexene	2.4	...	...	5.2	1.0[e]
cis-2-Butene	2.1	3.6[f]	...	2.0	2.0[e]
3-Methylheptane	2.0	0.08[f]	...	...	0.27[e]
Ethylene	1.3, 17[g]	0.2[d]	0.1[d]	0.33	0.3[d]

[a] Figures 8 and 9. [b] Table 46 (*20*). [c] k_{NO} is defined as the rate of nitrogen dioxide formation at the instant when the nitrogen dioxide concentration is one-half of its maximum value (*23*). [d] Niki et al. (*4*). [e] Glasson and Tuesday (*19*). [f] Schuck and Stephens (*22*). [g] Glasson and Tuesday (*5*).

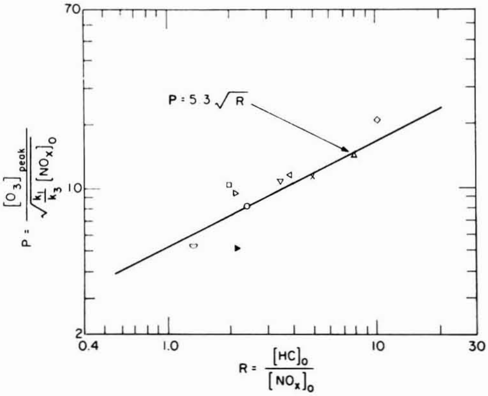

Figure 10. Peak ozone concentration *P* as function of concentration ratio *R* at which *P* occurs

○ Cyclohexene, present study; ▽ ethylene (*8*); □ 3-methylheptane (*9*); ▷ *cis*-2-butene $[\text{NO}]_o$ = 1.05 and 0.125 ppm; ▶ *cis*-2-butene $[\text{NO}]_o$ = 0.25 and 0.50 ppm (*10*); ▽ propionaldehyde (*11*); ◁ acetaldehyde (*11*); x propylene (*12*); △ formaldehyde (*11*); ◇ *n*-butane (*13*)

The foregoing discussion illustrates that to determine the peak ozone concentration produced in a given hydrocarbon–nitrogen oxide–air mixture, the value of either P or R for that hydrocarbon must be known. The values of P and R depend on all the rate constants in a complex manner. An inspection of the reaction equations (Table III) indicates that the rate constants which would most likely influence P and R are k_{24}, k_{25}, and k_{26}. In addition, P and R might also be related to the conversion rate of nitric oxide to nitrogen dioxide, characterized by a rate constant k_{NO} defined in Table IV. An attempt was made to correlate R with each of these rate constants. To facilitate this correlation the suggestion of Glasson and Tuesday (*19*) was followed, and a dimensionless relative rate constant called "reactivity" $\hat{k}$ was defined as

$$\hat{k} = \frac{k}{k_{C_3H_6}} \tag{41}$$

where $k_{C_3H_6}$ is the rate constant of propylene. The results, presented in Table IV, show only weak correlations between R and the reactivities $\hat{k}_{24}$, $\hat{k}_{26}$, and $\hat{k}_{\text{NO}}$, but indicate a strong correlation between R and $\hat{k}_{25}$. From a graph of R vs. $\hat{k}_{25}$ (Figure 11), the following approximate relationship between R and $\hat{k}_{25}$ was obtained

$$R = \frac{5.1}{\sqrt{\hat{k}_{25}}} \tag{42}$$

Thus, knowing the hydroxyl rate constant (k_{25}) for any given hydrocarbon, the value of R can be found from this expression, and this R value may then be used in Equations 39 and 40 to calculate the peak ozone concentration. Note that for ethylene, Figure 9 gives a value of R = 1.3. Glasson and Tuesday (*5*) report R = 5, while from their ozone formation rate data, the value of R = 17 can be estimated.

The foregoing results of the present investigation (but not those of previous investigators) were for a constant relative humidity of 50%. To assess the effect of relative humidity on the ozone formation, data were also taken at 100% relative humidity for the initial cyclohexene concentrations of 1, 2, 3,

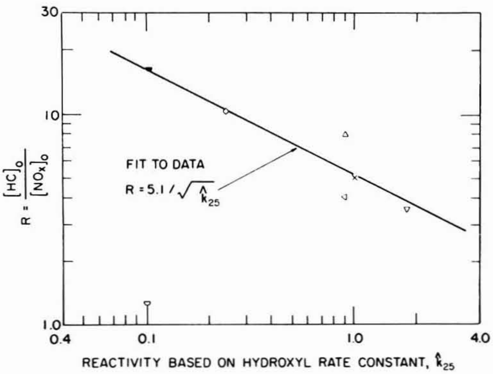

Figure 11. Variation in concentration ratio *R* with reactivity $\hat{k}_{25}$

◇ *n*-Butane (*13*), △ formaldehyde (*11*), x propylene (*12*), ◁ acetaldehyde (*11*), ▽ propionaldehyde (*11*), ▽ ethylene (*8*), ▼ ethylene (*5*)

5, and 10 ppm and nitrogen dioxide concentration of 1 ppm. These results are also shown in Figure 8 and indicate that within the humidity and concentration ranges tested here, the relative humidity does not affect the amount of ozone formed. This is in agreement with the observations of Bufalini and Altshuller (*15*) and Stephens and Price (*10*).

Finally, it is noted that the foregoing results are based on data obtained with reactive hydrocarbons. These results may also be valid for other types of hydrocarbons. However, for nonreactive (slow) hydrocarbons it may be difficult to verify these observations because of the surface effects inherent in smog chamber experiments.

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Characterization of Soluble Organic Matter in Leachate

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■ In this study, membrane ultrafiltration, gel permeation, gas chromatography, and specific organic analyses were used to separate and determine the main classes of soluble organics present in different leachate samples. The largest organic fraction consisted of free volatile fatty acids capable of permeating a 500-MW UF membrane. The next largest fraction was a fulvic-like material with a relatively high carboxyl and aromatic hydroxyl group density. A small percentage of the organics consisted of a high-molecular-weight humic carbohydrate-like complex also characterized by a significant amount of hydrolyzable amino acid.

The identification of general classes of organic matter present in wastewater, surface water, and groundwater is often difficult because of the complex nature of these organics. Investigators have studied several techniques for concentrating, separating, and identifying the different classes (*1–5*). The present study evaluated the applicability of membrane ultrafiltration to the separation of organic matter at high concentrations as found in heavily polluted groundwater samples. These samples, having chemical oxygen demand (COD) values ranging from 81 to 71 680 mg/l., were collected below solid waste fills (*6*). An in-depth knowledge of the organic matter composition of leachate and polluted groundwater is necessary to assess the potential attenuation of contaminants leached from the solid waste and to predict the effectiveness of treatment processes in removing such pollutants. Previous studies show ranges of organic matter concentration similar to those observed in the present study (*7–12*). The results also indicate that free volatile fatty acids can represent as much as 25% (*9*), 40% (*8*), 75% (*10*), 79% (*7*), or 80% (*11*) of the COD, as is also reflected by the high biochemical oxygen demand (BOD) relative to the COD. The present study used membrane ultrafiltration, gel permeation chromatography, and specific organic analyses to determine the composition of the unidentified major organic fractions.

Experimental

The ultrafiltration (UF) membranes used in this study were types UM05, UM2, UM10, and XM100A (Amicon, Lexington, Mass.) with nominal molecular-weight cutoffs of 50, 1000, 10 000, and 100 000, respectively. After ultracentrifugation of 1 l. of leachate at 30 000 rpm for 30 min, the supernatant was concentrated fivefold with a 500-MW UF membrane. The retentate was then desalted by diluting it to twice its initial volume with distilled water followed by reduction to the original volume. This step was then repeated. The percentage retained was calculated from a material balance. Following the ultrafiltration step, separate aliquots of the UF retentate were further separated into components of different molecular weights using Sephadex G-75 (1000–50 000 MW) and G-200 (1000–200 000 MW) columns (Pharmacia, Piscataway, N.J.). After the molecular-weight distribution of the 500-MW UF retentate was established by this method, other ultrafiltration membranes with cutoffs at higher molecular weights were employed to obtain sufficient quantities of each of the fractions of different molecular weights for chemical analyses.

The ultrafiltration membrane fractions and Sephadex fractions were characterized by measuring the total organic carbon (TOC; Beckman 915A TOC Analyzer, Fullerton, Calif.), COD, carbohydrates as dextrose (anthrone test), amino acids as lysine (ninhydrin test after 24 h acid digestion with 6 N HCl), carboxyl groups as acetic acid (hydroxyl amine test), carbonyl groups as acetophone (2,4-dinitrophenylhydrazine test), and aromatic hydroxyl groups as tannic acid (Folin-Denis test), as described by DeWalle and Chian (*13*). Dissolved free amino acids were measured with an automated Technicon TSI amino acid analyzer (Tarrytown, N.Y.). Each membrane fraction was also separated according to its polarity by extraction with two solvents: hexane which separates the less polar lipids, hydrocarbons, and fatty acids from the water phase; and, after pH adjustment of the aqueous layer to 2, with butanol which separates humic substances from the water phase (*3*).

Infrared (IR) spectra of the residues of the hexane and butanol extracts were obtained using a Beckman Model 20A IR spectrometer (Fullerton, Calif.). The free volatile fatty acids were analyzed with a Hewlett-Packard 5750 B gas chromatography (Palo Alto, Calif.) and a column consisting of 20% neopentyl glycol succinate and 2% phosphoric acid on Chromosorb PAW 60-80 mesh.

Results

Membrane Fractionation to Obtain Fractions of Different Molecular Weights. A leachate sample (code UI) obtained from a large experimental lysimeter at the University of Illinois (*6*) was extensively analyzed for organics. The sample, with a TOC of 17 060 mg/l. and a COD of 49 300 mg/l., had a corresponding iron concentration of 2200 mg/l. Since formation of colloidal iron hydroxides would interfere with the membrane separation process, the sample was collected under anaerobic conditions and processed as rapidly as possible through the ultracentrifugation and membrane ultrafiltration steps under a nitrogen atmosphere.

% TOC As	Fraction 1a	Fraction 2a	Fraction 3a
Carbohydrates	26	42	7
Aromatic Hydroxyls	4	2	5
Carbonyl Compounds	5	2	5
Carboxyl Compounds	5	5	6

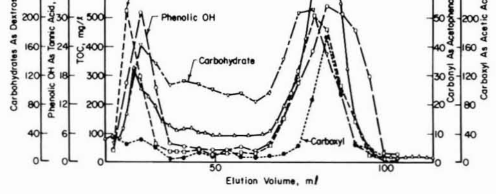

Figure 1. Eluate of 500-MW UF retentate of UI leachate sample separated on Sephadex G-75 column as characterized by total organic carbon, specific organics, and functional groups

Only 104 mg/l. or 0.5% of the volatile residue of 18 403 mg/l. was removed with the ultracentrifuge, indicating that most of the organics were present in the soluble fraction. Subsequent membrane ultrafiltration showed that 27.2% of the initial TOC was retained by the 500-MW UF membrane (Fraction 1b). When the 500-MW UF retentate was applied on a Sephadex G-75 column, the TOC distribution in the eluate showed that 22% of the 500-MW UF retentate, corresponding to 6% of the original TOC, was excluded from the column as it eluted between 20 and 36 ml (Figure 1), indicating a molecular weight greater than approximately 30 000–50 000. The application of the 500-MW UF retentate to a Sephadex G-200 column resulted in essentially the same elution pattern. This fraction, therefore, had a molecular weight considerably greater than 50 000 (*14*). The results in Figure 1 further showed that the majority of the 500-MW UF retentate consisted of organics with a molecular weight less than 1000–3000.

Substantial quantities of the different molecular-weight fractions were thereafter obtained using UF membranes having larger molecular-weight cutoffs. An aliquot of the original 500-MW UF retentate (Fraction 1b) was diluted to its original strength and pH and passed through a 10 000-MW UF membrane. The retentate (Fraction 3b) represented 21.8% of the original TOC. Fraction 3b, after being diluted to its original strength, was passed through a 100 000-MW UF membrane. The membrane retained 11.1% of the original TOC (Fraction 5b). The molecular weights obtained by membrane fractionation were several times higher than those estimated from the gel permeation data.

Specific Organic Analysis of Different Molecular-Weight Fractions. Extensive organic analyses were conducted on the organic fractions obtained from the gel permeation and membrane ultrafiltration steps. Analyses of the specific organics present in the Sephadex fractions showed considerable differences (Figure 1), with high concentrations of carbohydrates (relative to the TOC) observed in the high-molecular-weight fraction and substantial quantities of aromatic hydroxyl and carboxylic compounds present in the low-molecular-weight fraction. Although the TOC data indicated that Fraction 3a was rather homogeneous (Figure 1), the colorimetric tests showed that this was not the case, since the maxima of the different organic compounds did not elute at the same volume.

The relative contribution to the carbon in each molecular-weight fraction was also calculated (Figure 1). In so doing, it was assumed that the carbon in the model compounds used in the colorimetric tests reflected the actual structures and that a certain organic structure did not respond to more than one colorimetric test. A TOC/weight ratio of 0.4 for carbohydrates and carboxyl compounds and a ratio of 0.5 for aromatic hydroxyl and carbonyl compounds were used (*15*).

Organic analyses of the different molecular-weight fractions obtained with the membrane ultrafilters (Figure 2) also showed that the relative carbohydrate content decreases with decreasing molecular weight. These data therefore indicate that the carbohydrates and aromatic hydroxyl groups can be selected as indicators for the presence of high- and low-molecular-weight organics, respectively.

The values obtained from protein tests of the different membrane fractions followed a trend similar to those for carbohydrates in the fractions larger than 10 000 MW. A high content of amino acids was found in the 500-MW permeate, indicating the presence of free amino acids. Analysis of the unhydrolyzed 500-MW UF permeate with a Technicon amino acid analyzer showed, in order of decreasing concentration, the presence of ornithine, lysine, and valine. Dissolved free amino acids are generally detected when nitrogen is not a limiting nutrient source for bacterial growth.

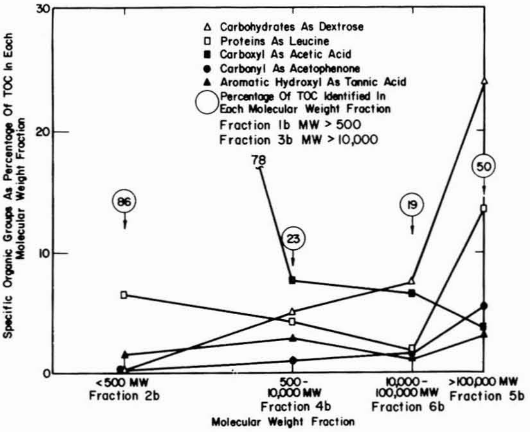

Figure 2. Characterization of different membrane ultrafiltration fractions for specific organics and functional groups

Analyses of the carboxyl compounds showed that the number of organics associated with this group increased in the membrane fractions having lower molecular weights (Figure 2), a result which agrees with those in Figure 1. The retentate of the 10 000-MW UF (Fraction 3b) and the permeate of the 10 000-MW UF (Fraction 4b) were titrated with NaOH. Following acidification with HCl and titration with NaOH, weak inflection points were noted at a pH of 4.3 and 4.37, respectively. A sharper inflection point was noted at 7.2 for both fractions. The density of carboxyl groups was calculated to be 10.1 meq/g C for Fraction 4b and 6.6 meq/g C for Fraction 3b. The corresponding densities as measured with the hydroxylamine test indicated that 8.8 and 5.2%, respectively, of the carbon of each membrane fraction was associated with the carboxyl group. Thus, both the titration and hydroxylamine test resulted in values of the same relative magnitude.

Owing to the presence of the free volatile fatty acids, which pass the 50-MW UF membrane, the highest percentage of carboxyl groups was present in the 500-MW permeate. GC analysis showed the presence of acetic (4370 mg/l.), propionic (1050 mg/l.), isobutyric (570 mg/l.), butyric (5620 mg/l.), isovaleric (1220 mg/l.), valeric (960 mg/l.), and hexanoic (2400 mg/l.) acids. The carbon from these free volatile fatty acids comprised 78% of the TOC of the 500-MW UF permeate or 49% of the initial TOC of the leachate sample.

The organic analyses showed that as much as 86% of the carbon present in the 500-MW UF permeate was identified, while 50% was identified in the 100 000-MW UF retentate. The intermediate fractions were least well characterized, indicating that they consisted of complex molecular structures. Of the total organic content of the sample, 71% was tentatively identified as being associated with specific groups of organics or functional groups.

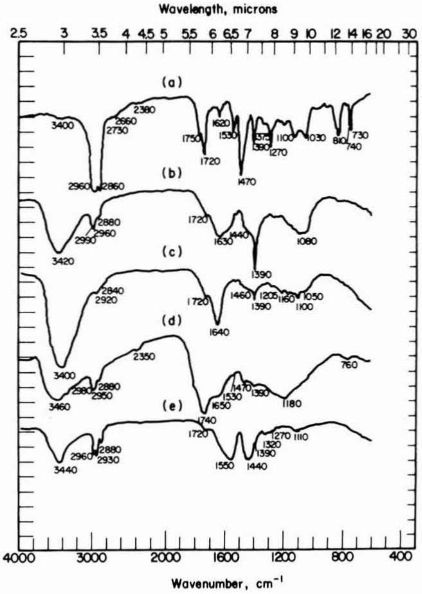

Figure 3. IR spectra of residue of hexane and butanol extracts
(a) Hexane extract of 10 000-MW UF retentate; (b) butanol extract of 10 000-MW UF retentate; (c) butanol extract of hydrolyzed 10 000-MW UF retentate; (d) butanol extract of 500-MW UF retentate; (e) hexane extract of 500-MW UF retentate

Solvent Extraction of Different Molecular-Weight Fractions. The last step in the characterization scheme consisted of hexane and butanol extraction to separate the different membrane UF fractions according to their polarity. The hexane extraction of the high-molecular-weight fraction (10 000-MW UF retentate) represented only 0.5% of the organic carbon, assuming an organic carbon/weight ratio of 0.75 as calculated for palmitic acid (Table I). The IR spectrum of the hexane residue of this fraction (Figure 3a), while showing the presence of impure mixtures, does suggest that this fraction consists primarily of fatty acids, some of which are esterified. If 50% of the weight of the butanol residue consisted of carbon, 3% of the organic carbon in the 10 000-MW UF retentate was comprised of this group (Table I). The residue of the butanol extract had a dark brown, oily appearance and an acidic and "moldy" odor. The IR spectrum was almost identical to a humic carbohydrate-like, high-molecular-weight fraction isolated from the effluent of an activated sludge unit (*5*). Further hydrolysis of the dry residue with HCl and subsequent drying indicated that most carbonyl groups were present as aldehydes and not as carboxyl carbonyls, while some hydrolyzable carbohydrates were also present (*17*).

Colorimetric tests confirmed the presence of carbohydrates

Table I. Effectiveness of Hexane and Butanol Extraction in Removing Organics from Different Molecular-Weight Fractions

Membrane fraction	Hexane extract as percentage of carbon	Extraction of specific organics	Butanol extract as percentage of carbon	Extraction of specific organics
High molecular weight (10 000-MW UF retentate)	0.5	0.8% of carbohydrates extracted with hexane	2.5	4% of carbohydrates and 100% of aromatic hydroxyls extracted with butanol
Intermediate molecular weight (500-MW UF retentate)	0		9	100% of aromatic hydroxyls extracted with butanol
Low molecular weight (500-MW UF permeate)	1.5	0.5% of carbohydrates and 10% of aromatic hydroxyls extracted with hexane	7	65% of aromatic hydroxyls extracted with butanol

and aromatic compounds in the dried solvent extracts. The above extraction results were also confirmed using model compounds. Butanol extraction removed 93% of a 1000-mg/l. tannic acid solution, thus demonstrating its affinity toward aromatic hydroxyl compounds. Only 14% of a bovine albumin solution was extracted, while no removal was observed with a starch solution.

Extraction of the 500-MW UF retentate with hexane resulted in no residue (Table I), indicating that such nonpolar organics are present only in the high-molecular-weight fraction (*18*). The butanol extract, however, represented as much as 9% of the TOC. The IR spectrum (Figure 3d) indicated that compounds in the carboxyl group were present in the highest amounts in this fraction, a result which agrees with those of the hydroxylamine test for carboxyls (Figure 2). Comparison with other IR spectra (*19, 20*) showed that this fraction resembled a fulvic acid.

The IR spectra of the hexane and butanol extracts of the 500-MW UF permeate indicated that the solvents extracted some of the free volatile fatty acids (Table I). Extraction of a 1000-mg/l. mixture of the C_1–C_6 free volatile fatty acids showed that the residue of the dried hexane layer represented only 1.2%, and the residue of the butanol layer 4%, of the initial fatty acid concentration.

Membrane Fractionation and Specific Organic Analyses of Other Samples. The effectiveness of membrane fractionation was also tested on two other leachate samples obtained from a control (a) and recirculation (b) pilot landfill of intermediate age, operated since the fall of 1971 by the City of Santa Rosa, Calif. (*8*). Analysis of the specific organics present in each fraction (Figure 4) showed a trend similar to that observed in Figure 2. The identified organics, however, represented a lower percentage of the organic carbon than in the UI sample. Since the landfill is located in a warmer climate, a larger percentage of the carbohydrates and proteins may have been degraded at the higher temperature. The carboxyl group, on the other hand, was present in relatively large amounts. As it represents one of the most oxidized forms of organic matter, a higher carboxyl group density would indicate a higher degree of oxidation. The greater stabilization of the California samples is further substantiated by the lower BOD/COD ratio, which ranged from 0.62 to 0.65 as compared to 0.80 for the UI sample.

Discussion

The results of the analysis of the organic fractions separated by membrane fractionation and gel permeation chromatography are in agreement with earlier but less comprehensive studies on humic substances in soil or water. Table II shows that significant amounts of carbohydrates and hydrolyzable amino acids are present in the high-molecular-weight fraction, while carboxyl and aromatic hydroxyl groups, color, and fluorescence are contributed by fractions of lower molecular weight (*21–27*). Most of the previous studies used functional-group analysis methods developed by soil scientists (*28*). Many such tests, however, give arbitrary results; the outcome of the carboxyl and aromatic hydroxyl test, for example, is dependent upon the generally unknown spectrum of dissociation constants (*29*). The colorimetric tests selected in the present study for functional group analyses are independent of this factor and may therefore be less arbitrary.

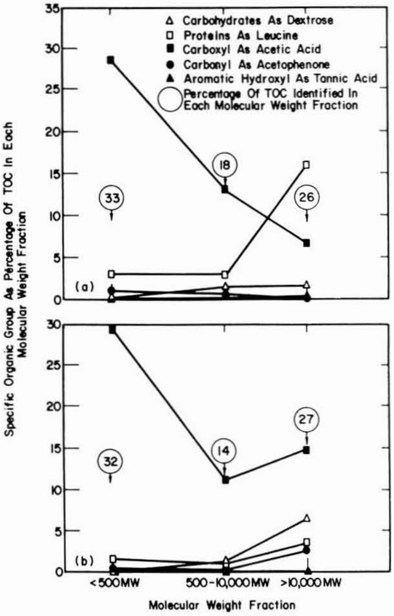

Figure 4. Characterization of different membrane UF fractions in leachate sample collected from control (a) and recirculation (b) landfill in Sonoma County

All of the studies, using samples from widely different environments, indicate a similar distribution of specific organics in the different molecular-weight fractions. This uniformity may indicate that similar bacterial or chemical processes govern the composition of the organics in natural environments. Several of the above studies do indicate that bacterial processes are the most important ones. Based on the identification of individual sugars in soil polysaccharides, Forsyth (*30*), for example, concluded that most were probably derived from microorganisms. The presence of relatively large amounts of hydrolyzable amino acids in the high-molecular-weight fraction may be the result of excreted bacterial amino acids that preferentially attach to this fraction (*31*). The aromatic compounds present in the UF retentates may have been excreted by fungi and bacteria followed by condensation to larger molecules as a result of the increase in the pH of the solution (*32*).

The solvent extraction results show that the hexane residue will slightly overestimate the amount of fatty acids and lipids, since free volatile fatty acids and humic fragments are coextracted. The butanol, used to extract the fulvic acid fraction, may also extract some of the free volatile fatty acids. Lamar and Goerlitz (*33*) found that although humic substances were the main fraction obtained and butanol extraction at acidic pH, up to 10% of the residue consisted of fatty acids. On the other hand, in the present study, butanol did not extract all of the fulvic-like material in the 500-MW UF retentate. DeHaan (*34*) similarly noted that only 50% of the color was extracted with butanol at a pH of 2, while butanol preferentially extracted organics with a high carboxyl, carbonyl, and aromatic hydroxyl content.

Conclusions

In the present study, membrane ultrafiltration, gel permeation chromatography, and specific organic analyses were used to separate and determine the main classes of soluble organics present in different leachate samples. With ultrafiltration a major fraction of the organics permeated a 500-MW membrane, and further analysis showed that most were present as free volatile fatty acids. The next largest fraction was a fulvic-like material with a relatively high carboxyl and aromatic hydroxyl group density. A small percentage of the organics consisted of a high-molecular-weight, humic carbohydrate-like complex, also characterized by a significant amount of hydrolyzable amino acids. Using different model compounds to reflect the actual organics, 75%

Table II. Organic Composition of Fractionated Humic Substances

Author	Origin	Organic fraction	Chemical composition
Dubach et al. (*21*)	Soil fulvic acid	High MW excluded from G-75	21% nitrogenous organics, 25% as carbohydrates
		Low MW included in G-75	9% nitrogenous organics, 5% as carbohydrates Specific absorb. increased with decreasing MW
Leenheer and Malcolm (*22*)	Soil fulvic acid	Neutral charged high MW fraction	43% carbohydrates, 20% nitrogenous organics
		Negative charged low MW fraction	10% carbohydrates, 14% nitrogenous organics contained most of color and carboxyl groups
	Riverwater organics	Neutral charged fraction	5% carbohydrates
Povoledo and Gerletti (*23*)	Lake sediment fulvic acid	Unfractionated	8% carbohydrates 1% hydrolyzable amino acids
		High MW excluded from G-25	Contains half of carbohydrates and proteins
		Low MW included in G-75	Contains most of the color, fluorescence and aromatic hydroxyls
Rashid and King (*24*)	Marine sediment	High MW excluded from G-200	2.4 meq/g (4.0 meq/gC) carboxyl groups 0.3 meq/g aromatic hydroxyl groups 28% nitrogenous organics
		Low MW included in G-50	3.6 meq/g (7.8 meq/gC) carboxyl groups 1.0 meq/g aromatic hydroxyl groups 26% nitrogenous organics
Reuter and Perdue (*25*)	River fulvic acid	High MW excluded from G-50	4.2 meq/g carboxyl groups
		Low MW included in G-50	9.6 meq/g carboxyl groups
Schnitzer and Skinner (*26*)	Soil fulvic acid	High MW excluded from G-50	4.8 meq/g (9.6 meq/gC) carboxyl groups 3.4 meq/g aromatic hydroxyl groups 7% nitrogenous organics
		Low MW excluded from G-10	8.7 meq/g (16.9 meq/gC) carboxyl groups 6.2 meq/g aromatic hydroxyl groups 2% nitrogenous organics C=O and C—OH decreased with decreasing MW
Swift and Posner (*27*)	Soil humic acid	Different Sephadex grades	28% nitrogenous organics in high MW fractions 13% nitrogenous organics in low MW fractions

of organic matter was tentatively identified. Solvent extraction of the different membrane fractions indicated the presence of lipids associated with the high-molecular-weight humic fraction. Butanol preferentially extracted aromatic hydroxyl compounds present in the intermediate-molecular-weight fulvic fraction. The distribution of specific organics in the various molecular-weight fractions showed a high degree of similarity to the results of other studies, indicating that universal bacterial processes may govern the character of naturally occurring organics.

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Impregnated Filter Sampling System for Collection of Volatile Arsenic in the Atmosphere

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An impregnated filter sampling system for the collection of volatile and particulate atmospheric arsenic is described. An aqueous glycerol and polyethylenimine polymer solution is used to impregnate Whatman filters. Laboratory studies show that for volatile arsenic trioxide the total collection efficiency of three impregnated filters in line averages approximately 96% at flow rates from 15 to 23 lpm. The less volatile hydroxy dimethyl arsine oxide is collected more efficiently than the inorganic oxide on both Nuclepore and impregnated Whatman filters. Particle loading on Nuclepore prefilters enhances the adsorption of volatile arsenic on these filters. Ambient measurements of atmospheric arsenic using this sampling system indicate that the major fraction of arsenic is collected on the Nuclepore prefilter and is thus apparently particulate.

The existence of a vapor phase for atmospheric arsenic has been proposed by several authors to explain anomalously high atmospheric particulate concentrations of this element (*1–3*). The high equilibrium vapor pressure of arsenic trioxide (As_4O_6) (*4*) has led to the suggestion that gaseous arsenic is released from high-temperature processes (*2, 5*) and caused concern regarding the efficiency of atmospheric arsenic sampling systems (*6*). Arsenic trioxide is the most volatile arsenic compound stable in air. This substance is weakly acidic and is most soluble in alkaline or organic solutions (*7*). Naturally occurring alkyl arsine oxides have also recently been found in air (*8*) and natural waters (*9*). They may also exist in soil-sediment ecosystems (*10, 11*). Impinger techniques (*6*) and absorption on silver coated glass beads (*8*) have been used for volatile arsenic collection in the atmosphere.

Impregnated filters have been used for ambient hydrogen sulfide (*12*), sulfur dioxide (*13, 14*), hydrogen chloride (*15*), and other inorganic halogen (*16*) gas collection. For certain applications, this collection method has some advantages over impinger techniques, especially with regard to field sampling and the capability to operate at higher flow rates.

Various organic bases have been tested in this laboratory as impregnating reagents for the collection of volatile arsenic trioxide and hydroxy dimethylarsine oxide. Most amines are too volatile and tend to "bleed" from the filters during air sampling. A nonvolatile organic base, a polyethylenimine, was found to perform satisfactorily for the collection of gaseous arsenic species over extended periods of time and still maintain highly basic conditions on the filter. In addition, the required impregnation levels were such that arsenic blanks could be routinely kept at or below 1 ng of arsenic per filter (47 mm diameter). This system could therefore be used for either low or high concentration arsenic sampling.

Experimental

Reagents. Reagents used were as follows: arsenic trioxide and hydroxy dimethylarsine oxide, J. T. Baker Chemical Co., Phillipsburg, N.J.; 1000 ppm (μg/ml) As reference solution, Fisher Scientific Co., Fairlawn, N.J.; PEI-6, polyethylenimine, Dow Chemical Co., Midland, Mich.; and glycerol (spectra grade), Eastman Kodak Co., Rochester, N.Y.

Filter Impregnation. Whatman No. 41 and 43 (Whatman, Inc., Clifton, N.J.) cellulose fiber filters were used for impregnation. Nuclepore polycarbonate filters (Nuclepore Corp., Pleasanton, Calif.) with a 0.4-μm pore size were used as described (not impregnated).

