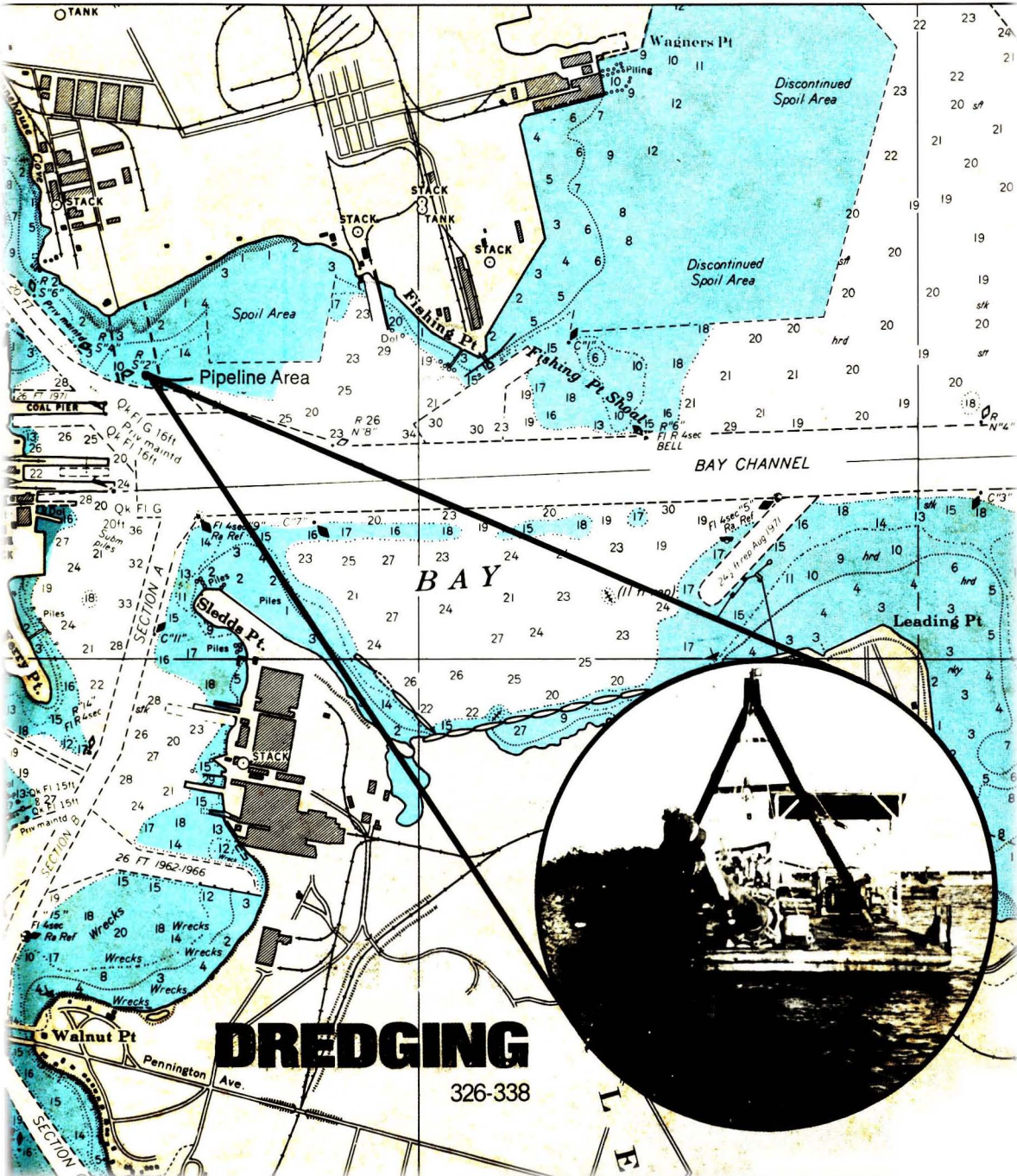


Environmental

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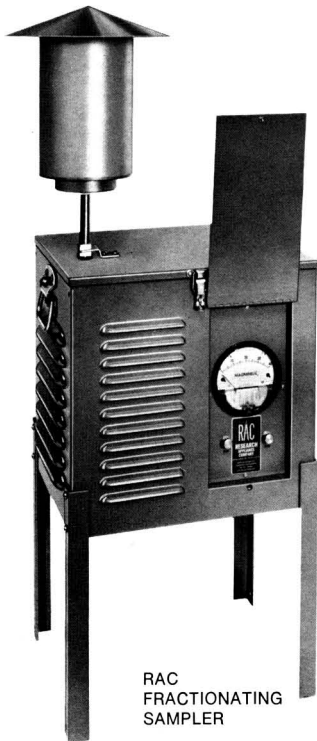
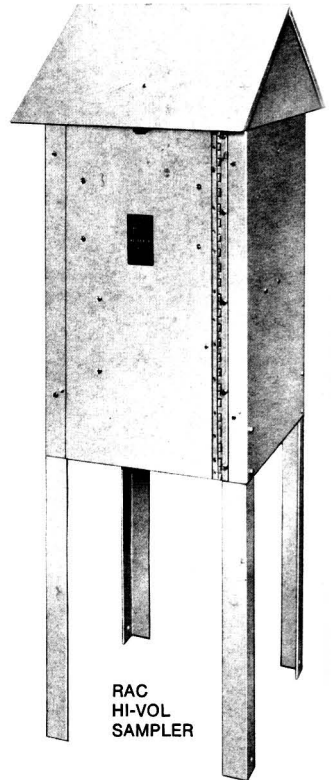
RAC offers a variety of precision instruments designed to collect samples of particulate matter suspended in ambient air. These instruments meet performance parameters established by the American Society for Testing and Materials (ASTM), Environmental Protection Agency (EPA), and National Air Sampling Network (NASN).

RAC hi-volume air samplers

This design meets ASTM 2009 specs—and exceeds EPA requirements—for accurate collection of suspended particulates in outdoor/indoor environments. Operating for 24-hr cycles (or longer), with constant flow rates ranging from 30 to 50 scfm, RAC Hi-Vols collect particles down to 0.03 microns dia on filter media with a 7 x 9" effective area. When equipped with optional accessories, these high-capacity units can operate as fully-automatic electronically-controlled systems that require only periodic filter replacement for continuous air sampling.

For details, write for BULLETIN 2338-B.

CIRCLE 16 ON READER SERVICE CARD



RAC total particulate membrane sampler

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

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

For details, write for BULLETIN 2349.

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RAC fractionating sampler

Designed to NASN requirements for more accurate determinations of suspended particle size distribution, this instrument uses a 5-stage cascade impactor to automatically segregate particulates and chemical components in ambient air. Particles ranging from 3.0 to 0.5 microns dia are separated and collected in the impactor. Smaller particles are collected in a 4" (100mm) dia inline, membrane-type backup filter.

Unit operates continuously at 4–5 cfm flow rates for a 24-hr cycle. Samples obtained with this instrument can be precisely evaluated by gravimetric or chemical analyses.

For details, write for BULLETIN 2354.

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STACK SAMPLING SEMINARS

RAC sponsors a series of 2-day technical how-to seminars on stack sampling parameters and procedures (EPA method). Write for descriptive folder. CIRCLE 19 ON READER SERVICE CARD

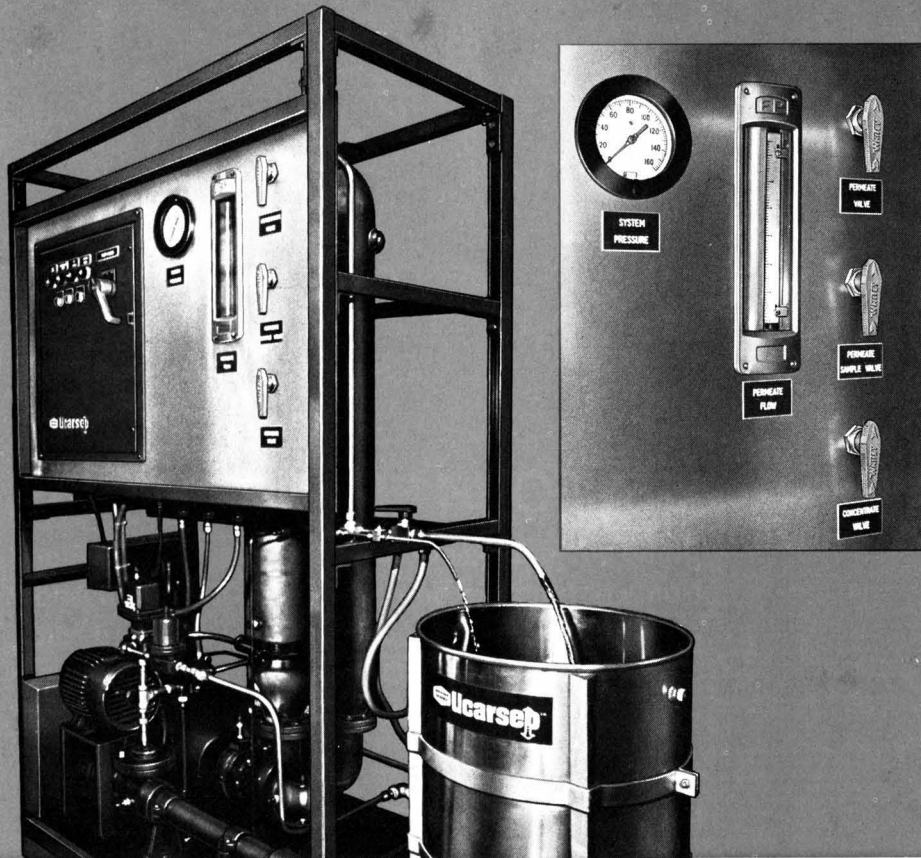


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But somehow the word "equivalent" makes us a bit uneasy. It sounds too much like "equal." And to the leader in the air analyzer industry that's not nearly enough. We're a lot more comfortable with "best." And "first." And "state-of-the-art."

So thanks, EPA, for certifying that the Thermo Electron Model 43 meets all Federal performance parameters. But we hope our customers remember that "equivalent" sometimes means a whole lot more.



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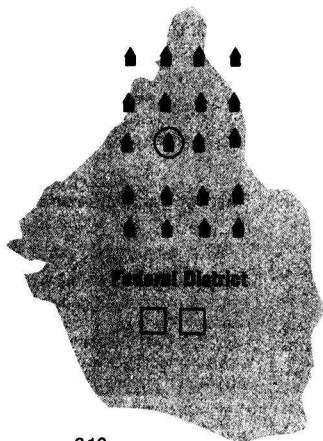
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Environmental Science & Technology

Volume 10, Number 4, April 1976

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CURRENT RESEARCH

Efficiency of membrane and Nuclepore filters for submicrometer aerosols 345

B. Y. H. Liu* and K. W. Lee

Efficiency of commonly used filters was measured using monodisperse aerosols and a new electrical aerosol detector. Particles of 0.03–1 μm were used with a pressure drop ranging 1–30 cm Hg. Efficiency ranged from 62–99.99% for Teflon filters and 0–80% for Nuclepore filters.

Organic photochemistry. Simulated atmospheric photodecomposition rates of methylene chloride, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and other compounds ■ 351

W. L. Dilling*, C. J. Bredeveg, and N. B. Tefertiller

Photolysis of 33 organic compounds was studied under simulated atmospheric conditions. Photodecomposition rates of several chloro compounds were determined in mixtures of other organics and gases. The presence of hydrocarbons reduced the decomposition rate for some chloroethylenes.

Toxicity of organic and inorganic arsenicals to an insect herbivore 356

A. P. Watson*, R. I. Van Hook, and D. E. Reichle

Four arsenicals were tested for effects on nontarget animal species. Resulting tissue concentrations of elemental As were higher for organic forms than for inorganic. Life expectancies were reduced to <10% that of unexposed populations by levels above 5 μg As/g.

Analysis of carbonaceous materials in southern California atmospheric aerosols 359

B. R. Appel*, Paul Colodny, and J. J. Wesolowski

A method for estimating elemental carbon and primary and secondary organic materials in particulates is described. It employs a combination of solvent extractions and carbon determinations. Data supporting the method are presented from four sampling sites.

Reverse osmosis separation of polar organic compounds in aqueous solution 364

H. H. P. Fang and E. S. K. Chian*

Twelve different reverse osmosis membranes were tested with 13 polar organic compounds. They were not separated as effectively as inorganic salts for all membranes tested. Separation of organic compounds with the same functional group increased with size and branching of the molecule.

Distribution of airborne polycyclic aromatic hydrocarbons throughout Los Angeles 370

R. J. Gordon

Samples of particulate matter were collected for a full year at 39 sites, and analyzed for 14 polycyclic aromatic hydrocarbons. Comparison of PAH patterns for different areas suggest that PAH in coastal areas are primarily from automobiles, but additional amounts inland apparently arise from nonautomotive sources.

PAN and oxidant measurement in ambient atmospheres 374

W. A. Lonneman*, J. J. Bufalini, and R. L. Seila

PAN and ozone levels were determined at four sites. High O_3 concentrations were generally observed when high PAN concentrations were measured, but O_3 /PAN ratios varied at all sites, and PAN concentrations could not be predicted based on O_3 levels alone. Observations concurred with simulated chamber studies and models.

Adsorption of polychlorinated biphenyls from aqueous solutions and sewage 381

John Lawrence* and H. M. Tosine

Adsorption of PCBs from aqueous solutions and raw sewage was studied with a variety of adsorbents. Activated carbons, XAD-2, and foams did well with aqueous solutions, but PVC was most efficient for sewage. A small-scale treatment unit was designed to demonstrate the method.

Apparent ionization constant of hypochlorous acid in seawater 384

Richard Sugam and G. R. Helz*

The ionization constant of hypochlorous acid in artificial seawater is determined by potentiometric titration. In typical estuaries, the nonprotonated form prevails. Equilibrium concentrations of HOCl are enhanced by low pH, low temperatures, and low salinity.

NOTES

Some relationships between exchangeable copper and lead and particulate matter in a sample of Hudson River water 386

E. J. Catanzaro

Concentrations of Cu and Pb from Hudson River water were determined by isotope dilution. More than 60% of Cu and Pb was associated with particles $>2\mu$ in size. Lead results were more variable than Cu, suggesting the presence of large Pb-rich particles, possibly from auto exhaust.

* To whom correspondence should be addressed.

■ This article contains supplementary material in microform. See ordering instructions at end of paper.

Credits: 314, Joe Kleim-Trenton; 321, Sam J. Irvin (Birmingham, Ala.); 326, 332, 338, ES&T's Julian Josephson

Cover: Linda McKnight

The Calgon® Adsorption Report

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

Industrial wastewater survey shows adsorption effectiveness.

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

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

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

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

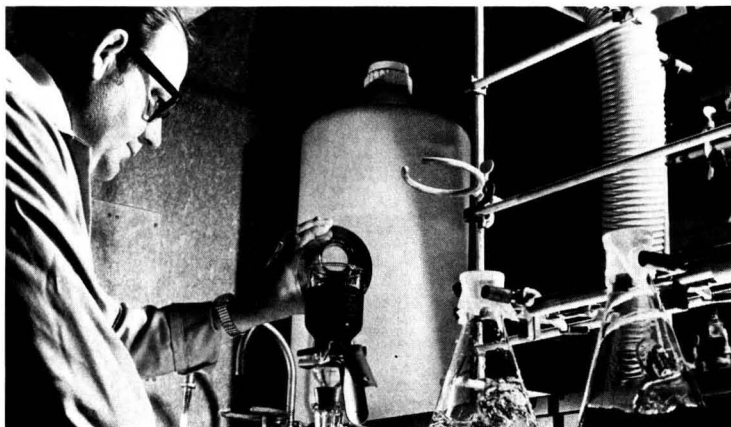
Fish toxicity tests compare raw and treated wastewater.

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

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

EFFECT OF CARBON TREATMENT ON TOXICITY OF BLUEGILL SUNFISH

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



Carbon isotherm tests at Calgon Water Laboratory

Toxic organics study shows carbon to be 98% effective.

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

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

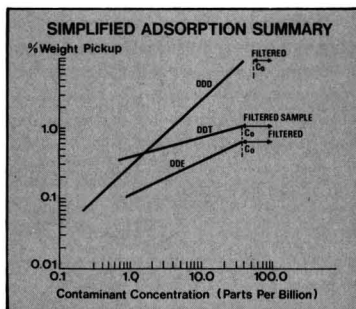
Report on studies.

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

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

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

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



Papers available.

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

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



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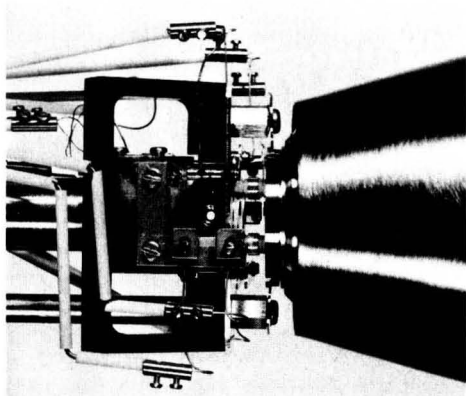
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Variable conductance enables you to get maximum and constant sensitivity in either mode under broadly varying flow conditions. Digital feedback temperature control maintains the source at precisely set temperatures for best spectrum reproducibility. A unique heat exchanger allows you to lower the source temperature as low as 50°C, to give you simpler cracking patterns and maximum molecular ion intensity.

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The RF voltage applied to the quadrupole rods has been increased to 6 kV peak to peak at over 2 MHz. As expected from the theoretical considerations, this achieves substantially greater high mass sensitivity and improved mass peak shapes, which contribute to the precision of the quantitative results.

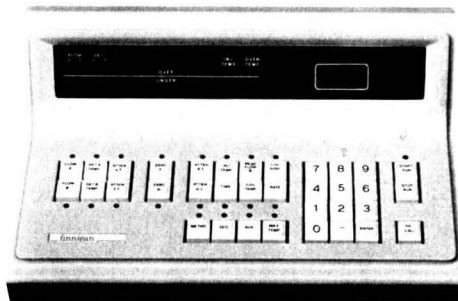
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Dregs on dredging

Public Law 92-500 specifically exempts the discharge of dredge or fill material from the EPA-administered NPDES Permit System and instead authorizes the Army Corps of Engineers to issue permits for the discharge of dredge material at specified disposal sites where navigable waters are involved.

Recently, the U.S. District Court for the District of Columbia ruled that the responsibility of the Army Corps of Engineers in this matter extends to all waters of the U.S., and ordered the Corps and EPA to work together in establishing appropriate regulatory procedures and discharge guidelines.

In this issue David Smith reviews the development process that has transpired since the Court ruling and offers *ES&T* readers an early glimpse of the regulations and guidelines that may formally be issued late this spring. In addition Professor G. Fred Lee offers an analysis of the directions in which greatly expanded research emphasis would be helpful to meet legal requirements.

Here again our legal mandates have outreached our ability to deliver. Difficulties in interpreting the phrase "navigable waters" will seem insignificant compared to defining the limits of "all waters of the U.S." Even without this expanded interpretation the environmental impact of dredging has been difficult to assess, and concern over chemical contaminants in dredge materials has added to the costs of some projects and delayed others. Our knowledge of the chemical and physical impacts of dredge material on water columns is inadequate and our ability to weigh social benefits and costs attendant with unnatural uses of coastal wetlands is primitive. We do not have an adequate technical basis for making the decisions now required by law.

The issue here, as in other aspects of P.L. 92-500, is the demand for more research, information and understanding as prerequisites for intelligent regulatory decisions.



LETTERS

Photochemical smog

Dear Sir: I wish to call attention to a potential hazard in controlling photochemical smog by reducing hydrocarbon (HC) emissions without a corresponding reduction in the emissions of the oxides of nitrogen (NO_x). If HC concentrations are reduced to keep hourly oxidant levels below the EPA ambient air quality standard of 80 ppb, and if NO_x concentrations are not correspondingly reduced, then on many days all the NO will not be oxidized. In the presence of NO, ozone levels are always considerably below the normal background level of 25 ppb, because of the rapid reaction between NO and O_3 . Thus on the days that NO is not completely oxidized, ozone levels will be considerably below background levels. If many such days should occur in succession, the bacteria count might increase, and this might enhance the incidence of disease (e.g., *streptococcus*

salivarius shows 90% mortality when exposed to 25 ppb O_3 at 60–80% relative humidity for 30 minutes).

Automobiles account for a greater percentage of the photochemically active HC than of the NO_x . (In Los Angeles it is about 90% for photochemically active HC vs. 70% for NO_x). However, the control devices presently being installed on cars are designed to control 80% of the HC and 40% of the NO_x . As a result the percentage reduction in photochemically active HC should be about 2–3 times as great as the percentage reduction in NO_x . This may not be a policy of wisdom.

Julian Hecklen, Professor of Chemistry
The Pennsylvania State University
University Park, Pa. 16802

Remote sensing

Dear Sir: Since the August 1975 issue of *ES&T* contained two lengthy articles (pp 714–725) on remote sens-

ing and its growing application to environmental monitoring and assessment it seems appropriate to bring the services of the EROS Data Center to the attention of your readers.

The EROS program was established by the Department of the Interior in 1966 as a departmental effort. The U.S. Geological Survey manages this program. Initial funding for the EROS Data Center occurred in 1971 and Data Center personnel moved into the permanent facility in January 1974.

The Center's primary responsibilities are to archive, reproduce, and distribute copies of remotely sensed photographic imagery and electronic data of the Earth's resources, and to provide a variety of professional services to further the understanding and use of the data.

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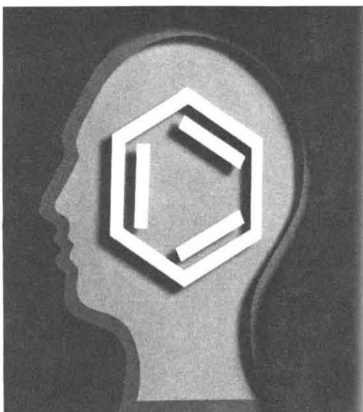
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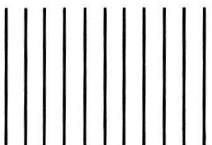
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assistance facility to provide domestic and international training, day-to-day technical assistance, cooperative demonstration projects, and digital analysis and processing capability.

Recent developments affecting the scope of activity of the EROS Data Center include the successful launch of LANDSAT-2 on January 22, 1975. LANDSAT-2 joins LANDSAT-1, which has exceeded its expected life by nearly two years and is still sending back quality data. The interest in the use of these data is reflected by increased demand by the domestic and the international community. From 10-15% of the orders received at the Data Center are from non-U.S. customers.

The EROS Data Center's Applications Assistance Branch has been expanded during the past year. The professional staff on this Branch includes applications scientists in mineral resources, land use and mapping, forest and rangeland management, and agriculture and soils inventory. The training and assistance functions are carried out by these professionals in the Applications Assistance Branch. Sixteen formal training courses are planned for this year, two of these to be interdisciplinary courses for foreign scientists.

Among the numerous cooperative demonstration projects currently underway are flood and floodplain analysis, South Dakota land use planning, Pacific Northwest land use analysis, forest defoliation mapping, and evaluation of the environmental impact of coal strip mining and strip mine reclamation.

The diversity of these programs and projects indicates that the users of the data produced are involved in varied disciplines. The largest segments of serious users of the data are private industry and government.

Requests for imagery (LANDSAT, SKYLAB, NASA aircraft, and USGS aircraft) should be directed to the User Services Section. Details regarding remote sensing applications and training courses can be obtained from the Applications Assistance Branch. Mail requests should be addressed to: EROS Data Center, Sioux Falls, SD 57198. Telephone inquiries should be made to (605) 594-6511.

Allen H. Watkins
EROS Data Center
Sioux Falls, SD 57198

It's your health

Dear Sir: Your editorial (*ES&T*, December 1975, p 1101) states without attribution: "Automotive air pollution kills 4000 Americans each year. Sulfur emissions from coal-powered plants will, if unchecked, kill 25 000 people in the next five years." I believe your readers should be told that these two sentences were lifted from a political speech by Representative Morris K. Udall (November 5, 1975), and that you and the American Chemical Society are in no way endorsing them. Unless such a specific disclaimer is published promptly, there is considerable risk that these sentences will become accepted as fact, and publication in this journal cited as "proof".

Perhaps a word as to the origin of these statements would be in order. The automotive number is misquoted from Volume 1 of the National Academy of Sciences report, "Air Quality and Automobile Emission Control" (September 1974, pp 11-12). An accurate, undistorted, and attributed paraphrasing of the sense of this report would be "A National Academy of Sciences study suggested that if air pollution is responsible for as much as 1% of urban mortality, this would represent 15 000 deaths annually, of which between 150 and 4000 *might perhaps* be due to automotive emissions." Whether even this very different statement than what was published could itself be *proven* by objective data is yet another matter.