A 10% (v/v) PEI-6 and 10% (v/v) glycerol solution in distilled deionized water was used for impregnation. The Whatman cellulose filters were soaked in this solution for 6 h. Filters were dried by placing them on a Teflon sheet in a laminar flow clean bench. Drying was facilitated by the use of a heat lamp. Filters were stored in sealed polyethylene containers until used.

Apparatus. Bendix (Environmental Science Division, Baltimore, Md.) 47-mm in-line filter holders and a 47-mm open face (Research Appliance Co., Allison Park, Pa.) filter holder were used in various arrangements during the testing of the impregnated filters. The filters were separated in the filter holder by 47-mm nylon screen (100 mesh).

A schematic of a typical laboratory sampling arrangement is shown in Figure 1. Ambient air can be prefiltered through a glass fiber filter (Gelman A, Gelman Instrument Co., Ann Arbor, Mich.) or a Whatman 42 filter before entering the sample stream. Arsenic vapors in the source flask diffuse into the air stream and pass through the sampling train. A Nuclepore filter or a nonimpregnated Whatman filter can be placed in line before the impregnated filters to observe their relative absorption of arsenic vapors or to separate particle and gas collection when ambient air is not prefiltered.

Procedure. Approximately 25 mg of the desired arsenic source was placed in a clean 250-ml filter flask and connected to the sampling train as shown in Figure 1. If no ambient air prefiltering was desired, the top of the filter flask was left open to allow unfiltered air to pass over the source. The depth of the filter flask minimized the entrainment of particulate ar-

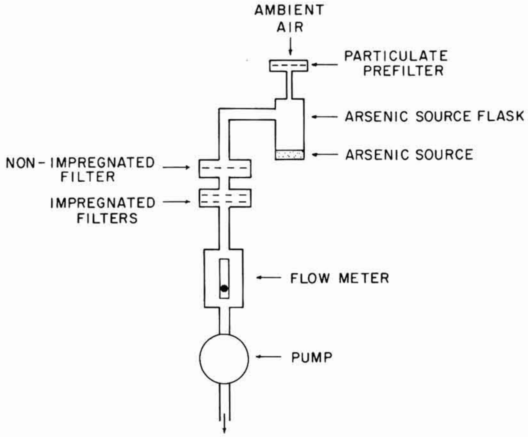

Figure 1. Schematic of typical impregnated filter test apparatus

senic from the source. Tests conducted with a condensation nucleus counter (Environmen/One, Model Rich 100, Schenectady, N.Y.) showed that condensation nuclei levels behind the ambient air prefilter were independent of the arsenic source flask at flow rates less than 16 liters per minute (lpm). Scanning electron microscopic analysis of the Nuclepore filters also confirmed that particles from the arsenic source flask were not being picked up by the airstream at flow rates of less than 16 lpm.

Entrainment of particles from the arsenic source flask was sometimes apparent at flow rates greater than 16 lpm. At these flow rates, double Nuclepore filters were placed in-line before the impregnated filters. With this arrangement of filters, all particles greater than 0.4 μm diameter were excluded from the test filters behind the first Nuclepore filter. Molecular absorption of the arsenic species on Nuclepore and impregnated filters could therefore be studied at the higher flow rates.

It is realized that the terms "molecular" and "vapor" are in fact only operational definitions dependent on the particle filtration efficiency of the Nuclepore filter. In this report a molecular vapor is defined as material passing through a 0.4-μm Nuclepore filter. Recent tests showed that Nuclepore filters with a pore size of 0.6 μm have a collection efficiency of greater than 50% for 0.05-μm diameter particles under filtration face velocities similar to those used in this study *(17)*.

The source flask was kept at room temperature (20 °C) so that the sublimed vapor concentration in the airstream sampled was dependent upon the vapor pressure of the arsenic species at that temperature and the quantity of source used. In general, the vapor concentration, determined by analysis of the collecting filters, was less than 200 ng As/m^3 of air for the conditions described previously. Raising the temperature of the source flask to increase the vapor concentration caused a much higher percentage of the vapors to condense on the Nuclepore filter than observed at room temperature. This effect, caused by a large vapor-filter temperature differential, is not present under most ambient conditions and was therefore avoided by keeping all apparatus and the source at room temperature.

For all samples, at least one Nuclepore filter or nonimpregnated Whatman filter was used as a prefilter in front of either two or three impregnated filters. Filter collection efficiencies were obtained by comparison of the amount of arsenic per filter relative to the total collected. Since only one arsenic source species was used in each test, the total arsenic could be determined from the in-series impregnated filters provided the last filter had no detectable arsenic at the end of the test run. The observation that arsenic levels decreased regularly to zero on the series of impregnated filters indicated that all of the arsenic was being collected.

Time and flow rates were recorded for all collections. Sampling times ranged from 24 to 48 h. After collection the filters were stored separately in acid-washed polyethylene vials for arsenic analysis by neutron activation. The sample holders, nylon spacers, stainless steel screens, and silicone rings were soaked in a very dilute ammonium hydroxide (pH = 8) solution, rinsed with distilled water, and dried in a laminar flow clean bench prior to sample collection. Sample holder filter blanks were routinely taken to ensure that the cleaning procedure eliminated all possible sources of contamination.

Neutron Activation. Samples and standards were irradiated for 6 h at a thermal flux of 4×10^{12} neutrons/cm^2/s in the Rhode Island Nuclear Science Center 2-MW swimming pool reactor. After a 24-h decay period, during which the high background activities of short-lived isotopes, mainly ^{38}Cl, were significantly reduced, each sample was counted for 2000 s on a 60 cm^3 Ge(Li) coaxial detector (resolution of 2.5 keV at the 1.332-MeV γ of ^{60}Co) interfaced to a computer-controlled 4096 multichannel analyzer (PHA-11, Digital Equipment Corp., Maynard, Mass.). Pulse height data were stored on magnetic tape for computer processing. The 0.559-MeV gamma ray of ^{76}As ($t_{1/2}$ = 26.4 h) was used for quantitation. A detection limit of 1 ng of As was readily obtained for these analyses.

Discussion

The collection efficiencies of arsenic trioxide vapors on impregnated cellulose filters are shown in Table I. No significant distinction between the efficiencies of the Whatman 41 and 43 filters was observed, and the data for these filters were therefore combined. Efficiencies did not show any significant variation over the range of flow rates (15–23 lpm) used for normal sampling. The efficiency did increase at the very slow flow rate of 2 lpm. Relative humidity also did not affect the performance of the filters. The glycerol and viscous polyethylenimine provided a moist surface which eliminated any dependence on atmospheric water content. The collection mechanism could tentatively be attributed to a solubilization in the basic reagent followed by a thermodynamically favorable oxidation to the less volatile pentavalent oxide species.

The collection efficiency is apparently most dependent on vapor contact time with the filter. These times range from 5.8 to 0.5 ms for the volumetric flow rates of 2–23 lpm through Whatman 41 and 43 filters of 0.2-mm thickness. Lowering the flow rate increases contact time but at the expense of increasing total sampling time to collect an equivalent volume. This may be quite disadvantageous when the flow rate must be reduced by a factor of 10 to obtain a collection efficiency greater than 80%. Efficiency control is therefore most easily obtained through filter thickness. The alternatives are to use one very thick filter of high efficiency or two or three thinner filters, each having a lower efficiency but having a combined

Table I. Gaseous Arsenic Trioxide Collection Efficiencies on Single Whatman No. 41 or 43 Filters

No. of samples	Flow, lpm[a]	Face velocity, cm/s[a]	Contact time,[a] ms	% Efficiency
3	2	3.5	5.8	85 ± 7
13	15	25.9	0.8	65 ± 6
4	19	32.9	0.6	65 ± 2
7	22	38.1	0.5	62 ± 8

[a] Flow data for the Whatman No. 41 or 43 filter, 35 mm effective diameter, 0.2-mm thickness.

Table II. Percent Arsenic (As_4O_6) Vapor Collection by Nuclepore and Nonimpregnated Cellulose Filters

Filter	No. of runs	Range	Mean
Nuclepore (0.4 μm)	12	0.2–18	6
Whatman 41	6	7–37	18

Table III. Percentage Desorption of Arsenic from Nuclepore Filter[a]

Arsenic source	No. of runs	Range	Mean
As_4O_6 sublimed from flask	3	<1–15	6
Ambient arsenic particulates	3	<1	<1

[a] Expressed as percent of arsenic assayed on two impregnated filters relative to the total of these filters and the Nuclepore filter.

efficiency equal to the thicker filter. The use of multiple filters has an advantage in that it enables the degree of vapor penetration to be accurately monitored for each sample. This is valuable when filter efficiencies have rather large variations and sample overloading is possible. Three impregnated filters, each having an efficiency of 65%, give an overall efficiency of 96%.

In these studies, impregnated filter overloading with As and a subsequent reduction in collection efficiency were not observed, even in cases where the total arsenic on an impregnated filter was as high as 5 μg. Once the arsenic vapor was collected on the filter, it had virtually no tendency to desorb. This was determined by passing arsenic free air through an impregnated filter already loaded with arsenic (collected as the vapor) and collecting any desorbed arsenic on a second impregnated filter that was placed in line behind the first. An average of 98% (four determinations) of the total arsenic was found on the first filter.

Absorption of arsenic trioxide vapors on Nuclepore and nonimpregnated cellulose fiber Whatman 41 and 43 filters was also investigated by passing arsenic vapors through double Nuclepore filters (the first being used for collection of any particulate arsenic) or a Nuclepore and nonimpregnated Whatman 41 or 43 cellulose filter and then through two impregnated filters. The percent collection of arsenic vapor by the Nuclepore or nonimpregnated cellulose filter, relative to the total collected on this filter and the impregnated filters, is shown in Table II. Absorption on Nuclepore filters ranged from 0.2 to 18% and averaged 6% of the total arsenic collected. Nonimpregnated cellulose filters collected between 7 and 37%, with a mean of 18%, of the arsenic trioxide vapors passing through them. The increase in efficiency of nonimpregnated cellulose compared with Nuclepore filters is probably attributable partly to the increased contact time for the much thicker cellulose filter (0.2 mm vs. 0.01-mm thickness). From this information, the use of the Nuclepore filter as a particulate prefilter is most appropriate when separation of the particle and vapor phases is desired.

Desorption of As from the Nuclepore filter was investigated by first collecting arsenic vapor or ambient particulate matter on the Nuclepore filter and then passing arsenic free prefiltered air through the Nuclepore. Two impregnated filters were placed in-line behind the Nuclepore to absorb any release of arsenic. The results are shown in Table III. Clearly, very little of the absorbed gaseous or particulate arsenic is desorbed from the prefilter.

The effect of particle loading of the Nuclepore filter on the absorption of arsenic vapors was evaluated by passing unfiltered laboratory air through the source flask and test filters for 48 h at a flow rate of 15 lpm. Considerable particle loading was evident on the Nuclepore filter. Total suspended particulates averaged 50–75 μg/m^3 in the test atmosphere. Under these conditions, a range of 13–22%, with a mean of 18% of the total gaseous arsenic, was collected on the Nuclepore filter. This mean value of 18% is three times the mean arsenic absorption given in Table II for Nuclepore filters alone (no particulates present). Particles do, therefore, alter the arsenic collection characteristics of the Nuclepore filter, although it is not known whether in this experiment the particles absorbed gaseous arsenic before contacting the filter or while lodged on the filter surface. However, because of the very short mixing times of the particles and vapor in this experimental system, nonequilibrium conditions very likely exist. It is proposed, therefore, that the 18% absorption of volatile arsenic on the Nuclepore filter in the presence of particulates represents a maximum in this experiment. At very high particulate concentrations, such as those found in industrial and some urban environments, arsenic vapor absorption on a Nuclepore prefilter could vary, especially as flow rates decrease, and should be evaluated before sampling under these conditions if an estimate of vapor phase arsenic is desired.

When hydroxy dimethylarsine oxide was used as the arsenic source, a maximum of 5% penetrated either a Nuclepore or nonimpregnated cellulose filter. The small amounts that did pass through were collected on the first impregnated filter. The quantities collected were much smaller than when similar quantities of the arsenic trioxide source were used. Thus, very little vapor was sublimed, and this was easily condensed on the first filter through which it passed. The much lower vapor pressure of this species relative to arsenic trioxide is the obvious reason for these observations. These results indicate that this sampling method would likely not separate an alkyl arsenical vapor from particulate As if they were both present. The highly volatile arsine species, such as arsenic hydride (AsH_3) and methyl arsines ($(CH_3)_xAsH_{3-x}$, $1 \leq X \leq 3$) were not extensively studied because of their instability in air. The detection of alkyl arsine vapors by Johnson and Braman (*8*) in a green house indicates, however, that these species may have short residence times in the immediate source vicinity before oxidation to the less volatile oxides.

Interferences. No specific interference studies were conducted since ambient air was used for all tests and the highly basic conditions on the filter allowed for the collection of halogen gases (determined by neutron activation analysis), nitrogen oxides, and sulfur dioxide. A distinct yellow color developed on the first impregnated filter in many cases and was especially distinct when samples were taken in high SO_2 environments such as smelters.

Results

Impregnated filters are presently being used to determine arsenic gas and particulate concentrations in various urban areas, in the vicinity of a smelter, and in remote marine regions. The objectives are to accurately determine total atmospheric arsenic concentrations and to ascertain where, under what conditions, and to what degree an ambient arsenic vapor phase exists. Some recent field data obtained using the described sampling systems are given in Table IV. The authors believe that from the experimental data presented in this report and the probability that arsenic trioxide and methyl arsenicals are the volatile species of arsenic potentially present in ambient air, these data represent total arsenic concentrations. No attempts to sample the filtered air by other techniques such as bubblers or vapor traps were made.

All samples were collected at ambient temperatures of less than 20 °C. The data in Table IV indicate that under these conditions, the major fraction of the atmospheric arsenic is retained on the Nuclepore filter, although as much as 20% of the total arsenic was found on the impregnated filters. Recent tests by an independent agency (*20*) have shown that this Nuclepore and impregnated filter system is highly efficient

Table IV. Atmospheric Arsenic Concentrations Determined in Various Environments

Sampling location	No.	Filter	As, ng/m^3
University of Rhode Island Chemical Laboratory	(1)	Nuclepore	0.37
		impregnated	0.02
	(2)	Nuclepore	0.26
		impregnated	0.05
Rural Coastal Rhode Island	(1)	Nuclepore	0.48
		impregnated	0.07
	(2)	Nuclepore	0.62
		impregnated	0.08
	(3)	Nuclepore	1.0
		impregnated	<0.02
Vicinity of Cu smelter	(1)	Nuclepore	8.3
		impregnated	2.3
	(2)	Nuclepore	480.
		impregnated	23.
	(3)	Nuclepore	250.
		impregnated	10.

for total arsenic collection under relatively high arsenic concentration conditions (up to 5 μg As/m^3) in the vicinity of a copper smelter. The same tests also demonstrated that glass fiber filters do not always efficiently collect atmospheric arsenic. It seems, therefore, that previous determinations of ambient atmospheric As concentrations may possibly be in error, the degree to which is dependent on the filtration system used and the conditions of sampling. Nuclepore filters of 0.4-μm pore size are, however, apparently suitable for most atmospheric arsenic determinations. Since the distribution between particulate and vapor phase arsenic may be related to collection temperatures, the impregnated filters may also be necessary under certain high-temperature sampling conditions. In addition, the impregnated filters can be useful in determining the arsenic filtration efficiency of other atmospheric aerosol collection systems.

Conclusions

Atmospheric sampling methods for arsenic should be capable of collecting both particulate and vapor phases. The high equilibrium vapor pressure of arsenic trioxide requires that this approach be strictly adhered to for sampling near high-temperature sources such as smelters, fossil fuel combustion facilities, and certain industrial processes. Volatile arsenic trioxide is apparently the major arsenic species produced by these processes (*18, 19*). This report demonstrates that impregnated filters are suitable for this application. There are several advantages in using impregnated filters. First, they can be used by themselves to collect a total particulate and vapor sample. If differentiation between particulate and gas phase is desired, a Nuclepore membrane filter can be used as a particle prefilter, since this filter has a relatively low collection efficiency for inorganic arsenic vapors. One should be aware, however, that substantial particle loading, as well as humidity, may affect vapor absorption on the Nuclepore filter. An alternative is to use the Nuclepore filter and impregnated filters as back-up filters to a cascade impactor. In this conformation, particle loading on the Nuclepore filter is substantially reduced.

Additional work is continuing to investigate the nature of the vapor-particle interaction observed on the Nuclepore filter and to determine the collection efficiencies of other impregnating reagents. Preliminary test results indicate that tetra butyl ammonium hydroxide is apparently a very efficient collection substrate for arsenic trioxide vapors.

Acknowledgment

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Regeneration of Fibrous Bed Coalescers for Oil–Water Separation

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■ The regeneration of fibrous bed coalescers operating on secondary oil-in-water emulsions was studied. Unstabilized or commercially available glass fibers were used, and the latter fibers were bound together into a rigid structure or stabilized by application of isobutyl methacrylate resin on the fibers and the subsequent heat treatment. The efficiency of these coalescers was close to 100% for several hours and then fell off rapidly. The cycle life, defined as the time when the concentration of the effluent emulsion reaches 5 ppm, was of the order of 6 h. Steam was an easily applicable and efficient regenerating agent. Steam regeneration of stabilized beds gave cycle lives 0.8 that of fresh bed. The cycle life of stabilized bed varied inversely with superficial velocity and was independent of inlet concentrations in the range of 100–200 ppm (v/v). The stabilized beds were regenerated three times without an appreciable decrease in cycle life.

Pollution of inland waterways and coastal waters by effluents containing waste oil from many industries and commercial and naval vessels has adverse effects on marine and human life. The oil can be present in the form of an emulsion of fine droplets due to wave action and particularly so if subjected to pumping. Primary emulsions (droplet size >10 μ) may be easily separated by gravity settling. However, secondary emulsions (droplet size <10 μ) have prohibitive residence times. As a result, various auxiliary procedures have been used to promote rapid coalescence of the secondary emulsion and subsequent separation by gravity settling (*1*).

One very effective method involves passing the emulsion through a fibrous bed. Many types of fibers (stainless steel, cotton, dynel, fiberglass, asbestos) have been used. When an emulsion is passed through the fibers, the holdup of the dispersed phase increases, and hence the pressure drop across the bed increases (*2*). Eventually, the increased holdup and the accompanying increase in the velocity through the bed cause incomplete coalescence or redispersion of the oil held up, resulting in appreciable oil showing up in the effluent. This behavior is in contrast to that of water in jet fuel where pressure drop buildup is very small over a period of months (*3*).

The unsteady state coalescence of oil–water emulsions has been reviewed by Shah (*4*). At present, filter/coalescers used for removal of oil from water are generally a cartridge type disposed of when saturated. The first use of fiber glass to remove oil from water was described by Burtis and Kirkbride (*5*) who used a 5-in. bed of compressed 7-μ fibers to remove salt water from crude oil. Redman (*6*) described cartridge-type coalescers with a fiber glass membrane with which thermal setting resins or binders were applied to retain its dimensional stability. A mathematical model was developed by Rosenfeld and Wasan (*7*). Langdon et al. (*2*) described the behavior of fibrous glass coalescer beds and their regeneration by methanol. The unsteady state behavior of stainless steel fiber beds with methanol regeneration was studied by Piekielny at ITT (*8*). Frauman et al. (*9*) developed a 40-gpm batchwise in situ regeneration separator using 60 pores/in. polyurethane foam. After the oil buildup in the bed was sufficient to prevent separation, the oil was removed by squeezing the bed.

Coalescer Cell (Figure 1). The coalescer bed (12) consists of coarse/fine/coarse fiber glass beds compressed between screens (11) to an overall length of ¼ in. as determined by the tie bolt nuts (13). The uncompressed bed consists of a 2-in. layer of coarse fiber glass (10.1 μ diam., Owens-Corning "Aerocor") both before and after a ½-in. layer of fine glass (3.2 μ diam., Owens-Corning FM-004). The internal diameter of the cell and compression tubes is 1⅜ in. These tubes are sealed by the external sleeve (6). The entrance compression tube (1) is provided with a valved air vent hole (5). The initial cell, used with methanol regeneration, was constructed of Plexiglas. However, steam regeneration required the cell to be constructed of aluminum.

Stabilized Fiber Glass. One ½-in. layer, 3 in. square, of 3.2-μ fiber glass is dipped into a 10% solution of isobutyl methacrylate resin (Lucite 45) in methylene chloride. The glass is then compressed to ¼ overall length between the two 2-in. layers of 10.1-μ coarse glass. The coarse glass layers are replaced with fresh layers of coarse glass again compressed to ¼ in. and heated at 100 °C for 1 h. After this treatment the fine glass layer is formed into a rigid and stable membrane, 0.028 in. thick. It is then removed and trimmed to the correct diameter of $1\frac{15}{32}$ in. for insertion into the coalescer cell between the two layers of coarse glass.

Methanol Regeneration. The entrance end of the cell, at the end of a run, is connected to a funnel filled with water, and the exit end to a water aspirator. Then alternately 500 ml of anhydrous methanol and 1000 ml of water are passed through the cell, care being taken that no air enters the cell at any time. When no turbidity is seen after the alcohol displacement with water, all oil is removed and the cell is reconnected for the next run.

Steam Regeneration. Steam close to saturation at 20 psi is passed through the cell open to atmospheric pressure for 3–5 min. Since the bed is unavoidably exposed to air after the regeneration, the cell is drained before and after the steam treatment.

Test Procedure. The test assembly is shown in Figure 2. Fifty gallons of tap water in tank (1) is first passed for 2 h through a filter (4) containing a 2-in. layer of coarse fiber glass and a 1-in. layer of fine fiber glass compressed to ¼ in. The test system including the cell is then completely filled with water, and all air eliminated. The emulsion is then prepared by

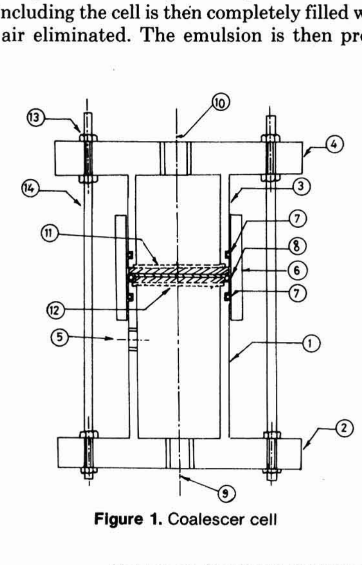

Figure 1. Coalescer cell

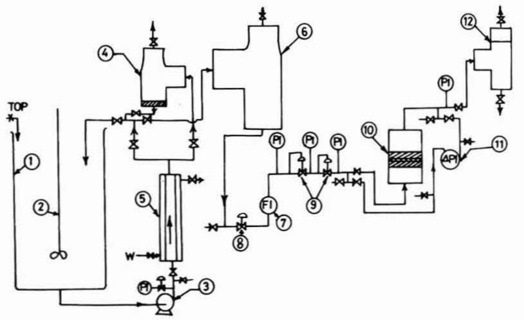

Figure 2. Assembly of apparatus

adding a measured amount of kerosine to the stirred (1750 rpm, 4½ in. diam. impeller) tank and circulating the mixture for ½ h through the 3450-rpm centrifugal pump. Temperature is manually controlled at 25 ± 3 °C by means of (5). The emulsion passes through the presettler (6) made from a 6-in. glass tee, a flow meter (7), and two back pressure regulators (9). The pressure drop across the cell is measured by a mercury manometer (11). The samples before and after the coalescer are diluted to a volume of 1-l. and dispersed in a Waring blender for 5 min. After standing 5 min, the turbidity is determined by means of a Hach 2100A turbidity meter. The calibration curve for the turbidity meter is shown in Figure 3. The typical inlet particle size distribution is shown in Figure 4.

Results and Discussion

Unstabilized and stabilized beds were tested in a coalescer cell of 1⅜ in. diam. (1.485 in.^{2} active area), at superficial velocities of 1 and 1.5 ft/min and inlet concentration of 100 and 200 ppm. Overall bed length in all cases was ¼ in., and the fine glass coalescer layer was nominally 0.028 in. The porosity of the unstabilized bed was 0.93, and the effective porosity of stabilized bed was 0.78. The temperature was kept at 25 ± 3 °C.

During the run, effluent concentration was essentially 0 ppm (nondetectable by turbidimeter, sensitivity ± 0.3 FTu). The bed was considered to have reached the breakthrough point when the effluent concentration was 5 ppm. Pressure drop across the bed increased with time as shown in Figure 5. Methanol or steam was used as the regenerating agent. The saturation (volume of dispersed phase held by the bed per volume of bed voids) was calculated by comparing pressure drops at breakthrough time and at zero time by Kozeny's equation:

$$\frac{\Delta P}{L} = K \frac{V\mu}{D_f^2} \frac{(1-\epsilon)^2}{\epsilon^3}$$

While comparing pressure drops, the effective fiber diameter was calculated assuming uniform distribution of the oil holdup by

$$\frac{n\pi}{4} \cdot D_{fe}^2 \propto (1-\epsilon_e)$$

$$\therefore \frac{D_{fe}^2}{D_{fo}^2} = \frac{1-\epsilon_e}{1-\epsilon_o}$$

$$\therefore \frac{\Delta P_o}{\Delta P_e} = \frac{(1-\epsilon_o)^2}{\epsilon_o^3} \cdot \frac{\epsilon_e^3}{(1-\epsilon_e)^2} \cdot \frac{D_{fe}^2}{D_{fo}^2}$$

$$\therefore \frac{\Delta P_o}{\Delta P_e} = \frac{(1-\epsilon_o)}{\epsilon_o^3} \cdot \frac{\epsilon_e^3}{(1-\epsilon_e)}$$

The saturation volume fraction is given by $S = 1 - \epsilon_e/\epsilon_o$. It varied from 0.13 to 0.26.

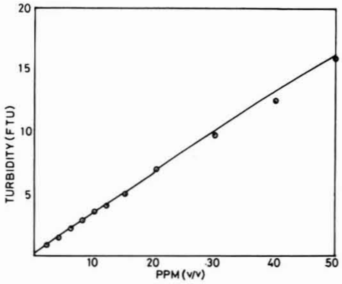

Figure 3. Calibration of turbidity meter

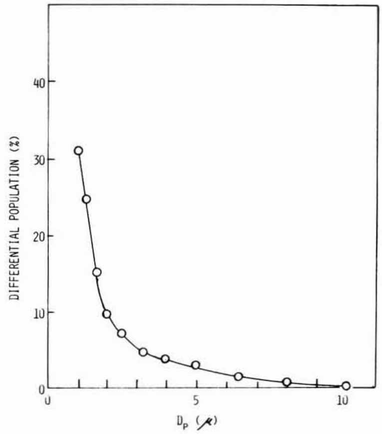

Figure 4. Inlet particle size distribution

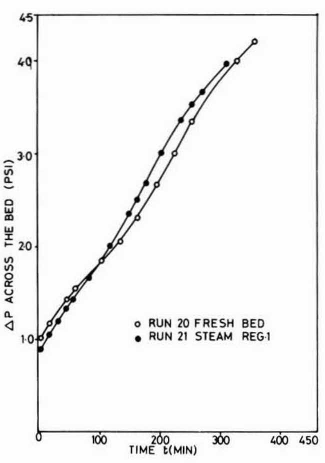

Figure 5. Pressure drop increase of stabilized fiberglass bed

Table I gives a summary of results obtained in this study giving breakthrough time, t_c, and rate of pressure drop increase, $\Delta(\Delta P)/\Delta t$, for the different types of bed, regenerating agents, velocities, V, and inlet concentration. The relative efficiency, referred to a steam regenerated stabilized bed as 1.0, $t_c \cdot V/300$, is also given.

The pressure drop, Δp, and rate of increase of Δp are the same for fresh and steam regenerated stabilized bed. Additionally, there is no Δp increase with passage of filtered water through the bed for periods up to 2 h. These observations establish the existence of unsteady state behavior due to oil

Table I. Summary of Results

Type of bed	Velocity V, ft/min	Inlet concn, C_{in}, ppm	Breakthrough time t_c, min	Rel efficiency, $\frac{(t_c)V}{(300)}$	$[\Delta(\Delta p)/\Delta t]_{av} \times 10^2$ psi/min
Unstabilized fiberglass					
Fresh	1.0	100	240	0.80	0.80
Methanol regenerated	1.0	100	135	0.45	1.88
Steam regenerated	1.0	100	195	0.65	1.50
Stabilized fiberglass					
Fresh	1.0	100	375	1.25	0.814
	1.0	200	340	1.12	1.070
	1.5	100	220	1.10	1.260
	1.5	200	200	1.00	1.020
[a]	0.45	100	765	1.15	1.0
Methanol regenerated	1.0	100	150	0.50	2.225
Steam regenerated					
First	1.0	100	300	1.0	0.989
Second	1.0	100	285	0.95	1.1
Third	1.0	100	315	1.05	1.0
	1.5	200	200	1.0	1.46
	1.0	200	280	0.94	1.16
Stainless steel fibers[b] (8 μ diam)	0.5	100	180	1.18	. . .
	1.0	100	100	0.34	. . .
	2.0	100	50	0.34	. . .

[a] Sampath (*11*). [b] Piekielny (*8*).

buildup in fibers and eliminate the possibility that the Δp increase is due to the filtration of impurities from the water or fiber migration.

Figure 6 compares the performance of stabilized and unstabilized beds with methanol and steam regeneration at standard operating conditions of 1 ft/min and 100 ppm inlet. The breakthrough time, t_c, for the stabilized bed is 1.5 times that of unstabilized bed. Steam regeneration is 50–100% more effective than methanol regeneration for unstabilized and stabilized beds, respectively. The relative efficiency of stabilized fibers regenerated by methanol is 0.5 that by steam regeneration. Unstabilized fibers, regenerated by methanol and steam, had relative efficiencies of 0.45 and 0.65, respectively, relative to steam regenerated stabilized fibers. Multiple regenerations of up to three times show little effect on the relative efficiency.

Figure 7 compares the performance of stabilized beds at different velocities and inlet concentrations. The fresh and steam regenerated beds for $V = 1.5$ ft/min have breakthrough time, t_c, 1.5 times shorter than the one for corresponding beds at $V = 1$ ft/min. At these two different velocities, the bed passes the same amount of kerosine. Piekielny (8) worked with stainless steel (8 μ) fibers and with methanol as regenerating agent. For bed length of 0.25-in. porosity of 0.92, and superficial velocities of 0.5, 1.0, and 2 ft/min, breakthrough times were 180, 100, and 50 min, respectively. These data show that

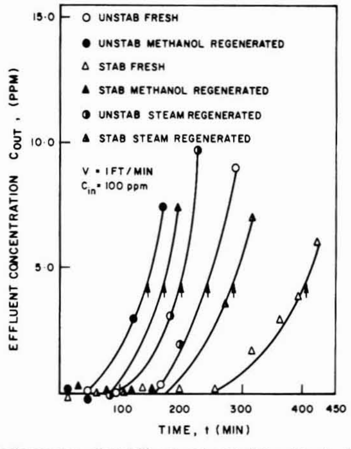

Figure 6. Performance of stabilized and unstabilized bed with methanol and steam regeneration

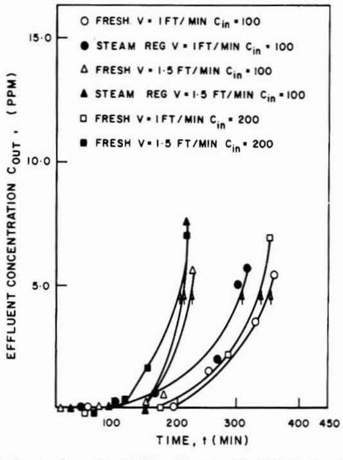

Figure 7. Performance of stabilized bed with different velocities and different concentrations

breakthrough time is inversely proportional to velocity. However, a change in inlet concentration from 100 to 200 ppm (Figure 7) does not affect breakthrough time significantly. Apparently, an increase in inlet concentration does not increase rate of saturation of bed due to accompanying increase in flow of coalesced drops on downstream side.

A major cost factor in using present day filter/coalescers is the replacement cost of the one-shot cartridges which are generally used. Since the steam cost is negligible, element cost will be reduced in direct proportion to the number of regenerations. Additionally the labor cost in regeneration is very small compared to that involved in changing elements. A design has been presented (*2, 10*) which allows large scale filter/coalescer units to be constructed using filter press construction and stabilized fiber glass medium.

Conclusions

Fibrous beds, stabilized by treatment with isobutyl methacrylate resin, were very effective for efficient separation of secondary emulsions of oil-in-water type. Coalescer life, defined as the time when effluent concentration reached 5 ppm (*breakthrough*), was 375 min for a fresh bed and 300 min after repeated steam regenerations. The same fiber glass bed used as available commercially with a phenol formaldehyde coating (unstabilized) gave life of 0.8 before and 0.65 after steam regeneration referred to steam regenerated stabilized beds as unity. Methanol regeneration of stabilized and unstabilized beds was much less efficient having efficiencies of 0.5 and 0.45 compared to the steam regenerated stabilized bed. A change in inlet concentration from 100 to 200 ppm does not affect the life of the bed. The operating life to breakthrough is inversely proportional to velocity.

Nomenclature

D_f = fiber diameter
D_{fe} = effective fiber diameter at breakthrough
D_{fo} = effective fiber diameter at time $t = 0$
D_p = drop size diameter
L = length of bed
V = superficial fluid velocity
ϵ = void fraction in bed
ϵ_o = void fraction in bed at $t = 0$
ϵ_e = effective void fraction in bed at breakthrough

$$= \frac{\text{Vol of bed} - (\text{Vol of fibers} + \text{Vol of oil holdup})}{\text{Vol of bed}}$$

$\Delta\rho_o$ = pressure drop across bed at time $t = 0$
$\Delta\rho_e$ = pressure drop across bed at breakthrough
S = saturation of bed = fraction void volume occupied by oil holdup
t_c = breakthrough time

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Sulfate Formation: Catalyst and Gas-Phase Composition Effects in Pulsators and Comparison of Three-Way with Oxidation Catalysts

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■ Results on SO_2 conversion over fresh and over well-characterized used fleet catalysts are presented. Evaluations are conducted with simulated exhaust from a laboratory pulse-flame apparatus. The experimental evidence indicates clearly the more demanding nature of the SO_2 oxidation as compared with CO or hydrocarbon oxidation. Hence, the SO_2 oxidation is more sensitive to space velocity, changes in the noble-metal makeup of the catalyst, and deactivation by poisoning. Mutual effects of exhaust and catalyst compositions are discussed. Finally, conversion measurements under steady-state conditions with synthetic gas mixtures are made for typical three-way catalysts.

Results on the formation of sulfate emissions over automotive oxidation catalysts heretofore have been obtained with flow reactors using synthetic gas mixtures blended to approximate burned gas (*1–4*) and with actual engine exhaust (*4–8*). The first approach was considered best suited to obtain basic data, and the second for measuring actual emissions.

For several years we have employed for the study of the main oxidation reactions and for catalyst characterization an apparatus which produces burned gas in the laboratory. The gas differs from actual car exhaust by a somewhat different hydrocarbon distribution (higher CH_4 content) since a constant boiling fuel, isooctane, has to be used. The apparatus, the pulse-flame combustor, has been described in detail (*9*). Results of the characterization of oxidation and three-way catalysts using this tool have been published (*10–12*), and good correlations with dynamometer and vehicle studies were obtained. The combustor permits control of some variables to a better degree than an engine. At the same time the gas composition is much closer to that prevailing with engine exhaust than could be obtained with any synthetic mixture. On the other hand, the catalyst flow conditions, generated by the pulsating flow frequency of about 60 pulses/min, differ

Table I. Characterization of Catalysts

	Catalyst and metal		
	Engelhard IIB, Pt–Pd	Matthey-Bishop 12C, Pt	Lab prep, Pd
Noble metal surface area (μmol CO/g)	0.98 ± 0.20	0.39 ± 0.10	0.71 ± 0.28
% Conversion at 500 °C			
CO	94.6 ± 2.1	93.2 ± 0.8	90.4 ± 2.6
HC	74.7 ± 4.1	76.2 ± 2.5	71.4 ± 5.9

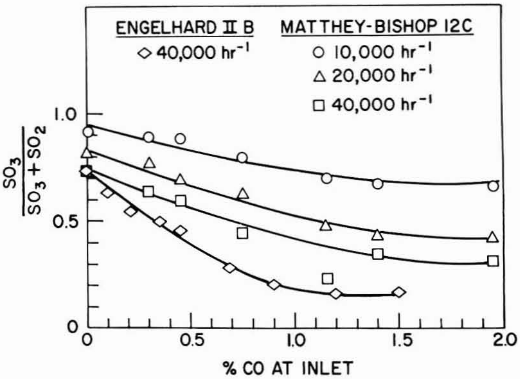

Figure 1. SO_3 formation on Engelhard IIB and Matthey Bishop 12C catalysts as function of CO concentration and space velocity

from those prevailing in flow reactors or in dynamometer and vehicle tests. While for CO and hydrocarbon oxidation these flow differences do not seem to affect catalyst performance, they might influence the oxidation of SO_2. One of the objectives was to explore the adaptability of the combustor for studies of sulfate formation. In the course of this work we were also able to reconfirm several previous observations concerning the effects of certain factors on sulfate formation.

In the case of the three-way catalysts the objective was to determine the SO_2–SO_3 conversion and compare it to the commonly used oxidation catalysts. Since three-way operation is restricted to a narrow band of air/fuel ratios around stoichiometric, this condition limits the equilibrium of sulfuric acid formation due to low partial pressures of oxygen (*13*).

Experimental

The combustion products of isooctane are passed over the catalyst, using a nearly adiabatic flame pulse. Details of the apparatus have been reported earlier (*9*). Two commercial catalysts were tested. One of them contained Pt and Pd (Engelhard IIB), while the other contained Pt alone (Matthey-Bishop 12C). In addition, a Pd catalyst was prepared in this laboratory. All three catalysts were monolithic but had different washcoats. Their activities for the oxidation of CO and hydrocarbons in pulsator tests and their metal surface areas are given in Table I, taken from ref. *11*.

In the present experiments, an excess of 5% oxygen over the amount needed to oxidize CO and hydrocarbons in the exhaust was used. The temperature across the catalyst was kept at 470 ± 25 °C, which is close to the temperature at which thermodynamics and kinetics allow maximum conversion of SO_2 to SO_3, as reported by Mikkor et al. (*2*). A sulfur dioxide level of 20 ppm in the gas phase was chosen for the experiments. This approximates the level which would result from fuel containing about 300 ppm sulfur when used in vehicles operating at an air–fuel ratio of about 15:1. Sulfur dioxide and trioxide were separated by the Gøksøyr-Ross method and analyzed by barium perchlorate–thorin titration in the manner described in ref. *1*.

It was first established that no sulfur was lost in the system by storage on catalyst or reactor walls during the steady-state operation of the experiments. For this purpose a calibrated amount of SO_2 in nitrogen was added to the exhaust and compared with the amounts of SO_2 and SO_3 deposited in the Gøksøyr-Ross train. Subsequently, the sulfur was added to the isooctane as diethylsulfide. The SO_2 concentration in the gas phase was calculated from the SO_2 + SO_3 collected in the Gøksøyr-Ross train, and the total flow, as measured by a wet test meter. The balance between sulfur in the carefully metered fuel and the total amount of SO_2 + SO_3 agreed within the reproducibility limits of the experiment (±5%). In a blank run, obtained at a catalyst temperature of 200 °C, less than 2% SO_3 was measured in the sulfur oxide mixture.

For a few comparison runs the same reactor setup was employed without isooctane combustion. Instead, a synthetic gas mixture of N_2, O_2, H_2O, SO_2, CO, H_2, and C_3H_6 was fed into the reactor system. The SO_2 conversion over the three-way catalysts was carried out in a simple flow reactor very much akin to that described in ref. *1*.

Results and Discussion

Pulsator Studies of Oxidation Catalysts. Figure 1 is a composite representation of the effects of gas composition, catalyst composition, and space velocity on the SO_2–SO_3 conversion under the pulsator conditions. It has been noted previously that all three factors affect the conversion rate (*2, 3, 7*).

The lowest curve shows the results obtained with an Engelhard IIB sample (atomic Pt/Pd ratio about one) at an average space velocity of 40 000/h (catalyst dimensions: diameter ¾ in., length ½ in.). With a very lean flame, which is practically free of CO and hydrocarbons, 75% of the fuel sulfur is converted to sulfuric acid. As the CO concentration is increased by decreasing the oxygen flow in the burner and increasing the secondary oxygen between flame and catalyst to maintain an excess of 5% oxygen, the SO_2 oxidation decreases. At 1% CO, only about 20% of the fuel sulfur is converted to sulfuric acid.

In a second series, a Pt catalyst (Matthey-Bishop 12C) was studied. In this case, the conversion was evaluated as a function of CO concentration and space velocity. Three different space velocities were obtained by employing catalyst lengths of 0.5, 1 and 2 in. These results are also shown in Figure 1. The line defined by the squares corresponds to the same conditions used for the Pt–Pd catalyst. While sulfuric acid formation in the absence of CO is the same in both cases, the Pt catalyst is less affected by the presence of CO than the Pt–Pd catalyst. As the space velocity is lowered by doubling the catalyst length (triangles in Figure 1), a general increase in SO_3 formation occurs. Doubling the catalyst length again results in further SO_3 increase (circles in Figure 1); here SO_2 conversion without CO is 92%; at 1% CO it is still 74%. Obviously, an increase in space velocity and the presence of CO both decrease conversion of SO_2 to SO_3.

A diminution of the activity of supported Pt catalysts for the oxidation of SO_2 to SO_3 by the addition of Pd in equiatomic amounts has been observed previously by Kobozev and Shekhobalova (*14*) for highly concentrated SO_2 streams. This holds also for the very dilute SO_2 streams used in this study. It is worth mentioning that in Kobozev's study very small additions of Pd to Pt had an enhancing effect on the SO_2 oxidation activity. Whether this holds under our conditions remains to be investigated.

Prudence requires at this point that it be recognized that

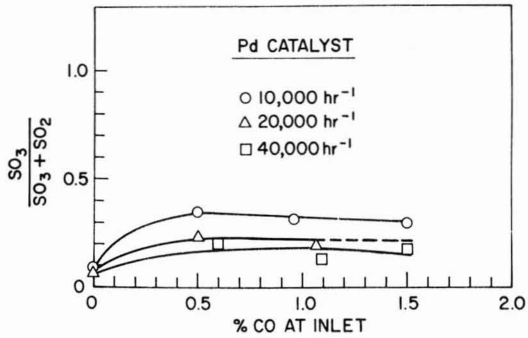

Figure 2. SO_3 formation on Pd catalyst as function of CO concentration and space velocity

although the stronger effect of CO in the case of the Pt–Pd catalyst as compared to the Pt catalyst appears to be associated with the compositional differences, it also might be due in part to differences in the physical properties of the two catalysts. It was pointed out by Hammerle and Truex (*3*) that smaller pore sizes in the catalyst washcoat can influence markedly the SO_2 conversion on Matthey-Bishop 3C catalysts, when operating in the pore-diffusion controlled regime.

A pure Pd catalyst is still less active for SO_2 oxidation than a mixed Pt–Pd catalyst, as seen in Figure 2. Again, this was noted previously for concentrated SO_2 streams (*14*) and for dilute streams by Hammerle and Truex (*3*). As could be expected, the increase in nominal space velocity decreases the conversion. The effect of CO addition to the strongly oxidizing stream is quite different from that observed either on Pt or on Pt–Pd catalysts. Small additions (0.5%) of CO enhance the conversion somewhat, while further additions have little effect. Comparison of Figures 1 and 2 shows that at a space velocity of 40 000/h and above 1% CO, the mixed Pt–Pd and the pure Pd catalysts convert about equal portions of SO_2 to SO_3.

Since the task of automotive catalysts is to oxidize carbon monoxide and hydrocarbons without oxidizing sulfur dioxide, one may strive to achieve the desired selectivity by several means. From equilibrium considerations, the oxidation of SO_2 to SO_3 can be prevented under certain conditions where CO and hydrocarbon oxidation is still relatively high, i.e., at temperatures above 550 °C and low excess oxygen. The condition of low excess oxygen is particularly of interest in the use of three-way automotive catalysts designed to operate close to stoichiometric air/fuel mixtures (*13*). Additional selectivity can be achieved by the large difference in the kinetics of the oxidation process. Clearly, the oxidation of SO_2 under the conditions of our experiments is space-velocity dependent, while hydrocarbon and CO oxidation is relatively independent of this parameter, as shown in Table II. The data in this table for CO and hydrocarbon oxidation correspond to the same runs of SO_2 oxidation in Figure 1.

It must be emphasized, however, that a stringent simultaneous control of NO, CO, and hydrocarbons by a three-way catalyst at stoichiometric air/fuel mixtures may require an additional lean oxidation catalyst downstream. In this implementation of the three-way catalyst approach, the problem of SO_2 oxidation may recur. In practice, the magnitude of this problem could be reduced significantly through appropriate oxidation catalyst sizing, the use of a Pt–Rh oxidation catalyst, as will be discussed later, and proper control of air addition between the reduction and oxidation catalyst beds.

The above data obtained with fresh catalysts showed already the kinetic selectivity between the more demanding oxidation of SO_2 and that of CO and hydrocarbons. Moreover, the performance of a catalyst exposed to car exhaust deteriorates because of poisoning, mainly by lead, and thermal sintering. It is therefore of interest to compare oxidation of hydrocarbons and CO on the one hand, and of SO_2 on the other, over aged catalysts. Four catalyst units from three different manufacturers were selected from cars which had undergone fleet testing with mileage accumulations between 20 000 and 50 000 miles. These catalysts were characterized by their BET surface areas, contaminant levels (Pb, Zn, P, S, and Fe) and other properties. Samples were taken either from the inlet or from the outlet portions of the monolith units. Table III lists the respective lead concentrations and the conversions of CO and hydrocarbons which were obtained by the pulse-flame test under standard conditions (1.1% CO, 3.5% O_2). Conversion of SO_2 was measured as before at an excess of 5% O_2, 20 ppm initial SO_2, and 470 °C, and is listed in the last two columns of the table for 0 and 1.1% CO. The data are listed in descending order of hydrocarbon conversion. Fresh samples of catalysts #1, 2A, and 2B are as effective as Engelhard IIB and Matthey-Bishop 12C catalysts in producing SO_3. A similar SO_2 conversion is expected for catalyst #3 because of a comparable Pt loading.

Comparison of the CO and hydrocarbon oxidation activity of the fresh (Table II) and aged (Table III) catalysts on the one hand and that of SO_2 oxidation on the other shows that the SO_2 oxidation is more vulnerable to deactivation. Although the aged samples contained appreciable amounts of lead, the CO activity was good and that of the hydrocarbons still appreciable. Table III and Figure 1, however, indicate a much more pronounced drop in the catalyst activity toward SO_2 oxidation.

A limited comparison of the pulsator results on aged catalysts with recent vehicle data is possible. It has to be emphasized, however, that data from different vehicles and different catalysts vary in the exact values of sulfate emissions, but indicate a clear trend of a substantial decrease in SO_2 conversion with mileage accumulation. Thus, Krause et al. (*7*), using a representative fleet of 20 catalyst-equipped vehicles, indicate an average drop in sulfate emissions from 22 to 6

Table II. CO and Hydrocarbon Conversions at Different Space Velocities and Concentrations

Catalyst	Nominal space velocity, 1/h	Concentration		Conversion	
		CO, mol %	HC,[a] ppm	CO, %	HC, %
Engelhard IIB	40 000	0.45	200	95	63
		0.70	460	91	67
		1.5	590	92	66
Matthey-Bishop 12C	40 000	0.75	585	94	74
		1.4	680	89	68
	20 000	0.75	585	96	79
		1.4	680	89	68
	10 000	0.75	585	98	77
		1.4	680	98	76

[a] Measured as hexane.

Table III. Activities of Fleet Aged Catalysts

		Conversion		SO_2 conversion	
Catalyst designation	Pb, wt %	CO, %	HC, %	Without CO, %	With CO (1.1%), %
2A—out	1.08	90.8	66.8	13.8	5.5
1—out	1.79	86.0	59.0	25.1	10.7
2B—out	3.83	87.0	58.0	14.4	6.0
2A—in	3.04	73.2	56.4	14.8	1.7
2B—in	5.95	83.9	55.4	20.6	6.2
3—out	2.50	75.7	50.0	10.5	1.7
3—in	6.69	61.3	39.7	11.6	3.6

mg/mile from a stabilized fresh condition to 24 000 miles. With further use the average sulfate emissions remained practically constant. Irish and Stefan (*8*) using one well-characterized vehicle found a sulfate decrease from 42 mg/mile at 4000 miles to 14 mg/mile at 50 000 miles. Considering the large decrease in sulfate emissions during the first 4000 miles by Krause et al. (*7*), the proportional decrease in sulfate emissions with mileage in refs. *7* and *8* should be considered as fair agreement. Again, the overall fleet results from ref. *7* indicate a lesser sensitivity of CO and hydrocarbon oxidation to catalyst aging, as was noted in the pulsator experiments.

Although the overall results of SO_2 oxidation behavior in the pulsator are consistent with observations on vehicles, we should indicate that in one respect the pulse-flame reactor may be considerably different. This has to do with the instantaneous space velocity over the catalyst during the pulse formation in the combustor. We have established that the conversion of SO_2 at a space velocity of 40 000/h is considerably higher in a steady state flow reactor using a mixture of N_2, O_2, H_2O, CO, and SO_2, than that at the same nominal space velocity in the pulsator. To obtain the effect of SO_2 conversion decrease by an increase in CO concentration, as noted in Figure 1, one requires much higher space velocities in the flow reactor. For example, at 1.2% CO, an 80 000/h value in the flow reactor is roughly equivalent to the 10 000/h space velocity in the pulsator relative to the conversion of SO_2 to SO_3. It is possible that, besides the instantaneous values of the flow in the pulsator exhaust, components absent in the synthetic flow or concentration gradients also contribute to the suppression of SO_2 formation.

The question naturally arises about what underlies the suppression of SO_2 conversion by the presence of CO, under overall oxidizing conditions. Is it selective reduction or competitive chemisorption? To answer this question, we have carried out a series of experiments that eliminates selective reduction as an explanation, which also would be thermodynamically untenable under exhaust conditions. A double catalyst was used in these experiments. The first catalyst was used to produce about 15 ppm SO_3 at a concentration of 5% O_2. The exhaust then contacted a second catalyst button after addition of one of the three gases: CO, H_2, or C_3H_6 at overall concentrations of 1, 0.5, and 0.1%, respectively. In no case was there a decrease of the SO_3 concentration from the second catalyst. In fact, some additional SO_3 was formed over the second catalyst, as expected from the previous experiments. Therefore, it is competitive chemisorption between CO and SO_2 that has to explain the suppression phenomenon. Direct confirmation of this hypothesis is being pursued in our laboratory by the infrared study of the competitive adsorption on Pt, Pd, and Rh catalysts.

Three-Way Catalyst Studies. As mentioned above, three-way catalysts operate under conditions where SO_3 formation is limited by equilibrium considerations. It is of interest to ascertain whether compositional differences between typical three-way and oxidation catalysts have an effect on the SO_2–SO_3 conversion under conditions where the thermodynamic limitations are largely removed. The SO_2 oxidation by oxygen was studied with nitrogen as a carrier gas, with and without the presence of carbon monoxide, but always with excess oxygen. A simple flow reactor was employed. All the catalysts were monolithic, made with the same honeycomb with 300 cell openings per square inch. Since the catalyst compositions are proprietary, they are identified by the code letters A, B, and C. Besides the differences in composition, it is likely that these catalysts differ also in the amount, morphology, and makeup of the porous washcoat.

Data obtained on fresh three-way catalysts are presented in Table IV. They indicate, indeed, that, as a class, the recent formulations of three-way catalysts are less active for the SO_2–SO_3 conversion than production catalysts. A comparison of the data at 0 and 1% CO with 1% O_2 again shows the general decrease of SO_2 conversion caused by the presence of CO. The various formulations differ among themselves in their activity for SO_2 oxidation and sensitivity to the presence of CO. Such differences are expected with samples of different compositions.

Table IV. SO_2 Oxidation on Fresh Three-Way Catalysts [a]

Temp, °C	Inlet composition, %		SO_2 conversion, %				Equil, [b] %
	O_2	CO	EIIB	A	B	C	
435	2.5	0	72	42	35	60	97.5
487	2.5	0	83	48	46	68	92.7
545	2.5	0	79	49	38	70	80.4
435	1.0	0	. . .	56	31	64	96.0
487	1.0	0	. . .	53	47	61	89.0
545	1.0	0	. . .	38	41	67	72.2
435	1.0	1.0	. . .	33	24	18	94.5
487	1.0	1.0	. . .	36	34	38	85.1
545	1.0	1.0	. . .	34	32	43	64.7
435	0.5	0	. . .	58	37	57	94.5
487	0.5	0	. . .	55	39	59	85.1
545	0.5	0	. . .	33	38	56	64.7

[a] Gas composition: SO_2, 20 ppm; H_2O, 10%; CO, 0 or 1%; O_2, 0.5–2.5%; N_2, balance. Space velocity: 40 000/h. [b] Thermodynamic equilibrium calculated from JANAF Thermochemical Tables (2nd ed.), National Bureau of Standards.

Table V. SO_2 Oxidation of Dynamometer Aged Three-Way Catalysts [a]

Inlet composition, %		SO_2 conversion, %	
O_2	CO	A	B
1.0	0.0	14	28
1.0	1.0	9	12
0.5	0.0	9	33

[a] Conditions of Table IV at a constant temperature of 487 °C.

Many three-way catalysts contain rhodium in various proportions to other noble metals (*12*). It is therefore of interest to examine a pure rhodium catalyst for the SO_2–SO_3 conversion. A monolithic catalyst prepared on the same honeycomb with an analyzed concentration of 0.15% Rh, and a surface containing 0.76 μg-atom of Rh per m^2, as measured by hydrogen titration, was tested for SO_2 oxidation in the pulse-flame apparatus. In a CO-free burned gas, the SO_2 conversions at space velocities of 40 000, 20 000, and 10 000/h are 15.9, 25.3, and 39.7%, respectively. These conversions are considerably lower than those obtained on the Pt and Pt–Pd catalysts of Figure 1. The activity of the pure Rh catalyst for SO_2 oxidation was still more sensitive to the presence of CO than that of the other catalysts. The presence of only 0.1% CO at the catalyst inlet, with 5% O_2, has limited the SO_2 conversion to below 15%, even at the lowest nominal space velocity of 10 000/h. The increase of the inlet CO to 1.0% caused a further decrease of SO_2 conversion to 5%. The results with the three-way catalysts and with the pure Rh catalyst confirm recent vehicle data (*7*), where it was implied that a Pt–Rh catalyst produced considerably less sulfate emissions than either Pt or Pt–Pd catalysts.

Finally, we have examined the deterioration of SO_2–SO_3 conversion after 470 h durability in engine dynamometer tests, using the three-way catalysts A and B of Table IV. The mileage accumulation tests on the dynamometer-mounted engine were carried out at an average air/fuel equivalence ratio of 0.94 with a fuel containing 0.02 g/gal Pb, 0.002 g/gal P, and 0.019 wt % S. After test completion, buttons cut from the inlet portion were examined in the flow apparatus. Table V gives the test results. Comparison with the data of Table IV for fresh catalysts indicates deterioration of SO_2 oxidation with use. The two three-way catalysts show a different decrease in their SO_2 oxidation activity in the dynamometer aging which may be associated with different formulations. It can, however, be stated that three-way catalysts show a higher sensitivity for the deactivation of the SO_2 oxidation than for the oxidation of CO and hydrocarbons, similarly to the conventional oxidation catalysts.

Conclusions

- The pulse-flame apparatus is suitable for the evaluation of SO_2 conversion and produces results in qualitative accord with vehicle data.
- The suppressing effect of carbon monoxide on SO_2 oxidation in simulated exhaust has been confirmed.
- Composition of the noble-metal catalysts has an influence on SO_2 oxidation.
- Three-way catalysts are less active for SO_2 oxidation than production oxidation catalysts.
- Catalytic oxidation of SO_2, being more demanding than that of CO or of hydrocarbons, is more sensitive to increased space velocity and the deactivation processes associated with prolonged catalyst use. This is observed for both oxidation and three-way catalysts.

Acknowledgment

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Migration of Trace Metals in Interfaces of Seawater and Polluted Surficial Sediments

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■ The migration of trace metals between the interface of seawater and polluted surficial sediments under different redox conditions was studied on three typically polluted nearshore surficial sediments. The experimental results obtained showed that under different sets of redox conditions over a period of 4–5 months of sediment/seawater contact time, three general trends could be observed: the released amount increased as the redox condition became progressively reducing (Fe and Mn), the released amount increased as the environment became more oxidizing (Cd, Cu, Ni, Pb, and Zn), and there was no significant change of concentration in interfacial water (Hg and Cr). An equilibrium model was set up to confirm the experimental results. After long-term incubation in a reducing environment, most of the trace metals analyzed closely followed the predictions from equilibrium calculations. Complex formation accounted mainly for the concentration levels analyzed. Under aerobic conditions after long-term incubation, most of the analyzed concentrations were either far below (Cd, Cu, Ni, and Pb) or far above (Fe and Mn) the equilibrium concentrations, probably due to the slowness in reaching the equilibrium condition or to the presence of unknown ligands.

Trace metals exist in different forms in the sediment–water system (*1–4*). Part of the trace metals may stay in interstitial waters as free or complexed ions or loosely adsorbed on solids. Some may incorporate with insoluble organic or inorganic matters of authigenic solids. Others may imbed in the crystalline structure of the sediment. The current awareness of trace metals as pollutants in aquatic systems has aroused much interest in the exchange of metal species between the sediment–seawater interface. This interface is considered to be the site of important interactions which greatly affect the behavior of trace metals in the overlying water.

Considering the extremely low levels of trace metals found in the present-day ocean, despite the continuous input from land sources, it would seem that sediments are the permanent sink of soluble trace metals. However, changes in the overlying seawater conditions may result in new sediment–seawater equilibria and affect the mobilization of trace metals.

Various mechanisms of metal mobilization have been proposed, for example, diffusion (*5*), desorption (*6*), dissolution (*7, 8*), redox reaction (*9*), complex formation (*6, 10, 11*), biological effects (*2*), or physical disturbance (*12*). Though some qualitative or semiquantitative information on the migration of soluble metal species is available, few data have been obtained under well-defined environmental conditions. The object of this study is to quantify the effects of environmental conditions and sediment types on the long-term migration of soluble metal species in a recently polluted sediment–seawater system.

Experimental

Sample Collection. The sediment samples used in this study were collected from Los Angeles Harbor. These were newly deposited fine-grained sediments derived mainly from the Los Angeles metropolitan area. From the previous sediment survey (*13*), three types of surface sediment samples were chosen: silty clay, sandy silt, and silty sand sediments (Table I). These sediment samples were sealed in plastic bags and stored in ice at 4 °C for transport to the laboratory.

Seawater from a reference station (3 miles outside the breakwater of the Harbor, 33°41.5′N, 118°14.5′W) was collected in polyethylene containers.

Experimental Conditions. Possible environmental factors affecting the migration of trace metals in the sediment water interfaces are: redox potential (*9*), pH (*14*), type and size of solids (*15*), ligands and chelating agent (*16–18*), and temperature. In this study the levels of dissolved oxygen (DO) and total dissolved sulfides [$S(-II)_T$] were used as indicators of redox conditions. The pH of the interfacial seawater is generally buffered by dissolution or precipitation of calcium carbonate or silicates within the sediment; therefore, no external control was used. After adding seawater to the sediment, bubbling of seawater by various gases was unacceptable for controlling the redox conditions since volatile substances were rapidly lost from the system. The containers were presoaked with seawater for several days prior to the initiation of experiments.

Preliminary experiments showed that when the seawater was used without prefiltration, a rapid growth of algae usually occurred due to the release of nutrients from the sediments. As a result, the experiment was conducted in a dark constant temperature chamber (12 ± 2 °C), and the seawater was prefiltered through a 0.05-μm millipore nitrocellulose membrane filter. The experiment was performed in a closed reactor using either ultrapurified air, oxygen, hydrogen sulfide, or nitrogen gases depending upon desired redox conditions. These gases, supplied through a tube connected to the top of the reactor (Figure 1), additionally served to compensate for volume loss during sample withdrawal.

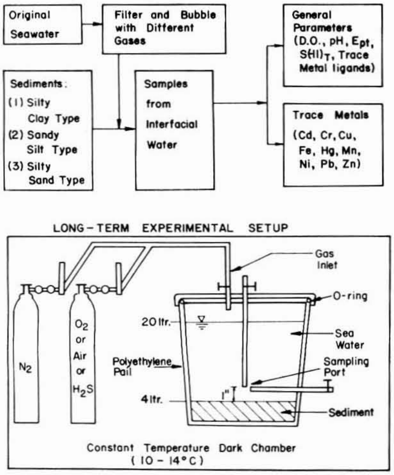

Figure 1. Flow chart and experimental setup on migration of trace metals between sediment–seawater interface

The operation of placing the sediments into the reactors was performed in a glove bag under a nitrogen atmosphere. Seawater was bubbled with appropriate ultrapurified gases before contacting the sediments. The sediment-to-seawater ratio in these reactors was fixed at about 1:4 (V/V). Three types of environmental conditions in the interfacial water were chosen:

Oxidizing condition:

$$DO = 5 \sim 8 \text{ mg/l.}$$

$$S(-II)_T = 0 \text{ mg/l.}$$

Slightly oxidizing condition:

$$DO = \leq 1 \text{ mg/l.}$$

$$S(-II)_T = \leq 0.05 \text{ mg/l.}$$

Reducing condition:

$$DO = 0 \text{ mg/l.}$$

$$S(-II)_T = 15 \sim 30 \text{ mg/l.}$$

The redox condition of the sandy silt sediment test was changed from reducing to slightly oxidizing conditions after one week of contact time to evaluate the effect of changing environmental conditions.