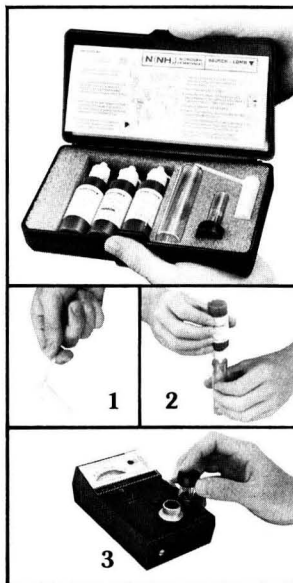
The coal-fired power plant assertion is misquoted from a speech by John R. Quarles (December 2, 1974), in which he said, "Other studies *indicate* that sulfur emissions, largely from coal-fired power plants, are *likely* to kill *as many* as 25 000 people between now and 1980" (emphasis added by me). Whether the studies mentioned by Mr. Quarles are themselves based on sound and interlocking clinical, epidemiological, and laboratory animal data, or whether they only represent first attempts to formulate a quasi-quantitative judgment in this uncertain and controversial area in the absence of such data, is also an open question—which is perhaps too important to be left to the experts in these fields.

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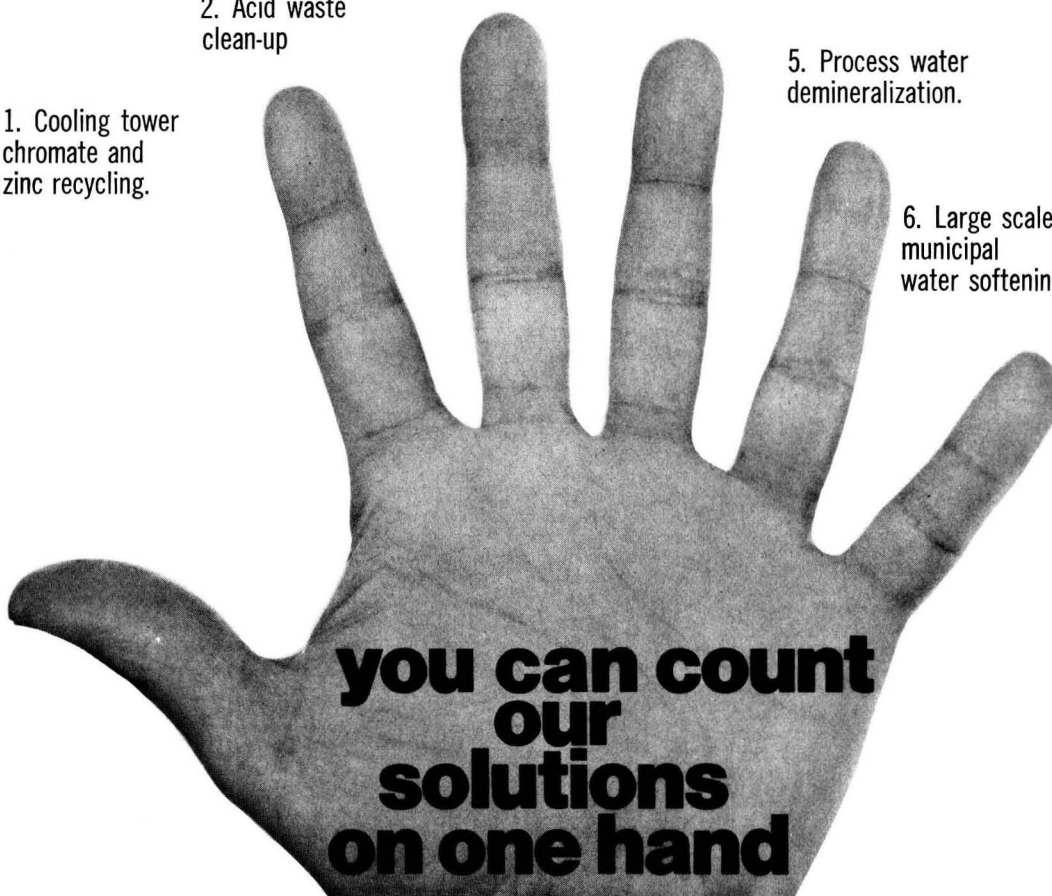
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CURRENTS

INTERNATIONAL

The European Community will spend about \$18 million on environmental R&D studies through 1980 to support efforts in member countries' national laboratories. The environmental studies are designed to collect data that will serve as a base for the eventual coordination and consolidation of environmental legislation throughout the Community. Four general study areas will be pursued. One will delineate the quantitative relationships between pollutants, including noise and waste heat, and their effects on man and his environment. A second concerns pollution control and prevention strategies; a third establishes an environmental chemicals data and information network; and a fourth will elucidate the function and structure of ecosystems.

WASHINGTON

The National Commission on Water Quality's final report has been transmitted to Congress. Ending a \$17 million, 3-yr study of the economic, environmental and social impacts of P.L. 92-500, the recommendations included maintenance of the July 1, 1977 date for compliance with uniform treatment requirements by industry and municipalities, but with flexibility to grant extensions on an individual basis. The 1983 interim water quality goal should be retained, but the 1983 requirements for application of uniform technologies should be postponed 5-10 yr. The 1983 goal should be met by applying the 1977 requirements to all dischargers. Effluent limitations for the elimination of discharge of toxic pollutants should be enforced immediately.

The Council on Environmental Quality's Sixth Annual Report has been published. New to the report are subsections called "Issues To Watch For." The report discussed the chemical basis of cancer, and emphasized cancer's prevention by stressing the need to devise tests to evaluate the risks. Among the highlights cited were the Supreme Court's decision that responsibility for attainment of ambient air standards rests with the states; the obligation of

about \$6.6 billion for municipal wastewater treatment facilities in fiscal 1975; an increase in ocean dumping by 20% in 1974; and a decrease in volunteer recycling centers for 1974. Included for the first time was a discussion of the environmental impacts of emerging energy technologies.

EPA's proposed budget for fiscal 1977 totals \$718 million, a decrease of \$53 million from the current operating budget (fiscal 1976). The greatest increase in fiscal 1977 is \$10.6 million for the water supply program to assist states in assuming enforcement responsibility for potable water supplies and underground injection control programs. The new budget shows no new funding authorization for municipal wastewater treatment facility grants; Section 208 planning grants are funded at \$15 million, down \$23 million from the fiscal 1976 level. Funding for several other programs was also reduced: pesticide programs by \$5.3 million; R&D programs by \$7 million; energy R&D programs by \$3 million; and radiation research programs by \$800 000.

The environment share in the total Federal R&D funding in 1976 is 4.6%, up from a 2.1% share in 1969 according to a National Science Foundation study. The environment function has shown an average annual growth rate of 17% over the term 1969-76. Of the \$985.2 million obligated for environmental R&D

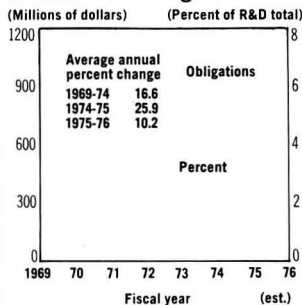
programs in 1976, 37.0% is allocated to health-related studies. Key components of these health studies are ERDA's biomedical and environmental research program (15.5%) and EPA's pollution effects research (5.3%). Thirty-three percent of the total obligations for the environment function in 1976 is allocated to pollution control and environmental protection; the key components here are EPA's energy-related environmental control programs, and water and air quality control.

The first insecticide made from a naturally occurring virus was registered by the EPA. The insecticide is effective against the cotton bollworm and tobacco budworm. Tests have shown the virus product to pose a minimal hazard to insecticide applicators and no adverse effects on beneficial birds, insects, or other wildlife. The insecticide is sold under the trade name Elcar by Sandoz, Inc. (Homestead, Fla.). In another pesticide matter, Russell E. Train, EPA administrator, will cancel the registrations of all mercury-containing pesticides used as bactericides or fungicides in paints and coatings, but will allow the continued use of mercurial pesticides as fungicides in the treatment of fabrics intended for continuous outdoor use, and for the control of Dutch elm disease.

STATES

Ohio is the only state that has not adopted air pollution regulations as mandated by the Clean Air Act of 1970. Under contention are SO₂ regulations, particularly in the industrialized cities of the upper Ohio Valley. The Ohio Environmental Agency's (OEA) proposed plans to control SO₂ were successfully opposed by eight electric utility companies. The U.S. EPA, superseding a state agency for the first time, began preparing regulations and an enforcement plan. These regulations are expected to be published this spring. The utilities claim that EPA's SO₂ data are incomplete and overestimate SO₂ concentrations in parts of the state. OEA agrees that SO₂ levels meet federal standards in all but nine counties; EPA may modify its proposed rules in light of data provided by the utilities.

Environment federal R&D obligations



New Jersey has expanded its water monitoring program in order to assess progress in cleaning up the state's surface waters. Under a joint federal/state effort, 200 water sampling stations throughout the state will be established. Water quality data began flowing into the Dept. of Environmental Protection's (DEP) Division of Water Resources last month from 100 stations now on-line and being monitored by the USGS. Once a month, state and USGS



N.J. deputy commissioner Ricci

personnel check sites and take water samples that are sent to state and USGS laboratories for analysis. Data collected from this monitoring network will be incorporated into a storage and retrieval system. Rocco Ricci, DEP's deputy commissioner, pointed out that the collected data consider major population centers, spreading industrial and commercial development, and human needs.

San Diego County, Calif., is the leader in gasoline vapor recovery programs, according to the U.S. EPA. The county regulations stipulate that at least 90% of the escaping vapors must be collected; the rules cover the storage and transfer of gasoline beginning at the bulk terminal and ending at the vehicle fuel tank. Vapors must be passed through vacuum-type disposal devices for collection into recovery units. Violators are subject to \$500 fines or six months in jail for each day a violation occurs.

The Northeastern Illinois Planning Commission (NIPC) has appointed a "208 Project" advisory body whose purpose is to advise NIPC on planning and evaluating alternative solutions to water-quality problems. The 28-member group will also help the NIPC select a final plan for the region as called for by Section 208 of P.L. 92-500. The planning program affects Cook, DuPage, Kane, Lake, McHenry, and Will Counties. Members of the advisory group were chosen from state and federal agencies, professional and trade associations and from major local environmental groups. The NIPC is forming other advisory committees whose members will be culled from public officials and the citizenry; some committees will be selected to focus on problems in major waterways.

California's movement to halt the spread of nuclear power received a significant boost recently. Three middle-level managing engineers, G. C. Minor, R. B. Hubbard and D. G. Bridenbaugh, from General Electric's nuclear reactor division quit their jobs to work for the coalition of California organizations that successfully put Proposition 15 on the ballot in the June primary; this initiative proposal could lead to the discontinuance of nuclear reactor operations in the state. E. A. Myers, Jr., vice-president, Southern California Edison Co., claimed that adoption of Proposition 15 would cost electric customers an average of \$225/household, severely restrict energy alternatives in the state and increase reliance on imported energy sources.

Maine's Solid Waste Management Regulations recently went into effect but for economic and/or technical reasons, few towns were expected to meet the new standards. Each town, therefore, will be allowed to submit an implementation schedule that will include compliance deadlines that it can meet. These schedules must be submitted to the Dept. of Environmental Protection by May 1 or it will be assumed that the town's waste disposal facility can comply with the new standards. To comply with South Dakota's solid waste regulations, all county and municipal waste systems must submit implementation plans to the Dept. of Environmental Protection by July 1, 1976. Implementation of the plans will occur on July 1, 1977.

AWARD

Thurston Larson of the Illinois State Water Survey (Urbana) has won the \$3000 Award for Pollution Control of the American Chemical Society (ACS) for 1976. Larson is assistant chief of the Survey, and is being recognized for



Larson wins pollution control award

his outstanding contributions to pollution control in the U.S., especially in the area of water quality and treatment. Also professor of sanitary engineering at the University of Illinois-Urbana, Larson has been very active with ACS, and headed what is now the Division of Environmental Chemistry in

1956. He led the ACS task force which prepared the report, "Cleaning Our Environment: The Chemical Basis For Action."

MONITORING

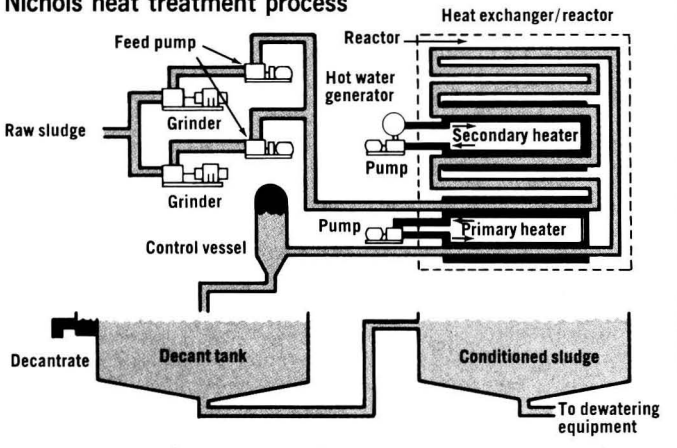
Measuring the amount of a given pollutant of a specific location, such as in a smokestack plume, is possible with an infrared laser. The wavelength of this laser will cause a molecule, such as NO, NO₂, SO₂, ozone, or CO₂, to fluoresce, according to the Pasadena (Calif.) office of NASA, patentee of the system. The system's two half cells are filled with pure nitrogen or helium and a measured amount of the pollutant to be determined. The laser is aimed at the plume, and the half cell containing the pollutant will absorb any fluoresced radiation from the plume. The difference in radiation intensities leaving the two half cell equals the intensity of the pollutant's fluorescence signal. That signal, in turn, is proportional to the pollutant concentration in the plume.

TECHNOLOGY

Methanol can be easily converted to a 75-80% yield of 90-100 research octane gasoline in one step, according to S. Meisel and his colleagues at Mobil Oil Corp. The trick is a single pass of methanol through a "molecularly engineered" zeolite catalyst whose cavities and channels are sufficiently constrained to provide 99+% conversion of methanol to a uniquely narrow range of hydrocarbons, none of which are larger than those in "gas". The methanol from which the "gas" can be made could be derived from coal, and the cost to produce "gas" from methanol by the Mobil process is estimated at 5¢/gal. The total cost for the "gas" would be double that of conventionally distilled "gas", but costs would rapidly decrease as coal-to-methanol processes improve, according to the Mobil scientists.

How can high-sulfur coal be made environmentally acceptable? One way is by powdering the coal and reacting it with hydrogen gas under pressure, and at 1000 °F. Coal is then partially converted to heavy oil and gaseous products. Remaining coal is treated at high temperature with oxygen and steam; this step provides hydrogen needed for the conversion process. This process was described by Richard Hutchinson, of the U.S. Army's Picatinny Arsenal (Dover, N.J.), who will assist ERDA in designing a coal conversion plant. A result of Hutchinson's work is a contract with Coalcon Corp. (New York, N.Y.) to build and operate a 2500 tpd demonstration plant to convert high-sulfur coal to clean fuels.

Nichols heat treatment process



A water desalination plant is worth its salt when it can treat about 150 000 gpd of city water. This is the case at Adelaide, Australia, where such a plant uses the Sirotherm process, developed by the Commonwealth Scientific and Industrial Research Organization (CSIRO), whose basis is resins regenerable by a simple hot-water wash. The plant, installed by ICI Australia Ltd., gets away from long and costly acid and alkali resin regeneration treatments. The process, according to CSIRO and ICI, is strongly competitive with reverse osmosis, electro dialysis, and other ion exchange techniques for desalination of water up to 3000 ppm salt, because of low energy needs and chemical usage, and simplicity. It could be very adaptable to purifying boiler make-up water, the process' developers believe.

A process to condition sewage sludge for effective dewatering with no chemicals is now being marketed in the U.S. and Canada by Nichols Engineering & Research Corp. The process uses a patented reactor design that obviates any possibility of sludge short-circuiting during the conditioning process. Also employed is a sludge-water-sludge heat transfer system aimed at eliminating plugging, as well as an indirect secondary heating system for thermal efficiency. Process heat is normally provided by recovery of waste heat in a Nichols-Herreshoff multiple hearth furnace. The system is based on experience gained in use of the heat treatment process in 40 plants operating throughout the world, according to Nichols.

A way of dewatering solids obtained in a gas-cleaning process is in use on two new Q-BOP steelmaking furnaces with which U.S. Steel replaced open-hearth furnaces at Fairfield, Ala. Each

furnace, capacity 200 tons/heat, is equipped with dual-stage wet scrubbers that remove 99+ % of particulate matter. The treatment technology to remove solids and return water to the scrubbers was supplied by Dorr-Oliver Inc. This technology involves primary degritting, sedimentation, and vacuum filtration. U.S. Steel plans to bring a third Q-BOP furnace on stream next year, and it, too, will be equipped with scrubbers employing Dorr-Oliver's solids removal technology.

INDUSTRY

Victor Wagner, president of the Water Pollution Control Federation (WPCF, Washington, D.C.), told the National Commission on Water Quality (NCWQ) that "a long-term federal funding commitment which maintains and bolsters the construction grant rate EPA has recently achieved" is essential. He also urged the NCWQ to "recommend funding all currently eligible projects at a rate of not to exceed 75%," on a case-by-case, cost-effective basis. Wagner warned that the industrial cost recovery provision of P.L. 92-500 "threatens to wreak havoc on the construction grants program," and called for its deletion. Also, in his testimony, he recommended mid-course corrections for 1983, and urged the elimination of national pretreatment requirements for industries discharging to municipal systems as "unrealistic and wasteful."

Richard Balzhiser of the Electric Power Research Institute (EPRI, Palo Alto, Calif.) called for identification of "the real threats to public health and the environment before mandating costly emission control systems for fossil-fuel fired electric power plants." He said that "tall stacks with supplemental controls are by far the

most cost-effective air pollution control technology available today," in response to the need for a balanced approach to air quality management. Balzhiser noted that a clear concept of what is to be controlled, and why, is vital, and pointed out that there is no definitive understanding of what stack emissions components constitute hazards. This understanding is needed before optimal control technology can be devised and perfected, he explained.

Union Carbide Corp. (UCC) has acquired the ultrafiltration and reverse osmosis (RO) technology of the Westinghouse Electric Corp. This technology covers products that use synthetic membranes to separate a wide variety of dissolved or suspended materials from liquids on the basis of molecular or particle size and shape. The Westinghouse technology complements UCC's own "Ucarsep" ultrafiltration systems. According to UCC, the Westinghouse product line can do many things "Ucarsep" systems cannot do, and UCC now has a complete line of systems. At present, membrane processes are a \$15 million industry, but UCC foresees total sales of \$200 million by 1986 in the U.S., because of material recovery, energy saving, and pollution control needs.

"Solar heating is now a commercial reality." George Lof, director of the Solar Energy Applications Laboratory, Colorado State University (Fort Collins, Colo.) made this statement at New York City when he received the Lyndon Baines Johnson Foundation Award on February 11. Over the short term, Lof expects that solar energy would be used mainly for heating, and that it is fast becoming competitive with oil (not gas) heating, and especially with electric heating where electricity has become costly. However, solar electricity will play no major role this century, according to Lof who noted that three times as much money is spent on solar electricity as on heating and cooling—"the proportion should be reversed," he said. He foresees the solar heating and cooling industry as a \$1 billion industry "in a few [10-15] years, with or without government help."

Lof on solar energy



INTERNATIONAL

Environmental improvement in Mexico

Pollution abatement makes severe demands on human and material resources, necessitating a more difficult allocation of such resources in this developing nation

Areas of environmental concern—air, water, solid waste, health, education and training—are at different stages of development in Mexico. In general, the water activity is the oldest, biggest, and most successful; air is the next in size but younger and with growing problems; solid waste is rather small yet making recognizable progress, as are health activity and education and training activity.

On Dec. 1, 1971, just one day before the first anniversary of the U.S. EPA, Mr. Luis Echeverría Alvarez became president of Mexico. Three months later saw the enactment of comprehensive legislation covering these environmental areas. By February 1972, approximately one year after the enactment of their federal environmental law, the Subsecretariat for Environmental Improvement became operational with the formation within it of a Technical Council, headed by Dr. Eduardo Echeverría Alvarez, brother to the president of Mexico.

By January 1974, a Program for Environmental Improvement (PEI) started under an agreement with the United Nations Development Program (UNDP). With \$2.8 million from the UNDP and \$4-5 million contributed from the Mexican government, the program is funded through 1977. Currently there are approximately 80 professionals involved in the PEI-UNDP project, and about 800 in the subsecretariat—80% at headquarters in Mexico City and the remainder throughout Mexico.

The Pan American Health Organization (PAHO) is the executing agency for the management of the program. Frank Butrico, chief of the PAHO Environmental Health Program at headquarters in Washington, D.C., explains that this agency provides technical support, including contracting for both short-term and long-term consultants and supplying equipment. Butrico explains that the program is structured so that there are national directors and international consultants in the different areas of envi-

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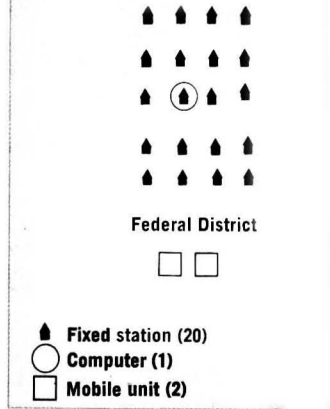
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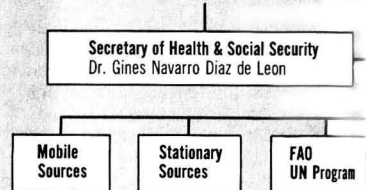
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Air monitoring network



Federal Government of Mexico



ronmental concern (see box); the international project manager is Edmundo Izurieta.

Overview

Dr. Enrique Sánchez Palomera, assistant director of the project and secretary general of the Technical Council of the National Secretariat of Health, summarized the overall activities in the PEI-UNDP program and of the subsecretariat. The latter includes the directorates for planning, investigation, control, operation, and coordination. At the technical council, integrated working groups of government, industry, and academic representatives provide advice on policy matters.

He says Mexico plans to establish primary waste treatment plants all over the country, but that it will be at least 10 years before this construction is completed. Some funding will be provided by taxing the polluters. Municipal funding will be provided for all communities through either national funding sources such as Nacional Financiera or through international lending agencies such as the World Bank.

Sánchez Palomera also noted that the major water activities are located in the Ministry of Hydraulic Resources (SHR, the Spanish acronym for Secretaría de Recursos Hidráulicos). The SHR concerns include expanded irrigation, complete inventory of water resources, and water supply and sewerage for all communities over 2500 population. (Another agency takes care of municipalities of less than 2500 people.)

He says that rules and standards for air emissions are limited currently to dust and smoke; however, a task group on stationary sources has been working on the SO₂ problem for about one year. He says that Mexico City has been compared in an air pollution sense with Denver, Colorado—both cities having air pollution at high elevations.

At the end of 1974, Mexico was chosen to participate in the UNEP GEMS program (*ES&T*, March 1975, p 230) for the monitoring of agricultural products that are exported to other countries including the U.S. This program of the United Nations Food and Agriculture Organization (FAO) picked 10 delegates from developed and underdeveloped countries as participants. Today, Mexico is working to maintain the required quality assurance of the analytical methods used for exported agricultural products. Engineer Delgado de Garay of the Mexican Department of Agriculture explains that sophisticated GC/MS instruments will be used to check pesticide levels on products exported to the U.S.

Dra. Lilia Albert, without question, is the best pesticide residue chemist in Mexico; she is located at the Polytechnic Institute of Mexico, CIEA-IPN (Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional). She told *ES&T* that U.S. methodology for pesticide monitoring was expensive and that she was examining less expensive Canadian protocols for such monitoring.

In the area of education and training,

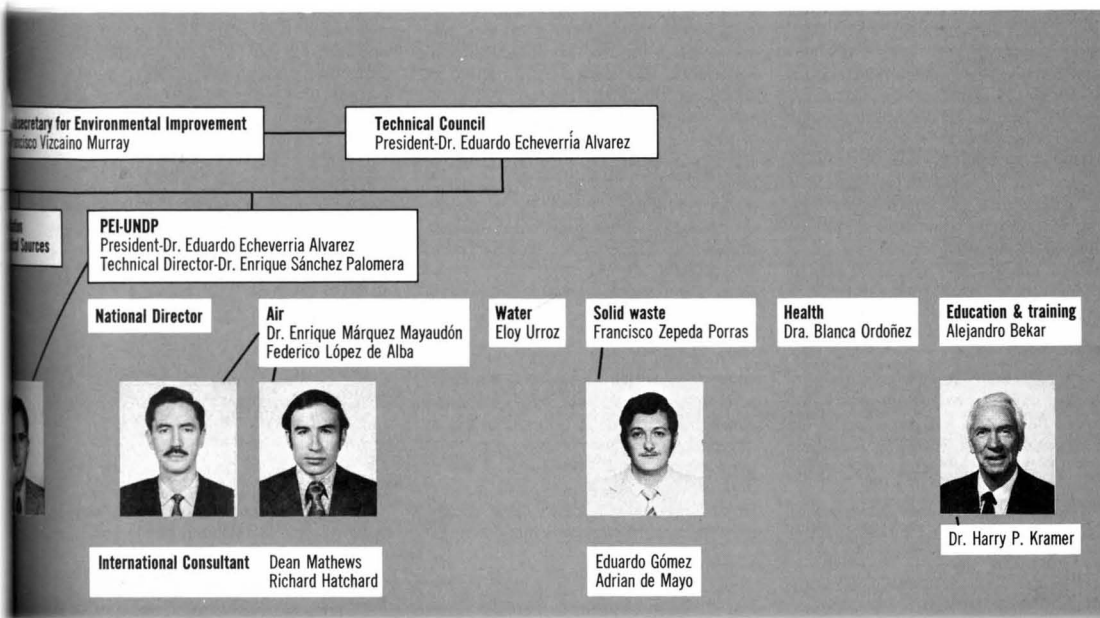
Dr. Harry Kramer, an international consultant to the PEI-UNDP program warned that assuring an adequate supply of trained, national personnel is one of the most difficult tasks that must be accomplished. As in other developing nations there is a shortage of trained manpower in Mexico, and the government is trying to establish a solid base for the development of the required professional and technical personnel.