Analytical Methods. The seawater samples for migration study were taken approximately 1 in. above the surface of the sediment. Samples for trace metal analyses were withdrawn regularly at 0, ¼, 1, 3, 8, 15, 30, 45, 60, 90, and 150-day intervals, and filtered through 0.05-μm millipore nitrocellulose membrane filters. The sample was immediately acidified to about pH 1 for sample preservation. Samples for the analysis of other parameters [DO, pH, $S(-II)_T$, trace metal ligands] were withdrawn at the same contact time as samples for trace metal analysis.

The analytical methods of possible trace metal ligands such as C_T (total carbonates), SiO_3^{2-}, NH_3, NO_2^-, NO_3^-, PO_4^{3-}, and $S(-II)_T$ were adapted from methods described by "Standard Methods" (*19*), Riley et al. (*20*), and Jenkins et al. (*21*). Since most trace metal concentrations were at very low levels, special care was necessary for the selection of containers, reagents, and cleaning procedures to eliminate contamination (*22–25*). In this study all containers for seawater samples were made of quartz, Teflon, or polyethylene. All reagents used were of the highest quality obtainable, for example, ultrapurified acids, double subboiled MIBK, and demineralized, double subboiled water.

A Perkin-Elmer atomic absorption spectrophotometer Model 305B equipped with a Heated Graphite Atomizer (HGA) Model 2100 and deuterium arc background corrector was used for the trace metal analysis. For Fe, Mn, and Cr, concentrations were sufficiently high, and background effects could be reasonably removed by using the HGA direct injection method (*33*). For Cd, Cu, Ni, Pb, and Zn, the APDC-MIBK extraction method was used for preconcentration as well as removal of interfering salts; this was followed by the HGA direct injection method. The APDC-MIBK extraction method used was mainly modified from the procedure suggested by Brooks et al. (*28*), Paus (*27, 28*), Ediger (*29*), Dudas (*30*), and Kinrade and VanLoon (*31*). The details are described elsewhere (*33*). The overall precisions of the soluble trace metal analyses based on about 20 samples (and at least two determinations on each sample) were Cd (6.7%), Cr (5.5%), Cu (4.0%), Fe (4.5%), Mn (4.9%), Ni (4.6%), Pb (7.3%), and Zn (12.9%).

Table I. Composition of Original Sediments (Units in ppm Unless Specified)

Parameters	Silty clay[a]	Sandy silt	Silty sand	Natural background level[b]
TOC, %	2.12	1.90	0.53	0.1–0.3
COD	117 000	52 300	29 200	6 000–10 000
IOD	1 570	538	383	40–100
TVS, %	10.1	4.59	2.80	1–2
Acid soluble sulfide	1 670	258	163	
Organic N–N	2 820	357	689	30–100
Total N–N	2 920	357	706	30–100
Total PO_4^{3-}–P	1 470	886	679	400–500
Cadmium	1.87	1.57	0.63	1–1.5
Chromium	187	174	114	10–30
Copper	152	89.9	45.7	5–10
Iron	32 000	22 200	15 500	12 000–15 000
Mercury	1.43	0.69	0.28	0.03–0.05
Manganese	414	411	319	
Nickel	42.8	31.1	20.6	15–20
Lead	177	93.6	64.8	20–50
Zinc	415	174	115	30–35
Particle size <5 μm, %	32	20	12	

[a] Classification of sediments is made according to method suggested by the U.S. Army Corps of Engineers. [b] Natural background levels in adjacent San Pedro Bay (from ref. *13*).

Results

General Parameters. The general characteristics of sediment and seawater samples before contacting are listed in Tables I and II. Generally, the levels of DO and $S(-II)_T$ in the interfacial water were maintained within the desired ranges. The changing pattern of pH for oxidizing and slightly oxidizing conditions was quite similar with pH decreasing from 8.2–8.6 to about 7–7.5 (same as the pH values of the pore water). For reducing conditions the pH levels were increased from 6.8 to about 7–7.5. Reducing conditions released more soluble nitrogen and phosphate compounds, about 10–20 times that of oxidizing conditions or the original seawater conditions (Table II) after long-term incubation. Clayey sediment showed higher releasing rates for these compounds.

The soluble silicate concentrations were increased from about 0.2 ppm to about 10–17 ppm (as Si) under all conditions. Total dissolved carbonates were increased from about 2.4×10^{-3} M to $8 \times 10^{-3} - 2 \times 10^{-2}$ M with higher rates of increase under oxidizing conditions.

Trace Metals. The results of the long-term migrations of trace metals are shown in Figures 2–8. These results indicate that the release of trace metals varied significantly with environmental conditions and sediment types. In general, concentrations of trace metals in the interfacial waters were at the sub-ppb levels. The experimental results can be categorized into three different groups:

- The release of trace metals increased as the redox conditions became more reducing. Fe and Mn were in this category (Figures 2 and 3).
- The release of trace metals increased as the environment became more oxidizing. This included Cd, Cu, Ni, Pb, and Zn (Figures 4–8).
- No significant change of metal concentrations in the interfacial waters; Cr and Hg were in this category. Throughout the experiment, concentration of Cr stayed between 0.4–0.9 ppb, while Hg concentration remained around 0.1 ppb.

In the second category, trace metal concentrations under a reducing environment increased gradually and eventually approached the values of a slightly oxidizing environment. Under the same redox conditions, the migration trend is independent of sediment types. The experimental results show that the trend of migration is controlled mainly by the redox condition of the overlying seawater and that the flux is controlled chiefly by the type of sediment.

The relation between the migration trend and redox condition also can be obtained from the sandy silt sediment experiment. In this experiment, oxygen was introduced into the reducing reactor after one week of incubation, changing redox conditions from reducing to slightly oxidizing conditions. After

Table II. General Characteristics of Original Seawater (ppb)

	Sediments tested		
Parameters	Silty clay	Silty sand	Sandy silt
NH_3–N	Trace	Trace	210
Soluble Organic–N	210	320	370
NO_2^-–N	26	2	3
NO_3^-–N	630	610	20
Soluble ortho–P (as P)	24	20	24
Soluble total–P	140	110	68
Total soluble silicon (as Si)	430	320	120
Cd	0.02	0.04	0.04
Cr	0.52	0.45	0.25
Cu	0.30	0.65	7.60
Fe	0.50	0.20	0.55
Hg	0.10	0.12	0.02
Mn	0.30	0.10	0.30
Ni	0.20	0.10	0.40
Pb	0.10	0.04	0.08
Zn	0.52	0.38	2.15

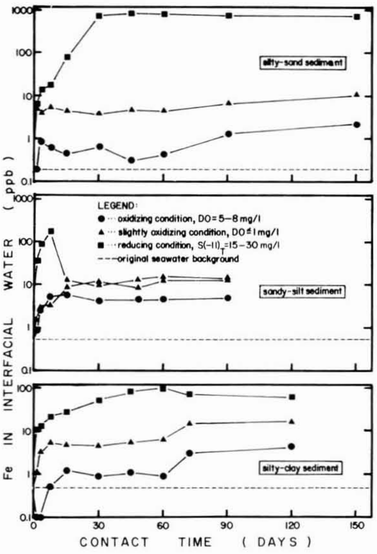

Figure 2. Concentration of Fe vs. contact time in sediment–seawater interface

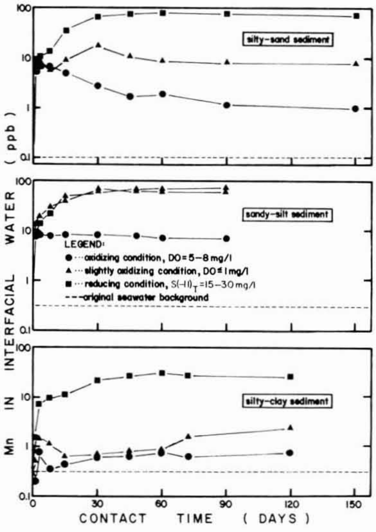

Figure 3. Concentration of Mn vs. contact time in sediment–seawater interface

changing the redox conditions from a reducing to a slightly oxidizing environment during the experiment, the concentrations of trace metals in the interfacial water approached those values in the original slightly oxidizing condition.

The geochemical partitioning of trace metals in the surface sediment (top 1 cm) was also performed (*33*). The trace metals associated with organic or sulfide solids in the sediment were gradually changed to solids of carbonate [$CdCO_3$, $Cu_2CO_3(OH)_2$, $NiCO_3$, $PbCO_3$], hydroxide [$Fe(OH)_3$], oxyhydroxide ($FeOOH$, $MnOOH$), oxide (MnO_{1-2}, Fe_2O_3) or silicate ($ZnSiO_3$) under aerobic conditions (see ref. *33* for details). The concentrations of trace metals in the interfacial waters were limited by the prevailing solids at different redox conditions discussed in the following section.

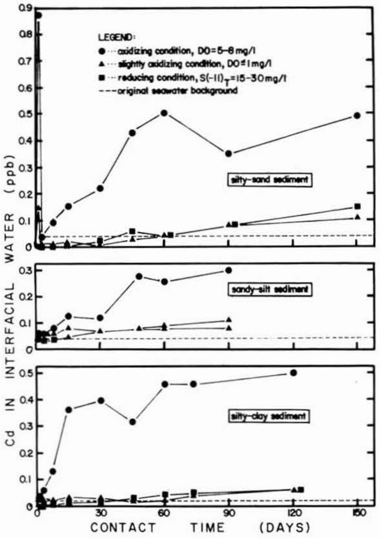

Figure 4. Concentration of Cd vs. contact time in sediment–seawater interface

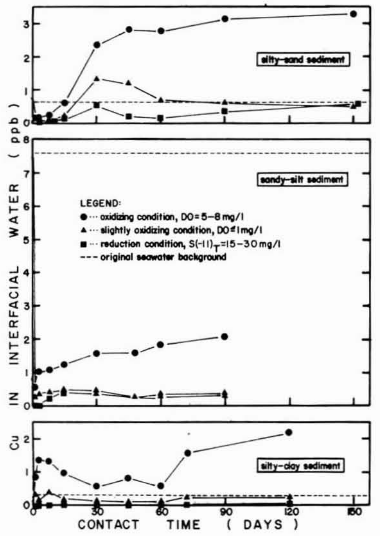

Figure 5. Concentration of Cu vs. contact time in sediment–seawater interface

Discussion

Metal Migration Under Reducing Conditions. Under the reducing environments, Fe and Mn were released to the interfacial seawater in significant quantities, while other metals (Cd, Cu, Ni, Pb, and Zn) were decreased in comparison with the original seawater background. This might be related to the formation of sulfide solids. Thermodynamic calculations (Eh-pH plot or ion-ratio methods) as well as experimental results of the geochemical partitioning of trace metals in the surface sediments (*33*) strongly support the argument that metallic sulfide solids are the predominant species. Over a 4–5-month period, these sulfide solids [except Cr, which might form $Cr(OH)_3$] would regulate the free metal ion con-

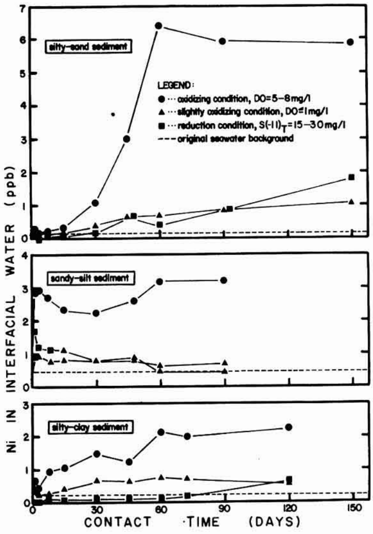

Figure 6. Concentration of Ni vs. contact time in sediment–seawater interface

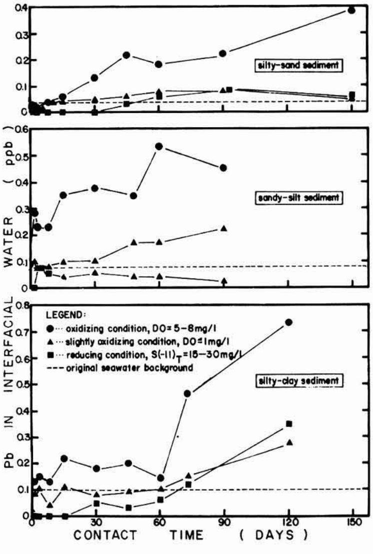

Figure 7. Concentration of Pb vs. contact time in sediment–seawater interface

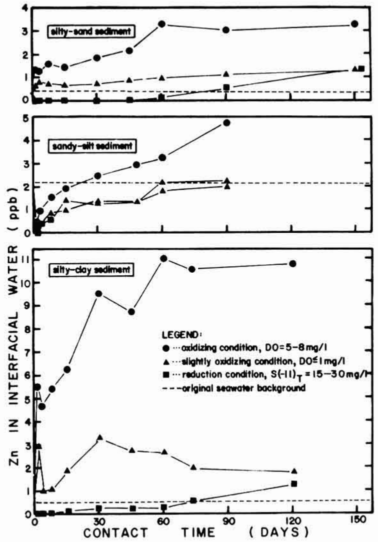

Figure 8. Concentration of Zn vs. contact time in sediment–seawater interface

centrations through dissolution or precipitation. In addition to the free ions, the total concentrations of trace metals in the interfacial waters would be also affected by the type and concentration of ligands present.

An equilibrium model controlled by sulfide solids [except Cr, which is controlled by $Cr(OH)_3$] was used to compare the metal concentrations from calculation with analytical results (Figure 9). This model was calculated at $T = 12$ °C, $I = 0.7$, by using the "K approach method" (*9*) assuming simultaneous equilibrium among major cations, trace metals, assumed controlling solids, and all known ligands. The total concentrations of known ligands are listed as follows:

Inorganic Ligands (units in M). $[C_T] = 8 \times 10^{-3}$, $[B_T]$ (total soluble borate) $= 6 \times 10^{-4}$, $[Si_T]$ (total soluble silicate) $= 5 \times 10^{-4}$, $[NH_3] = 4 \times 10^{-4}$, $[NO_2^-] = 7 \times 10^{-7}$, $[NO_3^-] = 1.4 \times 10^{-6}$, $[PO_4^{3-}] = 2.5 \times 10^{-5}$, $[S(-II)_T] = 5 \times 10^{-4}$, $[SO_4^{2-}] = 2.8 \times 10^{-2}$, $[F^-] = 8 \times 10^{-4}$, $[Cl^-] = 0.56$, $[Br^-] = 8 \times 10^{-6}$, and $[I^-] = 5 \times 10^{-7}$.

Organic Ligands. Data were mainly from mean values presented by Tatsumoto et al. (*34*), Park et al. (*35*), Duursma (*38*), Siegel and Degens (*37*), and Jeffery (*38*). A factor of 20 was applied based on the fact that the release of N and P compounds into the interfacial water was about 20 times higher than that in the average seawater. A total of 24 organic ligands was included (units in M): acetic acid (2×10^{-4}), alanine (1.12×10^{-6}), arginine (1.15×10^{-7}), aspartic acid (1.2×10^{-6}), citric acid (1.04×10^{-6}), cysteine (1.65×10^{-7}), glutamic acid (1.09×10^{-6}), glycine (4.0×10^{-6}), glycollic acid (7.89×10^{-6}), histidine (2.58×10^{-7}), *p*-hydroxybenzoic acid (4.35×10^{-7}), hydroxyproline (3.05×10^{-7}), lactic acid (1.11×10^{-7}), leucine (7.63×10^{-7}), lysine (6.85×10^{-7}), malic acid (1.49×10^{-5}), methionine (1.34×10^{-7}), ornithine (8.47×10^{-7}), proline (1.74×10^{-7}), serine (1.90×10^{-6}), threonine (8.40×10^{-7}), tryptophane (9.80×10^{-8}), tyrosine (5.24×10^{-7}), and valine (5.13×10^{-7}). It should be emphasized that this equilibrium model did not include organic compounds found in seawater for which stability data are not available.

The stability constants for metal-organic complexes were obtained from Sillen and Martell (*16, 17*); constants for metal-inorganic complexes were mainly from refs. *16–18* and *39–41*. The results of calculations are given in Figure 9. Final experimental data are also plotted for comparison with the theoretical calculations.

After long-term incubation the concentrations of Cd, Hg, Mn, Ni, and Pb in all tests and Fe in the clayey sediment test were close to the concentrations from equilibrium calculations. For Cr there is only a minor difference between the calculated value and the experimental results (e.g., at pH 7, the calculated value is about 5 ppb, and the experimental result was close to 1 ppb).

The closeness of the experimental results and the calculated values suggests that the formation of metallic solids plus the complex formation may, in fact, control the soluble concentrations of trace metals in the interfacial waters. The important thermodynamic data and the major soluble complexes are listed in Table III. From the calculations it can be shown

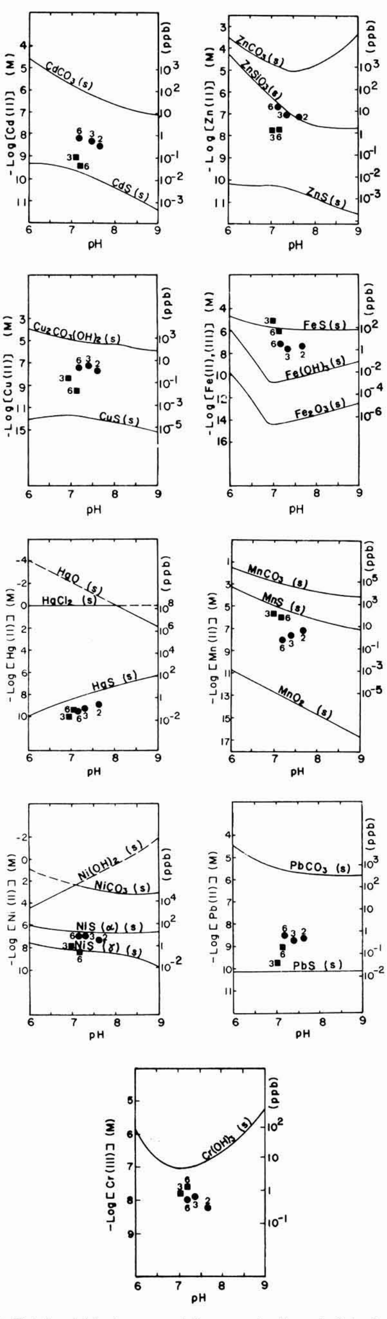

Figure 9. Total soluble trace metal concentrations in interfacial seawater by equilibrium model calculation (see text for explanation)

Square and circular symbols: final experimental results of trace metal concentrations in interfacial seawater under reducing and oxidizing conditions, respectively. Arabic numerals: type of sediment used: 2 = sandy silt, 3 = silty sand, 6 = silty clay

that the sulfide complexes are the most important soluble species for Cd, Hg, and Pb, organic complexes for Fe and Ni, chloride complexes for Mn, and hydroxide complexes for Cr.

For Cu, Zn, and Fe in the sandy sediment test, significant differences were found between the equilibrium calculations and the experimental results. The calculated value for Cu (most in the form of bisulfide complexes) is about 10^{-4} ppb which is much lower than the measured figures (0.02–0.55 ppb). The subsequent increase of Cu in the interfacial water may be due to slow precipitation or nucleation, or may be due to the existence of humic-copper complexes.

The calculated concentrations of Zn can only account for about 10^{-4} of the measured concentrations. The concentration of soluble Fe (about 750 ppb) in the sandy sediment test was higher than the calculated value (about 100 ppb). The differences for Zn and Fe are probably caused by the omission of humic substances in the equilibrium model. To reconcile the difference between calculated and experimental values, the minimum pK values for Zn-fulvic or Fe-fulvic complexes would have to be about 4.8–4.9 and 5.1–7.7, respectively (assuming fulvic acid = 3×10^{-5} M). These values are reasonable in comparison with the values suggested by Schnitzer and Hansen (*42, 43*), Geering et al. (*44*), and Schnitzer and Skinner (*45*). Therefore, it is reasonable to suggest that complexes of humic substances may become the predominant species for soluble Zn and Fe under the reducing condition. The possibility of the presence of colloids smaller than 0.05 μm leading to an overestimate of the soluble fraction for these metals also cannot be ruled out.

Metal Migration Under Oxidizing Conditions. Most of the trace metals, with the exception of Cr and Hg, were released under oxidizing conditions. From the geochemical fractionation study (*33*), after contacting these polluted reducing sediments with aerobic seawater, the controlling solids may change gradually from metallic sulfides to carbonate, hydroxide, oxyhydroxide, oxide, or silicate solids. As a result, the solubility of trace metals was also changed. Solubility of Cd, Cu, Ni, Pb, and Zn might be increased due to the formation of higher solubility solids, while solubilities of Fe and Mn might be decreased due to the formation of high oxidation states, lower solubility oxides or hydroxides. Therefore, the solid transformation and complexes formation also might become important factors for the migration of metals under the oxidizing environment. Through the thermodynamic calculation using the ligands as in the reducing conditions, except the following ligands, organic ligand concentrations ($\frac{1}{20}$ of the concentrations of the reducing condition), $[C_T] = 10^{-2}$ M, $[Si_T] = 4 \times 10^{-4}$ M, $[NH_3] = 0$, $[NO_2^-] = 0$, $[NO_3^-] = 4 \times 10^{-5}$ M, $[\Sigma PO_4^{3-}] = 2 \times 10^{-6}$ M, $[S(-II)_T] = 0$, it was found that only Zn is close to the experimental data, and most of the other trace metals analyzed were either far below the equilibrium concentration (Cd, Cu, Ni, and Pb) or far above the equilibrium concentration (Fe and Mn), as shown in Figure 9.

This discrepancy may be explained by the following phenomena:

Adsorption Effect. This effect could occur through the adsorption by clay minerals or hydrated oxides of iron and manganese. The formation of hydrated oxides of iron and manganese could happen under two circumstances: one is from the oxidation of the sulfide, hydroxide, or carbonate solids in the surface sediment; another is from the oxidation of the soluble species in the interstitial water (the original concentrations of Fe and Mn in the interstitial water were quite high, about 120–980 and 6–90 ppb, respectively). Due to the formation of these hydrated oxides, or due to the change of controlling mechanism from solubilities of sulfides to adsorption by other clay minerals, the soluble species of the trace metals (Cd, Ni, and Pb) could be scavenged. The concentration levels analyzed are probably a result of the competitive effect between the adsorption and dissolution mechanisms.

Low Oxidation Rate of Reducing Solids. The low oxidation rate of the reducing solids may also limit the migration of some metals from sediment to the interfacial water. From the geo-

Table III. Major Soluble Metal Species in Interfacial Seawater from Equilibrium Calculations (See Discussion Section for Details)

				Major soluble complex (at pH 7.5)		
Trace metals	Environmental condition	Assumed controlling solid	Solubility product Ksp (in pKsp)[a]	Major species	Formation constant, β (in log β)[a]	% of total soluble concn
Cd(II)	Oxidizing	$CdCO_3$	13.59	$CdCl^+$	2.69	56.5
				$CdCl_2^{\circ}$	2.69	15.2
				$CdCl_4^{2-}$	2.91	10.0
				$CdCl_6^{4-}$	2.25	9.1
				$CdCl_3^-$	2.78	9.0
Cd(II)	Reducing	CdS	26.96	$Cd(HS)_2^{\circ}$	15.21	97.2
				$Cd(HS)_3^-$	17.09	2.2
				$Cd(HS)_4^{2-}$	19.26	0.1
				$Cd(HS)^+$	7.94	<0.1
				$CdCl^+$	2.69	<0.1
Cr(III)	Reducing	$Cr(OH)_3$	33.52	$Cr(OH)_4^-$	33.12	90.2
				$Cr(OH)_2^+$	19.15	9.2
				$Cr(OH)^{2+}$	10.63	0.1
				Cr(citric acid)°	−5.55[b]	<0.1
				$Cr(serine)^{2+}$	8.79	<0.1
Cu(II)	Oxidizing	$Cu_2CO_3(OH)_2$	33.16	$Cu[B(OH)_4]_2^{\circ}$	12.55	33.6
				$CuCo_3^{\circ}$	6.77	30.1
				$Cu[B(OH)_4]^+$	7.13	27.7
				$CuCl^+$	1.58	4.6
				$Cu(CO_3)_2^{2-}$	10.01	3.1
Cu(II)	Reducing	CuS	36.38	$Cu(HS)_3^-$	−4.40[b]	99.4
				$CuS(HS)_3^{3-}$	−4.40[b]	0.5
				$Cu(histidine)^+$	11.71	<0.1
				$Cu(histidine)_2^{\circ}$	19.73	<0.1
				$Cu[B(OH)_4]_2^{\circ}$	12.55	<0.1
Fe(III)	Oxidizing	$Fe(OH)_3$	39.29	$Fe(OH)_4^-$	35.29	97.1
				$Fe(citric\ acid)^-$	28.14	1.5
				$Fe(OH)_2^+$	20.37	1.2
				Fe(*p*-OH benzoic acid)$^+$	15.2	<0.1
				$Fe[B(OH)_4]_2^+$	15.6	<0.1
Fe(II)	Reducing	FeS	16.90	$Fe(citric\ acid)^{2-}$	18.64	86.6
				$FeHPO_4^{\circ}$	7.03	9.0
				Fe^{2+}	. . .	2.4
				$FeCl^+$	0.38	0.9
				$FeCl_2^{\circ}$	0.81	0.7
Hg(II)	Oxidizing	$HgCl_2$	15.10	$HgCl_4^{2+}$	15.6	80.4
		HgO	26.24[b]	$HgCl_3^+$	14.8	15.4
				$HgCl_2^{\circ}$	13.9	4.1
				$Hg(OH)_2^{\circ}$	22.4	<0.1
				HgClBr°	2.01[b]	<0.1
Hg(II)	Reducing	HgS	53.89	HgS_2^{2-}	0.57[b]	98.5
				Hg(cysteine)°	46.2	1.2
				$HgS(HS)_2^{2-}$	−3.70[b]	0.2
				$Hg(HS)_3^-$	−3.50[b]	<0.1
				$HgS(H_2S)_2^{\circ}$	−4.25[b]	<0.1
Mn(II)	Oxidizing	$Mn(OH)_2$	12.19	$MnCl^+$	1.08	38.1
		$MnCO_3$	9.20	$MnCl_2^{\circ}$	1.52	34.0
		MnO_2	0.92[b]	Mn^{2+}	. . .	17.2
				$MnCl_3^-$	1.11	7.4
				$MnHCO_3^+$	1.8	2.1
Mn(II)	Reducing			$MnCl^+$	1.08	38.2
		$MnCO_3$	9.20	$MnCl_2^{\circ}$	1.52	34.1
		MnS (pink)	9.70	Mn^{2+}	. . .	17.2
		MnS(precip.)	15.70	$MnCl_3^-$	1.11	7.4
				$MnHCO_3^+$	1.8	1.7
Ni(II)	Oxidizing	$NiCO_3$	8.2	Ni^{2+}	. . .	47.0
		$Ni(OH)_2$	14.81	$NiCl^+$	0.72	38.4
		(fresh)		$NiCl_2^{\circ}$	0.70	10.0
		$Ni(OH)_2$	17.31	$NiSO_4^{\circ}$	2.18	4.2
		(aged)		$Ni(OH)^+$	4.70	0.3
Ni(II)	Reducing	NiS(α)	18.5	$Ni(cysteine)^+$	10.48	99.0
		NiS(γ)	25.7	$Ni(tyrosine)_2^{\circ}$	10.36[b]	<0.1
				$Ni(histidine)^+$	9.79	<0.1
				$Ni(histidine)_2^{\circ}$	17.76	<0.1
				Ni^{2+}	. . .	<0.1
Pb(II)	Oxidizing	$PbCO_3$	13.30	$PbCO_3^{\circ}$	7.4	64.6
				$PbCl_6^{4-}$	3.02	28.7
				$PbCl^+$	1.60	2.4
				$Pb(CO_3)_2^{2-}$	9.89	2.0
				$PbCl_2^{\circ}$	1.78	1.0

Table III. Continued

				Major soluble complex (at pH 7.5)		
Trace metals	Environmental condition	Assumed controlling solid	Solubility product Ksp (in pKsp)[a]	Major species	Formation constant, β (in log β)[a]	% of total soluble concn
Pb(II)	Reducing	PbS	27.65	$PbS(HS)^-$	-6.9[b]	83.9
				$PbS(H_2S)^\circ$	-6.8[b]	16.0
				$PbCO_3^\circ$	7.4	<0.1
				$PbCl_6^{4-}$	3.02	<0.1
				$PbCl^+$	1.60	<0.1
Zn(II)	Oxidizing	$ZnCO_3$	10.65	Zn^{2+}	...	38.1
		$ZnSiO_3$	21.03[b]	$Zn(OH)_2^\circ$	12.89	29.6
				$ZnCl^+$	0.43	18.0
				$ZnCl_2^\circ$	0.61	6.6
				$ZnSO_4^\circ$	2.27	4.3
Zn(II)	Reducing	ZnS	22.60	$Zn(HS)_3^-$	-3.0[b]	99.2
				Zn^{2+}	...	0.2
				$Zn(OH)_2^\circ$	12.89	0.1
				$ZnCl^+$	0.43	<0.1
				$ZnCl_2^\circ$	0.61	<0.1

[a] Sources of pKsp and log β values are cited in the text. All values of pKsp and log β are corrected to the conditions of $I = 0$ and $T = 12$ °C using the Davies modification of the Debye-Hückel expression and Van't Hoff equation. When the value of ΔHr (enthalpy of reaction) is unknown, then Ksp and β values for the other temperature (usually $T = 15 \sim 25$ °C) were used. [b] $HgO(s) + H_2O \rightleftharpoons Hg^{2+} + 2OH^-$; $MnO_2(s) + 2H^+ \rightleftharpoons Mn^{2+} + \frac{1}{2}O_2 + H_2O$; $ZnSiO_3(s) + H_2O \rightleftharpoons Zn^{2+} + 2OH^- + SiO_2(s)$; Cr^{3+} + citric acid $(H_3L) \rightleftharpoons CrL^\circ + 3H^+$; $CuS(s) + H_2S(aq) + HS^- \rightleftharpoons Cu(HS)_3^-$; $CuS(s) + 3HS^- \rightleftharpoons CuS(HS)_3^{3-}$; $Hg^{2+} + Cl^- + Br^- \rightleftharpoons HgClBr^\circ$; $HgS(s) + S^{2-} \rightleftharpoons HgS_2^{2-}$; $HgS(s) + 2HS^- \rightleftharpoons HgS(HS)_2^{2-}$; $HgS(s) + H_2S(aq) + HS^- \rightleftharpoons Hg(HS)_3^-$; $HgS(s) + 2H_2S(aq) \rightleftharpoons HgS(H_2S)_2^\circ$; Ni^{2+} + tyrosine$^-$ (or HL^-) $\rightleftharpoons Ni(HL)_2^\circ$; $PbS(s) + H_2S(aq) \rightleftharpoons PbS(H_2S)^\circ$; $PbS(H_2S)^\circ \rightleftharpoons PbS(HS)^- + H^+$; $ZnS(s) + H_2S(aq) + HS^- \rightleftharpoons Zn(HS)_3^-$.

chemical phase study (*33*), even with exposure of these polluted sediments in aerobic conditions up to five months, the sulfide solids still cannot be totally oxidized.

Among the metals studied, both HgS and $Cr(OH)_3$ have a low oxidation rate. This might account for the slow mobilization rates of Hg and Cr.

Other metallic sulfides (CdS, CuS, NiS, and PbS) have higher oxidation rates than HgS. Therefore, for these metal species, the higher solubility solids are more easily formed. Under the oxidizing conditions, the release of these metals will occur.

In the case of Mn, the equilibrium concentration probably is controlled by the presence of intermediate solids such as hydroxides (prochroite) or oxyhydroxide (manganite) and not higher oxides (pyrolusite). Therefore, the measured concentrations were greater than the calculated values using pyrolusite as the controlling solid.

Zn is the only element which reached the equilibrium concentration as calculated. This may result from the fact that ZnS had a very high oxidizing rate (*33*); thus, the equilibrium state could be reached rather quickly.

Formation of Humic Complexes. The soluble concentrations of Fe in the oxidizing condition were higher than the equilibrium concentration calculated by using amorphous $Fe(OH)_3$ as the controlling solid. These high concentrations of soluble Fe are quite possible from the formation of humic complexes as mentioned before. The polymolecular complex formation may also be applied to Mn to account for the high soluble concentrations.

Metal Migration Under Slightly Oxidizing Conditions. In general, the concentrations of trace metals in interfacial seawater under slightly oxidizing conditions were between the oxidizing and reducing conditions. Under oxygen-deficient conditions, due to the continued upward diffusion of dissolved sulfide, it is quite reasonable that the released amount of trace metals was between the oxidizing and reducing conditions. The soluble levels of metals were affected by the competition between the dissolution and the deposition mechanisms.

Conclusions

The experimental data show that the type of sediment (i.e., clay, silt, or sand) does not control the direction of metal migration. It is regulated mainly by the chemistry of the immediate overlying water as well as that of the interstitial water. The redox condition [especially the levels of DO and $S(-II)_T$] is the principal factor. In general, the concentrations of trace metals in the interfacial water were in the sub-ppb ranges.

The release (migration from sediment to interfacial water) of Fe and Mn increased as the redox conditions became more reducing. The released amount of Cd, Cu, Ni, Pb, and Zn increased as the redox conditions became more oxidizing. No significant change was observed for Cr and Hg under all redox conditions.

The possible mechanisms for migration of soluble trace metals between the sediment–seawater interface are chemical transformation, bio-oxidation, sorption, dissolution, precipitation, complexation, and diffusion. The first four mechanisms are likely to take place at the site of the sediment particle surface and finally form the solubility controlling solids of trace metals. On the other hand, the last three mechanisms are likely to take place in the bulk solution; they can further regulate the concentration levels and speciation of the trace metals in interfacial waters.

Under reducing conditions after long-term incubation, the analyzed concentrations of Cd, Hg, Mn, Ni, Pb, and Cr were very close to the solubility equilibrium calculations. Formed complexes were the main species to account for the concentration levels analyzed. The difference between the model and the experimental results for Cu, Zn, and probably Fe may come from the omission of humic-metal complexes.

Under aerobic conditions after long-term incubation, most of the analyzed trace metal concentrations were either far below (Cd, Cu, Ni, and Pb) or far above (Fe and Mn) the equilibrium concentration. These differences probably come from sorption phenomena as well as competitive effects between the dissolved oxygen and dissolved sulfides on the sediment surfaces. It is likely that the equilibrium conditions were not reached.

Despite the complexity of the metal chemistry in the sediment–water interface, this study shows that the behavior of metal species can be reasonably well predicted if the environmental conditions are known.

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Effects of Annual and Accumulative Applications of Sewage Sludge on Assimilation of Zinc and Cadmium by Corn (*Zea mays* L.)

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In 1967 relatively large demonstration and research programs were initiated to determine the feasibility of utilizing heated anaerobically digested sewage sludge from the Metropolitan Sanitary District of Chicago wastewater treatment plants as a fertilizer and soil amendment (*1*). When samples of digested sludge from the Southwest and Calumet wastewater treatment plants were analyzed in 1966, several heavy metals were found at concentrations considerably higher than amounts in normal soils. Therefore, one of the main objectives of the research was to monitor chemical compositional changes in soils, crop tissues, and water samples collected from large-scale field lysimeters.

Along with several laboratory and greenhouse studies conducted during the initial phases of the project (*2*), several field studies were established to assess the effects of long-term accumulations of sludge-borne heavy metals in soils on the macro- and micro-flora of sludge-amended soil (*3, 4*). Long-term field studies were considered from the beginning to be an essential part of the research program because it was recognized that the laboratory and greenhouse results were of little value in predicting environmental changes to be expected from full-scale sludge utilization programs. Melsted (*5*) discussed in some detail why data from short-term laboratory nutrient culture systems and greenhouse pot studies can seldom be applied to predict effects under field conditions.

The results presented here were from one of several field studies which were initiated in 1968 and 1969, involving annual applications of digested sludge at various loading rates and several crop species. During the existence of the continuous corn study discussed here, 16 chemical elements were monitored in soils and crop tissues more or less continuously while others were included occasionally. However, only analytical results for Zn and Cd were considered for discussion here because these two elements always occur in municipal wastewater treatment plant sludges at concentration levels (dry weight) several times higher than those in agricultural soils and in forms which can be readily assimilated and deposited in plant tissues (*3, 6*). Because of bioaccumulations in plant tissues, these two elements present the most obvious potential phytotoxic and/or animal health hazard.

■ Digested sludge from wastewater treatment plants was applied annually on a silt loam soil at various application rates where corn was continuously planted from 1968 through 1975. Sludge applications resulted in significant increases of total and 0.1 N HCl extractable Zn and Cd in the soil as well as in plant leaves and grain. Phytotoxic conditions were never observed, possibly because the main factor controlling the assimilation of Zn and Cd by corn was amounts of sludge-borne Zn and Cd applied immediately prior to planting, rather than total amounts applied in previous years. The organic component of sludge admixed with soil was not a major factor in protecting plants against excessive soil concentrations of Zn and Cd. If the digested sludge used here were applied annually at rates just adequate to provide supplemental nitrogen for corn, neither Zn nor Cd concentrations in grain would present a health hazard to animals as judged by levels reported in grain produced in normal environments. If sludge applications were terminated on maximum sludge-treated plots, apparently Cd contents of corn grain would decrease during the succeeding crop to levels within the upper range of concentrations reported in the literature for grains produced on soils not contaminated by additions of the element.

To our knowledge, these findings with regard to Zn and Cd are the first reported from long-term field studies where applications of digested sludge on land were similar to methods and rates which might be employed by those using sewage sludge as a soil amendment. In particular, the Zn and Cd data were interpreted from the viewpoint of determining the relationship between practical annual sludge loading rates, total accumulations of sludge-borne Zn and Cd in soils during successive years of applications, and resulting concentration enhancement of the two metals in crop tissues.

Experimental

Four replications of 6.1 by 12.2 m plots with four sludge treatments randomized within blocks were established in 1968 on Blount silt loam soil (Aeric ochraqualf, fine, illitic, mesic) occupying part of the cultivated area on the Northeast Agronomy Research Center near Joliet, Ill. Digested sludge was applied by furrow irrigation first in 1968 and annually thereafter during the growing season and sometimes during the fall after grain harvest. All plots were annually fertilized with a broadcast application of KCl to supply 134 kg K/ha, and control (zero liquid sludge) plots were further treated with annual broadcast fertilizer applications supplying 268 kg N/ha and 134 kg P/ha. As often as weather conditions permitted, liquid digested sludge was transported by truck-trailer tanks from MSD of Chicago Southwest or Calumet wastewater treatment plants and applied at liquid depths of 25.4 mm (maximum), 12.7 mm (one-half maximum), and 6.4 mm (one-fourth maximum) to each of the appropriate plots on the same day.

Immediately after ridges and furrows were established, corn (*Zea mays* L.) was planted at rates calculated to give a plant population of 60 000 plants per hectare on top of ridges spaced 76 cm apart. In general, sludge was applied for the first time each year when corn plants had reached a height of about 15 cm.

Samples of digested sludge were collected at the beginning and end of each irrigation event and composited before drying at 110 °C for a period of 24 h preparatory to later analyses.

Soil samples were collected each spring after plowing and before the ridging operation. Six core samples from 0 to 15.2 cm depth were collected and composited from each plot. They were then dried at 60 °C, crushed, split, and pulverized to pass a 60-mesh screen using a grinder equipped with tungsten-carbide faces.

Samples of corn leaves opposite and below the primary ear shoots were collected when about 10% of the plants had tasseled. Leaf samples were washed in distilled water immediately after cutting, dried at 60 °C, and ground in a Wiley mill. Grain samples, collected from larger shelled-grain samples used to determine yield responses, were dried and ground in the same manner as leaf samples.

Sludge and grain samples were prepared for analyses by slowly heating to 500 °C for 24 and 48 h, respectively, and subsequently dissolving the ash in 1 N HCl. Soil samples were prepared for determinations of total Zn and Cd by slowly heating to 500 °C for 24 h and digesting in concentrated HCl–HF from which residues were subsequently dissolved in 1 N HCl. Levels of Cd in grain, soil, and sludge samples were not significantly different regardless of whether organic matter was oxidized by ashing or perchloric-nitric digestion. But Cd levels were sometimes less in ashed as compared to digested leaf samples. Thus, leaf samples were wet ashed in HNO_3 at 90 °C and dissolved in 1 N HNO_3. The procedure for determining 0.1 N HCl extractable Zn and Cd from soils was essentially as outlined by Viets and Boawn (*7*), except only 1 g of soil was used and the time of shaking was 2 h. Sludge, soil, and plant tissue samples were analyzed for Zn and Cd contents by atomic absorption spectrometry with an instrument equipped to make simultaneous deuterium arc background corrections to the data. Total organic carbon contents of soils were determined by the Walkley-Black method as described by Allison (*8*).

Results and Discussion

The data presented in Table I show that annual liquid sludge loading rates varied from a low of 127 mm in 1972 to a high of 381 mm in 1971. Average solids content varied from a low of 1.91% in 1969 to a high of 3.38% in 1971. Thus, the annual applications of sludge-borne Zn and Cd varied from year to year depending on the depth of sludge that could be applied during the growing season and the concentration of solids contained in the digested sludge. On a dry weight basis, sludge used in the study had an average concentration of 200 ppm Cd and 4300 ppm Zn.

Corn grain yields (Table II) were significantly increased by sludge applications in 1970, 1973, and 1974. The most favorable response to sludge application was observed in years when weather conditions were somewhat unfavorable for the growth of corn. As judged by yields from control plots, both 1969 and 1975 were years in which weather conditions were exceptionally favorable for growth. In these two years, corn yields

Table I. Annual Maximum Applications and Amounts of Solids, Zn and Cd, Supplied as Constituents of Digested Sludge[a]

	Liquid sludge		Cumulative		
Year	Total annual depth, mm	Av solids content, %	Solids, mt/ha	Zn, kg/ha	Cd, kg/ha
1968	171	3.01	51.5	317	11
1969	254	1.91	99.8	787	28
1970	229	2.31	152.5	1201	48
1971	381	3.38	280.9	1806	77
1972	127	2.02	306.5	1905	81
1973	279	2.23	368.6	2122	88
1974	178	2.75	417.4	2358	101

[a] Sludge was applied during the growing season by furrow irrigation at a maximum application rate of 25.4 mm as often as weather conditions permitted. Appropriately lesser amounts were applied on the same day on 0.25 and 0.50 maximum-treated plots.

Table II. Grain Yields (mt/ha) from Plots Treated Annually with Various Rates of Digested Sludge and Continuously Planted to Corn for Eight Years (Adjusted to 15.5% Moisture)

	Sludge application rate, mm				
Year	0	6.4	12.7	25.4	LSD
1968	4.16	6.03	7.16	7.02	
1969	8.96	9.34	9.42	9.44	
1970	5.53	7.48	7.62	8.63	1.84[a]
1971	6.06	6.50	6.92	7.88	
1972	8.94	8.62	8.99	8.82	
1973	4.00	6.05	6.72	7.63	1.88[a]
1974	3.47	3.21	3.85	5.11	0.99[a]
1975	8.15	9.36	9.44	9.43	
Av	6.16	7.07	7.51	8.00	

[a] Significant at the 0.01 level of probability.

were not significantly higher on sludge-treated plots than on conventionally fertilized control plots; yields from maximum sludge-treated plots in 1969 were similar to those obtained from the same plots in 1975. That yields from maximum sludge-treated plots in 1975 were not less than those produced in 1969 is of significance because during the intervening years, 2041 kg Zn/ha and 90 kg Cd/ha were admixed with the soil as constituents of digested sludge.

According to amounts of sludge-borne Zn and Cd added to the soil during all years from 1968, at the beginning of the 1974 growing season the soil surface samples (0–15 cm depth) from maximum sludge-treated plots should have had concentration levels of roughly 1000 ppm of Zn and 40 ppm of Cd. This assumes none was lost by soil erosion or by leaching to or mixing with lower depths in the soil profile. But by comparison of calculated contents and total concentrations found in soil samples from maximum sludge-treated soil as presented in Tables III and IV, only about 46% of the added Zn and 40% of the added Cd were retained in the soil surface. Since all plant residues were returned (only 2.7 kg Zn/ha and 0.04 kg Cd/ha at most could have been removed from plots as constituents of harvested grain), and no perceptible amounts of soil erosion from nearly level plots were ever observed, low retention of the metals in the immediate soil surface is probably due to a combination of processes. Based on the authors' as yet unpublished data, it appears that the major portions of the metals unaccounted for in the soil surface were mixed to deeper depths by plowing and transported by percolating water to deeper soil depths than were sampled to obtain the results reported here. Nevertheless, the total soil Zn and Cd contents reported in Tables III and IV at the beginning of the 1975 growing season were about 50% greater than the highest concentrations reported for normal or uncontaminated agricultural soils (*9*).

Purves (*10*) stated that about 200 ppm of Zn, extractable from soils with 2.5% acetic acid, would indicate that harmful effects on plants are possible. Although not directly comparable because of the different acids used, 1974 concentrations of 0.1 N HCl extractable Zn in maximum sludge-treated soil (Table III) were very near phytotoxic levels as inferred from the statement by Purves (*10*). The inference is based on the fact that we have found 0.1 N HCl will extract from the soil used for this study about 1.4–2.0-fold higher concentrations of Zn than will 2.5% acetic acid. Where split soil samples collected from maximum sludge-treated plots in 1974 were dried at 60 °C, mean acetic acid extractable Zn contents were 154 ppm, but those which were air-dried contained 238 ppm of extractable Zn. At any rate, the additional 236 kg/ha of sludge-borne Zn applied in 1974 (Table I) did not adversely affect 1975 crop yields, even though critical phytotoxic soil levels were exceeded.

Concentrations of 0.1 N HCl extractable Cd shown in Table IV were within experimental error equivalent to total Cd contents in sludge-treated soil. (CV ranged from 2.5 to 4.2% for total Cd and from 1.0 to 8.5% for extractable Cd, depending on Cd levels in the soil). Evidently, 0.1 N HCl is an especially strong extractant for Cd and is no better than total soil contents as a tool for predicting phytotoxic levels.

Based on toxic levels for animals, plant levels at which appreciable Zn transfer from the vegetative portion of the plant to grain occurs, and levels known to be toxic to the plant itself, Melsted (*5*, p 127) suggested a tolerance level of 300 ppm in corn leaves at or opposite and below ear level at tassel stage. That tolerable levels of Zn in corn leaves were exceeded in samples from maximum sludge-treated plots in both 1972 and 1973 can be seen by the data exhibited in Table III. The highest Zn level of 381 ppm occurred in 1972; yet, no decrease in corn yields was observed (Table II). Also, the highest Zn level in corn grain from maximum sludge-treated plots occurred in 1970, a year in which corn yields were significantly increased by sludge applications.

Allaway (*11*) concluded that plants may accumulate up to about 3 ppm of Cd before severe plant growth depression occurs. This concentration corresponds to the tolerance level suggested by Melsted (*5*). But results reported in Table IV show that Cd concentrations in corn leaf samples from maximum sludge-treated plots in all years exceeded the suggested 3 ppm tolerance level by several times. Comparing grain yields from control with maximum sludge-treated plots, there is no evidence of the occurrence of a growth depression from Cd levels exceeding 20 ppm in leaf tissues (Table II). Higher levels of leaf Cd were associated with higher Cd contents in grain ($r = 0.79$, $Pr \leq 0.01$), but in spite of this, leaf-to-grain ratios of Cd concentrations varied from 36 in 1973 to 13 in 1974. The extremes of leaf-to-grain Cd concentration ratios were exhibited during two years when applications of sludge significantly increased grain yields.

To further examine the manner in which the most recent sludge application affected Zn and Cd concentrations in plant tissues as compared to total accumulative applied amounts, treatment mean concentrations (Tables III and IV) were used to calculate the partial and standard partial regression coefficients presented in Table V. Results of partial regression analyses showed that Zn concentrations in both leaf and grain tissues were increased to a greater extent by annual applications of sludge-borne Zn than by amounts accumulated during previous years of application. On the other hand, standard partial regression coefficients indicate that accumulative applications of sludge-borne Zn exerted a strong influence on levels of Zn in corn plant tissues. The importance of accumulative applications as indicated by the standard partial regression coefficients was exaggerated because the accumulative applications included the last annual application as well. Thus, the magnitude of the coefficient for the effect of accumulative levels was increased by the included annual application. This method of calculating the coefficients presented in Table V was used because annual sludge applications were never terminated during the data collection period. Although the results are not shown, the effects of annual vs. accumulative were separated by regressing the results from tissue analyses for any year (dependent variable) on sludge-borne metal applications during the preceding year (independent variable A) and accumulative sludge-borne metal applications (independent variable B) for the calendar year two years previous to the crop year. Using this approach, standard partial regression coefficients were almost equal, and the ratios of annual to accumulative partial regression coef-

Table III. Mean Dry Weight Contents of Total and 0.1 N HCl Extractable Zn (ppm) in Soil Samples from 0- to 15.2-cm Depths and Total Zn Concentration Levels in Corn Tissue Samples Collected from Control and Sludge-Amended Blount Silt Loam Plots

	Sludge application rates, mm									
Year	0	6.4	12.7	25.4		0	6.4	12.7	25.4	
	Soil total				LSD	Soil 0.1 N HCl extractable				LSD
1971	72	110	163	260	73[a]	13	41	98	181	63[a]
1972	62	137	199	329	67[a]	16	80	150	277	62[a]
1973	73	162	238	360	67[a]	13	81	118	244	65[a]
1974	78	173	264	460	131[a]	20	83	157	341	105[a]
	Leaf					Grain				
1970	58	85	138	212	82[a]	32	40	50	65	15[a]
1971	28	95	158	259	43[a]	24	37	36	53	10[a]
1972	56	139	253	381	136[a]	22	29	40	50	13[a]
1973	60	113	223	328	77[a]	29	37	51	58	6[a]
1974	59	122	193	293	104[a]	28	37	46	56	7[a]

[a] Significant at the 0.01 level of probability.

Table IV. Mean Dry Weight Contents of Total and 0.1 N HCl Extractable Cd (ppm) in Soil Samples from 0- to 15.2-cm Depths and Total Cd Concentration Levels in Corn Tissue Samples Collected from Control and Sludge-Amended Blount Silt Loam Plots

	Sludge application rates, mm									
Year	0	6.4	12.7	25.4		0	6.4	12.7	25.4	
	Soil total				LSD	Soil 0.1 N HCl extractable				LSD
1971	0.3	2.1	4.2	7.6	4.0[a]	<0.25	1.3	3.6	6.8	4.0[a]
1972	0.5	3.8	7.0	13.6	3.9[a]	0.27	3.1	4.7	12.1	3.3[a]
1973	0.7	4.7	7.9	13.2	3.6[a]	0.29	3.3	6.7	12.9	3.6[a]
1974	0.9	3.6	7.0	15.6	4.5[a]	0.58	3.8	7.3	16.4	4.9[a]
	Leaf					Grain				
1970	0.6	3.1	6.0	17.1	7.9[a]	0.30	0.60	0.79	1.00	0.20[a]
1971	0.5	4.9	11.8	25.4	7.3[a]	0.14	0.70	0.65	0.92	0.40[a]
1972	0.7	8.6	18.5	21.9	7.4[a]	0.14	0.45	0.83	1.10	0.52[a]
1973	0.8	3.5	12.0	22.1	5.7[a]	0.08	0.15	0.35	0.61	0.06[a]
1974	0.2	1.4	3.2	10.9	6.0[a]	0.09	0.18	0.40	0.81	0.22[a]

[a] Significant at the 0.01 level of probability.

ficients were 2.4 for leaf and almost 3 for grain Zn. Analyzing the data by this latter method perhaps simulated a more realistic chemical regime for sludge-borne metals than where the last annual application was confounded with accumulative or previous aggregate applications.

Results from partial regression analyses of Cd data indicate that the annual application rate of sludge-borne Cd was several times more efficient in determining Cd levels in corn plant tissues than were accumulative applications of the metal. Considering Cd in leaf tissues (Table V), the partial regression coefficient for annual application is 4.7 times greater than the coefficient for accumulative applications. Furthermore, the standard partial regression coefficients of 0.58 for annual and 0.42 for accumulative sludge-borne Cd applications accent the importance of the former over the latter source of Cd in determining levels in leaf tissues. Partial regression coefficients (Table V) for Cd contents of grain showed that annually applied sludge-borne Cd was 13 times more effective for increasing levels of the metal in grain than Cd applied as a constituent of sludge during all previous years. This conclusion regarding annual vs. long-term accumulative or aggregate applications as determinants of Cd levels in grain was confirmed by the standard partial regression coefficients (Table V). These data for Cd were also analyzed by the method for separating effects of aggregate applications from effects attributable to sludge applied during the crop year under consideration, as discussed above for Zn. From these latter regression analyses it was found that ratios of partial regression coefficients (not presented) for annual to accumulative applications were 5.7 and 17, respectively, for Cd concentrations in leaf and grain tissues. Corresponding ratios of standard partial regression coefficients were 1.9 and 4.8 for leaf and grain levels, respectively. Results from all regression analyses suggest that Cd levels will be reduced more rapidly in grain than in leaf tissues when sludge applications are terminated.

Coefficients presented in Table V and limits of applied Zn and Cd were used to develop surfaces presented as Figures 1–4. During the regression analyses, none of the quadratic terms was significant, and only in the case of Cd contents in grain did their use improve the fit of data on the surfaces ($Pr \leq 0.01$).

The surface depicting Zn contents in corn leaf tissue presented as Figure 1 shows that a single application of sludge providing 600 kg Zn/ha would have increased Zn contents of leaves from about 53 ppm to 227 ppm. Terminating sludge

Table V. Results of Regression Analyses Where Annual Mean Concentration Levels of Zn and Cd Were Considered as Functions of Amounts of Individual Elements Applied as Constituents of Sludge During Year Preceding Crop Year and as Cumulative Amounts Applied During All Years Since Corn Study Was Initiated in 1968[a]

	Leaf		Grain	
Variable	Partial regression	Standard partial regression	Partial regression	Standard partial regression
Zn(A)[b]	0.17[c]	0.30	0.020	0.29
Zn(B)[d]	0.12[c]	0.76	0.011[c]	0.61
Intercept	52.64[c]		30.06[c]	
R	0.96		0.81	
Cd(A)[b]	0.61[c]	0.58	0.08[c]	1.92
Cd(B)[d]	0.13[c]	0.42	−0.006	−0.47
$[Cd(A)]^2$			−0.001	−0.66
$[Cd(B)]^2$			0.0001	0.77
[Cd(A)] [Cd(B)]			−0.0003	−0.55
Intercept	0.93		0.187[c]	
R	0.88		0.96	

[a] Included in the regression analyses were data from 1970 through 1974 for both leaf and grain samples. The number of observations for each was 20, but each observation was the mean value calculated from the results obtained from samples collected from four replications. [b] Kg/ha of metal incorporated into the soil surface as a constituent of sludge immediately prior to planting corn. [c] Significant at the 0.01 level of probability. [d] Kg/ha of metal incorporated into the soil surface as a constituent of sludge during all years preceding the crop from which tissues were collected.

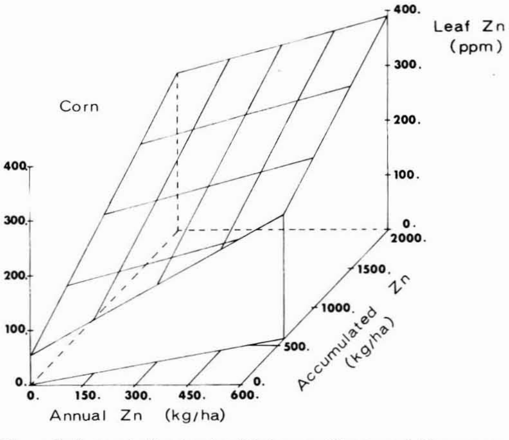

Figure 1. Concentration levels of Zn in corn (*Zea mays* L.) leaves expressed as functions of amounts of sludge-borne Zn incorporated into soil just prior to planting and amounts of sludge-borne Zn admixed with soil from cumulative amounts of sludge applied during the years 1968 through 1974. Surface generated by using relevant coefficients and statistics presented in Table V

applications after the soil had received a total accumulative 1479 kg Zn/ha loading rate would have caused an equivalent increased level of Zn in leaf tissues. Consequently, accumulative sludge-borne Zn will exert a prevailing influence for causing elevated Zn levels in corn leaf tissues only after amounts exceed annual loading rates by a factor of about 2.5 times. The levels of Zn in leaf tissues which could be expected from either the annual application of 600 kg Zn/ha or accumulative application of 1479 kg Zn/ha approach the suggested tolerance level of 300 ppm (*5*).

Although Zn contents in corn grain from maximum sludge-treated plots were only about one-fifth those found in corn leaves from the same plots, application of sludge-borne Zn affected concentration levels in each kind of tissue in much the same way, as evident by the surface presented as Figure 2. Incorporating 600 kg Zn/ha as a constituent of sludge into a soil like Blount silt loam for the first time immediately prior to planting will cause Zn concentration enhancements in grain to about the same extent as 1690 kg/ha of sludge-borne Zn would cause in the absence of further sludge applications. It appears unlikely that 2000 kg Zn/ha supplied in sludge over a period of several years would cause Zn concentrations in corn grain to be increased by more than 20 ppm if applications of sludge were terminated.

With regard to enhancement of Cd concentrations in corn leaf tissues, the surface exhibited as Figure 3 shows that sludge-borne Cd incorporated into soil immediately prior to planting was the major determinant of levels in such tissues when compared to amounts of the element supplied in sludge in previous years. If sludge applications were terminated after they had supplied a total 80 kg Cd/ha, the predicted level of Cd in leaf tissues would be only 11.4 ppm (calculated from coefficients in Table V). But because the data used in the generation of the surface depicted in Figure 3 were obtained from plots on which applications of sludge were never terminated, the levels of the metal in leaf tissue resulting from residual applications were probably considerably less.

Concentrations of Cd in corn grain from maximum sludge-treated plots were on the average less than 5% of amounts found in corn leaves from the same plots. Thus, as in the case for Zn, as seen from the surface presented in Figure 4, healthy corn plants had a considerable capacity for regulating changes in mineral composition of grain to a relatively low level. Also, as seen from the surface (Figure 4), the facility for regulating the concentration changes of Cd in grain was exerted to a greater degree at relatively high concentrations of Cd in soil and leaf tissues than at lower levels. This phenomenon for controlling levels in grain to a greater extent at higher levels in soil and leaves was not observed for Zn (Figure 3) although it may exist at some higher concentrations of Zn in sludges than those used in this study. Also, concentration levels of metals in grain may be determined to some extent by the fact that a relatively large proportion of the total plant root volume probably existed below the surface layer admixed with sludge at the time of grain formation.

As shown by the surface presented as Figure 4, the major factor which caused the higher Cd concentrations in grain was the amount of sludge-borne Cd incorporated into soil just prior to planting corn. Amounts of the Cd supplied in sludge applications in previous years were of little consequence in determining its level in grain. When the same data were analyzed by the linear regression method, the ratio of partial regression coefficients for annual to accumulated applications was 16.

In light of these findings, levels of Cd in grain from maximum sludge-treated plots will probably recede to expected normal or background levels after sludge applications have been terminated. Corn grain and grain of cereal crops produced in environments presumably having normal Cd levels have been reported to have Cd contents ranging from 0.1 to 0.5 ppm (*12*, p 303). It may be predicted from the surface for Cd concentrations in grain (Figure 4) that if sludge applications were terminated after total sludge-borne Cd applications amounted to 80 kg/ha, grain from the next succeeding crop would have Cd concentrations which would not exceed 0.45 ppm. Considerable support for this prediction is provided by the findings reported by Kirkham (*13*). She collected soil and plant tissue samples in 1973 from a site near Dayton, Ohio, where digested sludge was applied each year from 1930 until

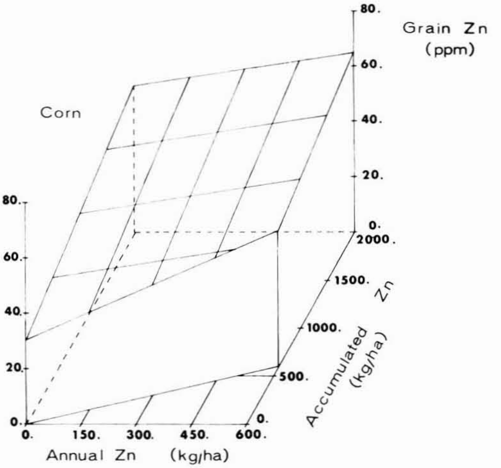

Figure 2. Concentration levels of Zn in corn (*Zea mays* L.) grain expressed as functions of amounts of sludge-borne Zn incorporated into soil just prior to planting and amounts of sludge-borne Zn admixed with soil from cumulative amounts of sludge applied during the years 1968 through 1974. Surface generated by using relevant coefficients and statistics presented in Table V

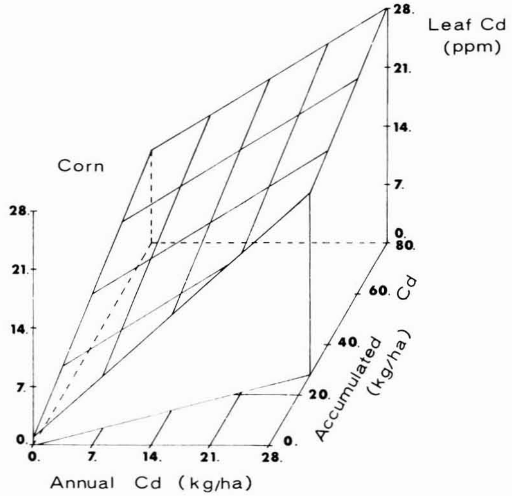

Figure 3. Concentration levels of Cd in corn (*Zea mays* L.) leaves expressed as functions of amounts of sludge-borne Cd incorporated into soil just prior to planting and amounts of sludge-borne Cd admixed with soil from cumulative amounts of sludge applied during the years 1968 through 1974. Surface generated by using relevant coefficients and statistics presented in Table V

applications were terminated in 1965 at a rate estimated to have been about 28 mt/ha/yr. According to her findings, total Cd concentrations in the 0–30-cm depth of soil had accumulated to 70.5 ppm, but 1973 corn grain contained only 0.9 ppm of Cd.