In the two areas—solid waste and health—Dr. Sánchez Palomera said that the city of Morelia has a pilot solid waste landfill operation. Rules, regulations, and advisory information on solid waste may be forthcoming before the end of this year. In the area of health, both air and water effects programs are underway, but the big concern to date is the bacteriological contamination of water.

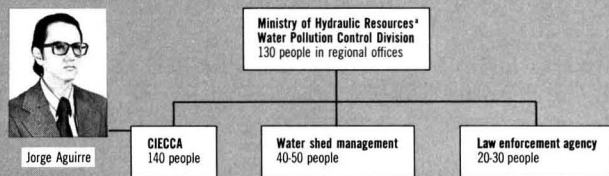
Water monitoring

Of the environmental disciplines, water has the most extensive monitoring program. There are 188 sampling stations located within 12 regional areas throughout the country. Each area has its own regional laboratory plus the support of some mobile units.

In his presentation at the Mexico City meeting of the First Chemical Congress of the North American Continent, Dr. Jorge Aguirre, who received his Ph.D. from the University of Texas at Austin, said that in Mexico they are interested in the effect of pesticides on the water resources. There is a shortage of water in the country and they are seriously



350 professionals in water in Mexico



*SHR, Secretaría de Recursos Hidraulicos

looking at extensive water reuse practices. Although the present supply for Mexico City seems assured until 1985, it may be necessary in the future to import water and to transport it from as far away as 200 km and pump it almost from sea level to about 2400 m.

Dr. Aguirre is director of a new center for water research and training, (CIECCA, the Spanish acronym for Centro de Investigación y Entrenamiento para el Control de Calidad del Agua). The idea of CIECCA, analogous to the EPA Taft Center in Cincinnati, started in 1971 through the efforts of a young, dynamic Mexican engineer, Eloy Urroz, who heads the water pollution control division of the SRH. The center became operational in 1973 and was recently expanded so that today it includes about 80 people and an operating budget of about \$1 million.

CIECCA conducts training courses similar to those offered at the Taft center. Initially conducted by EPA personnel, the courses are now offered by earlier-trained native sons. Aguirre relates that there are three basic courses:

- sampling techniques and field analysis (a 3-day course)
- water and wastewater analyses, based on extracted summaries of Standard Methods (a 2-week course)
- operation of primary waste treatment plants (a 2-week course).

Aguirre says that the first course was offered in April 1973. By now, more than 1000 people have taken one or more courses, and a small percentage has taken as many as four or five. The CIECCA director gave a breakdown of the trainees: 30% of them come from private industry, 30% were SHR personnel, 20% other government agency personnel, 10% university personnel, and 10% private individual and foreign exchange students.

Aguirre says that the law requires the monitoring of five water parameters—pH, temperature, oil and greases, settleable solids, and floatable materials. Wastewater discharges that are not in compliance with the five basic parameters by August 1977 will be subject to fines ranging from \$40–40 000.

Pesticides

At the meeting, Aguirre told the conference that in Mexico about 19 000 tons of pesticides are produced in the country each year, 80% of which are used on pests that attack the cotton crop.

In Mexico City, the government, which has a program for dairy supply,

was interested in learning what the pesticide levels might be in milk and how they got there. Alfalfa is grown by using the Mexico City wastewaters in the Tula irrigation district. This district was selected as an area that had about a 70-yr experience in continuous irrigation with wastewaters. Alfalfa is grown primarily in Tula, north of the Valley of Mexico, and most of the industry is located in the northern part of Mexico City on the way to the irrigation district.

CIECCA compared the pesticide levels in alfalfa and milk from this area with that of an unpolluted test site near a volcano on the eastern side of the Valley of Mexico, where the water for irrigation is different and there is no appreciable industrial pollution. The study took place during December 1974 and April and July 1975. Analyses of the milk showed the presence of 24 different pesticides, which were found by means of chemical reaction methods and gas chromatography with electron capture, followed by confirmatory TLC (thin-layer chromatography) work.

In this program they sampled and monitored the water that the cattle were drinking to see if it was the source of the pesticide. Values from some chlorinated hydrocarbons in the milk were above certain U.S. tolerable limits. Hence the federal government is faced with the implementation of strict rules for the application of pesticides before a serious health hazard develops from the presence of these materials in milk.

A significant finding by Aguirre's group was that the pesticides did not come from the irrigation water used in the growing of the alfalfa, but rather from direct application of the pesticide on the alfalfa crop that the cattle were fed.

From this study of pesticides in the water-fodder-milk cycle, the Mexican scientists concluded that irrigation water does not have a great effect in the pollution of fodder and crops, and even less in milk. Possible sources of contamination were evaluated, among which only water appears as a secondary medium of transport of pesticides.

Plans to look for the presence of other commonly used pesticides in this irrigation district, such as organophosphates, inorganic pesticides, and carbamates are being undertaken.

The CIECCA director explains that the Center performs analyses on both wastewater and stream samples and receives from 5000–10 000 samples/year. Only a few samples receive less than 10 individual analyses while some are subject to as many as 18 individual analyses.

CIECCA has three regional research centers, 15 regional laboratories, and nine mobile labs. The research centers are located in Guadalupe for limnological studies, in Monterrey for water reuse studies, and in La Paz (B.C.) for coastal water studies. These centers are equipped with ample laboratory facilities as well as classroom and research areas. However, the regional labs are less sophisticated than CIECCA's new facility at San Jeronimo, just off the outer beltway in Mexico City.

Aguirre mentioned that CIECCA is in the throes of setting up a computerized storage and retrieval system to handle analytical data generated by the water quality network. Adrian de Mayo, a member of the UNDP team in Mexico, who set up NAQUADAT systems in Canada and Brazil, is installing a similar system in Mexico. The systems are comparable to the EPA STORET system (*ES&T*, February 1971, p 115).

Work load at the center can be split into three categories. About 20% of the work is requested by government officials; 40% is related to water quality studies undertaken by the Water Pollution Control Division of the SHR; and 40% is produced by the internal research activity of the center.

Investigations

The water research activities at CIECCA (in addition to the training) are many and diffuse. In descending order of priorities, they include studies for:

- water reuse with agriculture primarily in mind
- adaptation of low cost waste treatment systems to Mexican conditions

- limnological condition of Chapala Lake

- coastal lagoon investigations to determine the effect of pollution on fish and shellfish productivity in Mexico's estuarine waters

- the impact of toxic substances—such as pesticides and heavy metals—and detergents on aquatic environments
- stream water quality surveys
- aquatic weed control.

Air monitoring network

Three cities in Mexico—Mexico City with 12.5 million population and a land area of 40 × 25 km; and two other cities, Monterrey and Guadalajara, each with about $\frac{1}{10}$ the population or 1.25 million people—are being monitored for air quality. The land area of Monterrey is 15 × 10 km; Guadalajara has a radius of 8 km.

At present, air rules and regulations only apply to dust and smoke (their terminology). Whereas perhaps only as many as 30 plumes can be observed in Mexico City now, only a few years ago there were literally thousands of them. Of course, the rainy season helps remove pollutants; the season is usually from the end of June until the end of October. Also, the general observation is that the haze peaks before noon each day and clears in early afternoon, for example, by 2:00 p.m.

On an inventory basis, there are 28 cement plants in Mexico. In Mexico City there are two, but one is the largest in the country with production of 3000 tons/day. There are four power plants in Mexico City with an aggregate SO₂ emissions burden of 400 metric tons/day and CO emissions greater than 5000 metric tons/day.

In mid-December, Mexican officials talked with their counterparts in the U.S. EPA on the monitoring of trans-frontier pollutants. Three U.S. cities are tagged with three Mexican cities to report on the air quality across the border. The pairings are Juarez-El Paso, Tijuana-San Diego, and Mexicali-Calexico, Calif.

Both manual and computerized automatic networks are in operation in Mexico City. Manual facilities are now going into Monterrey and Guadalajara, with a view to initiating automatic operations at a later date.

Engineer Federico López de Alba in the Mexican air monitoring network said that Mexico's automatic network cost \$1.8 million. The instrument package alone totals 20 instruments for SO₂, 20 for CO, 2 for NO, 3 for NO₂, 5 for ozone, 5 for dust, and 5 meteorological

stations. With the exception of the particulate counters, all instruments are made by Philips, including a Philips P855 computer with 16K connected by means of a telephone line to the devices of the 20 monitoring stations (see map), including the weather stations. The particulate counters are provided by a French company, Saphymo (Paris). Also, the Philips NO_x instrument can be set to read either NO or NO₂, but not both at the same time.

López de Alba further explains that the budget for operating the network would involve 15 persons and an estimated operating expense of \$200 000/yr, which includes maintenance of instruments and spare parts, and supports laboratory expenses of \$100 000/yr.

By March 15, 1976, 15 stations for SO₂ and CO were fully operational. On the map these include all stations with the exception of the four corners and No. 1. López de Alba says that by the end of July, the complete network will be validated. He explains that air quality assurance testing is being conducted on a station-by-station basis today. Validation of the network is assisted by George B. Morgan of the EPA Environmental Monitoring Support Laboratory, Las Vegas, Nev. (*ES&T*, December 1975, p 1109) and De Wayne Ehman of the Texas Air Control Board.

As mentioned earlier, air monitoring has begun in Monterrey and Guadalajara by collecting 24-h, Hi-Vol suspended particulate matter samples. The city of Monterrey has industrial air pollution problems arising principally from steel, chemical, and power plants. By the end of this year López de Alba explains that continuous SO₂ monitoring will be installed by industry. As a start, industry in Monterrey will be purchasing about \$500 000 of equipment, he estimates. The continuous monitoring system will include measurements for suspended particulate matter, carbon monoxide, and sulfur dioxide. To ensure that pollution levels are kept under control, the government has provided a manual backup system involving 10 monitoring stations. Here the fixed cost for the equipment is \$60 000, according to López de Alba, but the cost of the systems for industry will be borne by the industries.

Guadalajara, the third Mexican city to be monitored, is less polluted than either of the other two. Guadalajara's air pollution burden comes largely from motor vehicles. Plans are underway for a continuous monitoring system for CO emissions that is scheduled to start in

June 1977. It will involve two stationary stations and 4–5 mobile vans. Each station and mobile van will cost \$35 000 each. The funding is a 50–50 split; 50% federal government and 50% state government. The overall cost for equipment in Guadalajara is estimated at about \$250 000.

On the manual backup, Dr. Enrique Márquez Mayaudón, an M.D., who received a M.P.H. in industrial hygiene and occupational health from the University of Pittsburgh, told *ES&T* that the buildup of air pollution in Mexico City was noted before 1950. By 1960, there were many complaints, the public believing that the sources of pollution came from the oil refineries, power plants, cement plants, and other industrial sources.

Dr. Márquez Mayaudón said that by 1966 air monitoring started on a regular basis with 14 stations in the Valley of Mexico, which includes Mexico City. By 1970, there were some 250 dustfall jars in use and plates for sulfates.

He explains that 20 Hi-Vol samplers and 12 bubblers are now being used to check particulate matter and gases. In addition, they have plans to increase the number of stations as well as the variety of pollutants to be monitored.

In April 1975, they started to collect filters from the Hi-Vol samplers, for selected metal analyses by atomic absorption. Recently, he started up 10 Hi-Vol stations in Guadalajara and 10 in Monterrey. There are also 5 bubblers in each of these locations where SO₂ levels are being determined by using the procedures and methods employed by the Texas Air Control Board. He explains that the samplers collect for 24 h and rest for 96 h. In this way, samples are provided every fifth day.

Solid waste

The director of this program, Francisco Zepeda Porras, explains that 13 cities are included in the solid waste survey. There are full studies for six cities—Acapulco, Cancun, Mexicali, Tijuana, Atlixco, and Morelia—and partial studies for another seven cities—Villahermosa, Nuevo Leon, Veracruz, Monterrey, Guadalajara, Toluca, and Saltillo.

In summary, Dr. Sánchez Palomera says that Mexico is behind the U.S. on environmental improvement but it is working diligently on its environment problems. As with other developing nations, there is no question that environmental protection is necessary but rather how fast can Mexico economically afford to proceed. SSM

Monitoring air quality at power plants

Alabama Power installed a computerized system that meets federal, state & local requirements to track the buildup of air pollutants in real-time

Alabama Power Company, one of the operating companies of the Southern Company System, reported electrical energy sales totaling 25 billion kWh during 1974.

Last month, Alabama Power Company started operations of its real-time environmental data acquisition system capable of monitoring air quality and meteorological parameters at five of its large, coal-burning steam power plants. This data acquisition system was installed to comply with rules and regulations of the Alabama Air Pollution Control Commission and the Mobile County Board of Health. The system is a Leeds & Northrup LN 5400 digital computer system with L&N "Conitel" remotes for transmitting readings from the remote monitoring stations; it performs the following functions:

- provides for alarm and monitoring of episode conditions
- transmits data on more than 100 variables including SO₂ levels, opacity of flue gas from stacks, and meteorological information
- develops magnetic tape archive reports, data logs on SO₂ and flue gas opacity, SAROAD formatted magnetic tapes and programmed color CRT (cathode ray tube) (video) displays as guides to operation and for surveillance by pollution control authorities.

Gerald Aultman, who supervises the Environmental Systems Group for the Alabama utility, says that in addition to monitoring air quality on a 24-h basis, the system generates alarms if certain preset conditions are exceeded, and keeps records of the data for Alabama Air Pollution Control Commission and the Mobile County Board of Health. Aultman says that they plan to extend the system to one additional plant by late 1977.

J. E. Hubbard of the Environmental and Technical Services Department, which is responsible for data processing, formatting and reporting requirements to the regulatory bodies, says the system is designed to meet the monitoring requirements of both state and local air pollution control authorities.

According to Hubbard, the real-time environmental data transmitted from each plant site include:

- SO₂ levels at carefully selected locations around each plant

- opacity of the flue gas from the stack of each generating unit

- meteorological data including wind direction, wind speed, and air temperature at several elevations at each plant site.

In explaining the value of the color CRT display, Hubbard noted that the CRT can display a schematic diagram showing real-time values of all the key environmental conditions at any one of the plant sites. For example, it can graphically display vectors for the wind speed as well as show the relative locations of the various monitoring stations. In this way, Alabama Power personnel and agency personnel can monitor an episode condition at any generating plant site from a central location.

Evolution of system

In early 1973, state and local air pollution control agencies advised Alabama Power Company that in order for the utility to show compliance with stack emissions limitations and ambient air standards an ambient air quality and stack emission monitoring system would be required for five of its electric generation stations. The regulatory agencies specified that the system would be real-time, with a centralized location where air pollution regulatory personnel could observe conditions continuously, should an episode condition occur at any of the plant sites.

What the data acquisition system does:

- satisfies state and local air pollution control agencies
- develops magnetic tape archive reports in a prescribed format
- prints out data logs of SO₂ concentrations and stack flue gas opacities in prescribed format
- sounds an alarm (in the central station room) when SO₂ or stack opacity readings exceed a specified limit
- calls up, on demand, from the station operator any one of a number of programmed color CRT displays as a guide to operation or for observation
- provides the power pool coordinator, via a data link with Southern Services power system control center, real-time data on meteorological conditions at the generating plants.

Also, in the agreement, the agencies requested magnetic tape records be made available in a prescribed format to go into their data bank. Data on such tapes were to have a high recovery rate. For example, if any 5-min readout of any hour was missed, then that hour's data would not be acceptable for the data bank.

The utility determined from subsequent system design studies that one integrated computer system with high reliability and a central location under unified management would save many manhours in a year by reducing on-site maintenance visits.

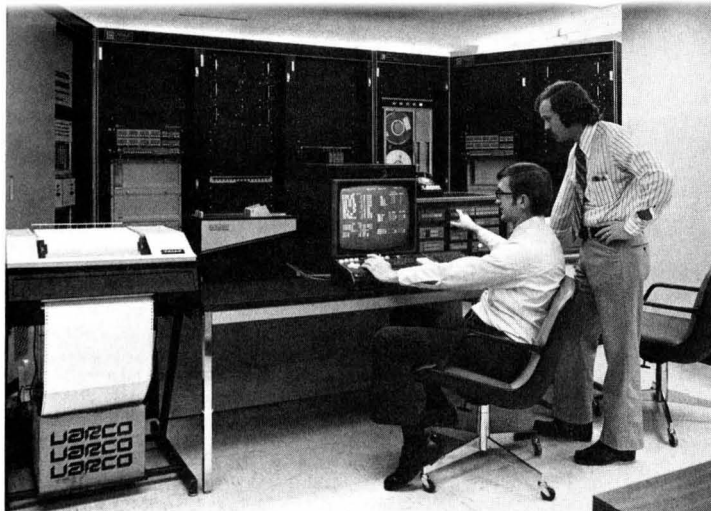
Aultman explains that an order for the LN 5400 system was placed in May 1974. The Environmental Systems Group was responsible for the installation of the system and is responsible for the equipment, sensors, and, in general, getting the data into the central station.

Typical operation

A typical plant site has three ambient air SO₂ monitors, a meteorological station, and flue gas opacity monitoring instrumentation. At each of the monitoring locations surrounding the five generating plants, an L&N "Conitel" remote is installed as a data concentrator for passage of the data back to the central station.

SO₂ concentrations in the vicinity of the plant area is the No. 1 concern. Placement of the SO₂ sensors at each plant were determined in close cooperation with the state and local agencies. This determination started with an Air Quality Display Model (AQDM), which calculated SO₂ concentration by using as variables plant stack height, emission rates, and Pasquill stability curves for wind. Results from the AQDM allowed isopleths for SO₂ to be plotted for each plant. These isopleths were used to pick the exact spots to place the monitoring stations. In fact, both first and second choice locations were picked considering likely areas of maximum SO₂ concentrations.

For actual measurement of SO₂ concentrations, Philips Model 9700 analyzers were chosen. These monitors are installed in portable weather-proof buildings made of reinforced fiberglass. Each building contains all the equipment required for the collection and transmission of SO₂ data, including radio equipment and the "Conitel" remote. These buildings can be moved to any monitoring location



Display. Aultman (l) & Hubbard communicate with all parts of system via CRT

that may be found or determined to be more desirable at any later date.

Temperature and barometric pressure measurements are made at the meteorological station. These data are transmitted along with the SO₂ measurements. Then at the central station the SO₂ values are corrected for standard temperature and pressure, 25 °C and 760 mm Hg.

Each day, the zero and span of the SO₂ instrument is checked by the system, which generates correction curves to be applied to the data until the next calibration occurs.

Opacity data

Opacity monitors are to be installed in the ductwork leading from each unit boiler to the stack. These monitors indicate the amount of particulate matter in stack emissions. Equivalent stack exit readings are possible by using a formula that compares the ratio of the duct width with the width of the stack opening.

In actual practice several generating units may be discharging into one stack, so the opacity, velocity, and temperature in the ductwork from each unit must be measured in order to show the contribution of each to the final stack exit.

Meteorological data

The meteorological station at each plant site includes a 195-ft tower. Temperature sensors are installed on this tower at 35-ft and 195-ft levels, to provide temperature gradient data. Instruments for wind velocity, wind direction, barometric pressure, solar radiation, dewpoint, and rainfall are also installed at the site. The instrumentation housing is similar to that at each SO₂ station.

Central station

At the Birmingham office building an operator can communicate with all parts of the system via the color CRT. He can

also initiate programs that perform all the system functions. In this way state and local control personnel can monitor the buildup of pollution levels. These officials, who have indicated appropriate formats for data reporting, can take these data, compile them with similar data from other SO₂ emission sources in the area, and use them in further data processing or analysis and interpretation.

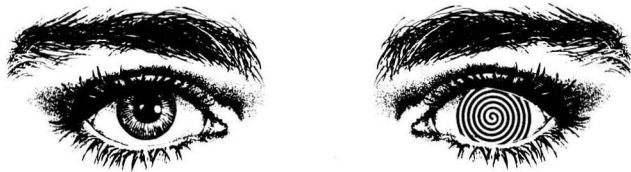
A special magnetic tape is generated

from the system archive tape in a standard format devised by the EPA and known as SAROAD (Storage and Retrieval of Aerometric Data) (*ES&T*, November 1970, p 902). When large amounts of data are requested by a regulatory agency, the computer can generate them on magnetic tape and the tape can be sent to the agency for direct use on their computer.

Alabama Power Company engineers are working on a real-time SO₂ dispersion model that will predict a plant's contribution to an episode condition in the area where the plant is located. This dispersion model is a 3-h predictive model that will use real-time inputs on meteorological conditions. An electric generating plant in Mobile, for example, is near other industrial SO₂ emission sources. This model will aid in indicating the contributions to an episode condition from any of the utility's generating plants.

With their new L&N system, Alabama Power is looking at additional uses for air quality as well as other environmental quality monitoring. Aultman and Hubbard indicated that although the system is fully responsive to the present requirements of the regulatory air pollution control agencies, the system software can be readily modified to adapt to any future changed monitoring or regulatory requirements, thus protecting against early obsolescent and facilitating system expansion.

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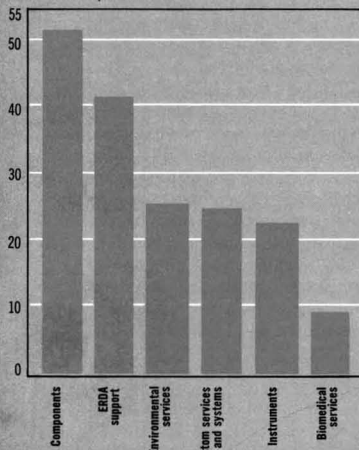
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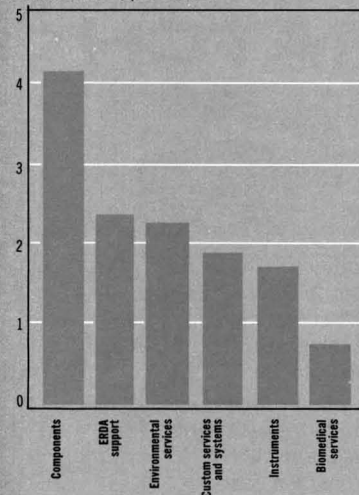
A unique combination of sophisticated scientific know-how, and business and management acumen, gave EG&G, Inc., a strong "track record", and indicates a bright future

EG&G at a glance
1975

Total sales \$176 million



Total income < \$13 million



During the 1930's, new types of photographs appeared on the scene. In these pictures, bullets were "stopped" in mid-flight, tennis balls were momentarily "flattened" by racquet impact, and numerous other high-speed, short-lived phenomena were depicted. The man who made all this possible, through the development of the modern stroboscope, was Harold Edgerton, then on the faculty of the Massachusetts Institute of Technology (MIT).

In 1947, Edgerton, along with Kenneth Germeshausen and Herbert Grier, also of MIT, organized a firm that was to become EG&G, Inc. (Wellesley, Mass.). At the time, the company was formed to continue classified research and development (R&D) and instrumentation work previously performed by these three founders for the Manhattan Project. It eventually became a systems contractor for the old Atomic Energy Commission for work at the Nevada and Pacific atomic test sites.

Generally, EG&G is a high-technology company that combines scientific know-how with strong profit motivation. Indeed, EG&G has reported a steady increase in annual operating income from \$6.83 million for 1970 to \$12.97 million for 1975. Even greater returns are expected for 1976.

Water soundings

The income sources of EG&G are broadly diversified. Principally, they consist of components, Energy Research and Development Administration (ERDA) contracts, custom services and systems, environmental and physics research, instruments, and biomedical services. These categories are listed in the decreasing order in which they earned operating income in 1974. The Environmental Group, in which is included the Environmental Equipment Division (EED), gave EG&G earnings of \$1.93 million in 1974, and \$2.26 million in 1975.

An element of EG&G's Environmental Group is Bionomics. It has two bases of operations—Wareham, Mass., and Pensacola, Fla. Kenneth Macek is Bionomics' manager.

One of the contracts EG&G received last year involves a 15-month water-

quality study at the Sunderset Nuclear Project for San Diego Gas & Electric Company, which is seeking background information before construction of a nuclear power generating plant near Blythe, Calif. At its Wareham laboratory, Bionomics is analyzing water samples taken from the Colorado River and two outfall drains, in support of this project.