In the absence of research results, Leeper (*14*) and Chaney (*15*) suggested that the sludge organic component complexes metals reducing their availability for absorption by plants, and that phytotoxic conditions in soil may not occur until the organic matter has been decomposed by microbial processes some time after sludge applications have been terminated. Their hypothesis was not supported by the findings reported here. Based on analytical results for organic C contents of sludge added to the soil and assuming none was lost by decompositional processes, the possible soil organic C contents were calculated and presented in Figure 5 along with observed soil organic C contents from plots treated with various application rates of sludge.

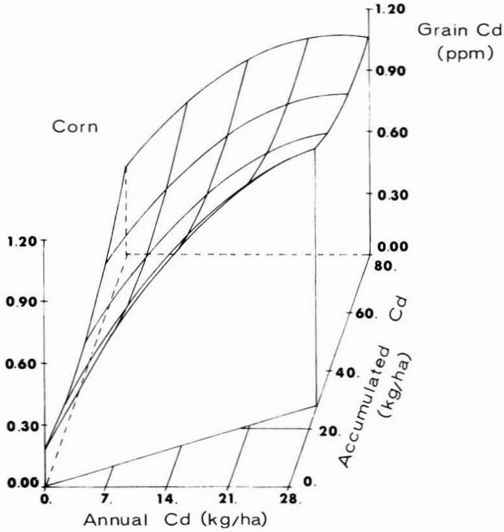

Figure 4. Concentration levels of Cd in corn (*Zea mays L.*) grain expressed as functions of amounts of sludge-borne Cd incorporated into soil just prior to planting and amounts of sludge-borne Cd admixed with soil from cumulative amounts of sludge applied during the years 1968 through 1974. Surface generated by using relevant coefficients and statistics presented in Table V

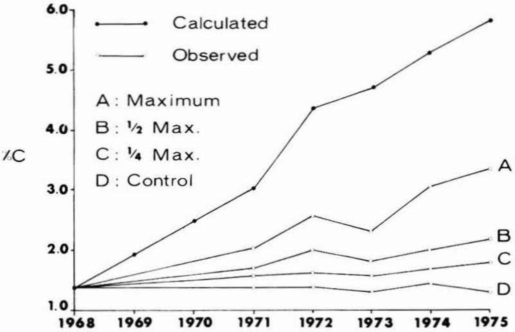

Figure 5. Calculated possible organic carbon contents in soil surface of maximum sludge-treated plots as compared to observed or measured contents in plots annually treated with various rates of digested sludge

Results from other studies (authors' unpublished data) indicate that the difference between calculated and observed concentrations in soils must be due to volatilization of C during microbial degradation of sludge organic matter. In 1975 about 55, 59, and 58% of the organic C added as a constituent of sludge during seven years of annual applications had been lost by volatilization processes from the maximum, one-half maximum, and one-fourth maximum sludge-treated plots, respectively. The percent of organic C lost by volatilization processes was calculated on the basis that the only organic C added to soils was that concomitantly applied with applications of sludge. However, additional organic C was returned to the soil as a constituent of the stover or plant residues. The amount of organic C returned to the soil as a constituent of undetermined amounts of plant residues probably varied with sludge treatment rates. Since corn grain yields were sometimes increased by higher sludge loading rates, correspondingly higher amounts of plant residues containing C were returned to plots treated with higher annual applications of sludge. The failure to measure plant residue quantities so that their C contribution could be taken into account leads to an underestimation of amounts of organic C lost by volatilization. The underestimation was probably greater where higher sludge loading rates were made.

If sludge-borne organic C on maximum-treated plots had not been volatilized, the organic C content of soil from this source alone should have been about 5.84% in the spring of 1975 (Figure 5). However, the observed organic C content was only 3.38% (CV = 0.79%) or about 2.0% higher than contents in control-plot soil. Observed levels as plotted in Figure 5 indicate that organic C may be approaching an equilibrium situation between amounts applied on sludge-treated plots and amounts lost by volatilization each year.

Along with the results from a study of biological activity in the soil where this study was conducted, it was reported that fats, waxes, oils, and resins comprised about 23–27% of total organic matter contents of the digested sludge used in the study (*4*). Results of soil organic matter fractionation studies showed that these compounds were the major ones being accumulated in soils as a result of sludge treatments. These kinds of organic compounds are relatively ineffective in complexing heavy metals to the extent that they would be unavailable for absorption by plant roots. Another reason for rejecting the hypothesis that organic matter supplied as a constituent of sludge protects plants against otherwise toxic concentrations of metals is the fact that sludge organic matter supplied to maximum-treated plots caused a relatively insignificant increase in the soil cation exchange capacity. The increase was from 12 meq/100 g to only 14.5 meq/100 g.

Contrary to what has been assumed by others, results reported here suggest that organic constituents or decompositional products of soil incorporated sludge organic matter temporarily maintain concomitantly applied Zn and Cd in forms readily available for absorption by plant roots, probably by chelation processes. Evidently, inorganic chemical reactions were more important in protecting plants against excessive contents of Zn and Cd accumulating in soil. If Zn and Cd supplied as constituents of sludge used to amend soils cause phytotoxic conditions, they will be observed while annual sludge applications are being made and not after they have been terminated.

The Blount silt loam soil employed in this study was poorly drained, and it was not known whether or not any subsurface drains existed in the part of the field where the study site was located. The soil had a low organic matter content when compared to associated prairie soils. Cultivated Blount silt loam is characterized by a very poor structure and tends to exhibit a severe crusting problem unless organic amendments are supplied. At the beginning of the study the soil pH was about 5.6, but by 1970 it had decreased to a value of 4.9 in the surface of maximum sludge-treated soil. In 1972 agricultural limestone was applied at rates calculated to increase soil pH to 6.5 in all plots. By 1973 surface soil in maximum sludge-treated plots had pH values that ranged from 5.1 to 5.5. By the spring of 1974, agricultural limestone applications had increased the soil pH in these plots to values that ranged from 6.1 to 6.3. The pH values attained in sludge-treated plots during the 1973 and 1974 growing seasons were very near the optimum pH of 6 for absorption and translocation of Cd to grain (*6*). Altogether, from the standpoint of the relatively low cation exchange capacity, poor drainage and soil structure, and adverse soil pH status, the potential for developing a heavy metal phytotoxic condition in soils and excessive accumulations of Zn and Cd concentrations in plant tissues was maximized in the study.

During the discussion of results major attention was given to data from maximum sludge-treated plots. But amounts applied on the one-fourth maximum-treated plots more nearly approach application rates where sludge is used just to supply supplementary nitrogen for high yields of corn. Since one of the major concerns about using municipal sludges as supplementary fertilizers is the potential hazard of cycling above normal levels of Cd in food chains, it should be noted (Table IV) that during the last three years of the study, Cd levels in grain from one-fourth maximum-treated plots never exceeded concentrations found in grain from more normal environments (*12*). None of the Cd concentrations found in grain from one-fourth maximum sludge-treated soil was greater than the 0.9 ppm reported by Kirkham (*13*). This is a concentration which she considered to be within the range normally observed in corn grain and corn meal.

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Interference in 2,4-Xylenol Procedure for Nitrate Determination in Atmospheric Aerosols

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■ The 2,4-xylenol method for determining nitrate in atmospheric particulate matter exhibited negative errors of up to a factor of 3 in the presence of motor vehicle-related aerosols. A correlation was observed between the magnitude of the error and the concentration of particulate lead. The concentrations of water-soluble halide, lead, and peroxide were determined but were insufficient to account for the negative interference. The vehicle-related material causing this interference remained unidentified.

As part of a program to characterize vehicular-related aerosols, sampling was conducted simultaneously upwind and downwind of a heavily traveled freeway in Los Angeles. The samples, collected on Whatman 41 filters, were analyzed for nitrate among other constituents. For several episodes two nitrate procedures were employed for analysis of the same aqueous extracts: the 2,4-xylenol method (*1*) and Technicon Industrial method 100-70W (*2*). The former is based upon formation of the deeply colored sodium salt of nitroxylenol. The latter involves reduction of nitrate to nitrite by a copper–cadmium reduction column followed by formation of a diazo compound with sulfanilamide.

The agreement between the two procedures proved to be highly variable. Table I gives the results obtained with the two procedures for samples collected simultaneously on both sides of the freeway. Also listed are the particulate lead values obtained by x-ray fluorescence on the filter samples prior to extraction. Wind direction correlated with the observed lead value; for a pair of samples, the higher lead values indicate the sampler which was downwind of the freeway during the time interval shown.

These results suggest that the degree of agreement between nitrate methods is relatable to the particulate lead concentration or other species proportional to the lead level. Such a correlation is revealed by Figure 1 which plots the ratio of nitrate results by the two methods against the observed total particulate lead.

Comparison of upwind-downwind nitrate levels for the same periods, as measured by the Technicon procedure, indicated, on the average, close agreement (east/west = 1.02). In contrast, the corresponding ratio as measured by the xylenol method was 0.66. Since direct emissions of particulate nitrate from motor vehicles are unlikely, close agreement in nitrate levels on both sides of the freeway is expected. Therefore, changes in the ratio of nitrate results by the two methods with increasing lead levels appear to reflect negative interference in the xylenol method.

As published by the Intersociety Committee, only chloride ion is reported to be a negative interferent with the 2,4-xylenol method at concentrations above 100 μg/ml. However, Holler and Huch (*3*) evaluated a series of potential interferents

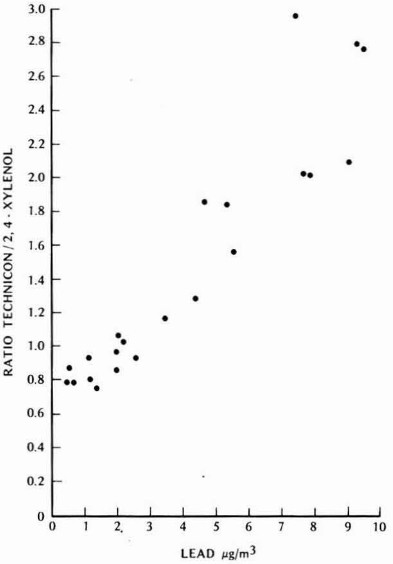

Figure 1. Ratio Technicon/2,4-xylenol nitrate against lead concentration

Table I. Comparison of 2,4-Xylenol and Technicon Methods for Nitrate on Samples Collected Adjacent to Heavy Vehicular Traffic [a]

	Nitrate east sampler			Nitrate west sample		
Time, PDT	**Xylenol**	**Technicon**	**Pb**	**Xylenol**	**Technicon**	**Pb**
0600–0800	3.43	3.52	1.13	1.69	3.00	5.52
0800–1000	3.63	3.71	2.56	3.10	3.97	3.46
1000–1200	1.08	3.32	9.45	3.45	3.34	1.97
1200–1400	1.08	2.62	9.05	3.78	3.25	1.36
1400–1600	0.95	2.30	7.85	2.73	2.50	0.644
1600–1800	2.21	3.20	4.39	2.86	2.85	0.519
1800–2000	0.89	2.17	7.69	2.62	2.42	0.472

[a] Nitrate values are in μg/ml of aqueous extract, and Pb values in μg/m^3. The coefficient of variation for the Technicon method ranged from 0.2 to 1.5%, for the xylenol method from 5 to 7%, and for the lead values from 3 to 4%. Samples collected August 20, 1974.

employing 3,4-xylenol rather than 2,4-xylenol. While concentrations of interferents were not given, a 34% negative interference was found with a Cl^-/NO_3^- ratio of 5:1 w/w. This increased to 40% at the ratio 10:1 w/w. Hydrogen peroxide yielded a 55% negative error at an H_2O_2/NO_3^- ratio of 10:1 w/w. Lead ion (from $PbSO_4$) showed no measurable effect at a Pb/NO_3^- ratio of about 100:1 w/w. Presumably, similar results should be observed with 2,4-xylenol as well.

To determine the cause of the negative interference, the total halide ion concentration was determined by the silver nitrate turbidimetric procedure (*4*). For the 22 extracts analyzed by the two nitrate methods, the range in total halogen (chloride plus bromide) concentration was from 0.3 to 1.1 μg/ml or about two orders of magnitude below the level reported for threshold interference effects by chloride ion (i.e., 100 μg/ml).

Since analysis of nitrate was done on extracts obtained with boiling water, extraction of significant amounts of lead was not expected. Nevertheless, the 22 extracts were analyzed for lead by atomic absorption. Of the 22 samples, only one exceeded the limit of detection, 0.5 μg/ml. The exception had a value of 0.8 μg/ml. Thus, if lead is the interfering species in nitrate determination by the 2,4-xylenol method, it is effective at quite low levels in contrast to the findings of Holler and Huch (*3*). Finally, a test for peroxides with a 10% potassium iodide solution proved negative with a representative set of the samples.

Conclusions

Regardless of the origin of interference, we can conclude the following:

- At atmospheric lead levels below ca. 2 $\mu g/m^3$, the ratio of Technicon nitrate to 2,4-xylenol nitrate was about 0.8.
- At lead levels above about 2 $\mu g/m^3$, the ratio increased sharply with increasing lead concentrations due to negative interference by a traffic-related aerosol constituent. This constituent appears to be something other than halide, lead, or peroxide.
- Because of the observed substantial interference in the 2,4-xylenol method, its use should be restricted to samples collected away from high-density vehicular traffic. [A recent comparison (*5*) of the xylenol and automated nitrate made by the Southern California Air Pollution Control District (Los Angeles) Zone with 24-h high-volume samples collected at the District's monitoring sites did not reveal significant differences between the two methods.]
- Further work is needed to elucidate the cause of the interference.

Acknowledgment

The particulate lead values quoted were obtained by R. D. Giauque, B. Garrett, and L. Goda, University of California Lawrence Berkeley Laboratory, by use of x-ray fluorescence analysis.

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Removal of Nitrogen Oxides with Aqueous Solutions of Inorganic and Organic Reagents

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■ The removal of nitrogen oxides with various inorganic and organic reagents is studied. The efficiency of the removal is best described as a function of the standard redox potentials of half reactions in which the reagents take part.

Great efforts have been made to find a system appropriate for the removal of nitrogen oxides with aqueous solutions of inorganic reagents in connection with air pollution control (*1–7*). Although a number of systems capable of removing nitrogen oxides are briefly reported in the "Official Patent Gazettes", little research related to the removal has been systematically carried out. We have studied the removal of nitrogen oxides of low concentration with aqueous solutions of inorganic and organic reagents and found that the removal efficiency is closely related to the oxidizing and reducing properties of the reagents.

Experimental

Method. The experiments were carried out in a flow system at room temperature. Nitric oxide or nitrogen dioxide (diluted with a nitrogen stream to 250 ppm) was bubbled through a Munenke scrubbing bottle in which 100 ml of aqueous solution of the inorganic or organic reagent was contained. The total flow was always kept at 820 ml/min, and the concentrations of nitrogen oxides at the inlet and the outlet of the scrubbing bottle were determined by a chemiluminescence-type NO_x analyzer (Yanagimoto Co. Ltd.).

Materials. The inorganic reagents used are listed in Tables I and II. The organic reagents used are also listed in Table V. They are all of extra pure grade and were used by dissolving in distilled water. Runs were carried out with aqueous solutions containing 0.4 and 0.1 mol/l. of inorganic and organic reagents, respectively, unless otherwise noted.

Results and Discussion

Removal of NO and NO_2. *Inorganic Reagents.* When NO or NO_2 containing gas is bubbled through the aqueous solution of the inorganic reagent, the nitrogen oxide reacts with the reagent and is removed. Tables I and II show the results obtained for various inorganic reagents. The efficiency $E_f(NO)$ or $E_f(NO_2)$ of NO or NO_2 removal in the second columns of the tables is defined as $E_f(NO) = 1 - (C_{NO(o)}/C_{NO(i)})$ and

Table I. NO Removal with Aqueous Solutions of Inorganic Reagents

Reagents	E_f(NO)	Remarks
(1) $FeSO_4$	0.19 → 0	
(2) H_2O_2	0.13	
(3) $KMnO_4$	0.8	NO_2 was evolved
(4) $Na_2Cr_2O_7$	0.06	
(5) NaClO	0.06	
(6) Na_2SO_3	0.075	
(9) $Na_2S_2O_3$	0.03	
(10) $NaClO_2$	1.0	NO_2 was evolved
(11) $SnCl_2$	0.05	
(12) $FeSO_4(NH_4)_2SO_4$	0.07	
(13) $FeCl_2$	0.14 → 0	
(14) CuCl	0	

Table II. NO_2 Removal with Aqueous Solutions of Inorganic Reagents

Reagents	$E_f(NO_2)$	Remarks
(1) $FeSO_4$	0.715 → 0.66	NO was evolved
(5) NaClO	0.14	
(6) Na_2SO_3	1.0	
(7) $NaHSO_3$	0.99	
(8) Na_2S	1.0	
(9) $Na_2S_2O_3$	0.67 → 0.60	NO was evolved
(10) $NaClO_2$	0.46	
(11) $SnCl_2$	1.0	NO was evolved
(12) $FeSO_4(NH_4)_2SO_4$	0.58 → 0.52	NO was evolved
(13) $FeCl_2$	0.755	NO was evolved
(14) CuCl	0.79 → 0.32	NO was evolved
(15) $NiSO_4$	0.19	
(16) $Na_2S_2O_4$	0.96	
(17) KI	0.83	
(18) $MnCl_2$	0.255	
(19) $CoSO_4$	0.290	

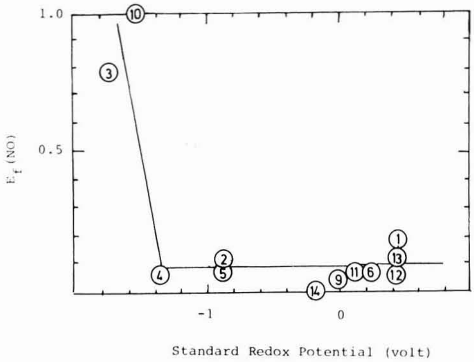

Figure 1. Standard redox potentials of inorganic reagents vs. efficiencies of NO removal

Numbers in figure: see Table I

$E_f(NO_2) = 1 - (C_{NO_2(o)}/C_{NO_2(i)})$, where the subscripts ($i$) and ($o$) represent the inlet and the outlet conditions, respectively. The arrows in the second columns indicate that the efficiency changes with time. From Table I, the strong oxidizing agents such as $KMnO_4$ and $NaClO_2$ remove NO efficiently, although NO is partly converted into NO_2.

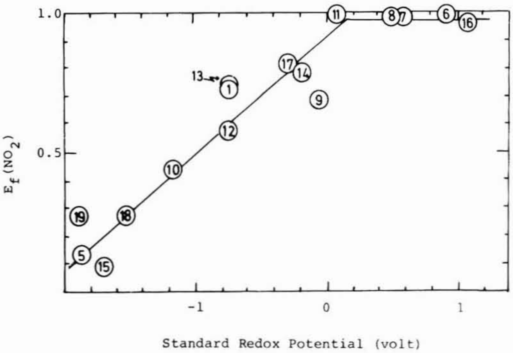

Figure 2. Standard redox potentials of inorganic reagents vs. efficiencies of NO_2 removal

Numbers in figure: see Table II. Concentration of reagent: 0.4 mol/l.

Table III. Standard Redox Potentials (*10*) Used in Figure 1

Reagents	Half reaction	Standard redox potential, V
$FeSO_4$, $FeCl_2$, $FeSO_4(NH_4)_2SO_4$	$Fe = Fe^{2+} + 2e^-$	0.44
H_2O_2	$4OH^- = H_2O_2 + 2e^-$	−0.88
$KMnO_4$	$MnO_2 + 2H_2O = MnO_4^- + 4H^+ + 3e^-$	−1.70
$Na_2Cr_2O_7$	$2Cr^{3+} + 7H_2O = Cr_2O_7^{2-} + 14H^+ + 6e^-$	−1.33
NaClO	$Cl^- + 2OH^- = ClO^- + H_2O + 2e^-$	−0.89
Na_2SO_3	$S^{2-} + 3H_2O = SO_3^{2-} + 6H^+ + 2e^-$	0.231
$Na_2S_2O_3$	$2S^{2-} + 3H_2O = S_2O_3^{2-} + 6H^+ + 8e^-$	0.006
$NaClO_2$	$Cl^- + 4OH^- = ClO_2^- + 2H_2O + 4e^-$	−1.55
$SnCl_2$	$Sn = Sn^{2+} + 2e^-$	0.136
CuCl	$Cu = Cu^+ + e^-$	−0.184

Table IV. Standard Redox Potentials (*10*) Used in Figure 2

Reagents	Half reaction	Standard redox potential, V
$FeSO_4$, $FeCl_2$, $FeSO_4(NH_4)_2SO_4$	$Fe^{2+} = Fe^{3+} + e^-$	−0.77
NaClO	$ClO^- + 2OH^- = ClO_2 + H_2O + 2e^-$	−1.82
Na_2SO_3	$SO_3^{2-} + 2OH^- = SO_4^{2-} + H_2O + 2e^-$	0.93
$NaHSO_3$	$HSO_3^- + 3OH^- = 2H_2O + SO_4^{2-} + 2e^-$	0.575
Na_2S	$S^{2-} = S + 2e^-$	0.506
$Na_2S_2O_3$	$S_2O_3^{2-} = (1/2)S_4O_6^{2-} + e^-$	−0.04
$NaClO_2$	$ClO_2^- + 2OH^- = ClO_2 + e^-$	−1.16
$SnCl_2$	$Sn^{2+} = Sn^{4+} + 2e^-$	−0.147
CuCl	$Cu^+ = Cu^{2+} + e^-$	−0.152
$NiSO_4$	$Ni^{2+} + 2H_2O = NiO_2 + 4H^+ + 2e^-$	−1.68
$Na_2S_2O_4$	$S_2O_4^{2-} + 4OH^- = 2SO_3^{2-} + 2H_2O + 2e^-$	1.12
KI	$I^- = (1/2)I_2 + e^-$	−0.267
$MnCl_2$	$Mn^{2+} = Mn^{3+} + e^-$	−1.51
$CoSO_4$	$Co^{2+} = Co^{3+} + e^-$	−1.82

On the other hand, Table II shows that NO_2 reacts readily with the strong reducing agents such as Na_2SO_3, $NaHSO_3$, Na_2S, $Na_2S_2O_4$, and $SnCl_2$. It was therefore suggested that the oxidation-reduction reaction is involved in the NO_x removal. The rate of the reaction is closely related to the thermodynamic quantity of the reaction such as the standard free en-

Table V. Removal of NO_2 with Aqueous Solutions of Organic Reagents

	Reagent	$E_f(NO_2)$	Remarks
(1)	p-Aminophenol	0.91	0.03 mol/l.
(2)	Neutral red	0.98	0.1 mol/l., NO was evolved
(3)	Xanthine	0.87	0.05 mol/l. + NaOH (0.05 mol/l.)
(4)	Hydroquinone	0.57	0.1 mol/l.
(5)	Pyrogallol	0.61	0.1 mol/l.
(6)	Methyl red	0.57	0.1 mol/l.
(7)	Crystal violet	0.81	0.01 mol/l., NO was evolved
(8)	Methyl orange	0.94	0.025 mol/l.
(9)	Pyoctanin blue	0.73	Saturated in water
(10)	Phenolphthalein	0.87	0.01 mol/l. + NaOH (0.06 mol/l.)

ergy of the reaction (*8, 9*). The efficiencies obtained at the initial period of the removal are plotted in Figures 1 and 2 against the standard redox potentials of possible half reactions in which the reagents take part. The redox potentials (*10*) used in Figures 1 and 2 are listed together with their half reactions in Tables III and IV, respectively. The reagents which have lower standard redox potentials than −1.4 V are effective for NO removal, whereas the efficiency of the NO_2 removal is increased as the redox potential of the reagent is increased.

Organic Reagents. Table V shows the results of NO_2 removal with aqueous solutions of various organic reagents. The organic reagents are also favorable for NO_2 removal. As Figure 3 shows, the relation similar to the plots in Figure 2 holds also for the organic redox system.

The standard redox potential of the reagents is therefore an important parameter for the prediction of the efficiency of NO_x removal when either an organic or inorganic reagent is employed. The oxidation-reduction reaction (the electron transfer from or to nitrogen oxides) should then be involved in the removal as one of the rate-determining steps.

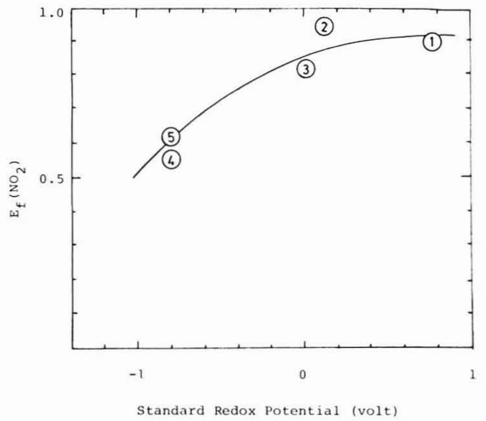

Figure 3. Standard redox potentials of organic reagents vs. efficiencies of NO_2 removal

Numbers in figure: see Table V. Standard redox potentials: Clark (*11*). Those for methyl red, crystal violet, methyl orange, pyoctanin blue, and phenolphthalein not available. Concentration of reagent: 2, 4, 5, 0.1 mol/l.; 1, 0.03 mol/l.; 3, 0.05 mol/l.

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Stain Method for Measurement of Drop Size

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■ A theoretical relation between water drop and stain diameters, *D* and *S*, presented elsewhere is in agreement with the empirical expression of $D = aS^b$, where *a* and *b* are constants. The present theoretical value of *a* depends upon impact velocity and the natures of the liquid and target surface, and the value of *b* equals ⅘. For large drops moving with terminal velocities, the value of *a* becomes insensitive to impact velocity, and the value of *b* becomes ⅔. Values of *D* are predicted to within ±16% for a wide range of drop sizes and velocities and to within ±2% for large drops moving at their terminal velocities.

A popular method for measuring the size of liquid drops is the stain technique wherein the drop is allowed to impact onto a target surface and leave a permanent impression or stain. Stains have been produced, for example, on solid surfaces coated with a layer of lampblack (*1, 2*), magnesium oxide (*3*), or liquid-sensitive films (*4, 5*), on Ozalid paper (*6*), and on filter papers (*7–11*). The drop and stain diameters, *D* and *S*, are reportedly related by the expression

$$D = aS^b \qquad (1)$$

where *a* and *b* are empirical constants. Numerical values of *a* and *b* appear to depend upon the specific experimental conditions (namely, the impact velocity of the drop and the nature of the target surface), i.e., *a* ranges from 0.33 to 0.47 (*6–8, 10*), while *b* ranges from 0.67 to 0.93 (*6–10*). While *b* = 0.67 according to "simple" geometry (presumably, the simple geometry assumes the volume of the impacted drop is proportional to the square of the stain diameter) (*7, 8, 10*) and *b* = 1.0 for the impacting drop taking a form of a spherical cap (*12, 13*), and *a* is predicted by the spherical model in terms of the contact angle between the liquid and the target surface and is not predicted by the "simple" model, a general theoretical model for a and b formulated in terms of the impact velocity of the drop and the natures of the liquid and target surface does not appear to have been previously given. This paper presents such a relation in terms of a previously reported model (*14*) for liquid drops impacting a target surface.

Consider a spherical liquid drop impacting a smooth, inert solid surface. Upon impact the drop tends to flatten into a disc and undergo dampened oscillatory motion. If the stain diameter is equal to the maximum diameter of the flattened drop, the ratio of the stain-to-drop diameter is proportional to the Weber number raised to ¼ power (*14*), and thus it can be shown that

$$D = \left(\frac{9}{4}\frac{\sigma}{\rho_\omega V^2 C^4}\right)^{1/5} S^{4/5} \qquad (2)$$

where σ is the surface tension of the liquid against air, ρ_ω is the density of the liquid, V is the impact velocity, and C is the ratio of the experimental to the theoretical stain diameter and denotes departure from the theoretical model. [To follow the symbols of Equation 1 which are familiar to stain workers (*6, 8–10*), a change of symbols of D to S and d to D from Equation 6 of ref. *14* was made.] Figure 1 plots experimental values for water drops impacting onto a bituminous coal surface (*14*). The observed value of b was ⅘ and was independent of drop size and velocity over the noted range of conditions, thus agreeing with Equation 2. The observed value of a was 0.2–0.6 and was independent of drop size but dependent upon drop velocity. Values of a ranging from 0.2 to 0.6 as shown in Figure 1 were agreeable for impact velocities of 1000–1500 cm/s and less agreeable for velocities outside this range, e.g., 0.71 vs. 0.60, i.e., $C = 1.1$–1.2 for the coal surface for an impact velocity of 250–450 cm/s and $C = 1.2$–1.5 for beeswax, cellulose acetate, and glass surfaces (*14*) for conditions for which high-speed photographs indicated that the impacting drop formed a reasonably flat disc. A smaller value of C was observed for a higher impact velocity, and photography indicated departure from a flat disc. Jarman (*9*) reported that $b = 0.82$–0.86 but did not report a value for a.

Most experimental studies of the stain method used drops falling at their terminal velocities. For a liquid drop larger than 1.5 mm in diameter, the terminal velocity (*15*) is

$$V = \left[\frac{3.0\, gD(\rho_\omega - \rho_a)}{\rho_a}\right]^{1/2}$$

where g is the gravitational acceleration and ρ_a is the density of the air. In this case,

$$D = \left[\frac{3}{4}\frac{\rho_a}{\rho_\omega(\rho_\omega - \rho_a)}\frac{\sigma}{g}\frac{1}{C^4}\right]^{1/6} S^{2/3} \qquad (3)$$

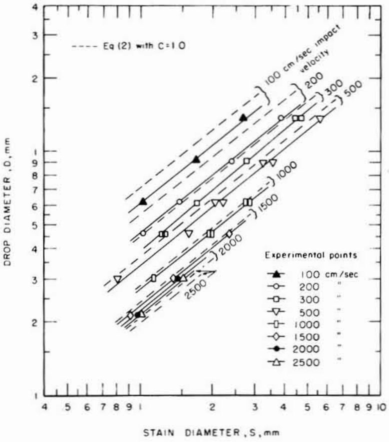

Figure 1. Relation between drop and stain diameters of water on bituminous coal surface at various impact velocities

[Deformation of water drops falling at terminal velocity was reported by, for example, Magono (*16*). We estimated the sphericity of the deformed drop to be >0.9 and a ratio of the maximum impact force to the air resistance to be 6×10^3; the deformation of the incident drop thus has a negligible effect on the stain diameter.] The theoretical value of b now has a constant value of ⅔ and is independent of drop size and velocity, agreeing with the results reported by Marshall et al. (*7*) and Fournier D'Albe and Hidayetulla (*8*) and approximately agreeing with the value of 0.74 reported by Engelmann (*6*) and 0.75 by Magarvey (*10*). The theoretical value of a is 0.43 for water if $C = 1.0$, agreeing with the reported values of 0.43 (*6, 7*) (the value of $a = 1.0$ reported in ref. *7* appears to be an error) and 0.47 (*8*), but not with the reported value of 0.33 (*10*). (However, the data in ref. *10* seemingly can also be satisfactorily matched by $D = 0.43\, S^{2/3}$.) These four references used absorbing paper as the target surface, and the close match between theory and experimental data implies negligible interaction between the impacting drop and the absorbing target surface during the ½ ms involved in the first spreading of the impacting drop (*14*).