Defense problems still play a large role in EG&G's activities. For instance, Bionomics is engaged in an 18-month, \$340 000 contract with the U.S. Army Medical Research and Development Command to evaluate effects of munitions compounds on aquatic ecosystems in the continental U.S.

Bionomics was formed in 1969 by a group of scientists, including Macek, who came from federal toxicology, water quality, and marine research laboratories. Its own laboratories are equipped with some highly sophisticated, state-of-the-art devices. Perhaps an idea of the services Bionomics provides can be gleaned from a partial list of present or former customers—Allied Chemical, Boston Edison, Du Pont, FMC Corp., Koppers, Monsanto, Procter & Gamble, Shell Chemical Company, and Velsicol Chemical Corp.

The principal function of Bionomics is to help to evolve a confident prediction that a given product or effluent will, or will not, have a significant impact on the aquatic environment. The approach to developing this confidence is to obtain relevant field data as much as possible. With such data, according to Bionomics, the accuracy of an environmental impact prediction can also be tested. However, where potential environmental safety of a particular material is expected to be relatively high, laboratory tests may be required.

Interdisciplinary services

Those who worked in oceanography may recall the name of the Geodyne Corp., a maker of data-sensing equipment and systems for the field, which was acquired by EG&G in 1968. EG&G's oceanographic group in Boston joined with Geodyne at its offices in Waltham, Massachusetts. In 1970, EG&G combined Cambridge Systems with Geodyne to form

the EED. To expand its activities further, the EED formed Environmental Consultants (EC) in 1971 to provide a full range of services related to aquatic, geophysical, and atmospheric measurements. EC's manager is Robert Ward.

The work that EC does is often highly interdisciplinary, and can involve air, water, or geological/geophysical matters. Among water projects, for example, are evaluations of navigation, safety, and potential oil spillage at prospective deep-water terminals. Such projects can call for studies of bottom and subbottom characteristics, currents, and temperature, for example, and the evolution of predictive mathematical models aimed at demonstrating effects of heated effluents in shallow coves.

A major project dealing with heated effluents was started about four years ago and is still active. This project involves



Robert Ward and Kenneth Macek
Environmental experts at EG&G

oceanographic and meteorological consulting work for the Atlantic Generating (nuclear) Station, offshore New Jersey, planned by Public Service Electric & Gas Company. The EC component of EG&G is a major contractor for this effort. Another contract involves subterranean mapping for the determination of optimum location of piping for dispersal of cooling-water effluent from the Jamesport nuclear plant of Long Island Lighting Company. Receiving waters would be the Long Island Sound (N.Y.).

One continuing effort comprises the joint ERDA/industry thermal dispersion study at the Pilgrim Station (nuclear), Plymouth, Mass. This exhaustive study involves EC and EG&G's Las Vegas, Nev., and Los Alamos, N.M., operations.

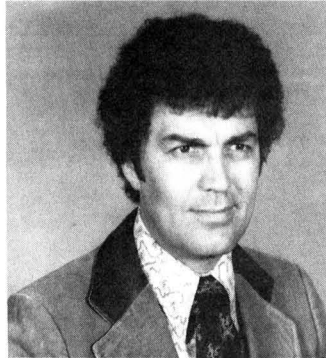
One deep-water terminal evaluation that EC did earlier was for Bonaire, Netherlands West Indies, and was commissioned by Northville Industries. Analogous surveys were, or are being conducted in Puerto Rico, Freeport (Bahamas), the Chesapeake Bay, and other locations.

Thus, EC has an extensive "track record" in environmental surveys for assessing the impact of nuclear (and also

fossil and hydro) power plants. This group also performs studies in ocean dumping, biology, ecological impacts, and offshore oil engineering. Among its approximately over 200 employees, EC has biologists, chemists, geologists, hydrographers, mathematicians, meteorologists, oceanologists, physicists, plant physiologists, and systems engineers.

International

Travel to many parts of the world, and you might meet with a representative of EG&G or one of its components. For example, EC is now involved in deep-water port studies on the Essequibo River, Guyana (South America). As part of these efforts, EC is training Guyana government personnel in operation and maintenance of applicable EG&G equipment so that the government can continue surveys when EG&G has completed its task.



Robert Ward and Kenneth Macek
Environmental experts at EG&G

EC'S Singapore offices has a contract with EBASCO Services, Inc. (New York, N.Y.) to study ocean circulation near a potential nuclear plant site near Bagac Bay, Philippines, which could be affected by plant discharges. Technical representatives of EC have also been engaged in preliminary efforts for possible nuclear plant studies in Egypt and Iran.

Finally, much of the international work involves the search for, and extraction of, oil. In support of oil projects, EG&G's Geophysical Engineering is conducting offshore surveys near Bangladesh, Indonesia, Malaysia, and Thailand.

Right place, right time

Among the factors in EG&G's growth is scientific know-how combined with capable management. The company's knack for being in the right place at the right time and having the facilities and people available when new requirements arose, has certainly given it a big boost. With energy, environment, and medicine at the forefront of immediate national needs—and many business and financial analysts feel that this is indeed the case—chances are that EG&G has a bright future to which to look forward. JJ

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Programs to develop control technology and to survey health and ecological effects are now underway as

The U.S. strives for energy sufficiency

Remember the Arab oil embargo? Almost three years ago Americans were spending hours in idling cars at filling stations for rationed gas being sold at ever-escalating prices and, when not in those lines, agonizing over increased home utility bills. This energy crisis spawned more than frayed nerves, short tempers, and less money for discretionary spending. Also to emerge from the damming of the foreign petroleum flow was a search for U.S. energy independence—a venture that has resulted in the formation of the Federal Interagency Energy/Environment R&D Program.

In-house and extramural research being conducted under this Interagency Program was described at the National Conference on Health, Environmental Effects, and Control Technology of Energy Use, held in February in Washington, D.C. The meeting was sponsored by EPA's Office of Energy, Minerals and Industry (OEMI) within the Office of Research and Development. To date there are 264 Interagency projects of which 150 are being implemented by agencies other than EPA (see box).

The road to formation

In the summer of 1973, President Nixon asked Dixie Lee Ray, then the chairman of the Atomic Energy Commission, to prepare a comprehensive national energy R&D plan. Completed that December, "The Nation's Energy Future," now commonly referred to as the Ray Report, called for a 5-yr, \$10 billion program to achieve energy sufficiency.

Coming on the heels of the Ray Report and the initial fiscal 1975 budget manipulations, which the report heavily shaped, was the establishment by the Office of Management and Budget of two interagency task forces under the auspices of the Council on Environmental Quality. The task forces, charged with recommending ways to achieve an effective integrated

federal energy-related environmental R&D program released two reports in November 1974: "Health and Environmental Effects of Energy Use" and "Environmental Control Technology for Energy Systems."

In the first report, the working group identified

- pollutant characterization, measurement and monitoring
- ecological effects and transport processes
- health effects
- integrated assessment

as information required to assess the impact of each major step—extraction, processing or conversion and utilization—of any energy technology.

The second report addressed program areas for control technology, which included extraction and beneficiation; fossil fuel combustion; synthetic fuels; and advanced systems and conservation. To facilitate the expected near-term reliance on coal, the report placed the highest priority on R&D directed to flue gas cleaning and resource extraction.

Interagency efforts

These three reports have served as guides to the Interagency Program in existence since fiscal 1975. Participating in this program are 12 federal departments or agencies (see box) with the lead agency, the U.S. EPA, responsible for coordination and planning. General direction within EPA is assumed by OEMI.

This Program was funded at \$134 million in fiscal 1975 and at \$100 million in fiscal 1976. About 40% of this funding is called "pass-through" funds, which OEMI administers, for research implemented by other agencies. For the near-term the Interagency Program plans to support the expansion, in an environmentally acceptable manner, of the extraction and combustion of coal (and oil and gas), and to direct efforts toward the support of EPA's regulatory role; mid- and long-term emphasis will be placed on anticipatory R&D to prevent environmentally adverse consequences of a new energy source.

The philosophy of the Interagency Program is typified by ERDA's goal, as expressed by Roger Le Gassie, assistant administrator for planning and analysis, which is to have the environmental information at hand when the energy decisions have to be made. ERDA and the other participating agencies feel that environmental protection must be a part of any energy development. But, once the

information on energy options and the environmental effects of these options is available, it must be disseminated to the public who will make the ultimate decisions.

For the next 25 years the U.S. will depend heavily on its coal, oil and gas resources and, to an increasing extent, nuclear energy. To be phased in, but with longer time schedules, are synthetic fuels, geothermal energy, breeder reactor and fusion power and solar energy. In the striving for energy sufficiency, all the ramifications—social, economic, legal, ecological, safety, health and institutional—of each energy development will be considered.

Coal: A case study

To meet the nation's more immediate energy demands, the diminishing domestic oil and gas reserves place the greatest burden on the extraction and direct combustion of coal. But as EPA's Stephen Gage, deputy assistant administrator for Energy, Minerals and Industry pointed out, the extraction process will be limited mainly, though not entirely, by the availability of water resources, particularly in the vast coal fields of the western U.S.

Underground and surface mining can cause heavy metal and acidic pollution of surface and subsurface waters; spoilation (erosion) of the land; fugitive dust problems; and loss of fish and wildlife. As Peter Lederman, EPA, demonstrated with his audiovisual presentation, surface mining is essentially a rape of the land if reclamation is not practiced. Reclamation, however, is particularly difficult in the arid or semi-arid western U.S., where most of the future coal mining is expected to occur.

A major problem with direct coal utilization is that uncontrolled or poorly controlled combustion releases particulate matter, SO_x, NO_x, and trace metals to the air. Among other problems, particulate matter and SO_x can lead to increases in cardiovascular diseases and deaths while NO_x can cause eye and respiratory irritation.

The physical and chemical processes available to clean coal are able to remove significant quantities of the precursors to the pollutants SO_x and NO_x, now released to the atmosphere with the combustion of coal. The technical feasibility of these cleaning processes has been proven according to the EPA, and the use of these pre-combustion methods may, in some

Strip mining operations near Elkins, W. Va., and . . .



Projects within the Interagency Energy/Environment R&D Program

	Control technology	Ecological effects	Characterization, measurement, and monitoring	Health effects	Integrated assessment	Total
EPA ^a projects	54	23	20	12	5	114
Non-EPA ^b projects	48	36	32	26	8	150

^a OEMI, coordinator; ^b Within Agriculture, ERDA, Federal Energy Administration, HUD, Interior, NASA, National Bureau of Standards, National Institute of Environmental Health Sciences, NIOSH, NOAA, TVA.

cases, be less costly than flue gas desulfurization, but the range of application of these methods may not be so broad as other emission control strategies.

Cleaning of coal combustion flue gases to remove SO_x and eventually NO_x (the Japanese are approaching commercial application of NO_x flue gas treatment on gas- and oil-fired boilers) eliminates some air pollution problems, but methods to dispose of the resulting sludge and fly ash are still required. And, the emission of volatile trace elements such as mercury and fine particulate matter, is not halted by this control technology.

Fluidized-bed combustion of coal is now being studied and may offer major solutions to the control of atmospheric pollution (see *ES&T*, February 1976, p 120).

Basic studies

To prevent unacceptable degradation of environmental quality, the Interagency Program has made measurement and monitoring an integral part of studies on the sources, transportation and fate, effects on man and the environment, and available control technology of pollutants. A major thrust has been in the development and intercalibration of instrumentation for measuring air, water and terrestrial residuals. EPA, with the assistance of several other agencies, is integrating air, water and land-use data for the energy development areas in the western U.S.

NASA, for example, is developing advanced optical techniques for remote and in situ monitoring of the effects of mine-mouth power plants, and the degree to which mining sites have been rehabilitated. The National Bureau of Standards is developing standard reference materials to eliminate the bias in the measurement of air pollutants, while the USGS is developing flumes and weirs for measuring sediment-laden stream flows. For

... reclamation efforts three years later



measuring workplace hazards, NIOSH plans to develop a fibrous aerosol survey meter and a portable, personal gas chromatograph.

Health effects: An overview

In his remarks, David Rall, Director of the National Institute of Environmental Health Sciences, emphasized the diversity and multiplicity of compounds to which man is exposed and which singly or in combination are potentially toxic. Since these substances do not exist in the environment in isolation, the opportunity for synergistic or additive effects is enormous. Yet, Rall pointed out, knowledge of the toxicology of these combined effects is not adequate at present. He and George Stapleton of ERDA called for the development of innovative methods to obtain this needed information.

A fundamental objective of the health effects aspects of energy-related pollutants being studied by EPA, ERDA, NIEHS and NIOSH is an understanding of basic molecular interactions that lead to cellular damage and the repair and recovery processes that compensate for the initial damage. Broad avenues of study include the carcinogenesis, mutagenesis and teratogenesis of energy-associated pollutants. The science of mutagenesis is in high gear with new rapid, reliable screening methods being developed or perfected. But in the case of teratogenesis, scientists are not even certain how to test for teratogenic effects.

A major program in ERDA addresses the potential health problems associated with coal liquefaction and gasification. An early phase of ERDA's research is the presumptive identification of mutagenic or carcinogenic compounds, via newly developed microbial and multitier screening techniques. Only these compounds will be subjected to the more laborious and expensive animal bioassays

to describe precise dose-effect relationships. On another front, EPA has undertaken clinical and epidemiological studies to assess the effects in normal, susceptible and stressed populations exposed to effluents associated with coal conversion and utilization.

ERDA, along with EPA and NIEHS, is also pursuing efforts to develop methods in human and animal populations that will function as early indicators of physiological damage or the progression of a disease after its induction.

Among its many efforts, NIEHS is developing the methodology for teratogenicity testing. A long-range objective is the use of "embryo culture" to study the mechanism of teratogenic effects, and to rapidly predict human teratogens. Of particular concern to the agency is the latent or abeyant effects of in utero chemical exposure on physiologic functions such as behavioral responses.

In summarizing the occupational hazards of developing energy technologies, the NIOSH representative, Kenneth Bridbord, cited the need to study such acid aerosols as nitric acid and NO_x. NIOSH suspects that NO_x aerosols may, among other things, contribute to the development of chronic diseases, including cancer.

With the increased emphasis on energy conservation and the concomitant requirement for new and existing insulation materials, Bridbord highlighted the potential for increased health problems to workers engaged in the manufacture of these materials. In residential and commercial buildings, recirculation of exhaust air to reduce heating or cooling of make-up air may aggravate or create new indoor air pollution problems; NIOSH is now developing criteria for recirculating systems, and EPA is characterizing and assessing health implications of pollutant levels and concomitant control measures in the indoor environment. EPA's studies are in conjunction with HUD's and ERDA's development of voluntary energy conservation standards for buildings.

In closing, Bridbord applauded the federal effort to reduce community and environmental exposures to energy-related pollutants, but he decried the lack of emphasis to develop control technologies to protect the worker by reducing occupational hazards. LRE

Experts met in Mobile to try to dig up solutions to the many and varied problems involved in . . .

...Handling and using dredged material

"What does violence to the environment is bad engineering. What does violence to economics is also bad engineering," Arthur Fox, Jr., president of the 72 000-member American Society of Civil Engineers (ASCE, New York, N.Y.), reminded a dinner session of the ASCE Specialty Conference on Dredging and its Environmental Effects. He told the meeting that full weight must be given to both environmental and economic impacts of dredging or deciding not to dredge. The conference, strongly supported by the U.S. Army Corps of Engineers, and especially the Corps' Mobile (Ala.) district, was held at Mobile in late January; attendance exceeded 400.

Actually, some violence has been done to the aquatic environment by dredging and filling operations. True, dredging of navigable waters of the U.S. has required a Corps permit under the River and Harbor Act of 1899, but such permits were generally granted when it was deemed that no impairment of navigation would ensue. In 1958, the Corps began to examine dredging permit applications with somewhat more environmental scrutiny. The National Environmental Policy Act (NEPA, 1969), 1972 water pollution laws (P.L. 92-500), and 1973 ocean dumping laws (P.L. 92-532) provide that the Corps must carefully weigh environmental, as well as economic and navigational factors in any decision to grant, delay, or deny a dredging permit.

The Corps' power to deny a dredging permit has also been established in the courts. A landmark case (1969), involving a proposed mobile home park on Boca Ciega Bay, Fla., known as the Zabel v. Tabb case, helped to establish this power (see box).

It can take time!

To assure conformity with applicable federal, state, and local laws and regulations, the processing of a dredging permit application can take time and money. Col. Frank Boerger (USA, ret.), former San Francisco District Engineer, told the conference that monitoring and reporting alone can cost \$3000-80 000, depending upon proposed

project size. Total costs of obtaining a permit, for the San Francisco Bay area, for example, could be \$10 000, if 15 000 yd³ are to be dredged, or \$120 000, if 300 000 yd³ are to be dredged. Assurance of conformity to environmental guidelines has contributed to these totals. Costs of disposing contaminated dredged material (DM) at sea in deeper water, at least 14 mi out from the Bay area, as now required, could be as high as \$10/yd³.

Col. Boerger showed a flow chart that outlines the procedure to obtain a Bay dredging permit. He said that an average application takes about 140 days to clear the Corps, and 244 days to clear California authorities. The situation becomes even more involved when a state requires an environmental impact report (California, for example, almost always requires such a report). Also, in most cases, the federal government requires an environmental impact statement for a project of any consequence.

Social benefits

Why, then, go through all this "hassle" for a dredging permit? After all, as R. Pope of Gulf South Research Institute (Baton Rouge, La.) pointed out, the lease value of a tidal marsh or wetland,

for example, might often be only about \$1/acre/yr. Would they not be more valuable dredged and filled in for some "good" economic purpose, such as an industrial or commercial development, resort, mobile home park, or the like?

Pope answered this question by reminding the conference that this concept is indeed still extant, and that Louisiana alone, for instance, is losing some 16 mi²/yr of wetlands to "progress", with little or no attention paid to social costs of dredged material disposal. He also warned that with no wetlands, the shrimp, crab, and fish resource would be badly curtailed—in many cases, to the vanishing point—and that about two-thirds of Atlantic and Gulf seafood resources are estuary- and wetland-dependent. Pope called for thinking in terms of benefits of coastal wetlands and marshes to society as a whole, rather than to a given developer, company, or individual.

What are some of these social benefits? For openers, a coastal marsh can act as a buffer against storm surges. Also, it can serve as a seafood nursery ground; Pope estimated a biomass of 1400 lb/acre/yr, on the average. Moreover, the wetland could in some cases handle otherwise expensive tertiary sewage treatment needs, and help balance nature's nitrogen, phosphorus, and sulfur cycles for next to nothing, Pope told the conference. These lands may perhaps be used for aquaculture, as they are indeed so used in parts of Indonesia and Japan. Pope put a money value on the social benefits of coastal wetlands, based on the free work they do—\$82 000/acre (capital) or \$4100/acre/yr (operating).

Drinking water sources

A large proportion of the downstate Illinois population depends on small water impoundments, with average depths of 10 ft at their dams, for drinking water. W. J. Roberts, of the Illinois State Water Survey (Urbana), said. He noted that water demand there increases by 2.5%/yr, while the impoundments are losing an average of 0.6%/yr of storage capacity to sediment (sedimentation rate of 7 tons/



ASCE president Fox

"Weigh economics with environment"

acre/yr). Therefore, the lakes, which vary in area from 100 to 2500 acres, will eventually be abandoned, have their spillways raised, or be dredged periodically, and the dredged material put somewhere, since the region is running out of impoundment sites.

One place for DM disposal is the impoundment levee; only how high can one go on building levees? However, much of the sediment to be dredged is nutrient-laden, and, as Roberts told the meeting, a farmer was able to use some of this impoundment DM to raise 45 bu/acre of winter wheat with no fertilizer. Lately, an Illinois town was able to dredge its impoundment with a machine specially made for small dredging needs, and operable by one person. Total dredge/DM disposal costs, Roberts said, were pegged at 76¢/yd³. Incidentally, Roberts mentioned that it was envisioned that DM not having structural value (levees, for example), or agricultural use, might be employed in abandoned Illinois strip mine reclamation.

On the Vicksburg Bluffs

About 400 million yd³ of material—about 350 million yd³ for channel maintenance alone—are dredged annually in the U.S. How can better disposal or resource recovery methods for this material be devised? In 1972, a potential \$30 million expenditure was authorized to address these and related problems through the 5-yr Dredged Material Research Program (DMRP). Of major concern, however, is the significance of chemical contaminants associated with dredged sediments (this issue, p 334). The U.S. Army Engineer Waterways Experiment Station (WES) at Vicksburg, Miss., is the lead agency for the DMRP, which is being conducted by WES' Environmental Effects Laboratory (EEL). John Harrison, one of the Mobile conference session chairmen, is chief of the EEL. Indeed, the WES was very heavily represented at the conference, both on the speaker's podium, and among the attendees.

Normally, the trend has been to fill in wetlands for "progress", or to destroy marshes as an ancillary cost of some human endeavor. To be sure, nature itself sometimes destroys marshes through water level increases or decreases, or by other means. However, what about restoration or creation of marshes for the safeguarding of wetland resources?

The WES/EEL is experimentally creating wetlands or tidal marshes on coasts near Astoria, Ore., Brunswick, Ga., Galveston, Tex., and some other locations. River sites include Dyke Marsh, Va. (Potomac River, about to start work), and Windmill Point on the James River, near Hopewell, Va.

To prepare a marsh site such as Windmill Point with DM, for example,

the WES had to do some critical planning and engineering. Although the point is so far upstream that the James River is fresh, a tide range of 2–3 ft prevails. Thus, the level of the proposed site must be such that it is mostly submerged at flood tide, and exposed at ebb tide, and contains some areas of higher ground. Then, the plants most suitable for growing on the site and holding it in place must be put in. Add to all this the logistical questions of obtaining necessary equipment, supplies, and personnel to dredge, deposit material, and form the site to the required shape and level. Finally, exhaustive sediment and water quality tests must be run, analyzed, and catalogued, in order to determine potential impacts.

Conrad ("Pete") Kirby, the EEL's environmental resources division chief,

Dredging: A landmark decision

During the 1960's, Alfred Zabel, a real estate developer, applied for a permit to construct a bulkhead and bridge, and to dredge and fill, and to use the dredged material to establish trailer parks in filled tidelands. Col. R. B. Tabb, then Jacksonville (Fla.) District Engineer of the Corps, refused to grant the permit because he felt that the real estate project would harm the ecology of Boca Ciega Bay, Fla., where the structures and trailer parks were to be built. Col. Tabb cited the River and Harbor Act of 1899 and the Fish and Wildlife Coordination Act of 1958 as the laws which allowed him to deny the permit.

Zabel sued Col. Tabb in the U.S. District Court, Middle District of Florida, on February 17, 1969. The decision was that the Secretary of the Army (represented by the District Engineer) did not have the authority to deny the permit under the 1899 Act, even if considered together with the 1958 Act, as long as the proposed project did not interfere with navigation. The Corps was directed to issue a permit, but was given a stay from granting this permit pending appeal.

The appeal was heard in the U.S. Court of Appeals, Fifth Circuit, on July 16, 1970. The lower court decision was reversed; the Act of 1958 and NEPA (1969) were said by the appellate judges to give the Secretary of the Army (and his representatives) grounds to deny permits for ecological reasons. This appeal decision is considered by many to be an environmental legal landmark.

The case went to the U.S. Supreme Court. On February 22, 1971, the High Court refused to review the Appeals Court decision on the Zabel v. Tabb case.

told ES&T that the James River site was eminently successful last year. Indeed, 95 species of marsh plants took hold and flowered in two months—before the EEL had time to experiment with species it had selected (finally, the EEL reserved a part of the site for its selected species). EEL's contractor, Environmental Concern, Inc. (St. Michael's, Md.), had its representative call EEL to inform Kirby that "the thing looks like a cornfield!" It has proved very attractive to waterfowl.

The warmer-climate brackish-water DM site near Brunswick, Ga., has had successful growth of certain selected species, and work there continues. Another disposal site example is one of sand in open water, enough to form a small island off the Mississippi coast, upon which certain grass species have begun to establish themselves.

Nuisance or resource?

Be it nuisance or resource, DM, at the tune of 20 million m³/yr is a commodity with which The Netherlands must contend. Jaap de Nekker and Kees d'Angremond of that country told the conference that much of this material consists of harbor mud that is cheaper to dredge and use than is North Sea sand. However, much of this mud, carried to Holland by the Rhine River, is contaminated with biocides, heavy metals, and toxic organic chemicals.

Important uses for DM are for land stabilization, beach fills, and dune erosion countermeasures, in the Rhine Delta land reclamation project and elsewhere. Where mud is used, it is shrunken by dewatering to make a base for the next layer. Also, it could be used for many non-agricultural purposes, including strip mine fill; or even for agricultural purposes, if it is uncontaminated or sufficiently decontaminated. The mud, properly cured, seems to develop physical properties suitable to support urbanization and industrial areas.

Finally, a very important use of DM is for establishment of polders—land reclaimed from the sea bottom. Two large polders, Nordoostpolder and Flevoland, were built with DM in what used to be the salt Zuider Zee, now, the fresh IJsselmeer. These polders now hold thriving communities, such as Flevoland's Lelystad, for example. A third polder, Markerwaard, should be under construction in the next few years.

In time to come, in the U.S., The Netherlands, and hopefully, other countries, environmental aspects of dredging will be increasingly taken into account. Because of food resource bases and other social and natural benefits, as well as stiffer environmental regulations, the notion that a dredger need concern himself only with navigational matters will become more and more a thing of the past. JJ

FEATURE

New federal regulations for dredged and fill material

Aided by EPA guidelines, the U.S. Army Corps of Engineers regulates the discharge of these material, through a permit program, to all waters of the U.S.

David D. Smith

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In March 1975, the U.S. District Court for the District of Columbia ruled that the responsibility of the U.S. Army Corps of Engineers to regulate the discharge of dredged or fill material to navigable waters *extends to all waters of the U.S.* At the same time, the court directed the Corps to revise its regulatory procedures accordingly, and the U.S. Environmental Protection Agency (EPA) to issue the applicable discharge guidelines forthwith. The court ruling stemmed from a suit brought by the National Resources Defense Council and the National Wildlife Federation against the Corps and EPA alleging non-compliance with certain provisions, primarily Section 404, of the Federal Water Pollution Control Act Amendments (P.L. 92-500).

After several months of intensive joint efforts, coordinated by the Office of Management and Budget, the proposed Corps Regulations and EPA proposed Guidelines were published as separate documents in the Federal Register in May 1975. The Corps received more than 4500 comments on the Regulations; EPA received 92 comments on the Guidelines. After review and analysis of the comments, the Corps issued the Interim Final Regulations for Discharge of Dredged and Fill Material in July 1975. In September 1975, EPA issued the Interim Final Guidelines to be applied by the Corps in evaluating a proposed discharge of dredged or fill material in navigable waters. Both the Corps Regulations and EPA Guidelines allowed 90 days for additional public comment.

The comment period has closed and both agencies are analyzing the more than 2000 comments received. The final regulations, possibly incorporating some changes based on the comments, are expected to be issued late this spring.

While this feature summarizes the key points of the Regulations and Guidelines, prospective permittees are cautioned to consult the complete text in the *Federal Register*, because of the large number of modifying conditions and provisos and the complicated language contained in these documents.

Background

P.L. 92-500 prohibits any individual from discharging pollutants into a waterway from a point source unless the discharge is authorized by a National Pollutant Discharge Elimination System (NPDES) permit issued by the EPA or an EPA-approved state agency. The single point source pollutant discharge excepted from this NPDES permit program is the discharge of dredged or fill material.

Section 404 of P.L. 92-500 authorizes the Secretary of the Army, acting through the Chief of Engineers, to issue permits for the discharge of dredged or fill material into navigable wa-

ters at specified disposal sites. Section 404 also provides that guidelines developed by EPA be applied by the Corps in selection of disposal sites and in the application review procedures prior to issuance of permits.

Federal regulatory control of construction and related activities in navigable waters dates back more than 75 years. The River and Harbor Act of 1899 gave responsibility and authority to the Department of the Army, acting through the Corps, for regulatory permits authorizing structures and work in or affecting the navigable waters of the U.S. For disposal of dredged material at sea, the Marine Protection, Research and Sanctuaries Act of 1972 (P.L. 92-532) provides for the Corps to issue permits, under criteria established by the EPA, for transport of dredged material for dumping in ocean waters.

Prior to the 1975 court decision, the Corps had limited the exercise of its responsibilities under Section 404 to the navigable waters of the U.S. Navigable waters are those waters that are presently navigable, have been historically navigable, or that could be reasonably developed to be navigable.

The 1975 decision expanded the Corps' jurisdiction to include the "waters of the United States," a vague phrase not defined by Congress or the courts. The fact that the phrase had not been defined necessitated an effort of many months duration by the Corps and EPA to arrive at a more or less workable definition of the new geographic limits and types of activities included within the Corps' expanded jurisdiction.

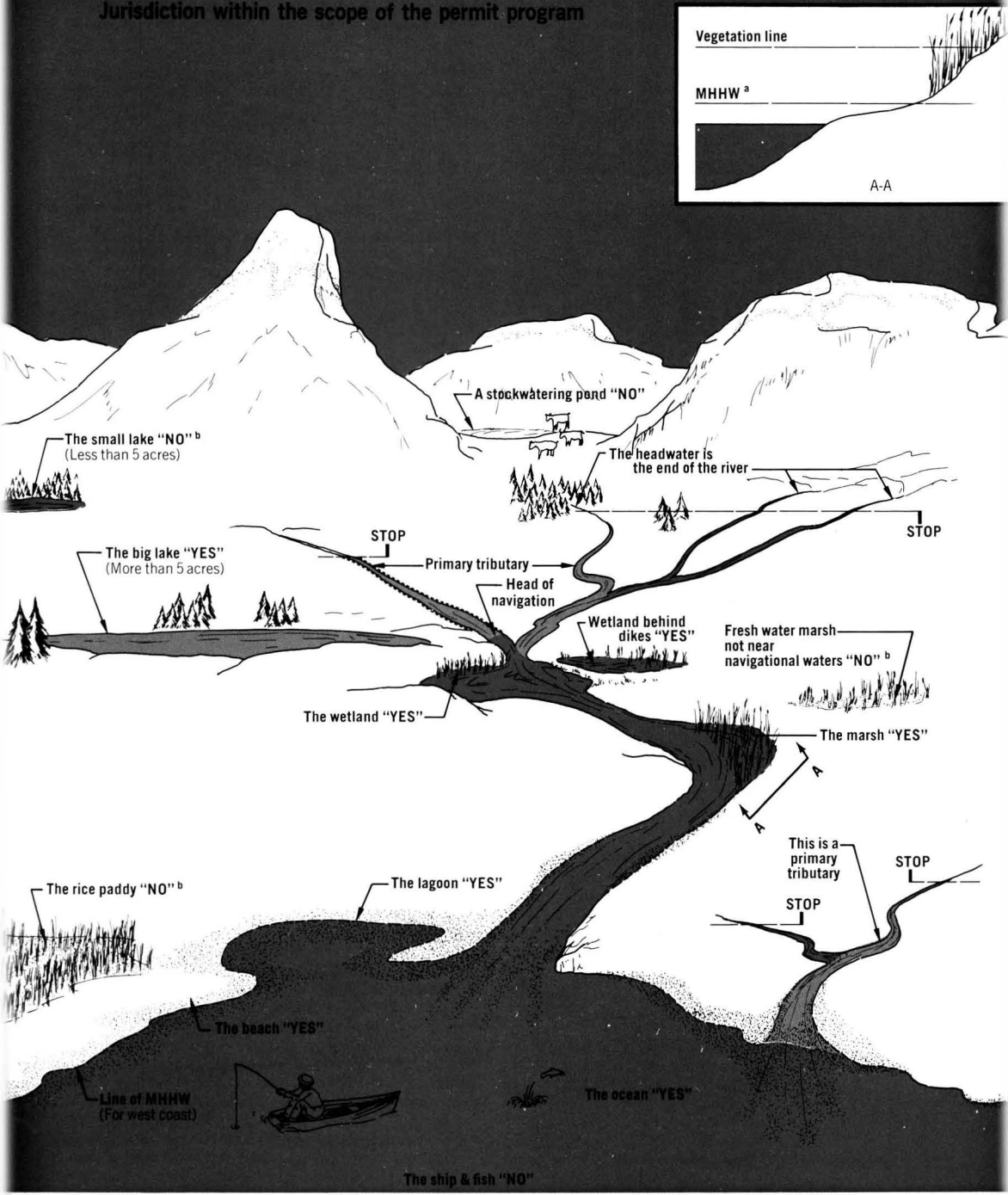
The extent of the Corps' jurisdiction and the sequence in which the phases of the permit program will be implemented are illustrated in Figure 1. In addition to the discharge of dredged or excavated material, a number of other types of activities (Table 1) come within the purview of these regulations and will be regulated by the Corps.

The Corps has emphasized that it plans to proceed slowly in expanding its authority. The expansion, a three-phase program, will occur over the next two years.

- Phase I, which became effective July 25, 1975, extended the Corps' regulation of disposal of dredged or fill material (which had been applicable to the traditional "navigable waters of the United States") to include contiguous or adjacent wetlands.
- Phase II, which becomes effective July 1, 1976, will expand the Corps' regulatory permit program into primary tributaries of "navigable waters of the United States," natural lakes greater than five acres in surface area, and their contiguous or adjacent wetlands.
- Phase III, effective July 1, 1977, will extend the Corps'

FIGURE 1

Jurisdiction within the scope of the permit program



----- On inland fresh waters our jurisdiction is to the "ordinary high water mark."

^a mean higher high water

^b Unless the district engineer finds it necessary for the protection of water quality

STOP Jurisdiction ends if the normal flow is less than 5 ft³/s

	Starts
Phase I	25 JUL '75
Phase II	1 JUL '76
Phase III	1 JUL '77

TABLE 1

Activities requiring permits under SECTION 404^a

Discharge of dredged material

- Discharge of material dredged or excavated from any waters of the U.S.
- The addition of dredged material to a specified disposal site
- The runoff of overflow from a contained land or water disposal site

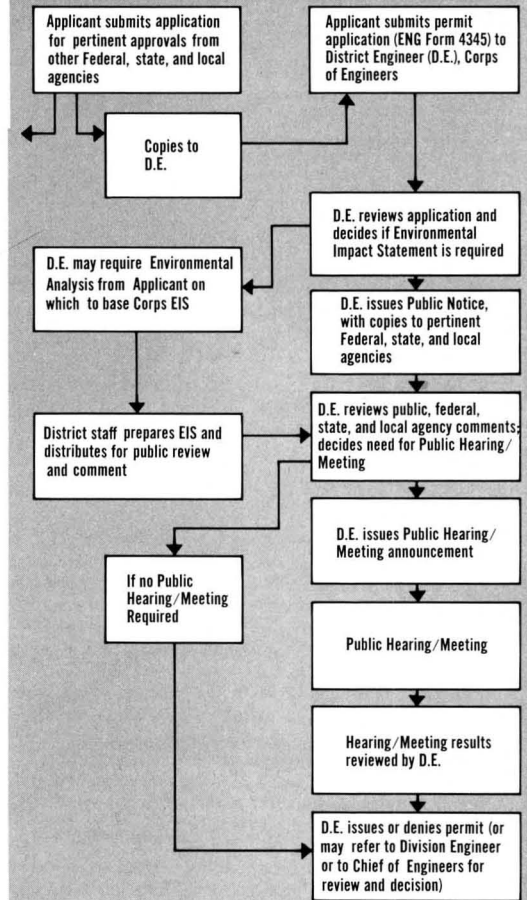
Discharge of fill material

- Placement of fill in construction of any structure in navigable waters
- Building of any structure of impoundment requiring rock, sand, dirt, or other pollutants
- Site development fills for recreational, industrial, commercial, residential, and other uses
- Causeways or road fills
- Dams and dikes
- Artificial islands
- Property protection and/or reclamation devices such as riprap, groins, seawalls, breakwaters and bulkheads and fills
- Beach nourishment
- Levees
- Sanitary landfills
- Fill for structures such as sewage treatment facilities, power plant intake and outfall pipes, and subaqueous utility lines
- Artificial reefs

^a Under Section 10 of the River and Harbor Act of 1899 a permit for structures or work in navigable waters is required.

FIGURE 2

Corps permit application processing steps



authority into other waters of the U.S. generally up to the headwaters where the streams flow less than five cubic feet per second.

The Corps has stressed that it will use common sense, good judgment, and moderation in carrying out the purpose of the Section 404 permit program, and that public cooperation and voluntary compliance will be encouraged. Prosecution will be recommended only when all other options have been exhausted.

Permit application processing

Permit application procedures include the principal steps to be taken by the applicant and the district engineer shown in Figure 2 and discussed below. Additional steps or variations in the procedures may be required in specific Corps Districts to facilitate coordination with state and local agencies.

Using ENG Form 4345, the applicant prepares his application according to directions furnished in the Corps' pamphlet "Applications for Department of the Army Permits for Activities in Waterways." The form and pamphlet are available from the district engineer.

There will be some exceptions to the requirement for the full-scale permit processing procedure. These include general permits, short-form application procedures, and abbreviated processing for certain small-scale bulkhead and fill activities.

The general permits and short-form procedures are yet to be worked out. It is known, however, that general permits are intended for certain clearly described categories of structures or work, and would be authorized only for those activities that are substantially similar in nature, that cause only minimal adverse environmental impact when performed separately, and have only a minimal adverse cumulative effect on the environment.

Once issued, a general permit normally would preclude the need for any further permit for similar work and would prescribe conditions to be followed in the future performance of such work. This mechanism is intended to facilitate the Corps' administrative management of the regulatory program. It is the Corp's intent to use the general permit for many categories in Phases II and III prior to the effective date of those phases, and to urge district engineers to utilize the general permit mechanism as extensively as possible.

An abbreviated permit processing procedure is also provided for minor bulkheads and fills that are constructed in waters other than navigable waters of the U.S. provided they are less than 500 ft in length, constructed for property protection, and involve the discharge of less than an average of one cubic yard per running foot.

Because the Corps Regulations require extensive coordination with federal and state agencies, and with the public during the application processing procedure, it is anticipated that processing time will be substantial. Although the Regula-

tions state that in processing permit applications, the district engineer will be guided by specific time limits these steps, totaling 135 days, may represent only a fraction of the processing time required for a major project.

The time for processing an application depends on such factors as the size and nature of the activity, the magnitude of the environmental impacts, the number of federal and state agencies involved, whether or not an EIS must be prepared by the Corps, and the degree of environmental opposition to the project. Based on experience in California, authorization of a Corps permit for a moderately sized coastal project without major adverse environmental impacts would probably take another 3–4 months after the issuance of the Public Notice by the district engineer. By contrast, a large industrial dredging or fill project with substantial adverse environmental impacts, thus requiring preparation and review of an EIS, would probably require 12–15 months before the permit was issued or denied.

The evaluative process

Using guidelines developed by the EPA, the district engineer makes an "Ecological Evaluation" of the proposed discharge to determine whether to allow or deny the discharge. In making this decision the district engineer also evaluates information contained in environmental impact assessments, environmental statements (if required), and appropriate coastal zone management programs and/or river basin plans. Taken into account are the physical effects, the chemical-biological interactions of the proposed discharge, and a series of considerations dealing with the selection of disposal sites and the stipulation of conditions for the proposed discharge.

The "Ecological Evaluation" laid out in the Guidelines is a step-by-step process. At one extreme, that of general permits, the review is minimal as long as there is reason for the district engineer to believe that environmental protection, specified in a published general permit, is met. Where permits are required on a case-by-case basis, the district engineer must first consider the necessity for testing.

If testing is required, the Guidelines specify that the elutriate test may be used to predict the effect on the water column. When an inventory of the total concentration of chemical constituents in the sediment is indicated, a total sediment analysis may be required. The district engineer may specify use of bioassays, biological community structure studies, and evaluation of biological indicator species within the limitations permitted by the state of the art. The Guidelines emphasize that no single test or approach is applied in all cases to evaluate the effects of proposed discharges of dredged or fill material.

Information obtained about a proposed operation, whether or not tests are required, must be interpreted in terms of the operation's predicted effect on the aquatic environment including its substrate and margins, the biota inhabiting such areas, and human uses thereof. Particular emphasis is to be given to municipal water supply intakes, shellfish, fisheries, wildlife, recreational activities, threatened or endangered species, benthic life, wetlands, and submerged vegetation. In order to avoid unreasonable burdens on applicants in regard to the quantity and types of data to be provided, the district engineer must consider the economic cost of performing the evaluation, the utility of the data to be provided, and the nature and magnitude of any potential environmental effect.

EPA, in conjunction with the Corps, will publish a procedures manual to provide details on technical evaluations, in-

cluding a description of tests, definitions, instructions on sample collection and preservation, analytical procedures, calculations, and references. Until this manual is issued, the district engineers offer technical guidance.

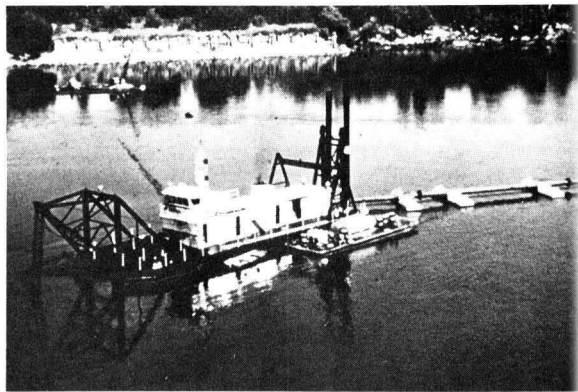
The most severe environmental impact covered by the Guidelines, from a national perspective, is the degradation or destruction of aquatic resources by filling operations in wetlands. The evaluation procedures for determining these environmental effects are relatively straightforward: "the guiding principle should be that destruction of highly productive wetlands may represent an irreversible loss of a valuable aquatic resource."

The evaluation of physical effects at proposed disposal sites other than wetlands is not so straightforward. For example, the significance of water column physical effects (such as reduction in light transmission, esthetic values, and direct destructive effects on nektonic and planktonic populations) are not readily predicted by current technical approaches. On the other hand, evaluation of the significance of the effect on the benthos (covering of benthic communities with a subsequent change in community structure or function) can be estimated, prior to the discharge activity, from a knowledge of the hydrodynamics of the disposal site, mode of discharge, volume of materials, particle size distribution and types of dredged or fill material, and from a knowledge of the benthic community.

The Guidelines recognize that "ecological perturbation caused by chemical-biological interactive effects resulting from discharges of dredged or fill material is very difficult to predict," and research has not clearly demonstrated the extent of these interactive effects. The principal concerns regarding open water discharge of such material focus on the potential effects of contained chemical contaminants on the water column or on benthic communities.

An elutriate test may be used to predict the effect on water quality from the release of contaminants from the sediment to the water column. The elutriate is the supernatant resulting from prescribed manipulations of one part bottom sediment from the dredging site with four parts water (vol/vol) collected from the dredging site.

Major constituents in the elutriate to be analyzed are determined by the district engineer after evaluating comments received from EPA's regional administrator, and considering



A hydraulic suction dredge is performing maintenance dredging

known sources of discharges in the area and known characteristics of the extraction and disposal sites. The data on elutriate concentrations should be used in conjunction with other available information that aids in the evaluation of impact on water quality.

In addition, the district engineer may specify bioassays if he believes that they will be of value for determining such effects as toxicity, stimulation, inhibition, or bio-accumulation. The district engineer may also use an appropriate benthic bioassay when such procedures will be of value in assessing ecological effect and in establishing discharge conditions. However, because evaluation of the chemical-biological interactive effects on benthic organisms is extremely complex, it requires procedures at the forefront of the current state-of-the-art. Although research has shown that benthic species can ingest contaminated sediment particles, no model exists to describe the degree to which contaminants are dissociated from the sediment and incorporated into benthic body tissues thereby gaining entry to the food chain.

Unless the district engineer determines otherwise, dredged or fill material may be *excluded* from the evaluation procedures described above for assessing the potential chemical-biological interactive effect if, for example, the material:

- is a naturally occurring sedimentary material (sand or gravel) with particle sizes larger than silt
- is intended for beach nourishment or restoration
- is substantially the same as the substrate at the proposed disposal site.

Selection of sites and conditions

In evaluating whether to permit a proposed discharge into navigable waters, consideration is given to the need for the proposed activity, the availability of alternate sites and methods of disposal that are less damaging to the environment, and water quality standards as are appropriate and applicable by law. Specific objectives to be considered in the evaluation are summarized in Table 2.

The EPA Guidelines require that particular consideration be given to preventing degradation of existing water uses at proposed disposal sites. The considerations specified can be grouped in two categories: prohibitory and precautionary. In the former category no disposal site may be designated or a

TABLE 2

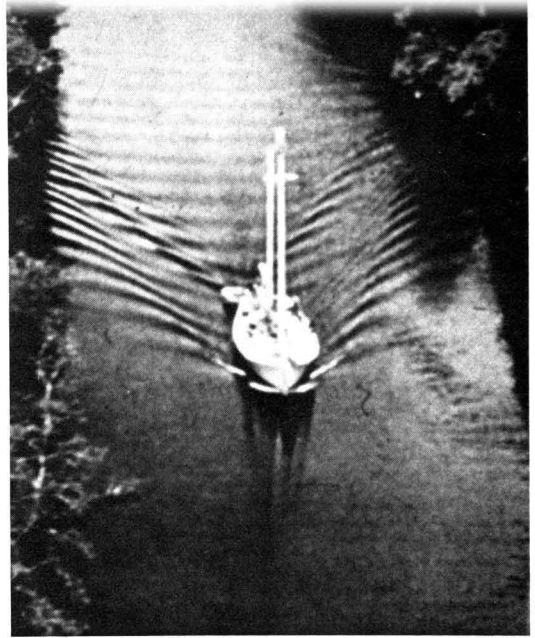
Objectives in evaluating a proposed discharge

AVOID discharge activities that will:

- significantly disrupt the chemical, physical and biological integrity of the aquatic ecosystem, of which aquatic biota, and substrate, and the normal fluctuations of water level are integral components
- significantly disrupt the food chain including alterations or decrease in diversity of plant and animal species
- inhibit the movement of fauna, especially their movement into and out of feeding, spawning, breeding and nursery areas
- destroy wetland areas having significant functions in maintenance of water quality
- degrade water quality

MINIMIZE discharge activities that will:

- degrade esthetic, recreational, and economic values
- cause adverse turbidity levels
- destroy or isolate areas that serve the function of retaining natural high waters or flood waters



The Corps permit program applies to coastal and inland waters, including adjacent wetlands

discharge allowed that will adversely affect a public water supply intake, concentrations of shellfish, or jeopardize the continued existence of threatened or endangered species. In the latter category, the precautions are that in designating a disposal site or allowing a discharge, avoid significant disruption of and/or minimize impact on marine or aquatic sanctuaries; areas of dispersed shellfish populations; wildlife habitat, food chain, and community structure; areas of submersed vegetation or significant biological productivity; wetlands, and recreational areas.

The specified disposal site should be confined to the smallest practicable area consistent with the type of dispersion determined to be appropriate under the EPA Guidelines. For instance, wide dispersion of a very thin layer of clean dredged material over a bay bottom may be more desirable in some localities than mounding dredged material in a restricted area.

After areas become candidates for designation as disposal sites, the district engineer may review them to assess the cumulative effects of existing and proposed disposal activities in those areas. The district engineer will consult the appropriate regional director of the EPA, the Fish and Wildlife Service, the National Marine Fisheries Service, and the Soil Conservation Service, as well as the heads of appropriate state agencies.

Consistent with the objectives of the Guidelines, the mixing zone is the smallest practicable zone within each specified disposal site in which desired concentrations of constituents must be achieved. In determining the acceptability of a proposed mixing zone, the district engineer and EPA's regional administrator will consider the:

- surface area, shape and volume of the discharge site
- current velocity, direction and consistency at the discharge site
 - degree of turbulence
 - stratification attributable to causes such as salinity, obstructions, and specific gravity
 - any on-site studies or mathematical models that have developed with respect to mixing patterns at the discharge site
- other factors prevailing at the discharge site that affect rates and patterns of mixing.

Overview

The district engineer will use what the Corps terms a "General Balancing Process" in reaching his decision on whether or not to authorize a given activity and in specifying conditions under which that activity may occur, if authorized. In addition to the anticipated environmental effects of the activity, he must also weigh such factors as economics, flood damage prevention, navigation, recreation, and the needs and welfare of the public.

Broadly speaking, the district engineer's evaluation of the environmental effects of a dredged or fill material discharge in the "balancing process" is based on the application of EPA Guidelines. The selection of disposal sites in navigable waters is also in accordance with these Guidelines. Further, the administrator of EPA can prohibit or restrict the use of any defined area as a disposal site if he determines that the discharge of dredged or fill material will have an unacceptable adverse effect on municipal water supplies, shellfish beds and fishery areas, wildlife or recreational areas.

Because there is no single technical evaluation procedure applicable for nationwide use, the Guidelines provide for various types of test procedures, including chemical mechanical analyses, elutriate tests, total sediment chemical analyses, bioassays, and biological evaluations. The Guidelines emphasize that such technical evaluations should be required only when a case-by-case review indicates that the results of such testing will provide information necessary to reach a final decision. When used carefully, the results of an appropriate technical evaluation in a given case will serve as one of many factors considered in the decision-making process.

It is important to recognize that the EPA Guidelines have been developed to comply with P.L. 92-500. These Guidelines are imposed on a permitting system that has been in existence for many years in historically navigable waters but that is yet to be introduced in many inland waters under the Corps phased implementation plan. For this reason, and because of the complex nature of the Guidelines, the process of implementation will, in itself, be developmental in character, and will place considerable reliance upon the judgment of district engineers and their advisors. It is significant that the Guidelines specify that they will be reviewed at least once every three years and revised as indicated by the accumulation of information from pertinent research.

Because of the very broad geographic extent of the permit program and the complexity of the Regulations and Guidelines, it is virtually certain that a great deal of patience will be required by all parties.