The theoretical model giving Equations 2 and 3 assumes the liquid drop impacts an inert surface with sufficient velocity to spread into a flat disc, and such a model cannot explain b larger than ⅘. It is, however, likely (*12, 13*) that the value of b approaches 1.0 for a small, low-velocity drop as a limiting approximation.

Measurement of drop size is inherently important to such problems as scavenging of airborne particles by raindrops (*6*), suppression of dust by water sprays (*14*), and elimination of drop carryover from cooling towers which may damage the environment (*11*). While a calibration curve relating D and S must be experimentally determined if an appreciable interaction with the target surface is expected or if the drop size or velocity is outside the present range (Figure 1), the present flat-disc model hopefully provides a clearer understanding of the stain technique and should be sufficiently precise for most purposes. Thus, even ignoring the effect of C, one obtains the drop size within ±16% from Equation 2 for drop sizes from 0.2 to 1.44 mm and drop velocities from 100 to 2500 cm/s, and within ±2% from Equation 3 for large drops (1.5 to ~7 mm, the critical size for drop breakup, e.g., ref. *8*) moving with terminal velocities. Somewhat surprisingly, the present model also appears to be useful for a filter-paper target surface.

Acknowledgment

The author thanks Welby G. Courtney for his valuable suggestions during preparation of the text.

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PAN Measurement in Dry and Humid Atmospheres

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■ The effects of water on the gas chromatographic (GC) analysis of peroxyacetyl nitrate (PAN) are not observed in our laboratory studies. A series of PAN calibrations demonstrates the independent nature of water and PAN on our GC systems. On the basis of these results, the water anomaly observed by others is probably unique to their system.

A recent publication by Holdren and Rasmussen (*1*) dealt with the effect of moisture on peroxyacetyl nitrate (PAN) analyses. In brief, the authors reported on a series of experiments that were performed with a variety of GC–electron capture systems which demonstrated a reduced response for PAN when samples were at relative humidities of 30% or lower. They observed as much as a tenfold decrease in PAN response when the relative humidity of the sample air was near 0%. The authors suggest that a possible cause for this water anomaly was a column sample interaction.

In the past 10 years, we have performed many GC–electron capture analyses for PAN and PAN-type compounds in both ambient atmospheres and smog chamber irradiation studies of hydrocarbon–nitrogen oxides mixtures. In those studies air samples of PAN were analyzed at relative humidities ranging from 30 to 100% with no apparent water vapor effect upon the PAN response. The lack of such an effect, however, was more clearly demonstrated during instrument standardization where PAN standards in both humid and dry atmospheres were analyzed with no apparent effect on PAN response. Presented here are the results of three such calibrations.

Experimental and Discussion

The GC system for PAN used in our smog chamber studies was a 9 ft × ⅛ in. o.d. glass column packed with 10% Carbowax 600 on Gas Chrom Z. This length of GC column was used to permit resolution of alkyl nitrate products. Retention times for PAN and water vapor with this system were 8.8 and 23 min, respectively. The GC system was operated at 30-min intervals to analyze the chamber contents. A typical procedure for standardization was to replace one of the 30-min chamber samples with a series of PAN calibrations. These standardizations were performed by the dynamic dilution of calibrated cylinders of PAN with dry nitrogen. An example of such a calibration is shown in Figure 1. In this case, a 10.2 ppm PAN standard was dynamically diluted by a factor of 170 with dry nitrogen to produce a PAN sample of 60 ppb which was injected onto the GC column. Dry nitrogen or air was the preferred diluent since either eliminated the necessity of waiting for the resolution of a water peak. In this way, PAN standards could be repeated several times during this 30-min time period.

Generally, the first PAN standard sample was injected onto the GC immediately after the resolution of the PAN peak from the previous chamber sample. This permitted a 14-min period for the elution of the first PAN standard peak before the elution of the water peak from the previous chamber sample. A second PAN standard sample was injected onto the GC column immediately after the elution of the first PAN standard peak. A graphic illustration of these standards is shown in Figure 1. In effect, Figure 1 shows two identical 60 ppb PAN samples on the GC column, one with water at approximately 50% relative humidity from the previous chamber sample with the possibility of a water–PAN interaction and one without water and no possibility of a interaction occurring.

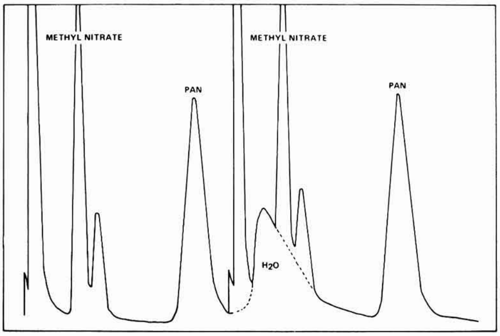

Figure 1. Dynamic calibration for PAN using 10.2 ppm standard cylinder of PAN in dry nitrogen and cylinder of prepurified grade nitrogen, February 2, 1971

Column used was 270 cm × 3.2 mm o.d. glass column packed with 10% Carbowax 600 on Gas Chrom Z

If PAN and water interactions occurred in the GC system, one would expect to see a definite difference in response between the two PAN standard samples; however, no difference was observed. Similar calibrations were performed many times during a two-year chamber program with PAN concentrations ranging from 25 to 300 ppb with no water anomalies observed.

In field study calibrations, the usual procedure for PAN standardization is the syringe injection of an aliquot from a concentrated PAN standard bag into a second bag containing a metered volume of dry air or nitrogen. The concentrated PAN bags are calibrated by IR absorptivities (*2*). For example, in one specific case, a 10-cc aliquot of a 108 ppm PAN sample was injected into a Tedlar (PVF) bag containing 100 l. of dry nitrogen. Since Tedlar is permeable to water from the surrounding atmosphere, the water content inside the bag increased with storage time. Results of two such calibrations are given in Figures 2 and 3. Since the permeation rate of water through Tedlar is 2.8 g/(100 in.^{2}) (24 h) (mil) at 39.5 °C (*3*), it takes very little time for the relative humidity in the bag to

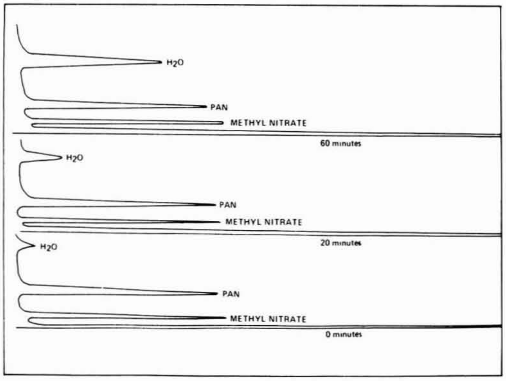

Figure 2. PAN standard of 10.6 ppb concentration in dry nitrogen prepared in a 2 mil Tedlar PVF bag, August 21, 1975
Column used was 90 cm × 3.2 mm o.d. glass column packed with 10% Carbowax 600 on Gas Chrom Z

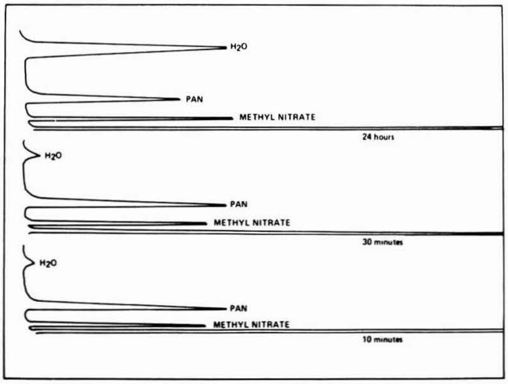

Figure 3. PAN standard of 31.0 ppb in dry nitrogen prepared in 2 mil Tedlar PVF bag, August 21, 1975
Column used was 90 cm × 3.2 mm o.d. glass column packed with 10% Carbowax 600 on gas Chrom Z

approach the relative humidity of the surrounding atmosphere. In these experiments the relative humidity of the surrounding atmosphere was approximately 50%.

If the water anomaly occurs at low relative humidities, one would expect a difference in PAN response between the first sample at less than 10% relative humidity and the third sample at approximately 50% relative humidity. Since this was not observed, we conclude that the water anomaly does not occur in our GC system. In fact, in one instance (Figure 3), the PAN peak decreased approximately 15% after 24 h storage; however, this decrease was due to PAN deterioration on the surfaces of Tedlar as indicated by a corresponding increase in methyl nitrate—a usual degradation product (*4*).

Based on these results and our experiences, we suggest that the anomaly reported by Holdren and Rasmussen (*1*) is probably related to the preparation of the GC–electron capture system. When using columns prepared from either Carbowax 400 or 600, we experienced difficulties whenever the GC substrate was heated to 100 °C for conditioning purposes. At these temperatures the substrate appears to decompose as evidenced by a pungent odor. When this occurred, the PAN response deteriorated, and quantitative elution of PAN was impossible. When the GC substrate was prepared and conditioned at considerably lower temperatures (approximately 40 °C), we detected no odor, and we observed quantitative elution of PAN at good sensitivities (less than 1 ppb). On occasions stored substrates at room temperature developed similar pungent odors suggestive of autooxidation; such substrates would not permit quantitative elution of PAN at good sensitivity. At times, we have been suspicious of column deterioration due to impurities in some of the cylinders of carrier gas used.

Our experience also suggests that column tubing material is an important factor. We have used only glass tubing in an effort to assure completely inert surfaces. We have attempted to replace glass with either stainless steel or Teflon for better rigidity and durability, but have not been completely satisfied with these alternatives.

Brass and copper surfaces as well as heated inert surfaces seem to cause loss of PAN. For this reason, only glass, Teflon, and stainless steel materials have been used for the sample valve and connecting tubing in the construction of the GC system. Detector temperatures for our systems have been maintained anywhere from 25 to a maximum of 50 °C. At these low temperatures, however, deterioration of detector sensitivity due to deposit buildup occurs more readily; therefore, overnight heating of the detector at 150 °C was frequently performed.

Conclusion

The problems observed by Holdren and Rasmussen (*1*) reflect a water vapor effect that is unique to the system used by these investigators. It is possible that their system has active sites that cause PAN loss. If so, water vapor may deactivate such sites resulting in a greater PAN response.

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CORRESPONDENCE

SIR: Lonneman has concluded that the moisture anomaly in the analysis of peroxyacetyl nitrate reported by Holdren and Rasmussen (*1*) was unique to their system.

In response to the claim that our observations were unique, we reference several other investigators' comments upon this effect. Nieboer and Van Ham (*2*) have recently reported that "the elution gas stream was previously humidified by passing it over $Na_2S_2O_3 \cdot 5H_2O$ (analytical grade Merck), because it appeared that the height of the PAN peak depends on the relative humidity of ambient air if dry elution gas was used". This article appeared in the literature at the same time as our original article and thus could not be included in our list of references. Stephens and Price (*3*) stated that "the diluent should be air of normal humidity so that the chromatogram will be a realistic one". Although there was no further explanation given, it appeared that this author too had experienced some moisture difficulty when analyzing for PAN. Penkett and Sandalls, in correspondence (*4*) with our laboratory, indicate their data show an increased response to PAN analyses by pretreating the column substrate with acetone. The authors suggested that the acetone treatment temporarily reduced the active sites present on the column and that PAN analyses were substrate sensitive.

We feel that there is a definite problem in analyzing for PAN under varying humidity conditions. Why or how it happens is uncertain. We definitely believe it is not unique to our laboratory, and investigators reporting PAN measurements should be aware of this fact.

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SIR: When my original manuscript was submitted to *ES&T*, the Holdren and Rasmussen (*1*) article was the only report I was aware of that suggested a water effect on the response of PAN in a gas chromatograph–electron capture system. Therefore, the use of the term "unique" seemed to be appropriate. The article by Nieboer and Van Ham (*2*), which reported a water vapor effect on the peak height of the PAN peak, did not come to my attention until sometime later and was not referenced in my manuscript. In their report (*2*), however, the authors did not go into the details of this interference. Also, it is not clear from their description the magnitude of this effect. One could conclude from their report that variation in the water vapor content may have affected the geometry of the eluding PAN peak but did not necessarily affect the peak area response of PAN.

Stephens and coworkers have published several articles pertaining to the measurement of PAN in ambient atmospheres without the suggestion of a water interference. The statement made by Stephens and Price in the 1973 publication (*3*) that "the diluent should be air of normal humidity so that the chromatogram will be a realistic one" can be interpreted in many ways. Since this comment was not expanded upon, one could conclude that the authors intended this as an instructive statement and were not referring to any water anomaly problems.

The purpose of my manuscript was to present PAN and water data at similar concentrations and relative humidities as those reported by Holdren and Rasmussen and to show that these were free of water anomaly effect. I also included a brief outline of past experiences and difficulties in the construction of a suitable GC system for PAN. These difficulties are apparently shared by other experimenters who have attempted this analysis. The purpose of my manuscript was not to discredit the work of Holdren and Rasmussen, but to point out that their results are not necessarily observed in all GC systems for PAN analysis.

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INDUSTRY TRENDS

Stuart Finley Inc. (Falls Church, VA) is offering a film called, "Which Energy," that provides an in-depth look at near-, mid-, and far-term options available for ensuring adequate energy supplies.

Dow Chemical U.S.A. (Midland, MI) has opened its first toluene diisocyanate plant at Freeport, TX. The chemical is used to make urethane products. Dow says that pollution control regulations affecting the plant will be met or bettered.

The **Michigan Energy and Resource Research Corp.** (Detroit), which organized Michigan's bid for the new Solar Energy Research Institute, accepted General Motors as a member.

Northeast Utilities (Hartford, CT) announced that a record 73.8% of the electricity it supplied came from nuclear generators. This was for September, during which Northeast supplied 1.582 billion kWh in Connecticut and Massachusetts.

Inco Ltd. (Copper Cliff, Ont., Canada) has installed 60-mgd automated reactor clarifiers as part of a $6 million water treatment complex. Inco now recycles 87% of its water; remaining effluent more than meets Ontario environmental guidelines.

The **Beverage Industry Recycling Program** (Phoenix, AZ) collected more than 446 600 lb of newspaper for recycling in October, and consistently bought it at 1¢/lb.

Natural Energy Corp. (Washington, DC) has acquired rights for worldwide distribution of solar energy equipment made by Central Boilers Co., Ltd. (Hod-Hasharon, Israel), believed to be the world's largest solar energy collector maker.

Union Camp Corp. (Wayne, NJ), a large forest products company, has donated 2850 acres of land to the State of Florida for preservation as part of Florida's Endangered Lands Program.

Titan Group, Inc. (Paramus, NJ) has contracts totaling over $30 million for wastewater treatment plants near Dallas and Fort Worth, TX, and at Plainville, CT.

The **Syracuse Research Corp.** (Syracuse, NY) has been awarded an EPA contract to study methyl halides for the EPA's Office of Toxic Substances.

Scott Paper Co. (Philadelphia, PA) is to join the City of Oconto Falls, WI, in an agreement for treatment of plant wastes in a system to be built by the City.

AAF-Ltd. (Montreal, Canada), a subsidiary of American Air Filter Co., Inc., will provide an AAF-Elex electrostatic precipitator, valued in excess of $800 000, to Inland Cement Industries, Ltd., of Canada. Precipitator rating is 265 000 cfm.

Neptune Microfloc, Inc., has a $2.8 million contract to supply the Puerto Rico Water Resources Authority with complete wastewater treatment systems for 4 steam electric generating plants.

Varian Associates (Palo Alto, CA) received 3 ERDA contracts for solar-electric power development, totaling about $450 000. These are continuing contracts that emphasize gallium-arsenic cells and films.

FMC Corp. will supply an open-tank pure-oxygen wastewater treatment system for a $8.5 million upgrading and expansion of the Joe W. Lovell Wastewater Treatment Plant at Murfreesboro, TN.

Johnson-March Corp. (Philadelphia) will provide and install a complete dust control system for the lignite-handling operation of Brazos Electric Power Cooperative (San Miguel, TX), on a turn-key basis.

B. F. Goodrich has installed a catalytic incinerator air pollution control system at its tire cord treating unit at Martha Mills, GA. This lower-temperature system is believed to be the first ever in the textile industry.

Wheelabrator-Frye Inc. will provide a clean air system to U.S. Steel Corp. The system uses fabric filters, and will handle 825 000 cfm.

Met-Pro Corp. and **Met-Pro Systems, Inc.** have moved to new facilities at Harleysville, PA. All of Met-Pro's 5 subsidiaries are involved in environmental and pollution control work.

Aluminum Co. of America (Alcoa, Pittsburgh, PA) announced that its technology for aluminum smelter pollution control—a dry scrubbing technique—has been licensed to the Anaconda Co. It recycles more than 98% of total fluoride content.

Dames & Moore (Los Angeles) will complete a series of meteorological and geotechnical studies for environmental/safety analysis reports for Pennsylvania Power & Light Co.'s Susquehanna Steam Electric Station.

The **American Iron and Steel Institute** sees this year as "the best year ever for garbage recycling."

Fluor Engineers and Constructors, Inc. (Los Angeles, CA) has received a $9 million contract from ERDA to design and engineer a new high-capacity facility to solidify liquid nuclear wastes.

York Research Corp. (Stamford, CT) has expanded its laboratory facilities, reflecting a growing emphasis on sanitary microbiological and water quality determinations for permit compliance, wastes, and other customer needs.

The Standard Oil Co. (Ohio) has created a well-equipped fleet of environmental control vehicles to contain and clean up petroleum product spills on land and water.

Engineering-Science, Inc. (Arcadia, CA) and Petrotechna, S.A. (Paris, France) have formed a partnership to offer pollution control engineering services in European Common Market countries.

Kaiser Engineers (Oakland, CA) has been selected by ERDA to build a key facility for a magnetohydrodynamic (MHD) method of generating electricity from coal. In MHD, hot coal gases (over 4500 °F) are directed through a magnetic field.

The **Chemical Industry Institute of Toxicology** (CIIT, Research Triangle Park, NC) has approved construction of a 57 000-ft^2 laboratory for testing, research, and training programs.

Pennwalt Corp. (Philadelphia) estimates that its environmental cleanup market grew by 26.2% over 1971–1975.

Computer Network Corp. (COMNET, Washington, DC) was selected by EPA to provide computer resources, telecommunications, and user support for agency-wide data processing requirements. Value will exceed $20 million, and should double COMNET's current revenue.

Basic Technologies, Inc. (West Palm Beach, FL) is building 2 brackish-water desalination plants, totaling 270 000 gpd, for use at Riyadh and Medina, Saudi Arabia. The contract is worth about $500 000.

Rockwell International's Atomics International Division (Canoga Park, CA) has a $1.26 quality-assurance program contract for air monitoring laboratories in the western U.S. The contract is with EPA.

RaySolv, Inc. (Linden, NJ) has recently completed a 50 000-cfm system, using activated carbon, to reduce emissions and recover solvent, for General Motors. Emission control is 99% efficient.

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U.S. Reduction Co., an **American Can Co.** (Greenwich, CT) subsidiary, has scheduled a $2 million plant at Anniston, AL, to extract non-ferrous materials from crushed automotive scrap.

Jacobs Engineering Co. (Pasadena, CA) has concluded a nationwide study of hazardous waste disposal practices in the petroleum refining industry for the EPA.

Stone & Webster Engineering Corp. (Boston, MA) will design a 12-MW pilot plant to burn coal in a pressurized fluid bed, for ERDA.

American Lurgi Corp. (Hasbrouck Heights, NJ) is to design, procure, and construct a Lurgo sulfacid plant and sulfuric acid concentrator system for SO_2 effluent abatement for Gulf & Western's New Jersey Zinc Division at Palmerton, PA.

Standard Havens, Inc. has provided air pollution control systems for two spreader-stoker boilers (70 000 cfm) for Ashland Oil Co.

United Nuclear Corp. has been awarded a $87 million contract addition by ERDA for production of nuclear components.

CEA*Carter-Day Co. (Minneapolis, MN) has a dust collection system contract from Great Lakes Coal & Dock Co. (St. Paul, MN). Two large fabric filters will clean air at 58 000 cfm.

The **American Paper Institute** (New York, NY) has asked the Federal Energy Administration to set a realistic energy-saving target under the Energy Policy and Conservation Act of 1975.

Gorham International Inc. (Gorham, ME) will prepare a multi-client study of energy conservation potentials and alternatives in the pulp/paper industry.

AG Brown Boveri & Cie (Baden, Switzerland) said that manufacture of motor-generators for the Mapragg pumped-storage station of Kraftwerke Sarganserland AG, near Bad Ragaz, Switzerland, is proceeding according to schedule.

Arthur D. Little Inc. (Cambridge, MA) is to design prototype appliances that save fuel by integrating separate functions in one piece of equipment. The company also sees a solar heating market of $800 million–$1.5 billion by 1985.

J.T. Baker Chemical Co. (Phillipsburg, NJ) has appropriated $2.5 million more for waste treatment plant expansion to achieve further BOD reduction.

Eco-Research Ltd. (Pointe Claire, Québec, Canada) will construct and evaluate a pilot plant for the "ICI Deep Shaft Effluent Treatment Process" at Coopérative Agricole de Granby's milk processing plant.

NEW PRODUCTS

Data acquisition system

System can log, trend and "alarm" up to 1000 points. It will accept input from thermocouples, resistance thermometer detectors, voltage or current transmitters and contact closures. It displays 3+ or 4+ digit measurements. Leeds & Northrup **131**

Timer-counter

This 5-digit timer, frequency meter and event counter is computer compatible. Features include a 20-bit BCD output, and remote controllability via logic levels. McKee-Pedersen Instruments **132**

Grab sampler

The capped sampling bottle is clamped onto a 6-ft long grab sampler and submerged. The cap can be removed, the sample collected and the cap replaced without the operator touching the bottle or getting wet. Wheaton Instruments **101**

Flow rate/suspended solids analyzer

The sonic device simultaneously measures volumetric flow rates and concentration of suspended solids via a single pair of transducers. These readings can be combined to yield a mass-flow reading. Mapco Inc. **102**

Sound level meter

The meter spans 30–120 dBA in two switch-selectable 50-dB ranges, and readings are displayed on a digital and linear analog meter. The unit will "hold and display" the maximum level measured on the digital display while the analog meter indicates lower levels. GenRad **103**

Fly ash collector

This fabric-filter-type collector is designed to clean flue gases from coal-fired boilers. The unit requires little compressed air for operation and purge times are controllable. American Precision Industries **104**

Non-PCB fluid

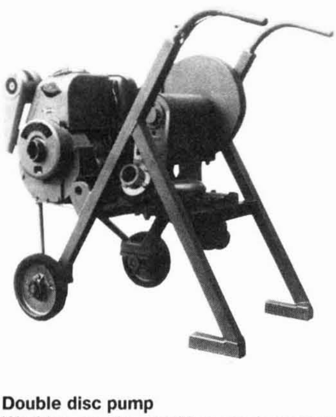
This fluid was developed for use in power capacitors where once PCBs were used. The new fluid, isopropylbiphenyl, is combustible. Westinghouse Electric **105**

Subsurface sludge injector

For use in the land application of liquid wastes, the device allows the sludge to be pumped directly into the ground from a treatment plant or holding facility; the soil surface is the cover. Briscoe Maphis **106**

TOC analyzer

The on-line monitor is fully automatic. Results appear on a chart record every 12 min. The analyzer can monitor ranges from 0–1 to 0–5000 mg/L carbon. Delta Scientific **107**



Double disc pump

Working on the positive displacement principle, the two flexible discs serve as impulsion members and as suction and discharge valves. Discs are available to handle high-temperature slurried and petroleum products. At 750 rpm maximum speed the pump will deliver 120 gal/min. The pump is self-priming. Zodiax **108**

Bubble generator

This technique makes it possible to visualize the photograph patterns of air flow for use in pollution studies with urban topography models, atmospheric modeling and room ventilation studies. Sage Action **109**

Potable gas monitor

Worn on a worker's belt, the instrument will detect and monitor combustible, toxic and oxygen deficiency simultaneously. Alarms and indicator lights signal the gaseous condition. The unit is impervious to temperature, humidity or electronic drift changes. Dynamation **110**

Chemical resistant finish

This finish was designed for coating fiberglass fabrics used in dust collector bags. National Filter Media **111**

Water sampling system

The system is clog-resistant and self-cleaning claims the manufacturer. The automatic system operates on air and hydrostatic pressure. Samples in almost any amount of suspended solids can be collected and stored. Environmental Measurement Systems **112**

Instrument shelter

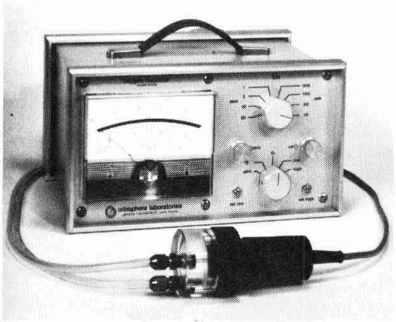
This portable shelter is designed to protect air-quality monitors and data processors. The shelter is temperature controlled. Radian **113**

Mist eliminator

Device is designed to replace high-velocity equipment in the sulfuric acid industry. The unit is easier to install, offers better collection efficiency and requires less maintenance. Collection efficiency is at least 95% on particles 1–3 μ in size. Monsanto Enviro-Chem Systems **114**

Deep-sea movie camera

The camera offers high-speed and elapsed time underwater photography in the 16-mm movie format. The camera is useful in environmental studies, observation of sediment transport and in corrosion studies. The camera is pre-tested to 13 000 m. Benthos 115

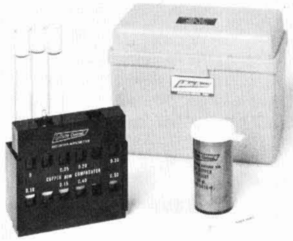


Dissolved oxygen analyzer

Designed for very-low-level oxygen measurement in biochemical studies of oxygen uptake and metabolism. The instrument's ranges are: 0–10, 0–30, 0–100, 0–300, 0–1000, 0–3000, 0–10 000 and 0–30 000 ppb or μg/L; accuracy is ±1% or 0.5 ppb, whichever is greater. Orbisphere 116

Level alarm/control system

The system prevents spills from storage tanks of fuels and chemicals. It is modular and is readily adapted to any number of levels and tanks or bins. Amiprodux 117



Copper test set

The single-reagent with no chemical extractant requirement test measures copper in a range of 0.05–0.50 ppm in treated water and wastewater. LaMotte Chemical 118

Settling pit cleaning system

A submerged pump and variable speed feeder automatically and hydraulically removes settled solids from settling pits. The system can be programmed to handle a wide range of particle sizes and concentrations. It finds application in sludge-collection facilities. Colerapa Industries 119

Scanning fluorescence detector

The spectrofluorimeter is designed for use in high-speed liquid chromatography. It permits emission spectra to be recorded on the peaks in a chromatogram, thus aiding positive identification of the peak. The detector is able to routinely measure substances in the picogram range. Perkin-Elmer 120

Charcoal tubes

Used as the collecting medium, these tubes are designed to collect potentially hazardous airborne chemicals in the workplace. The small sealed-glass tube, containing a precise amount of NIOSH-approved charcoal is connected to a low-flow personal air sampling pump for the OSHA'specified flow rate and collection time. Du Pont 121

Glassware carrying cases

These fitted cases are designed for use with the company's manual industrial stack sampling systems. Two different cases are available for transporting EPA Method 5 glassware in foam inserts. EPA Method 6 (SO_2) and EPA Method 8 (sulfuric acid mist and SO_2) glassware can also be fitted in the carrying cases. Lear Siegler 122

Reverse osmosis element

The 8-in. diameter element for use in large-capacity reverse osmosis desalination systems can be shipped and stored dry. The unit is intended for use in feedwater with total dissolved salts of 750 ppm; operating at 400 psi it can produce 4000 gal/day. Hydranautics 123

Potable air sampler

The self-lubricating motor allows the sampler to be used over long periods of time without interruption. The unit can be made for use with 220 V ac or dc current. Staplex Company 124

Charged droplet scrubber

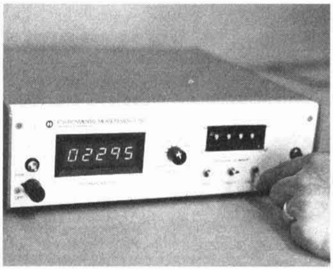
The scrubber traps gaseous and solid emissions from industrial stacks. These scrubbers are currently in use in steel, paper and chemical plants in the U.S. and Japan. TRW 125

Solar concentrator/collector

The unit uses focusing reflectors to concentrate and collect solar heat. The concentrator weighs less than 70 lb and measures only 4 × 6 ft; it is designed to perform better than flat-plate collectors. The unit contains no glass; it can be used for hot water or pool heating. Solarcell 126

Chlorine titration system

The system measures total residual chlorine, free residual chlorine and combined residual chlorine in chlorinated water supplies. It finds application in municipal water-treatment systems and in manufacturing plants that use bleach. The method of titration used—amperometric—is unaffected by oxidizing agents, temperature variations, turbidity or color. Fisher Scientific 127



Distance proportional air sampler

The device is a timer that controls sampling devices while traveling in a moving vehicle. The device monitors the vehicles rate of speed and adjusts the sampling rate to be proportional to the speed. The sampling density is selectable. Environmental Measurements 128

Process refractometer

The instrument continuously measures and identifies various chemical substances in liquids. The unit operates within any range from 0.00005–0.1 R.I. units, full scale, to an accuracy of 1% and a sensitivity of 1.4%, full scale. Anacon 129

Digital humidity indicator

The instrument is designed for direct measurement of relative humidity in environmental studies. Readout is linear over the range of 0–100% relative humidity; automatic temperature compensation for the humidity sensor is operative from −5 to +75 °C. Phys-Chemical Research 130

pH/temperature recorder

This cordless recorder simultaneously records temperature and pH on the same chart. By using a time-sharing system with one galvanometer, the full chart width is used for each parameter but with different line intensities for easy identification. Analytical Measurements 133

Cooling tower control system

This 3-speed solid-state system automatically controls the water temperature of cooling towers. Each system module will control up to 4 zones with one or two fans in each zone. Suntech 134

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

NEW LITERATURE

Boiler energy recovery. Catalog describes boiler energy recovery systems for boiler sizes of 100–2000 boiler hp (3500–75 000 lbs/h of steam). Payback of 1½ years is estimated. Isothermics, Inc. **151**

Community noise. "Here's How" Bulletin 4.1223.0 tells how noise level of four induced-draft fans of 785 000 cfm was reduced by 15 dB(A), and that nearby residents' complaints ceased. Industrial Acoustics Co., Inc. **152**