Additional reading

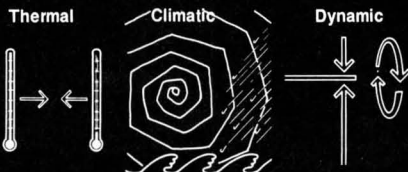
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CIRCLE 6 ON READER SERVICE CARD

Dredged material research problems and progress

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Each year, approximately 400 million yd^3 of sediment are dredged from U.S. waterways in order to maintain a desired navigation depth. Prior to about 1970, the dredged sediments, frequently called spoil, were disposed of in the most economical manner, in nearby waterways or on nearby land. In the late 1960's, however, state and federal pollution control agencies became increasingly concerned about the environmental impact of dredged material disposal. Particular attention was focused on the significance of chemical contaminants associated with the dredged sediments.

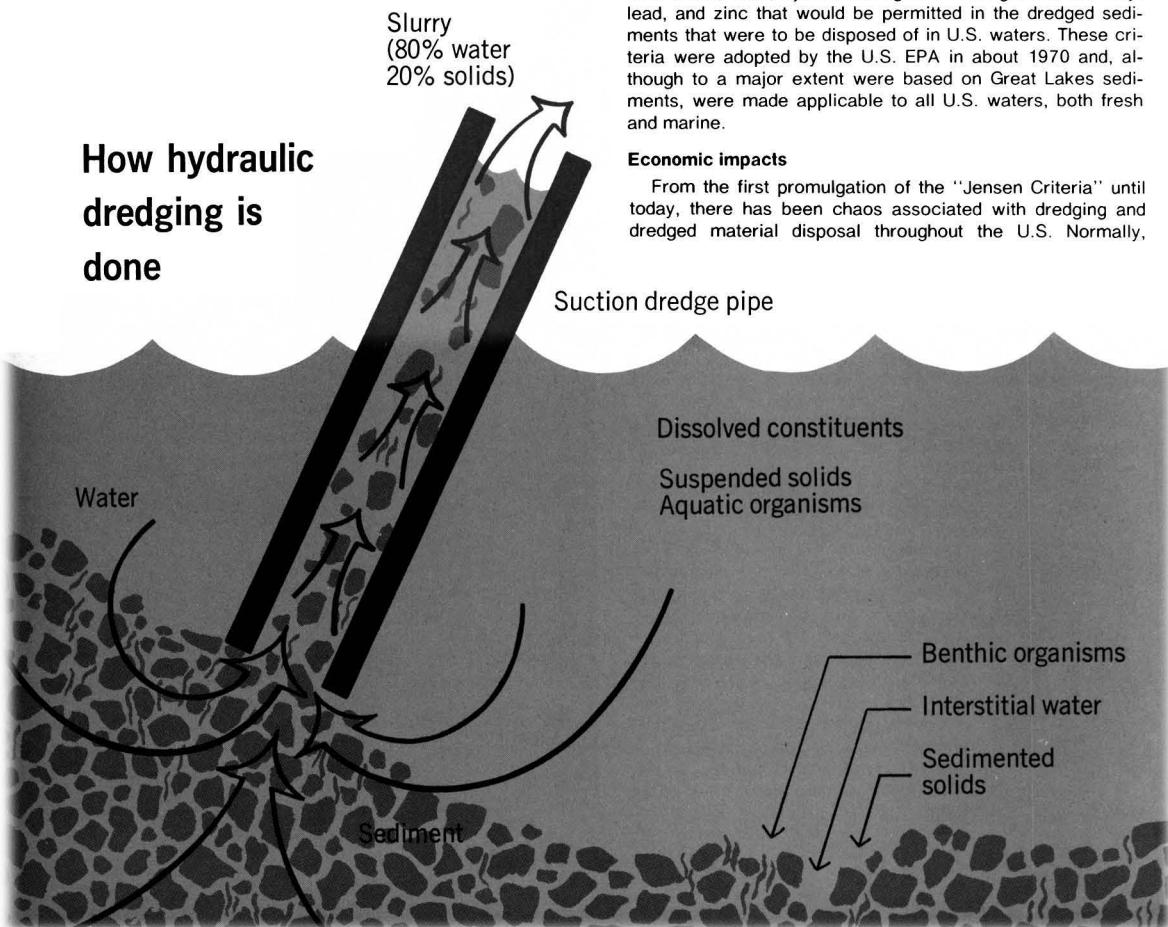
During the late 1960's, the U.S. Army Corps of Engineers Buffalo District, at the request of the Federal Water Quality Administration, initiated studies on the pollutional characteristics of sediments taken from selected Great Lakes harbors. These studies showed that, based on the classical parameters used to characterize the pollutional tendencies of municipal and industrial wastes, many of the Great Lakes harbor sediments were grossly polluted.

As a result, the Federal Water Quality Administration (FWQA), one of EPA's predecessors, proposed what are frequently called the "Jensen Criteria" for dredged material disposal. These criteria specified the maximum amounts of volatile solids, COD, Kjeldahl nitrogen, oil and grease, mercury, lead, and zinc that would be permitted in the dredged sediments that were to be disposed of in U.S. waters. These criteria were adopted by the U.S. EPA in about 1970 and, although to a major extent were based on Great Lakes sediments, were made applicable to all U.S. waters, both fresh and marine.

Economic impacts

From the first promulgation of the "Jensen Criteria" until today, there has been chaos associated with dredging and dredged material disposal throughout the U.S. Normally,

How hydraulic dredging is done



The U.S. Army Corps of Engineers has \$30 million earmarked for the DMRP. How can the program be optimized? Some suggested approaches to this research are presented here

about \$200 million are spent each year on dredging U.S. waterways. For fiscal year 1975, the expenditure was \$232 million for fiscal year 1976, it is estimated to be \$241 million.

In some parts of the U.S., environmental regulations had little or no effect on the costs of dredged material disposal. In other areas, however, their effects have been quite pronounced—frequently on the order of 10–20%. At several places in the U.S., environmental considerations have made the cost of dredged material disposal and, therefore, dredging prohibitive. This has been especially important in New England. Thus, certain harbors and waterways are silting in and eventually will become unusable.

Of great significance is the fact that many dredging projects that were originally scheduled to be conducted during the past year are being delayed because of potential environmental impact associated with chemical contaminants present in the sediments. The total cost of this situation is impossible to assess accurately.

One of the basic questions that must be resolved at this time, therefore, is whether the approach that was adopted as a result of the FWQA promulgating the "Jensen criteria" was technically, economically, and ecologically sound. In the opinion of many, it was not justifiable, based on information available at the time the FWQA first promulgated these criteria, nor is it justifiable based on information available today.

On the other hand, there is every reason to believe that in some instances the disposal of contaminated sediments may be adverse to water quality at the disposal site. Therefore, what is needed is a procedure by which the potential significance of chemical contaminants in dredged sediments can be assessed prior to dredged material disposal. This would help to ensure that the large amounts of chemical contaminants associated with some dredged sediments are not significantly adverse to aquatic life and water quality at the dredged material disposal site.

A research overview

The primary concern of this research is the significance of chemical contaminants in dredged sediments. Under certain conditions, disposal of dredged sediments (even independent of chemical composition) can be adverse to aquatic life, particularly benthic organisms at the disposal site. This situation is related to the problem of burying of organisms. This kind of problem must be approached differently from that associated with chemical contaminants in dredged sediments.

It is also clear that the decision by the Office of Management and Budget to support a major research effort in this area is justified because this effort could provide the information needed to determine the actual effect of dredging and dredged material disposal on environmental quality. From a strictly economic point of view, if in five years, the \$30 million, 5-yr Dredged Material Research Program (DMRP, this issue, p 326) results in saving approximately two cents per cubic yard dredged, this saving alone would pay for the total cost of the research program. It is difficult to envision a situation in which a concentrated effort of the type being conducted by the DMRP could not result in much greater savings in the cost of dredging than the cost of the program.

In addition to the U.S. Army Corps of Engineers Dredged Material Research Program being conducted at the Waterways Experiment Station (WES—Vicksburg, Miss.), research



Disposal. Dredged material is in the process of being slurried to a disposal site

is also being conducted in the Corps of Engineers districts. There has been an attempt to coordinate these multiple research efforts between the districts. Generally, the DMRP focuses on development of a set of guidelines that can be utilized by a Corps district to evaluate the environmental aspects of dredging and dredged material disposal.

The research sponsored by the Corps districts usually focuses on specific problems within the district. For example, one of the more intensive studies is being conducted by the San Francisco District. This district has conducted a multi-million dollar, multi-year study on some aspects of the environmental impact of dredging and dredged material disposal in San Francisco Bay. Particular attention has been given to situations that are peculiar to the Bay.

The U.S. EPA has also sponsored some research on dredging and dredged material disposal. These efforts must be considered relatively modest in comparison with the Corps of Engineers activities in this area.

Probably the most important current pending regulations governing dredging and dredged material disposal to which research must be addressed are set forth in the September 5, 1975, *Federal Register*. These regulations (this issue, p 328) are designed to meet requirements set forth in the water pollution law, P.L. 92-500, Section 404. While there is some difference between the approach given in these regulations, which are currently "interim final" and the guidelines pursuant to the ocean dumping law P.L. 92-532, basic differences are minor. Ultimately, it is likely that P.L. 92-532, the Canada-U.S. Water Quality Agreement, and the "Ocean Dumping Treaty" will all base their procedures for determining whether a particular sediment dredged from a U.S. waterway may be deposited at a particular location pursuant to the approach outlined in the September 5, 1975, *Federal Register*.

Needed: More field studies

Particular emphasis must be given to field studies designed to evaluate the actual environmental impact of a particular dredged material disposal operation at a variety of locations throughout the U.S. Far too much of the money that had been available for both the Corps and the EPA was devoted to what might be termed mechanistic-type research projects rather than to investigations of what actually happens during a dredged material disposal operation. The apparent basic philosophy of those initiating this type of research was that rather than study each and every situation, it would be far better to understand the mechanism of release of contaminants from dredged sediments and then, based on this understanding, predict what might happen at another site.

Unfortunately, the aqueous environmental chemistry of trace contaminants associated with natural water sediments is such that the likelihood of understanding the mechanism of release of a wide variety of contaminants to the water or aquatic organisms at the disposal site is nil in the foreseeable future. The more or less classical approach of a laboratory study in which different variables are controlled and varied one or two at a time, as has been taken with part of the dredged material research dollars during the past several years, has proven to be of limited value. What is needed is a series of field studies in which the physical, chemical, and biological characteristics of the sediments and disposal site are determined with enough reliability to detect sufficient change in the numbers and types of disposal site organisms to justify alternate methods of dredged material disposal.

One of the primary problems with laboratory studies for dredged material research is that, at this time, there is not an adequate understanding of the field situation suitable to permit simulation in the laboratory. Thus, detailed field studies, rather than laboratory studies should have been the first phase of research. These could have been followed by laboratory studies, once understanding of the actual operating systems is sufficient for the proper design of the laboratory investigations.

Another major problem with laboratory studies of dredged sediments is that frequently, the sediments have been substantially altered from their natural state by sampling and subsequent handling. Thus, the results of these studies would have little or no applicability to the real world. It is important that any studies on the significance of chemical contaminants associated with dredged sediments be conducted in such a way as to preserve sediments and their contaminants in their original form.

Focus of field studies

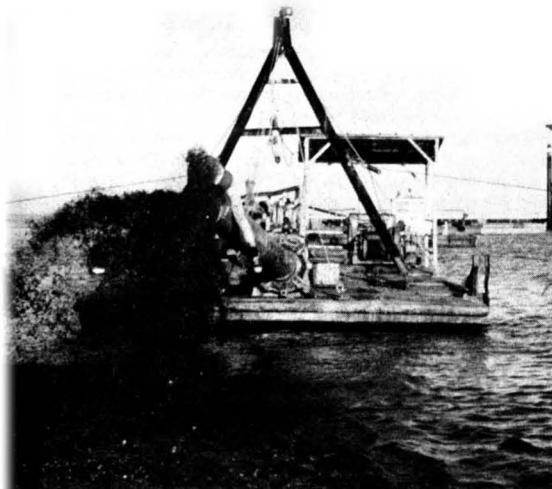
Any field studies must include detailed studies of actual dredging operations. Information is urgently needed on the water-sediment ratio used in hydraulic dredging for various types of dredging operations, and the degree of mixing of hydraulically and mechanically dredged sediments in the disposal site water column. For example, the Elutriate Test currently specified in the September 5 *Federal Register* is designed for hydraulically dredged sediments. However, a substantial quantity of sediment is mechanically dredged (especially in New England). Hydraulically dredged sediments are typically slurried in a one-to-four or one-to-five sediment-water ratio. By comparison, the amount of water associated with mechanically dredged sediments is normally much smaller. The result is a much more compact sediment; in some instances, a cohesive mass that settles to the bottom rapidly and with very little interaction between it and the disposal site water column.

Field studies must assess the rate of mixing of the contaminants from the dredged material disposal operation with the water column at the disposal site or, if in a diked area, with the nearby waters that receive the overflow. The September 5 *Federal Register* specifies that the District Engineer shall determine the mixing zone associated with a particular disposal operation. The perimeter of this mixing zone is to be used as a basis for judging the significance of chemical contaminant release in the disposal site. The Corps of Engineers DMRP is doing some work in this area, which, however, needs to be greatly expanded. Greater attention should be given to field studies that can be used to develop generalized mathematical models that could be applied to any area once the overall dominant characteristics such as water depth, currents, type of dredging, and disposal operations are defined. Chemicals that should receive attention in any field research program include the heavy metals; organics, with particular emphasis on the persistent organics such as the chlorinated hydrocarbon pesticides and PCB's; and aquatic plant nutrients such as nitrogen and phosphorus compounds.

Some current constraints

The DMRP as well as some of the various Corps district studies have indeed included detailed field studies. However, many of these studies have been conducted under very significant constraints that were in part related to the way in which the Corps can fund research. Studies of the type that are needed are extremely expensive, often requiring something on the order of a million dollars per year per site.

This estimate is based to some extent on the amount of funds that has been spent by various electric utilities studying the environmental impact of using once-through cooling at electric generating stations. A number of utilities have spent between \$1-2 million/yr for several years to assess the environmental impact of once-through cooling on receiving water quality. The disposal of dredged sediments in water or on land with overflow of supernatant water to the nearby water course is a similar problem and will require similar funding. Thus far, the amount of funding available for research in this area has fallen considerably short of this amount. This is certainly the most significant deficiency with respect to research in this area. Instead of the present few million dollars per year, \$10-15 million/yr should be spent for a 5-yr period at selected locations in the U.S., in order to evaluate the actual



Utilization. Material is being piped to a place where some new land area is to be created

environmental impact of disposal of dredged sediments properly.

Some of the other important problems with respect to conducting studies of this type are the funding constraints that are placed on governmental agencies. These include limitation of contracts to a 1-yr period, and limits on the total funding that can be readily allocated to one investigator during a specified contract period.

The various constraints discussed above, as well as others, lead to situations in which high-intensity short-term programs, such as the current efforts in dredged material research in the U.S., often have a relatively low efficacy. It is the author's opinion, however, that based on his personal experience with a number of studies of this type in the environmental quality area, the current Corps of Engineers DMRP efficacy is at least equal to, and in general, better than most of the previous or current efforts to provide information on a specific aspect of environmental quality that could be used to determine public policy in a specific area.

Research needs

It is important to break down potential environmental impact of chemicals associated with dredged sediments into a short-term, high-intensity effect related to the release of contaminants to the water column at the disposal site or in the overflow waters from a diked disposal area, and the long-term chronic exposure that could occur to benthic or epibenthic organisms that inhabit or attempt to inhabit the dredged material disposal site, once the sediments have been redeposited on the bottom. These two areas have distinctly different characteristics and must be treated differently.

Field studies on the significance of chemical contaminants in dredged sediments must focus on at least two, and in some cases three, distinct areas. In coastal zones, the focus must include the potential environmental impact of disposal in nearby open waters and in diked disposal areas in the water and on land. In some parts of the country, deep ocean disposal must also be considered. The latter is frequently being used for disposal of highly contaminated sediments.

In some areas, regional agencies have adopted the policy that disposal of contaminants associated with dredged sediments has less environmental impact in deep waters than in shallow waters. This supposition has not been borne out by any experimental results. A number of aquatic scientists question whether barging to deep water is an ecologically safe method of dredged material disposal. This is an area that is not receiving sufficient attention at this time and should be studied, in order to evaluate the actual environmental impact

of deep water disposal of dredged sediments on aquatic ecosystems.

One of the areas of primary emphasis in dredged material research has been on evaluating the significance of chemical contaminants associated with dredged sediments disposed of in waters near the dredging site. As noted above, this was the most frequent method of dredged material disposal prior to adoption of bulk chemical "Jensen Criteria" by the EPA and its predecessor organizations. In accordance with these criteria, almost all polluted and non-polluted sediments were disposed of in nearby water courses, or on land whose overflow water quickly returned to the water course.

A substantial part of current efforts within the DMRP conducted at WES and in the district is devoted primarily to evaluating the impact of dredged material disposal in water. Some of these studies are deficient in that they are devoted to evaluating the environmental impact of relatively clean sediments. Few of these studies actually involve evaluating the impact of what most individuals would consider grossly polluted sediments.

An exception to this is the work done at Galveston, Tex., where the study compared the environmental impact of disposal of dredged sediments from the Galveston Entrance Channel (relatively non-contaminated) to that of sediments from the Texas City Channel, a heavily industrialized area. This study focused on the effect of the dredged material disposal on water column characteristics. With respect to these characteristics, it was found that the grossly polluted sediments had the same environmental impact as the clean sediments. Neither would have a significant deleterious effect on organisms present in the water column at the open water disposal site.

Another area that is not receiving sufficient attention in the current Dredged Material Research Programs conducted by the Corps and the U.S. EPA is the environmental impact of the overflow waters from diked disposal operations. This method of disposal has been adopted in numerous places throughout the U.S.—especially the Great Lakes—as a means of disposal of more polluted sediments. Dredged material disposal in diked areas either in water or on land and with overflow of the supernatant water to the nearby watercourse may be ecologically more damaging than open water disposal. This is because most of the significant contaminants associated with dredged sediments would be present in the overflow waters that would enter what are generally the most sensitive areas of a water body; for example, the near-shore waters in which larval forms may be present. These are areas with relatively lower mixing than open waters, where generally, the contaminants are rapidly dispersed.

An effort at least equal to the open water disposal research efforts should be mounted immediately in order to enable the District Engineer to evaluate the environmental impact of open water vs. diked disposal area disposal properly. Such research would be particularly important in the Great Lakes region where each of the states bordering on the lakes (except Ohio) has arbitrarily adopted a policy of a complete diked disposal operation at a cost of tens of millions of dollars. Based on the information available, no one can be certain that the diked disposal operations currently being implemented will have less environmental impact than the formerly used and less expensive open water disposal techniques.

Contaminated sediment uses

It is likely that some dredged sediments in U.S. waterways may contain chemical contaminants that could have a significant adverse effect on water quality at a particular open water or on-land disposal site with overflow to the nearby watercourse. Therefore, it is important that work be conducted on methods of treating these contaminants from on-land disposal in order to prevent contamination of surface or groundwaters. This is an area that is receiving some attention in the current Dredged Material Research Program. However,

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it is an area that needs greatly increased research with particular emphasis on its engineering and economic aspects.

Based on current information, beneficial uses or reclamation of areas that have been used for dredged material disposal in the past should receive a lower priority for research dollars associated with dredged material disposal. It is doubtful that in the foreseeable future the public will spend any substantial amount of money for habitat development associated with dredged material disposal. While some beneficial uses, such as reclamation of mined land, can be made from dredged sediments, generally this does not appear to be an area of great promise. It certainly should receive a relatively low funding priority compared to the other more pressing problem areas that exist, such as those enumerated above.

How research can pay off

The current dredged material disposal regulations promulgated in the September 5 *Federal Register* require a case-by-case approach to evaluate the potential environmental impact of dredged material disposal on receiving water quality. This approach is technically sound, but places a considerable burden on the District Engineer who must evaluate a number of specific points delineated in the regulations. The ongoing research in this area will make significant strides toward helping the District Engineer make this evaluation. However, even with the completion of the DMRP there still will be numerous questions that have not been properly and adequately addressed.

It is strongly recommended that, in light of the September 5 *Federal Register*, a significant increase in funding available for dredged material research be allocated and that these funds be used specifically to evaluate the environmental impact of chemical contaminants associated with dredged sediments. There is every reason to believe that such expenditure will more than pay for itself by reducing costs of dredging and dredged material disposal and by providing guidance to development of the best overall methods of disposal that encompass environmental impact, and technical, legal, and social factors.

Additional reading

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G. Fred Lee is currently director of the Center for Environmental Studies at the University of Texas at Dallas. He is also one of the consultants to the Corps of Engineers Dredged Material Research Program and an advisor to the International Joint Commission Research Advisory Board, as well as the EPA Grosse Ile Laboratory for dredging research on the Great Lakes.

Coordinated by JJ

Pyrolysis systems that convert municipal solid waste to useful materials are options to current disposal methods

Fuel and feedstock from refuse

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Disposal of refuse and conservation of energy have become major problems of immediate concern. Municipal solid waste consists of a wide variety of organic and inorganic material and its composition is highly variable, depending on such factors as geographic location, time of year, local regulations, and standard of living. The present rate of generation is about 5 lb/day/capita with a resulting heating value of 3000–6000 Btu/lb. By the year 2000, it is expected that a half billion tons per year of refuse will be generated with an energy potential of 60 billion watts.

The composition of the refuse is also expected to change in future years: the plastic and paper content is expected to increase significantly while the inorganic fraction (metals, glass) is projected to decrease. The net result is a projected large increase in the heating value per pound of refuse. If these projections are accurate, a viable means for energy recovery from solid waste should become increasingly attractive in the near future.

The current options available for disposal of solid waste are: ocean dumping, landfill, separation, biodegradation, incineration and pyrolysis (Table 1). Both ocean dumping and landfill are expected to reach a saturation point with regard to available sites and environmental insult. Indeed, in many heavily populated areas, these disposal methods are no longer acceptable. Separation is concerned with physical segregation of refuse into components such as metals, glass, and paper for recycling to ease the load on the virgin material supply. There are a wide variety of biodegradation approaches under consideration—composting, aerobic digestion, anaerobic digestion, biochemical conversion—and resource re-

FIGURE 1

Resource recovery systems

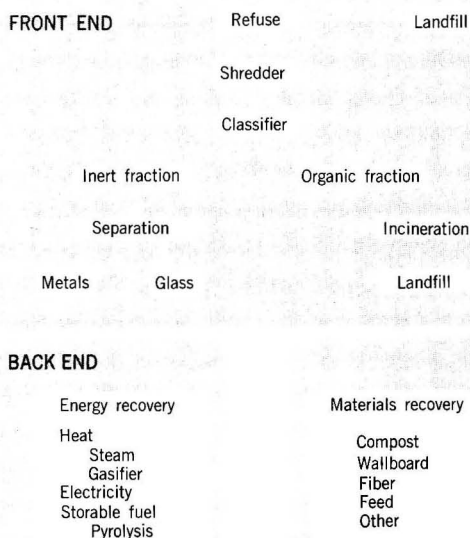


TABLE 1

Features of waste disposal options

Option	Environ- mental insult	Volume reduc- tion	Mass reduc- tion	Resource recovery		
				Ma- terials	Steam/ electric	Fuel/ feed- stock
Ocean dump- ing	•					
Landfill	•					
Separ- ation		•	•	•		
Biode- grada- tion				•		•
Incin- eration	•	•	•		•	
Pyrolysis		•	•	•	•	•

covery can be achieved in some cases; however, the processes generally require lengthy residence times and are quite susceptible to stability problems.

The remaining options for waste disposal are incineration and pyrolysis. Both have the potential for volume and mass reduction and energy recovery. Incinerator processes can be coupled to steam and electrical generating plants, but emission control equipment can be costly. If a storable and/or transportable fuel or chemical synthesis feedstock is desired with minimal environmental problems pyrolysis—the thermal degradation with incomplete combustion—may be a viable alternative. Process development is not well advanced, however. The first commercial scale plants are just now coming on-stream, and the design and operation of a pyrolysis process is somewhat of a speculative venture, with considerable confusion regarding vendor technical and economic claims.

Figure 1 diagrams resource recovery options from solid waste. The "front end" section is concerned with materials recovery with disposal of the organic portion by landfill or incineration. The "back end" portion is concerned with the recovery of the organic portion and its reuse as a fuel or raw material for a product.

General considerations

The fuel/feedstock products from a pyrolysis reaction system can be liquid, solid and/or gas. Typical gas heating values of 100–600 Btu can be achieved; liquid fuel heating values are in the 10 000–11 000 Btu/lb range while solid fuel values are approximately 6000–9000 Btu/lb. The yields and relative proportions of the different phases as well as the chemical composition of each phase are dependent on the reactor type, heating method, and process variables. Several basic reactor types have been used for pyrolysis reactions. The most common (Figure 2) are shaft, rotary kiln, and fluidized bed.