Air cleaning. Brochure GL 202-096 covers filter bags that use a patented reverse air cleaning method. Many applications, including product recovery. General Resource Corp. **153**

Submersible pump. Bulletin 728.1 announces a new submersible water pump that handles unscreened raw sewage, nonabrasive solids, and industrial waste sludge. Goulds Pumps, Inc. **154**

Turn-key services. Brochure describes company's turn-key services for customers with stack, water, or solid waste pollution problems, or all three. Midwesco Energy Systems **155**

Safety color codes. Guide can be used to determine color coding for first-aid equipment, caution areas, radiation hazards, and other industrial safety and material identification. Based on standards adopted by OSHA. Carboline Co. **156**

Welding dust collector. Report tells about performance tests of a Torit TD 4600 filter-cartridge collector with regard to control of fumes and dust from welding stations. OSHA standards met. Torit Division, Donaldson Co., Inc. **157**

pH, redox receiver. Data Sheet C2.1122-DS describes 7076 pH and redox receiver with easy-to-read digital display. Leeds & Northrup **158**

Wet scrubber. Brochure describes operating principles and specifications of the Model FRP-100 Low Energy Wet Scrubber for economical particulate control and SO_2 removal. Century Industrial Products **159**

Waste handling. Literature tells how Corra-Trough Belt Conveyors meet needs of municipal and industrial waste treatment facilities for handling sludge, centrifuge cake, and the like. The Bucket Elevator Co. **160**

Mass spectrometry. Brochure describes company's services, especially for customers without in-house mass spectrometry or gas chromatography/mass "spec" capabilities or equipment. Shrader Analytical & Consulting Laboratories, Inc. **161**

Heavy metal removal. Write-up describes precipitation-absorption process for removing non-complexed and non-chelated heavy metals from metal finishing plant effluents. Economical and highly effective, according to company. Waste Water Technology Corp. **162**

Reverse osmosis. Leaflet discusses osmosis/ultrafiltration techniques that can be applied to industrial, toxic, radioactive, or sewage effluent cleanup, and recovery of dissolved solids. Harwell **163**

Water service. Brochure describes water services, such as predictive studies, surveys, and analysis/assessment planning that the company offers. The Research Corporation of New England **164**

Waste reduction. Bulletin 32-109 describes a Waste Disintegrator/Macerator that will chew almost all solids, including glass, into pieces of about 3/16 in. in size. BIF Sanitrol **165**

Ultrafiltration. Booklet has up-to-date listing of almost 1000 literature references to use of the firm's ultrafiltration devices and membranes. Amicon Corp. **166**

Dams. "Water for People . . . Water for Industry" tells of company's experience with planning and design of both concrete and fill dams. Harza Engineering Co. **167**

Coal firing. Bulletin No. 122 explains how coal can be ground for better, more efficient firing. 4000 grinding units now in operation. C-E Process Equipment. **168**

Water/waste filtering. Permutit Bulletin No. 2225 describes the latest pressure filters for water/watewater treatment. Construction and performance features are discussed. The Permutit Co., Inc. **169**

AA Spectrophotometers. Brochure describes IL 51 series atomic absorption (AA) spectrophotometers, and provides much instructional material. Instrumentation Laboratory, Inc. **170**

Spray dryers. Brochure tells company story and illustrates capabilities to create spray dryer systems for many requirements. Most liquid-based products can be dried. Anhydro, Inc. **171**

Resource recovery. Brochure discusses importance of resource recovery from solid waste, and company's capabilities and experience in that field. Raytheon Co. **172**

Refractory dryout. Case histories describe services in drying out refractory materials for the oil, gas, and petrochemical industries. Much downtime was saved. Hotwork, Inc. **173**

U/V sterilizer. Bulletin describes operating principles of an ultraviolet (U/V) water sterilizer. Construction, flow rates, and specific applications are discussed. Xodar Corp. **174**

Fire protection. Brochure describes piping systems that give most economical means of putting in fire protection. Victaulic Co. of America **175**

Surface aerators. Monograph tells how to optimize horsepower selection and aeration basin size for low-speed surface aerators at wastewater treatment plants. Envirex **176**

Chlorine control. Bulletin 4770-1 describes and illustrates automatic chlorination switchover system for continuous water and wastewater treatment. Capital Controls Co. **177**

Construction castings. Catalog "R" describes wide range of construction castings for many needs, including catch basins, sewage collection, and other applications. Neenah Foundry Co. **178**

Reverse osmosis. Specification literature can be of help to people working on problems of water desalination, and tells how reverse osmosis components can do the job. Hydranautics **179**

Fluid couplings. Bulletin D-1100 tells how fluid couplings transmit power from a motor to a load efficiently, without mechanical connections. Used for pumps, crushers, and other machines. American-Standard **180**

Shredder. Bulletin No. 915 describes shredder for both wood and bark products. Sizes ranging from 24 in. diameter and 12 in. wide to 60 in. diameter and 120 in. wide are available. Gruendler Crusher & Pulverizer Co. **181**

Environmental testing. Brochure describes company's capabilities for testing services for air, water, and noise pollution in many different situations. Environmental Testing Services, Inc. **182**

Solid waste services. Brochure, "Solid Waste Management & Resource Recovery . . . the Weston Way," outlines a broad range of services for private, industrial, and government clients. WESTON Environmental Consultants-Designers **190**

Composting. Information is available that describes composter system for processing sewage sludge, refuse, feedlot wastes, wood wastes, garbage, and food wastes into compost. Eagle Crusher Co., Inc. **191**

Oil and solvent salvage. Mini-catalog lists liquid claritation products and systems that can salvage up to 95% or more of old industrial oils, petroleum solvents, coolants, and insulating oils. Velcon Filters Inc. **198**

Coal gasification data. News release tells of collection of government documents on coal gasification and liquefaction dating 1910–1975. Standard microfiche. UPDATA **199**

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

South Texas water. Report 210, Volume I describes ground water resources in 17 countries from the San Marcos River to the Rio Grande. Featured is the Carrizo Aquifer. Texas Water Development Board, 1770 North Congress Ave., Austin, TX 78701 (write direct).

Solar Energy. Questions are answered with regard to investment and savings. Document SE-101. ERDA Technical Information Center, Box 62, Oak Ridge, TN 37830 (write direct).

Solid waste management. Bibliography SW58.26. Available information materials 1966–1976. By Julie L. Larsen. Solid Waste Information, U.S. Environmental Protection Agency, Cincinnati, OH 45268 (write direct).

"Energy vs. Ecology . . . The Great Debate." Allis-Chalmers Corp. film shows how coal can be used with no environmental disruption. Film won major award. Modern Talking Picture Service, 2323 New Hyde Park Road, New Hyde Park, NY 11040 (write direct).

Refinery gas analysis. Paper by Shell Oil engineer reprinted in recent issue of "*Current Peaks*," company publication. Carle Instruments, Inc., 1141 East Ash Ave., Fullerton, CA 92631 (write direct).

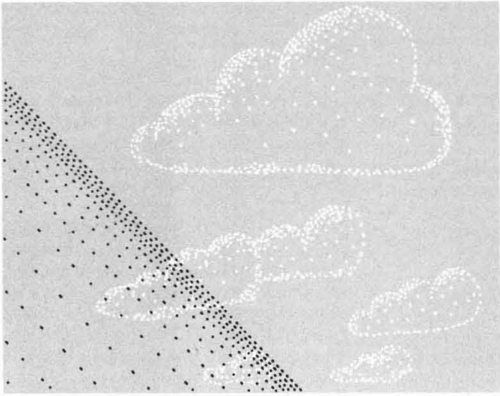
Fibrous glass exposure. Discussion of worker exposure to fibrous glass. NIOSH-76-151, single copies. Clearing House for Occupational Safety and Health Information, 4647 Columbia Parkway, Cincinnati, OH 45226 (write direct).

Cold-weather sludge handling. Study is entitled: "Low Temperature Oxygen Single-Sludge Nitrification With Phosphorus Removal." Cold-weather aerobic sludge digestion and ozone disinfection. Air Products and Chemicals, Inc., Allentown, PA 18105 (write direct).

TECHNOLOGIES. Resource Recovery Plant Implementation: Guides for Municipal Officials. SW-157.2. Solid Waste Information, U.S. Environmental Protection Agency, Cincinnati, OH 45268 (write direct).

Quantum Chemistry Program Exchange. Facilitates software exchange between quantum chemists. Very useful for analysis. Quantum Chemistry Program Exchange, Chemistry Building 204, Indiana University, Bloomington, IN 47401 (write direct).

Oil regulations. Guidelines of environmental concern in Europe. CONCAWE report 6/76. Stichting CONCAWE, 60, van Hogenhoucklaan, The Hague 2018, The Netherlands (write direct).



BOOKS

Atmospheric Pollution. Michel Benarie, Ed. x + 650 pages. Elsevier/North Holland, Inc., 52 Vanderbilt Ave., New York, N.Y. 10017. 1976 $49.75, hard cover.

Air pollution research has one goal: to fight and eliminate nuisances arising from such pollution. Here, such research is deeply discussed, and topics include air chemistry, aerosols, monitoring, NO_x, particulates, surveys, and international coordination. Papers are from the 12th International Colloquium, Paris France, and the book is one of Elsevier's *Excerpta Medica* series.

The Accident Hazards of Nuclear Power Plants. Richard E. Webb. x + 288 pages. The University of Massachusetts Press, P.O. Box 429, Amherst, MA 01002. 1976 $6.95, paper.

The nuclear controversy rages on, and here is a book that points out dangers of nuclear accidents. However, it does not suggest that nuclear reactors pose the greatest risk of harm, since risk assignment is very difficult. Nevertheless, actual hazard possibilities are listed, and they cover strontium-90 release; design basis *vs.* worst possible accidents; breeder reactor explosion risks; near-accidents that occurred; and other pertinent subjects.

Energy From Solid Wastes. Paul N. Cheremisinoff and Angelo C. Horresi. v + 505 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, NY 10016. 1976. $35, hard cover.

Sometimes, what is "a lotta garbage" can be good, especially if it provides environmentally clean fuels and energy. This volume (Volume 1 of the Pollution Engineering and Technology Series) describes practical solid waste-to-fuel projects involving direct burning, pyrolysis, gasification, liquefaction, and other approaches. Resource recovery is also covered, as are experiences worldwide.

Nature, Mother of Invention: The Engineering of Plant Life. Felix R. Paturi. 208 pages. Harper & Row, Publishers, Inc., 10 E. 53rd St., New York, NY 10022. 1976. $10.95, hard cover.

In many fields—chemistry, ballistics, aerodynamics, engineering—nature was there before man. However, in nature, nothing is wasted. Growth and decay merge into each other, and pollution, thus, cannot exist. However, man pollutes through the development of new forms. The author tells why man cannot expect to survive unless the human race resigns itself to the equilibrium needed for survival by imitating nature.

Nitrogen, Phosphorus, and Sulphur—Global Cycles. B. H. Svensson, R. Soderlund, Eds. 192 pages. Editorial Services, Swedish Natural Science Research Council, Box 23136, S-104 35 Stockholm, Sweden. 1976. S. Kr. 40 (about $10), postpaid, paper.

This report brings together present knowledge of biogeochemical cycles of nitrogen, phosphorus, and sulfur in a multidisciplinary way. Natural cycles and man's impacts are covered, as is environmental stress brought on by excesses of these elements. The study leading to this report was funded by UNEP and other bodies. Ask for Ecological Bulletins/NFR 22.

Proceedings of the Second International Symposium on Ozone Technology. Rip G. Rice, et al, Eds. xii + 725 pages. Ozone Press Internationale, P.O. Box 366, Jamesville, NY 13078. 1976. $40, paper.

The symposium took place at Montreal, Canada in May 1975. Principal subjects covered were uses in industry; treatment of phenols; water disinfection; treatment of cyanide-containing water; and ozone *vs* chlorine. The International Ozone Institute (Syracuse, NY) sponsored the symposium.

Chemical Carcinogens. Charles E. Searle, Ed. xxvi + 788 pages. American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. 1976. $67.50, hard cover.

What do vinyl chloride, N-nitrosamines, and benzo $[\alpha]$ pyrene have in common? They, and hundreds of other compounds from many sources appear to cause cancer. This ACS book describes most recent research in this direction, and illustrates it with many tables, as well as over 750 structural formulas.

Strategies for Marine Pollution Monitoring. Edward D. Goldberg. x + 310 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1976. $21.50, hard cover.

What must be monitored? How are pollutants analyzed? What are the best sampling methods? How can programs for local or regional marine monitoring be created? The author provides guidelines for programs aimed at answering these questions, tells specifically what to look for, and how to go about determining pollutant levels by the latest quantitative methods.

The Economics of Refuse Collection. Peter Kemper, John M. Quigley. xvi + 181 pages. Ballinger Publishing Co., 17 Dunster St., Harvard Square, Cambridge, MA 02138. 1976. $13.50, hard cover.

Of the resources devoted to solid waste collection/disposal, more than 80% goes for collection. Costs, demands, and methods of public and private waste collection are analyzed; organization of the economic sector is discussed, and alternative financing methods are covered. The authors recommend ways of improving efficiency.

Pesticides in the Environment, Volume 2. Robert White-Stevens, Ed. xvi + 458 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, NY 10016. 1976. $37.50, hard cover.

In this volume, the role of fungicides in crop production, control of nematode diseases in plants, pesticides in ornamental/landscape plantings, and control of certain parasites in animals are discussed. The book's contents are based on experimental evidence and practical field experience.

Ponds as a Wastewater Treatment Alternative. Earnest F. Gloyna, et al, Eds. xii + 447 pages. Center for Research in Water Resources, The University of Texas at Austin, Austin, TX 78712. 1976. $20, hard cover.

This volume considers anaerobic waste stabilization ponds, facultative waste stabilization ponds, and polishing waste stabilization ponds. Pond technology, design, and operation are discussed, as is impact of pond effluents on receiving waters, and auxiliary processes that may be needed to achieve certain water criteria.

Corrosion Resistant Materials Handbook. 3rd ed. Ibert Mellan. x + 685 pages. Noyes Data Corp., Mill Rd., at Grand Ave., Park Ridge, NJ 07656. 1976. $39, hard cover.

Corrosion is a problem in many systems, including those for abating pollution. It is always helpful to include corrosion-resistant materials wherever possible, and this book presents those that are known at present, so that the engineer and scientist will have the widest possible choice at his command. Many performance statistics are given.

Nature by the Month. Andrew A. Wilson. viii + 80 pages. The Interstate Printers & Publishers, Inc., 19-27 North Jackson St., Danville, IL 61832. 1976. $2.95, paper (less educational discounts).

This book was prepared to assist children and parents, as well as teachers, in learning about the ties between man and nature. It is written in very simple wording in order that it may be useful to a very wide readership.

Nuclear Energy and National Security. 88 pages. Committee for Economic Development, 477 Madison Ave., New York, NY 10022. 1976. $4, hard cover; $2.50, paper.

This report says that the U.S. must remain a leader in nuclear energy if it wants to do something about stopping or slowing the spread of dangerous nuclear materials in the world. It calls for a U.S. energy policy that deals with foreign and domestic aspects of the energy problem; negotiations for safeguards and inspection standards that are tighter; and strengthening of the U.S. as a major reactor fuel supplier.

Environmental Toxicity of Aquatic Radionuclides. Morton W. Miller, J. Newell Stannard, Eds. xv + 333 pages. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, MI 48106. 1976. $27.50, hard cover.

This book considers biogeochemistry of transuranic radionuclides, and models for radionuclide release and distribution. It also covers ecological factors of radionuclide toxicity. All these subjects were discussed at the Eighth Rochester International Conference on Environmental Toxicity, held in June 1975.

Solid Waste Planning in Metropolitan Regions. Michael R. Greenberg, et al. 218 pages. The Center for Urban Policy Research, Rutgers University, New Brunswick, NJ 08903. 1976. $10, paper.

Solid waste is a readily available, and still largely untapped resource. Landfilling will be increasingly withdrawn from the land-use market. Thus, reuse for materials and energy will become the name of the game more and more. This book explains what the options and alternatives are in making all this come about.

Papers Presented Before the Third Symposium on Coal Utilization. iv + 233 pages. National Coal Association, 1130 17th St., N.W., Washington, DC 20036. 1976. $8, paper.

Looking for a way out of the energy crisis? One way is use of coal, but certain technological and environmental matters must be addressed. This volume examines some of these problems, and covers desulfurization, gasification, fly ash utilization, use of elemental sulfur, and many other topics.

Energy Demand Studies: Major Consuming Countries. Paul S. Basile, Ed. xiv + 553 pages. The MIT Press, c/o Uniserv Inc., 525 Great Road, Littleton, MA 01460. 1976. $20, hard cover.

This book presents analyses of 1972 demand as a base, and projections of demand to 1985. The basis on which these projections rest is explained.

MOTOR Auto Repair Manual 1977. Louis C. Forier, Ed. 1376 pages. MOTOR, 1790 Broadway, New York, NY 10019. 1976. $21, hard cover (sold to the auto repair trade).

This manual is a guide to repair and tune-up of American-made cars. More than 100 pages are devoted to emission controls. Detailed illustrations and step-by-step instructions are provided.

The New American Dream Machine. Robert L. Sansom. 251 pages. Anchor Press Doubleday, 245 Park Ave., New York, NY 10017. 1976. $8.95, hard cover.

Remember the Santa Barbara (CA) oil spill? Fires on the Cuyahoga River (Cleveland, OH)? These and other events helped to bring about much of the recent environmental legislation. In turn, there was controversy ranging from doomsaying environmentalism to *laissez-faire* industrialism. The author, formerly EPA's assistant administrator for air and water programs, examines the early phases of the environmental movement.

Industrial Wastewater Management Handbook. Hardam S. Azad, Ed. xix + 546 pages. McGraw-Hill Book Co., 1221 Ave. of the Americas, New York, NY 10020. 1976. $27.50, hard cover.

This handbook aims at solving wastewater management problems in the largest water polluting industries. It shows how to minimize industrial wastewaters through product recovery, water reuse, stream segregation, better housecleaning, and other methods. The editor is director of environmental projects for NUS Corp. (Rockville, MD).

MEETING GUIDE

February 23 St. Louis, Mo.
Corporate Readiness for Compliance with the New Toxic Substances Control Act. Manufacturing Chemists Association

Write: George W. Ingle, Manufacturing Chemists Association, 1825 Connecticut Ave., N.W., Washington, D.C. 20009

Feburary 23–25 Washington, D.C.
Economic Growth with Environmental Quality. Environmental Industry Council

Write: Environmental Industry Council, 1825 K Street, N.W., Suite 210, Washington, D.C. 20006

March 5–9 Atlanta, Ga.
42nd North American Wildlife and Natural Resources Conference. The Wildlife Management Institute

Write: Wildlife Management Institute, 1000 Vermont Ave., N.W., 709 Wire Building, Washington, D.C. 20005

March 8–10 New Orleans, La.
1977 Oil Spill Conference. Environmental Protection Agency, American Petroleum Institute and U.S. Coast Guard

Write: Ms. Retha Odom, Shell Oil Co., 50 W. 50th St., New York, N.Y. 10020

March 9–11 Long Beach, Calif.
First Annual Conference and Exhibit on Ports, Harbors and Related Facilities. American Society of Civil Engineers, U.S. Army Corps of Engineers and others

Environmental topics will be discussed. *Write:* A. J. Favata, American Society of Civil Engineers, 345 E. 47th St., New York, N.Y. 10017

March 14–16 Washington, D.C.
4th Annual Energy Technology Conference & Exposition. Government Institutes, Inc.

Write: Ms. Nancy McNerney, Director of Information, Energy Technology Conference, c/o Government Institutes, 4733 Bethesda Ave., N.W., Washington, D.C. 20014

March 20–25 New Orleans, La.
173rd ACS National Meeting. American Chemical Society (ACS)

Write: A. T. Winstead, ACS, 1155 16th St., N.W., Washington, D.C. 20036

March 21–23 Chicago, Ill.
Third Annual Conference & Exposition. American National Metric Council

Theme is Trans Metric. *Write:* George B. Buchanan, American National Metric Council, 1625 Massachusetts Ave., N.W., Washington, D.C. 20036

March 21–23 Philadelphia, Pa.
Symposium on Municipal Wastewater and Sludge Recycling on Forest Land and Disturbed Land. Institute for Research on Land and Water Resources and the School of Forest Resources in Cooperation with Continuing Education, The Pennsylvania State University

Write: Dr. William E. Sopper, Institute for Research on Land and Water Resources, The Pennsylvania State University, University Park, Pa. 16802

March 21–24 Omaha, Neb.
1977 Land-Use Symposium. Soil Conservation Society of America and others

Theme is "Land Use: Tough Choice in Today's World." *Write:* Soil Conservation Society of America, 7515 Northeast Ankeny Rd., Ankeny, Iowa 50021

March 21–25 Nashville, Tenn.
Development of Design Criteria for Wastewater Treatment Processes. Dept. of Environmental Engineering and Policy Management and the Center for Environmental Quality Management, Vanderbilt University

Write: Prof. W. Wesley Eckenfelder, Jr., Vanderbilt University, Box 6222, Station B, Nashville, Tenn. 37235

March 22–24 San Diego, Calif.
2nd Bi-Annual ATP Methodology Symposium. SAI Technology Co.

Environmental applications will be discussed. *Write:* Conference Coordinator, SAI Technology Co., 4060 Sorrento Valley Boulevard, San Diego, Calif. 92121

March 22–24 Chicago, Ill.
Packaging of Hazardous Materials for Transportation. Hazardous Materials Advisory Committee

Write: Willis W. Bixby, Secretary/Treasurer, Hazardous Materials Advisory Committee, Suite 1107, 1100 17th St., N.W., Washington, D.C. 20036

March 27–30 New Orleans, La.
INFO 77: Nuclear Power and the Public. Atomic Industrial Forum, Inc.

Write: Conference Office, Atomic Industrial Forum, Inc., 7101 Wisconsin Ave., N.W., Washington, D.C. 20014

March 27–31 Kansas City, Kan.
Second Energy-Environment Conference. American Defense Preparedness Association

Write: Commander Sullivan, American Defense Preparedness Association, Union Trust Building, 15th and H Streets, N.W., Washington, D.C. 20005

March 30–31 Washington, D.C.
5th Annual Government Affairs Seminar. Air Pollution Control Association

Theme is "The New Washington Takes a Look at the Old Clean Air Act." *Write:* Public Relations Dept., Air Pollution Control Association, P.O. Box 2861, Pittsburgh, Pa. 15230

Courses

February 23–24 Madison, Wis.
The Impact of Health System Agencies on Health Facility Planning and Design. Dept. of Engineering, University of Wisconsin–Extension

Fee: $125. *Write:* Dr. Raymond C. Matulionis, Program Coordinator, University of Wisconsin–Extension, Dept. of Engineering, 432 North Lake St., Madison, Wis. 53706

February 27–March 2 Rochester, N.Y.
EPA Pesticide Applicator Certification Training and Examination for Category No. 7 Food Processing. Environmental Management Association

Fee: $75. *Write:* Environmental Management Association, 1701 Drew St., Clearwater, Fla. 33515

February 28–March 3 Research Triangle Park, N.C.
Source Sampling for Particulate Pollutants, Course No. 450. Air Pollution Training Institute (APTI)

Fee: $140. *Write:* Registrar, APTI, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

February 28–March 3 Portland, Ore.
Control of Gaseous Emissions, Course No. 415. Air Pollution Training Institute (APTI)

Fee: $88. *Write:* Registrar, APTI, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

February 28–March 3 Dallas, Tex.
Statistical Evaluation of Air Pollution Data, Course No. 426. Air Pollution Training Institute (APTI)

Fee: $88. *Write:* Registrar, APTI, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

March 3–4 Madison, Wis.
Coal Gasification & Liquefaction. University of Wisconsin–Extension

Fee: $150. *Write:* Dept. of Engineering, University of Wisconsin–Extension, 432 North Lake St., Madison, Wis. 53706

March 7–11 Austin, Tex.
Flood Plain Hydrology. University of Texas at Austin, College of Engineering

Enrollment is limited to 30. Fee: $300. *Write:* Registrar, Flood Plain Hydrology, c/o Engineering Institutes of the College of Engineering, Cockrell Hall 2.102, The University of Texas at Austin, Austin, Tex. 78712

March 14–18 New York, N.Y.
Principles and Practice of Air Pollution, Course No. 452. Air Pollution Training Institute (APTI)

Fee: $110. *Write:* Registrar, APTI, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

(continued on page 208)

CHEMICAL CARCINOGENS

A tape recorded in-depth look at the problem of hazardous substances in the environment.

5 Speakers
Length: 164 Minutes
14 Figures

The Speakers:

H.H. Fawcett—Purpose of Symposium
B. Carroll (N.I.O.S.H.)—Toxic Substances List—What, Why, How, For Whom
W.F. Malone (Nat'l. Cancer Inst.)—Occupational Cancer Control and Prevention
N. Meade (EPA)—Actual vs. Acceptable Risks from Asbestos
W.S. Wood (Wood Assoc.)—Engineering Approach to Control of Chemical Carcinogen Exposure

PRICE: $18.00 (Cassettes Only)
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PROGRESS IN CANCER CHEMOTHERAPY

Tape recorded discussions about new drugs that look promising in the battle against cancer.

5 Speakers/167 Minutes/85 Figures

The Speakers:

A.C. Sartorelli (Yale U.)—Optimization of the Antineoplastic Potential of α-(N)-Heterocyclic Carboxaldehyde Thiosemicarbazones (HCT)
D.W. Henry (Stanford Res. Inst.)—Adriamycin
N.R. Bachur (Nat'l Cancer Inst.)—Biochemical Pharmacology of the Anthracycline Antibiotics
A.J. Lin (Yale U.)—Potential Bioreductive Alkylating Agents
G.P. Wheeler (Southern Res. Inst.)—Review of Studies on the Mechanism of Action of Nitrosoureas

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CONTROL OF ATHEROSCLEROSIS

A tape recorded symposium detailing the latest advances toward controlling atherosclerosis and reducing coronary heart disease which kills 600,000 Americans each year.

6 Speakers/210 Minutes/125 Figures

The Speakers:

R.I. Levy (Nat'l Heart & Lung Inst.)—Lipids in Atherosclerosis
G.F. Holland (Pfizer)—Recent Advances in the Discovery & Development of Antihyperlipidemic Agents
R.M. Tomarelli (Wyeth)—Antihypercholesterolemic Activity of WY 14,643, a 2-Pyrimidinylthioacetic Acid Derivative
R.A. Parker (Merrell-National)— 5-(Tetradecyloxy)-2-Furancarboxylic Acid (RMI 14,514) & Related Hypolidemic Fatty Acid-like Alkyloxyarylcarboxylic Acids
L.R. Mandel (Merck)—Studies of the Mode of Action of Halofenate
L.A. Kelly (Sandoz)—Studies of a Series of Compounds which Reduce Serum Cholesterol With and Without Accumulation of Sterol Precursors of Cholesterol

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INTERFERON

Interferon may play an important role in protecting against virus infections, cancer, and other diseases. The potential for interferon is examined in this tape recorded symposium.

4 Speakers
Length: 143 Minutes
44 Figures

The Speakers:

S. Baron (Nat'l. Inst. Allergy, Infect. Dis.)—Biological Aspects of the Interferon System
H.B. Levy (N.I.A.I.D.)—Mechanism of Antiviral Action of Interferon
J. Vilcek (New York U.)—Interferon Induction with Polynucleotides and Viruses
J.F. Niblack (Pfizer)—Synthetic Inducers of Interferon

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Selective Insect Control

Tape recorded symposium examines the potential of growth regulating chemicals as selective insect control agents.

3 Speakers
Length: 135 Minutes
95 Figures

The Speakers:

L.I. Gilbert (Northwestern U.)—Biochemical and Physiological Aspects of Insect Growth and Development
J.H. Law (U. Chicago)—Juvenile Hormone Synthesis and Action in Insects
J.W. Barnett (Ciba-Geigy)—Recent Developments in Insect Growth Regulators

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Progress Toward Synthetic Oils

Shale, coal, oil-bearing sands all offer an opportunity to add to our energy reserves. The potential for each is examined in this tape recorded symposium.

4 Speakers
Length: 125 Minutes
47 Figures

The Speakers:

H.W. Sternberg (Lawrence Livermore Lab.)—The Nature of Coal Liquefaction Products
S.K. Kunchal (Paraho Oil Shale Demo.)—Energy and Dollar Requirements in an Oil Shale Industry—Based on the Paraho Process
G.A. Myers (Atlantic-Richfield)—Prerefining of Shale Oil
R.H. Fischer (Mobil)—Non-Hydrogenative Demetalation of Residua Using Manganese Nodules

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MEETING GUIDE *(continued)*

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Design Fundamentals or Particulate Collection for Air Pollution Control. American Institute of Chemical Engineers (AIChE)

Registration limited to 60. Fee: $150 (members); $175 (non-members). *Write:* AIChE, Continuing Education Dept., 345 E. 47th St., New York, N.Y. 10017

March 21–23 Los Angeles, Calif.
6th Annual Gas Chromatography Short Course. Occidental College

Fee: $200. Write: R. L. Amey, Dept. of Chemistry, Occidental College, Los Angeles, Calif. 90041

March 21–23 Houston, Tex.
Environmental Health Management. International Safety Academy

Fee: $300. *Write:* Conference Registration, International Safety Academy, P.O. Box 19600, 10575 Katy Freeway, Houston, Tex. 77024

March 21–25 Research Triangle Park, N.C.
Meteorological Instrumentation in Air Pollution, Course No. 447. Air Pollution Training Institute (APTI)

Fee: $174. *Write:* Registrar, APTI, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

March 23–24 Houston, Tex.
Processing of Solid Wastes for Resource and Energy Recovery. American Institute of Chemical Engineers (AIChE)

Registration limited to 60. Fee: $150 (members); $175 (non-members). *Write:* AIChE, Continuing Education Dept., 345 E. 47th St., New York, N.Y. 10017

Call for Papers

February 15 deadline
Ninth Mid-Atlantic Industrial Waste Conference. Bucknell University and others

Conference will be held August 8–9 at Lewisburg, Pa. *Write:* Dr. William Snyder, Chemical Engineering Dept., Bucknell University, Lewisburg, Pa. 17837 or Dr. Michael LaGrega, Civil Engineering Dept., Bucknell University, Lewisburg, Pa. 17837

March 1 deadline
1977 Scenic River Symposium. Dept. of Landscape Architecture, Louisiana State University in conjunction with Gulf Coast Regional Conservation Committee, Sierra Club

Conference will be held June 17–18 at Baton Rouge, La. *Write:* Mr. Charles F. Fryling, Jr., Dept. of Landscape Architecture, Louisiana State University, Baton Rouge, La. 70803

March 4 deadline
1977 Spring Meeting. American Geophysical Union

Conference will be held May 30–June 3 at Washington, D.C. The Meteorology Section will hold a session on "Weather Dependence of Energy Demands and Energy Consumption." *Write:* Meetings, American Geophysical Union, 1909 K St., N.W., Washington, D.C. 20006

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