Shaft reactors are conceptually the simplest and the lowest in capital cost. In the vertical type, the feed material is fed at the top of the reactor and settles into the reactor under its own weight. Generated pyrolysis gases pass upward through the shaft and are removed from the top. Typical feed mechanisms include screw conveyors, rotary devices, and rams. A residue discharge device and gas takeoff manifold must be provided. The horizontal shaft type incorporates a feed conveyor system, either mechanical or molten bed, through the reactor housing and refuse is continuously pyro-

lyzed from the conveyor system. Feed and discharge problems are minimized but the reliability of conveyors at elevated temperatures can be a problem. Both types of shaft reactors are constructed of metal capable of withstanding temperatures of 500–3000 °F, or are lined with a refractory material.

The rotary kiln is a cylinder rotated upon suitable bearings and usually slightly inclined to the horizontal. Typical length/diameter ratios are in the range of 4 to 10. Feed material is charged into one end and progresses through the kiln by means of rotation and slope of the cylinder to the opposite end where it is discharged. Feed and discharge mechanisms must be provided. The metal cylinder is normally lined with refractory brick. The rotary kiln has mixing advantages over the shaft reactor but sealing the rotating cylinder from the stationary feed and discharge ports can be a problem.

The fluidized-bed reactor consists of a bed of solid particles such as sand, suspended by an upward flowing gas stream. For pyrolysis applications, the solid particles are heated (in the same vessel or an external vessel with circulation) and serve as the heat source for the pyrolysis reactions. A chemical reaction involving the solid particles may take place. The major advantage over other reactor types is im-

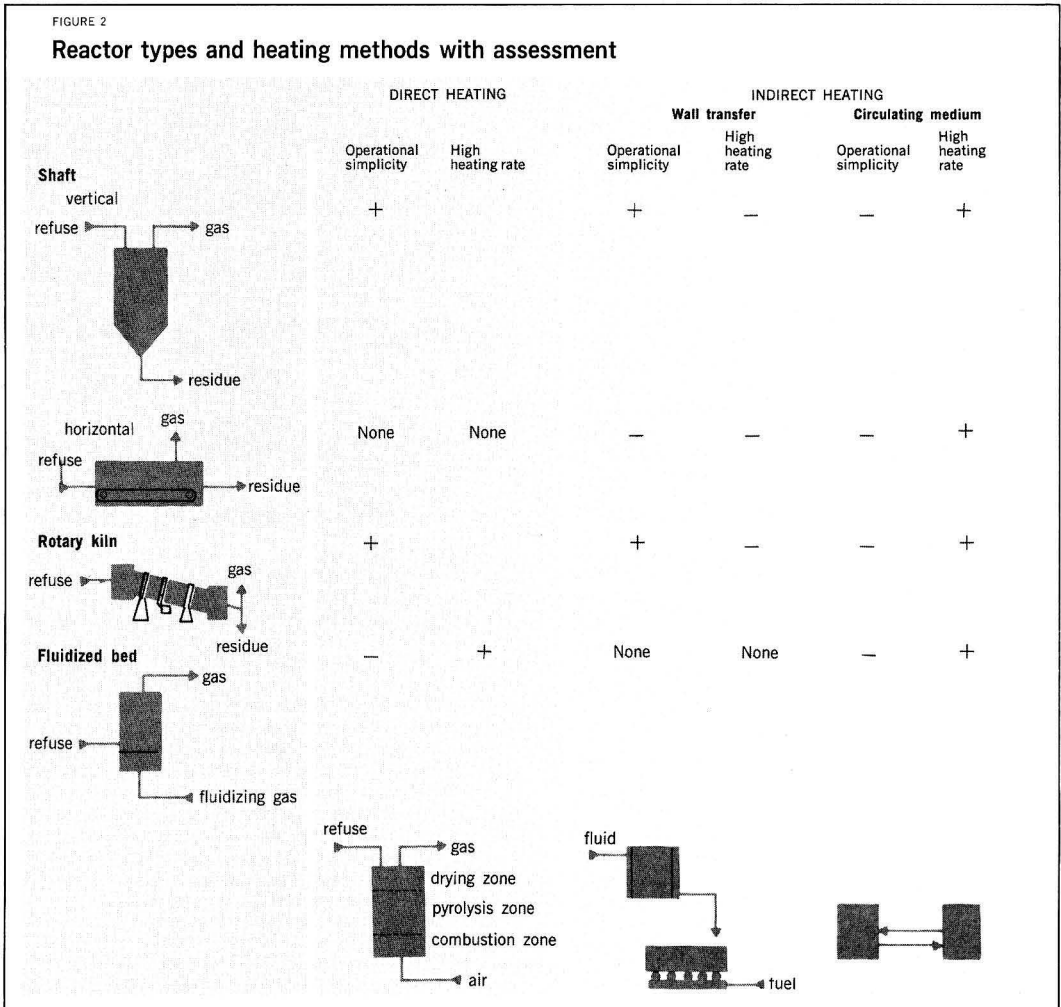


FIGURE 3

Typical steps in preprocessing refuse

	Municipal solid waste	100%	
		Refuse storage	
		Primary shredding	
		Drying	
Heavies shredding		Air separation	
Air separation		Secondary shredding	
Magnetic separation		Mechanical separation	
Nonferrous metals, glass, dirt or cleanfill	Ferrous metal	Pulverized solid fuel	Moisture
12%	6.5%	70%	11.5%

proved heat transfer and temperature control. The primary drawbacks include erosion and carryover problems associated with the solid particles, gas velocity control and solids transfer, and separation problems.

Pyrolysis reactions require a heat source. Two distinct heating methods are used—direct and indirect. In a direct method, heat is supplied to the reaction mixture by partial combustion of refuse and/or supplementary fuel within the pyrolysis reactor. Oxygen must be supplied and the reactor product gas contains a significant amount of CO_2 and H_2O , with resulting reduced heating value. If air is used as the oxygen source, the environmental problems of NO_x formation must be considered, as well as the further dilution of the pyrolysis gas by large amounts of nitrogen. With indirect heating methods, the primary heating zone is separated from the pyrolysis vessel. This separation can be achieved by a heat conduction barrier such as a wall, or by transfer of a separate medium such as sand between the combustion and pyrolysis vessels. Wall heat transfer methods are generally unacceptable in solid waste applications because of large resistances such as refractory linings, slag coating, and corrosion problems. The use of a separate medium from a heat transfer viewpoint is desirable but can present major problems with regard to solids transfer and separation. Indirect methods are generally less efficient than direct methods but avoid the problems of excessive CO_2 and H_2O formation (and reduced heating value) and high NO_x and N_2 content. Schematics of various heating methods are illustrated in Figure 2. The general relationships of reactor type and heating method to operation simplicity and high heating rates are also shown in Figure 2. For example, a rotary kiln system with indirect heating via a circulating solid medium would be expected to have excellent heat-transfer characteristics but severe solids handling and separation operational problems.

Process variables

The key reactor variables with regard to manipulating product yields and composition are temperature, residence time/heating rate and residue feed conditions. Unfortunately, very little quantitative information has been published on the variable relationships.

A key reactor control variable is the temperature of pyrolysis. The decomposition of the organic material begins at about 360 °F. Current processes under development operate

in the 500–3000 °F range. At high temperatures (3000 °F), the reactor products consist primarily of gas and slag phases. The gas consists of low-molecular-weight hydrocarbons and other gases such as hydrogen, carbon monoxide and carbon dioxide. The slag consists of a fused mass of solid residue. As the temperature is lowered, the gas phase becomes richer in higher molecular weight hydrocarbons and a liquid phase may also be present. The solid residue phase also becomes more heterogeneous at lower temperatures.

A batch reactor study using refuse from which glass and metal components had been removed reported the relation of temperature to product distribution (see Additional reading). The amount of gas increases with temperature while the amount of residue declines. The liquid fraction remains fairly constant over the temperature range studied. With regard to the gas phase composition, the major change with increasing temperature is a decrease in carbon dioxide and an increase in hydrogen. The gas heating value peaks at about 650 °C, roughly corresponding to the peak in the methane curve.

Residence times/heating rates are generally defined in terms of the time required to bring the residue particles to a uniformly desired temperature. Levels currently under investigation are generally less than one hour. A batch reactor (1 gram sample closed crucible) study has reported the effect of heating rate on the nature of the pyrolysis product (see Additional reading). Shredded newspaper was used as feed. The heating rate for the batch reactor was reported by the time required to heat the refuse to 800 °C (1500 °F). Gas yields increased sharply at high heating rates (low time to 800 °C) with corresponding decrease in residue. The hydrocarbon liquid phase seemed to peak at a heating rate corresponding to about 25 min, while the water phase fell off at the higher heating rates. The gas composition curves indicated that high heating rates corresponded to an increase in carbon monoxide and a decrease in carbon dioxide. The heating value curve reached a minimum at a heating rate corresponding to 40 min.

Pyrolysis reactors have been designed to handle a variety of refuse feed conditions. Thus some systems will accept raw municipal refuse while others may require some preprocessing such as size reduction or separation of different types of inorganic material. Conceptually, a system that is designed to handle a raw feed can also accept a preprocessed feed. Preprocessing decisions are sometimes dictated by inorganic product-utilization considerations but also have a direct effect on required reactor equipment such as feed and discharge devices. In general, a dried, finely shredded feed with solid inorganics removed is most desirable.

Typical process steps involved in preprocessing refuse are shown in Figure 3.

The processes

Table 2 lists 24 pyrolysis projects in progress or completed. The processes are grouped by reactor type where possible (all other processes are lumped into the "other" category that includes process work that is inadequately described in the literature (some under the guise of "proprietary information"), or is strictly research scale in nature (batch reactors, subcomponent and systems studies). All of the commercial status processes listed are in the design, construction or startup phase. A classification of the various pyrolysis systems according to heating method, temperature and reactor type is given in Table 3. There is no column for slagging-temperature indirect-heating systems since direct heating is the only practical way of achieving the high temperatures (>2200 °F) required for slagging.

TABLE 2

Status of pyrolysis projects

Process	Heating method		Product distribution			Feed conditions			Reactor Temp. (°F)	Status			
			Solid (Btu/lb)	Liquid (Btu/lb)	Gas (Btu/ft ³)	Raw	Size reduction	Separation		Research	Pilot plant (tpd)	Commercial (tpd)	
	Direct	Indirect											
Shaft-vertical													
Union Carbide	•				300	•			3000			5	200
Garrett		•	9700	10 500	550		•	•	900			4	200
Torrax Systems, Inc.	•				150	•			3000			75	
Urban Research and Development Corp.	•				150	•			2600			120	
Ga. Tech.	•		10 000	13 000	200		•		750			25	
Battelle	•				170		•		1800			2	
Shaft-horizontal													
Kemp Corp.		•	•	•	•		•		1100			5	
Barber-Colman		•			500		•	•	1200			1	
Rotary kiln													
Rust Engineering		•			450				1250				260
Monsanto	•		2500		130		•		1800			35	1000
Devco	•		•		•		•	•	1000			120	1500
Pan American Resources, Inc.		•					•		2000	•			
Fluidized bed													
W. Virginia Univ.		•			450		•	•	1400	•			
Coors	•				150		•	•	1400			1	
A.D. Little		•			•		•	•		•			
Others													
Battelle	•								1800	•			
Hercules			•							•			
Bureau of Mines	•				500		•	•	1800	•			
N.Y. University	•								1700	•			
Univ. of Southern California		•								•			
Anti-Pollution Systems, Inc.										•			
Univ. Calif	•									•			
Wallace-Atkins	•		3000	16 000	500				1600	•			
Resource Sciences	•						•		1800			2	

TABLE 3
Process classifications

Reactor type	Direct heating		Indirect heating (nonslagging)	
	Nonslagging	Slagging	Wall transfer	Circulating medium
Shaft-vertical	Ga. Tech. Battelle	URDC Torrax Union Carbide		Garrett
Shaft-horizon- tal			Kemp	Barber- Colman
Rotary kiln	Monsanto Devco		Rust Pan Am. Res.	
Fluidized bed	Coors			West Va. Univ. A. D. Little

A description of selected processes from Table 3 follows (see Additional reading for further information). The Garrett Research and Development Co. (central research organization for the Occidental Petroleum Corporation) has modified a coal conversion process to convert municipal refuse to synthetic fuel oil. A 200 ton/day demonstration plant is being built for San Diego County, Calif. The process involves extensive preparation, consisting of the following steps:

- primary shredding of the raw refuse to approximately 2 in.
- air classification to remove most of the inorganics
- drying to about 3% moisture
- screening of the dry material to further reduce the inorganic content (less than 4% by weight)
- recovery of magnetic metals and glass
- secondary shredding of the organics to about 28 mesh.

The organic material is then fed to a vertical shaft pyrolysis reactor at a reactor temperature of about 900 °F yielding products consisting of char, oil, gas, and water phases. An indirect heating method is used. Under optimum liquefaction conditions, oil yields of about 40% by weight are obtained. The gas and part of the char is used on-site for process heat.

The Union Carbide Corporation has developed a slagging temperature pyrolysis system, called the Purox System, which utilizes nearly pure oxygen for the combustion of the pyrolysis char (see *ES&T*, May 1975, pp 423-427). The major advantage of using pure oxygen is the fact that the pyrolysis gas is virtually free of nitrogen. The heating value of the pyrolysis gas is still only about 300 Btu/scf compared to 1000 Btu/scf for natural gas. The primary combustible components of the pyrolysis are hydrogen and carbon monoxide. Water shift reaction, carbon dioxide removal, and methanation could be used, if desired, to convert this gas to natural-gas-quality methane. On-site production of the oxygen for the Purox process is estimated to require approximately one-third of the energy available in the pyrolysis gas.

The Barber-Colman process reactor is a closed horizontal shaft with a circulating molten lead bed as the heat transfer medium. The refuse is first fed to a metal detector where large chunks greater than six inches are removed. The remaining material is then shredded to about two inches before being fed to the reactor via an air lock. The pilot plant reactor has a capacity of about 1500 lb/day and is 6-ft long, with a rectangular cross section of 10-in. depth and 18-in. width.

The refuse "floats" on the molten lead surface that is circulated via a gas lift pump. The lead bath is heated from the

top by standard radiant tube burners located in the vapor space. The refuse is pyrolyzed from the lead surface at a temperature of about 1200 °F, producing a gas with a target heating value of about 500-700 Btu/scf. About one-fourth of the gas is used in the "gas lift" system; the remainder of the gas would be available for sale.

Some material will dissolve/settle in the lead bath and will have to be removed periodically by batch processing. Thus, at desirable intervals, a portion of the lead bath must be withdrawn and reclaimed and clean lead must be added to the reactor. Inert materials that remain on the surface are removed by means of a mechanical rake device at the opposite end of the reactor from the refuse feed part. Some low-pressure steam is generated in the process.

The Monsanto "Landgard" process (see *ES&T*, February 1975, pp 98-99) has been tailored to meet the needs of the city of Baltimore where a 1000 ton/day plant has been built. Shredded waste four inches in size is conveyed to a storage system from which it is continuously fed into a refractory-lined rotary kiln. A fuel (oil) and air stream are fed into the opposite end of the kiln. Countercurrent flows of gases and solids expose the refuse feed to progressively higher temperatures, 1800 °F maximum, as it passes through the kiln, so that first drying and then pyrolysis occurs. Hot residue is discharged from the kiln into a water-filled quench tank. A conveyor then elevates the residue into a flotation separator. Light material floats off as a carbon-char slurry, which is thickened and filtered to remove the water, then conveyed to a storage pile prior to truck transport from the site.

Heavy material is conveyed from the bottom of the flotation separator to a magnetic separator for removal of ferrous materials. Recovered metals are deposited either in a storage area, or directly into a railroad car or truck. The balance of the heavy material, now called a glassy aggregate, passes through screening equipment and is then stored on-site. This glassy aggregate can be used in building asphalt roads.

Pyrolysis gases are drawn from the kiln into a refractory-lined afterburner, where they are mixed with air and burned. The afterburner prevents discharge of combustible gases to the atmosphere and subjects the gases to temperatures high enough for destruction of odors.

Hot combustion gases from the gas purifier pass through water tube boilers, where heat is exchanged to produce steam. The steam will be used for heating and air conditioning of buildings in downtown Baltimore.

Exit gases from the boilers are further cooled and cleaned of particulate matter as they pass through a water spray scrubbing tower. Scrubbed gases then enter an induced draft fan that moves the gases through the entire system. To suppress formation of a steam plume, the gases are passed through a dehumidifier in which part of the water is removed and recycled, and then the gases are discharged to the atmosphere.

Normally, all water leaving the system is carried out with the residue, or evaporated from the scrubber. All process water is cleaned and recycled.

Research on combustion and pyrolysis in fluidized beds at West Virginia University has led to a proposal for a two-bed system for the pyrolysis of refuse. The inert bed material (sand) would be circulated between the separate combustion and pyrolysis beds, carrying combustion heat to the pyrolysis bed and pyrolysis char to the combustion bed. Since air is excluded from the pyrolysis bed, the pyrolysis gas produced is relatively free of undesirable nitrogen. Such gas, with a heating value between 400-500 Btu/scf, is probably directly

marketable to certain utility or industrial customers, and it also has the potential to be upgraded to pipeline quality methane. Temperatures of approximately 1800 °F in the combustion bed and 1400 °F in the pyrolysis bed have been recommended. A portion of the pyrolysis gas is cleaned, probably after cooling, and recirculated by blowers to be used as the fluidizing gas in the pyrolysis chamber. Preheated air for combustion of the char is used to fluidize the combustion bed.

Pyrolysis alternatives

Because the field of refuse pyrolysis is relatively new, it is very difficult to make definitive statements regarding the desirability of various systems. In particular, there is the possibility that some process now at the conceptual or experimental stage may become, in the future, clearly preferable to the systems that have presently been demonstrated. On the other hand, some process that appears to be very promising at the conceptual or experimental stage may become technically or economically infeasible when construction of a commercial plant is attempted. Since at least five commercial plants for pyrolysis of refuse are currently under construction, it can be expected that some of the data necessary for informed decision-making will become available within the next few years. These five plants represent only four types of processes, whereas Table 3, for example, contains sixteen possible (but not necessarily feasible) combinations of reactor types and heating conditions, with example processes listed for nine of these combinations. Thus, there are many types of processes that may be feasible, but for which operating data may not be available for some time.

Anyone faced with making an immediate choice of a pyrolysis process for some commercial application would surely be very interested in data from successful pilot plant operations. Table 2 shows at a glance that the largest scale pilot operations have been limited to two types of processes: vertical shaft and rotary kiln, both with direct heating. More limited scale pilot plants have demonstrated vertical and horizontal shafts with indirect heating and a fluidized bed. Obviously the data from the larger scale pilot plants can be extrapolated more reliably to commercial plant operation.

The relative economics of the various alternatives will depend greatly on the local markets for various fuels and/or reclaimed materials, as well as on the processes considered. Economic comparison for selected pyrolysis systems have been published. Net amortized cost estimates generally fall in the range of \$3–10/ton of refuse.

The fuel product from the processes that have been tested in the four largest pilot plants (those greater than 35 tons per day) is a low heating value gas containing much nitrogen, since these processes use air for the oxygen source in direct heating. It seems unlikely that it will ever be economical to transport this gas any significant distance, but it is usable in boilers located near the source. In the high-temperature vertical-shaft processes (Urban Research and Development Corp. and Torrax Systems, Inc.) no preprocessing is required for the reactor, but it could be added, if justified, by markets for the byproducts. Since some preprocessing is required for the rotary kiln processes (Monsanto and Devco), some byproduct reclamation may be included at small additional cost. The Union Carbide process is basically similar to the other high-temperature vertical-shaft processes, but the use of pure oxygen improves the quality of the fuel gas. The quality of the raw Union Carbide gas could still not justify transportation very far, but it could be upgraded to methane by known

chemical procedures if desired. Also, the very small amount of nitrogen in the Union Carbide gas minimizes one of the potential air pollution problems of the other direct heat processes. A disadvantage of the Union Carbide process is the hazard associated with separation and use of pure oxygen.

Processes using indirect heating also avoid the problems of nitrogen in the fuel gas (Kemp, Barber-Colman, Rust, West Virginia University, A. D. Little). This lack of nitrogen, along with the moderate temperatures used in these processes, give fuel gases with improved heating value, as well as potential for methanation. The still lower temperature processes concentrate on production of liquid fuel (Garrett) or char (Georgia Tech). All of these processes require preprocessing of refuse and are quite compatible with byproduct reclamation.

Again, it should be emphasized that the local markets for various forms of fuel and for various byproducts can be expected to be the controlling factors in economic comparisons.

Additional reading

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CURRENT RESEARCH

Efficiency of Membrane and Nuclepore Filters for Submicrometer Aerosols

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■ The efficiency of several commonly used membrane and Nuclepore filters has been measured using monodisperse aerosols and a new electrical aerosol detector. Particles in the 0.03- and 1- μm diameter range were used and the filter pressure drop was varied between 1 and 30 cm Hg. The filters tested include Teflon membrane filters of 0.5-, 1.0-, 5.0-, and 10.0- μm diameter pores and Nuclepore filters of 0.6-, 1.0-, 3.0-, 5.0-, and 8.0- μm pores. The minimum filter efficiency ranged from a low of 62% for the 10- μm Teflon membrane filter to a high of greater than 99.99% for the 0.5- and 1.0- μm Teflon filters. For the Nuclepore filters, the minimum filter efficiency ranged from a low of zero for the 8- μm filter to a high of 80% for the 0.6- μm filter. In general, the membrane filter was considerably more efficient than a Nuclepore filter of the same or a comparable pore size. The results suggest that the classical filtration mechanisms of interception, impaction, and diffusion are operative in these filters.

We report here on a new experimental technique for measuring the efficiency of filters. The technique, based on the use of monodisperse aerosols and a new electrical aerosol detector, provides a simple and convenient means for measuring filter efficiency over a wide range of particle sizes. We describe here its use in studying membrane and Nuclepore filters and report on the experimental results.

The technique described in this paper is similar to the conventional "DOP Test", which has been used extensively for testing filters, particularly for testing high performance, absolute filters. In the conventional DOP test (1), a monodisperse aerosol of DOP (dioctyl phthalate), usually 0.3 μm in diameter, is generated. The aerosol penetration through the filter is then measured with a light-scattering photometer. Since small particles below about 0.2 μm in diameter do not scatter sufficient light to be detected by the photometer, the method is limited to large particles in the light-scattering range only. In the present technique, monodisperse DOP aerosols are also used. However, the aerosol penetration is measured with an electrical aerosol detector that has a considerably wider particle size range than the photometer. In addition, with the new monodisperse aerosol generator used, the size of the aerosol can be changed easily and quickly, thus enabling the filter efficiency to be measured over a broad range of experimental conditions.

One of the principal objectives of this investigation is to measure the efficiency of membrane and Nuclepore filters as a function of particle size. Previous filter efficiency measurements, such as those reported by Lockhart et al. (2), were generally limited to particles of a single size, usually 0.3 μm in diameter. Data on the size dependence of filter efficiency is important in view of the great variety of aerosols these filters are used to collect. In addition, we wish to measure the filter efficiency under conditions of high filter

pressure drops. In these experiments, the filter pressure drop was varied between 1 and 30 cm Hg. Such high filter pressure drops are frequently encountered in actual practice because of the high flow resistance of the filter media and the need to obtain high sampling flow rates in order to increase the amount of aerosol material collected for analysis.

The efficiency of a filter may be defined as the fraction of particles retained by the filter following the passage of the fluid through the filter. If V_2 is the volume of gas passing through the filter, and N_1 and N_2 are the number of particles—assumed monodisperse—incident upon and penetrating through the filter, then the filter efficiency is given by

$$\eta = 1 - P \quad (1)$$

where P is the aerosol penetration defined by

$$P = \frac{N_2}{N_1} = \frac{N_2/V_2}{N_1/V_2} = \frac{C_{2,2}}{C_{1,2}} \quad (2)$$

To allow for the possibility that the volume of gas may not remain constant across the filter due to high filter pressure drop, we have let V_2 be the gas volume referred to conditions downstream of the filter. Consequently, in Equation 2, $C_{2,2} = N_2/V_2$ is the downstream particle concentration and $C_{1,2} = N_1/V_2$ is a reference particle concentration based on the upstream particle number, N_1 , and the downstream gas volume, V_2 . If the pressure drop across the filter is small and the volume expansion of the gas negligible, then $C_{1,2}$ becomes the same as the upstream particle concentration. Under these conditions, the aerosol penetration can be defined as the ratio of downstream and upstream particle concentrations, as Equation 2 shows. It is clear from this analysis, to define the aerosol penetration as the ratio of downstream and upstream particle concentrations as is usually done, it is necessary that the filter pressure drop be small. For high filter pressure drops and non-negligible expansion of the gas, the correct definition based on Equation 2 must be used.

Experimental

Figure 1 is a schematic diagram of the filter testing apparatus used. The filter to be tested is placed in a filter holder and the particle concentration, $C_{2,2}$, downstream of the filter is measured with an electrical aerosol detector. Parallel to the filter holder is an expansion valve that can be used to expand the aerosol to a low pressure with a minimum of particle loss. By our measuring the particle concentration downstream of the expansion valve and correcting for the loss of particles in the expansion system, the reference particle concentration, $C_{1,2}$, can be determined. The aerosol penetration and filter efficiency can then be calculated by means of Equations 1 and 2.

To measure the filter efficiency, pinch clamp 2 is first closed and pinch clamp 1 opened to allow the flow to pass

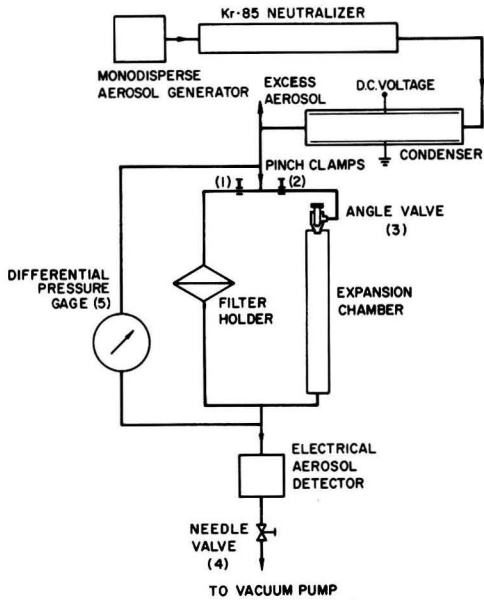


Figure 1. Experimental system for measuring filter efficiencies

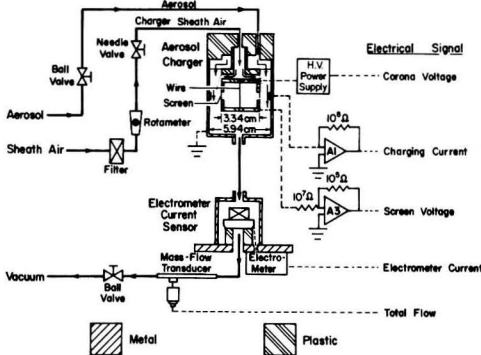


Figure 2. Schematic diagram of electrical aerosol detector

through the filter. The needle valve 4 is then adjusted until flow through the filter produces the required pressure drop, as indicated by the differential pressure gage 5. The aerosol is then applied to the filter inlet, and the downstream particle concentration, $C_{2,2}$ measured with the electrical detector. Next, pinch clamp 1 is closed and pinch clamp 2 opened to allow the flow to pass through valve 3 and the expansion chamber. Valve 3 is then adjusted until the same flow and pressure drop are obtained. The aerosol concentration is similarly measured. If $C_{3,2}$ is the aerosol concentration downstream of the expansion valve, then the measurement described above will give the ratio

$$P_1 = \frac{C_{2,2}}{C_{3,2}} = \frac{C_{2,2}/C_{1,2}}{C_{3,2}/C_{1,2}} = \frac{P}{P_2} \quad (3)$$

from which we have

$$P = P_1 P_2 \quad (4)$$

In the above equations, P denotes the aerosol penetration through the filter, P_2 , the penetration through the expan-

sion valve, and P_1 , the relative penetration through the filter with respect to that through the expansion valve.

Aerosol Generation and Neutralization. The aerosols used in these experiments are monodisperse aerosols of DOP generated by the atomization-condensation technique previously described by Liu and Lee (3). The technique involves first producing a polydisperse aerosol by atomization using a syringe-pump atomizer and a DOP-alcohol solution. The polydisperse DOP aerosol is then made uniform by vaporization and condensation. The generated aerosol is moderately monodisperse with geometrical standard deviations of 1.2-1.4. The particle size can be varied between 0.03- and 1.3- μm diameter by changing the solution concentration. The generator output is very stable with output concentration varying by less than $\pm 2\frac{1}{2}\%$ over a period of 1 h or more.

Since aerosols generated by the above technique are electrically charged, they must be neutralized in order to avoid unwanted electrostatic effects. This was accomplished by passing the aerosol through a Krypton 85 "neutralizer". In the Kr-85 neutralizer, the aerosol is exposed to the ionizing β radiation from a 2-mCi radioactive Kr-85 source and the particles are brought to a state of charge equilibrium with the bipolar ions. More details concerning the Kr-85 neutralizer and the charge equilibrating process are given in References 4 and 5.

Although the aerosol emerging from the Kr-85 neutralizer is not completely neutral, the residual charge on the particles is small. Further, since a substantial fraction of the particles are uncharged, it is possible to obtain a truly neutral aerosol by further precipitating the charged particles from the aerosol stream. This can be accomplished by applying a high voltage (several thousand volts) on the condenser shown in Figure 1. In a few cases this was done and the filter efficiency was measured with this neutral aerosol and compared with that measured when the charge equilibrated aerosol from the Kr-85 neutralizer was used. No difference was found. It was concluded that the filter efficiency could be measured with the charge equilibrated aerosol from the Kr-85 neutralizer without further precipitating the remaining charged particles from the aerosol stream.

The Electrical Aerosol Detector. Figure 2 is a schematic diagram of the electrical aerosol detector used. The detector is comprised of a diffusion charger, which places a unipolar, positive charge on the particles, and a Faraday cup which collects the charged particles by filtration and measures the collected particle charge by a sensitive electrometer. A flow transducer in the detector enables the aerosol flow rate to be measured. The device is a simplified version of the commercial electrical aerosol analyzer (Model 3030, Thermo-Systems, Inc., 2500 N. Cleveland Ave., St. Paul, Minn. 55113) previously described (6). In the present case, the mobility analyzer tube, which provides the size discriminating capability for the electrical aerosol analyzer, is eliminated. The device is thus used as a sensor for aerosol concentration only.

The electrical aerosol detector is capable of measuring the relative aerosol concentrations accurately. This is due to the fact that the output of the electrometer is proportional to the rate of charge collection by the Faraday cup. Thus, when all operating parameters that affect the particle charge, such as the charger pressure and flow, and ionizing voltage, and current, are kept fixed, particles will emerge from the charger carrying a specific number of charges, and the rate of charge collection by the Faraday cup will be proportional to the concentration of particles in the aerosol stream. This is true both for monodisperse aerosols of a given particle size and for polydisperse aerosols of a constant size distribution. The measurement accu-

racy of the instrument for relative aerosol concentration is determined only by the linearity of the electrometer, which is very good owing to the use of negative feedback and high amplifier gain.

The Filter Holder. When measuring filter efficiency with the above apparatus, filters and filter holders of two different sizes had to be used because of the different flow characteristics of the filters and the flow requirement of the electrical detector. The total flow passing through the filter and the electrical detector was varied in these experiments between 1.5 and 35 standard liters per minute. To produce the required pressure drop at these flows, a 25-mm diameter or a 47-mm diameter filter was used. The small filter was used when the filter pore size was large and the flow resistance low, while the larger filter was used when the filter pore size was small and the flow resistance high.

The filter holders used in these experiments were standard commercial filter holders purchased from the Millipore Corp. (Bedford, Mass. 01730). The specific filter holders used had 120-mesh stainless steel screens placed on the downstream side of the filter to provide the needed mechanical support. The collection efficiency of these filter screens for aerosol particles was measured in a few cases and found to be essentially zero. Thus, the measured filter efficiency can be considered as that due to the filter medium alone.

The Expansion System. To measure the reference particle concentration, $C_{1,2}$, with the electrical detector, it was necessary to expand the aerosol from the ambient atmospheric pressure to a low pressure, which was varied between 1- and 30-cm Hg below the ambient. To minimize particle loss during the expansion, an angle valve with a 5.6-mm diameter orifice was used as shown in Figure 1 to produce the required pressure drop. The aerosol jet emerging from the valve orifice was directed into a cylindrical chamber, 3 cm in diameter by 35 cm long, where the particles were slowed down by air resistance. This minimized the particle loss due to impaction. However, some losses remained that must be accounted for experimentally in the filter efficiency measurements.

To determine the particle loss in the expansion system, we utilized the fact that the charged equilibrated aerosol from the Kr-85 neutralizer also carried a net overall charge. This charge, which was negative, appeared as a consequence of the greater mobility of the negative ions and the higher rate of combination between the negative ions and aerosol particles. By sampling this negatively charged aerosol from the Kr-85 neutralizer upstream and downstream of the expansion system with the Faraday cup and measuring the corresponding current with the electrometer, the particle loss can be determined. It should be noted that this negative particle charge was very low, being on the order of a fraction of an elementary unit per particle for a 1- μ m diameter aerosol. Its effect on particle motion during the expansion process was totally negligible. This charge is used here merely as a "tag" for determining the relative aerosol concentrations.

In performing the above measurement with the charged equilibrated aerosol, we found that the ions contained in the aerosol stream would interfere with the measurement. Although positive and negative ions were produced in equal numbers in the Kr-85 neutralizer, the greater mobility of the negative ions caused them to more readily diffuse to the neutralizer chamber walls than the positive ions. This resulted in an ion cloud having a positive space charge. To avoid sampling this positively charged ion cloud in the Faraday cup, the aerosol stream was first passed through a condenser as shown in Figure 1, where a low applied voltage (about 5 V) on the condenser caused the ions to be pre-

cipitated while allowing both the charged and uncharged aerosol particles to pass through.

The performance of the expansion system as determined by the procedure described above is shown in Figure 3. It is seen that aerosols of up to 0.49- μ m diameter can be expanded by this system at up to 10-cm Hg pressure drop with less than 10% loss. Larger particles and high pressure drops resulted in greater losses. However, these losses can be taken into account in the filter efficiency measurements.

Effect of Ions. During the course of the experiments, a question arose as to whether the positively charged ion cloud, carried by the aerosol stream into the filter holder, could cause the filter medium to become positively charged, thus causing the aerosol particles, which had a small negative charge, to be collected with enhanced efficiency. A few experiments were consequently performed in which a low voltage (about 5 V) was applied to the condenser shown in Figure 1 to remove the ions from the aerosol stream. By measuring the filter efficiency with and without this applied voltage on the condenser, the charge effect due to the ions could be determined. Again, no difference was found. It was concluded that the presence of

Table I. Pertinent Filter Parameters

Filter	Mfg code	Nominal pore diameter, μ m	Pore density, pores/cm ²	Porosity, %	Thickness, μ m
Nuclepore	N060	0.6	3×10^7	8.4	10
	N100	1	2×10^7	15.6	10
	N300	3	2×10^6	14.1	10
	N500	5	4×10^5	7.8	10
	N800	8	1×10^5	5	10
Fluoropore	FH	0.5	—	85	125-150
	FA	1	—	85	125-150
Mitex	LS	5	—	60	125-150
	LC	10	—	68	125-150

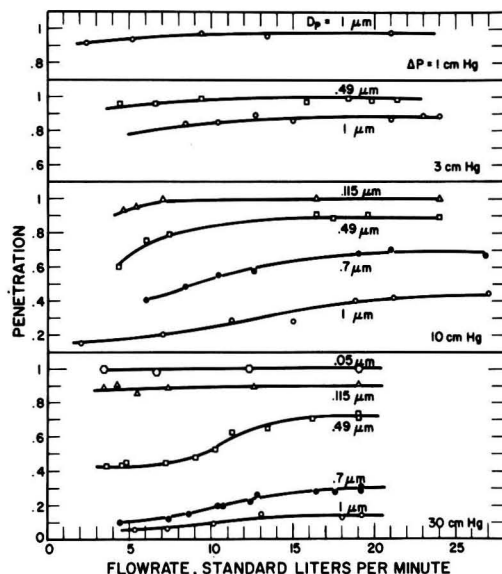


Figure 3. Penetration of aerosols through expansion system

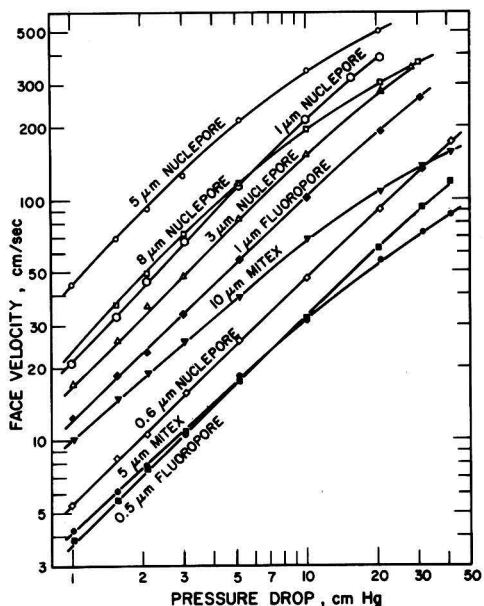


Figure 4. Experimental relationship between inlet face velocity and filter pressure drop

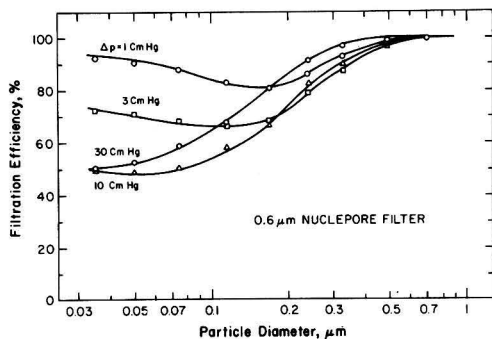


Figure 5. Efficiencies of 0.6- μm Nucleopore filter

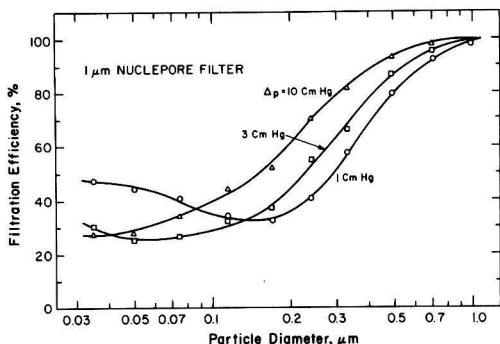


Figure 6. Efficiencies of 1.0- μm Nucleopore filter

the positively charged ion cloud in the aerosol stream did not significantly affect the measurement results.

Results

A total of nine filters were tested with the technique just described at pressure drops of 1-, 3-, 10-, and 30-cm Hg. The filters tested include the polycarbonate filters of 0.6-, 1.0-, 3.0-, 5.0-, and 8.0- μm pores manufactured by the Nucleopore Corp. (7035 Commerce Circle, Pleasanton, Calif. 94566) and the Teflon filters manufactured by the Millipore Corp. The Millipore filters are marketed under the tradenames of Fluoropore filters (0.5- and 1.0- μm pores) and Mitex filters (5.0- and 10- μm pores). The pertinent filter parameters, taken from manufacturer's literature, are summarized in Table I. The relationship between filter pressure drop and inlet face velocity for these filters has also been determined experimentally. The result is shown in Figure 4.

In performing the filter efficiency measurements, we had chosen to set the filter pressure drop, rather than the inlet face velocity, to various preselected values for the following reason. At a given pressure drop, the velocity of the fluid through the individual filter pores, and hence the efficiency, is fixed. However, at a given inlet face velocity, the fluid velocity in the pores will depend on the number of pores in the filter. Thus, two filters with the same pore size but different pore densities, will have the same efficiency when tested under the same pressure drop conditions, but will give different results when tested at the same inlet face velocity. Thus, more reproducible results can be expected when pressure drop is chosen as the parameter to be varied, since the results will then be independent of the actual pore densities in the filter. This conclusion has been confirmed by our experimental results.

The results for the Nucleopore filters and those for the 5.0- and 10.0- μm Mitex filters are shown in Figures 5 through 9. The results for the 0.5- and 1.0- μm Fluoropore filters are not shown graphically, since for these filters, the efficiency was greater than 99.99% over the entire operating range. These results indicate that the membrane filters are considerably more efficient than Nucleopore filters of the same or a comparable pore size. For the Teflon membrane filters, for instance, the minimum efficiencies range from a low of 62% for the 10- μm Mitex filter to a high of >99.99% for the 0.5- and 1.0- μm Fluoropore filters. In comparison, the Nucleopore filters have minimum efficiencies that range from essentially zero for the 8- μm pore filter to a high of only 80% for the 0.6- μm filter. It should be noted that all

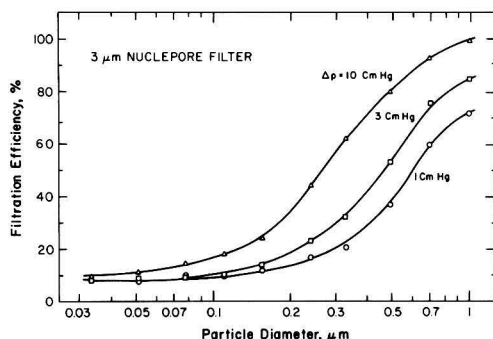


Figure 7. Efficiencies of 3.0- μm Nucleopore filter

filter efficiencies referred to here were measured with a clear filter—i.e., the measurements were made prior to significant clogging of the filter had occurred.

A detailed examination of the filter in the electron microscope shows that there is a considerable difference among the filters in terms of their physical structure—a difference that can account for the different filtration characteristics observed. The Nuclepore filter (Figure 10) has pores that are essentially straight, near circular holes. The Fluoropore filter (Figure 11) has a fibrous structure with the finest fibers measuring approximately $0.2 \mu\text{m}$ in diameter. The structure of the Mitex filter (Figure 12) differs from both the Nuclepore and Fluoropore filters. The Mitex filter is made up of two distinct layers, the structure of which is quite irregular. The path of the fluid in the filter must be quite tortuous and the greater collection efficiency of the filter in comparison with the Nuclepore filter can most likely be attributed to this fact.

According to the classical theory of aerosol filtration, particles are captured in a filter by the mechanisms of interception, impaction, and diffusion. When capture by interception and impaction is important, the filter efficiency will increase with increasing particle size and increasing fluid velocity or filter pressure drop. When capture by diffusion is important, the efficiency will decrease with increasing particle size and pressure drop. The combination of these mechanisms will lead to the existence of a particle size at which the penetration is a maximum and the filter efficiency, a minimum. Below the most penetrating size, particle collection is primarily by diffusion; above the most penetrating size, interception and inertial impaction are the predominant particle-collecting mechanisms. Further, the most penetrating particle size should decrease with increasing filter pressure drop due to the increased particle inertia and the decreased particle residence time and diffusion in the filter medium.

The behavior of the 0.6- and 1.0- μm Nuclepore filters shown in Figures 5 and 6 is seen to be consistent with the above behavior predicted according to the classical theory based on the mechanisms of interception, impaction, and diffusion. In particular, the existence of a most penetrating particle size is clearly evident from these curves. Further, the most penetrating size is seen to decrease with increasing filter pressure drop. It is of interest to note that for both filters, the filter efficiency approaches 100% as the particle size approaches the filter pore size, as one would expect.

In contrast to the above, the data shown in Figures 7

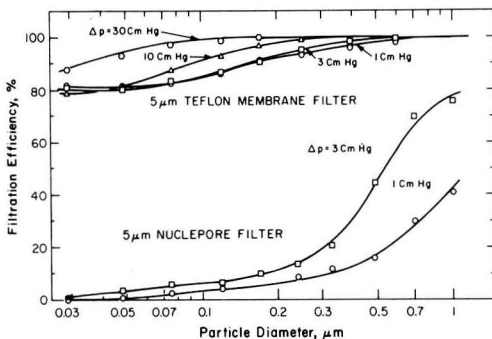


Figure 8. Efficiencies of 5.0- μm Nuclepore and 5.0- μm Teflon membrane (Mitex) filter

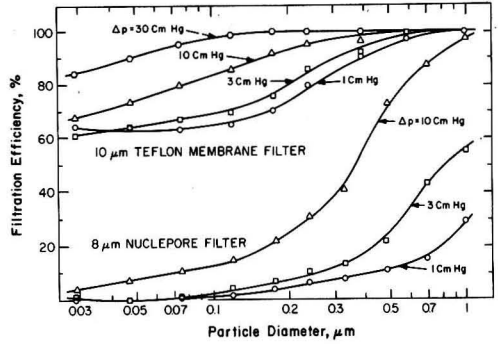


Figure 9. Efficiencies of 8.0- μm Nuclepore and 10.0- μm Teflon membrane (Mitex) filter

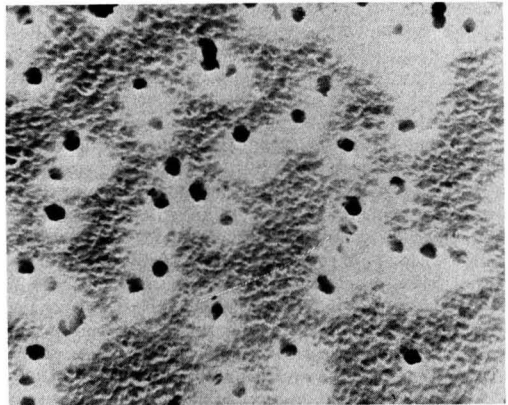


Figure 10. Electron microscope picture of 3- μm Nuclepore filter

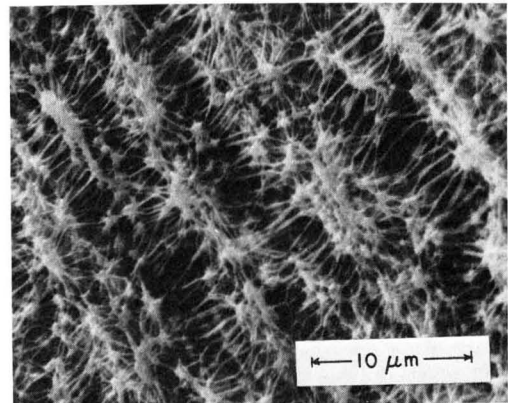


Figure 11. Electron microscope picture of 0.5- μm Fluoropore filter

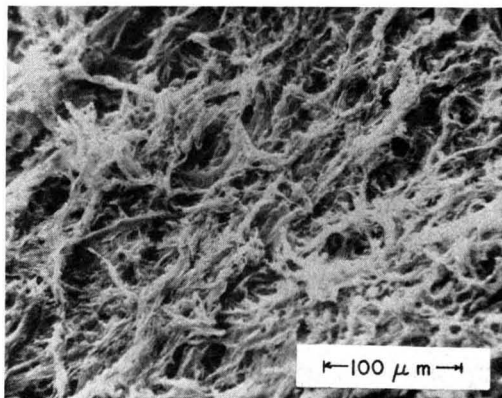
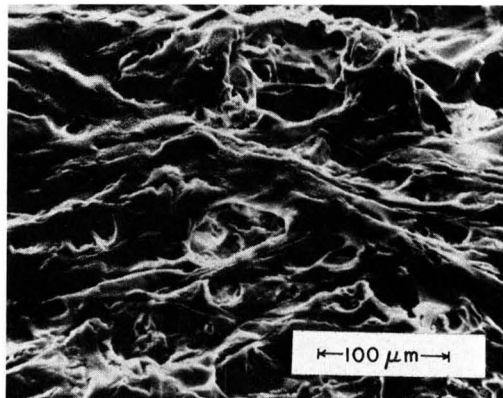


Figure 12. Electron microscope picture of 5- μm Mitex filter showing (a) its outer surface structure and (b) its inner surface structure

through 9 show no clearly defined particles sizes at which the penetration is maximum. For these filters, the efficiency generally tends to increase with increasing particle size and increasing filter pressure drop. This suggests that under the conditions of these experiments, the filtration mechanism in these filters is mainly interception and impaction, with diffusion having only a minor and insignificant effect.

A comprehensive theory of aerosol filtration for Nuclepore filters has been developed by Spurny and coworkers (7). Detailed tables have been prepared by Spurny and Lodge (8), giving the theoretical filter efficiency as a function of particle size and velocity of flow for different filter pore sizes and different thicknesses of the filter media. Unfortunately, the conditions used by Spurny and Lodge in the preparation of the filter efficiency tables were not the same as those encountered in the present experiments, and no detailed comparisons of the data with the theory can be made without extensive further calculations. Such calculations would be beyond the scope of the present paper.

In the theory of Spurny et al., as in all other filtration theories developed up to the present time, the gas flow is assumed incompressible. At the higher pressure drops encountered in the present experiments, the gas undergoes substantial expansion in volume and the incompressibility assumption is no longer valid. Further theoretical development is needed to obtain a theory that is applicable to the

filtration of aerosol particles for conditions of high pressure drops and for compressible gas flow.

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Organic Photochemistry

Simulated Atmospheric Photodecomposition Rates of Methylene Chloride, 1,1,1-Trichloroethane, Trichloroethylene, Tetrachloroethylene, and Other Compounds

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■ To estimate the decomposition rates of chloro compounds in the atmosphere, we carried out laboratory studies on the photolysis rates of the four title compounds, six other chlorohydrocarbons, and 23 other organic compounds under simulated atmospheric conditions. In the presence of nitric oxide, vinylidene chloride, *cis*- and *trans*-dichloroethylene, trichloroethylene, and vinyl chloride decomposed at moderate rates (estimated half-lives of 5–12 h under bright sunlight) when compared with a series of standard hydrocarbons. Chlorobenzene, tetrachloroethylene, and 1,1,2-trichloroethane decomposed slowly (estimated half-lives 20–40 h). Methylene chloride and 1,1,1-trichloroethane did not decompose (half-lives >250 and >>1700 h respectively). The photodecomposition rates of several chloro compounds were determined in mixtures with other organic compounds and also in the presence of nitrogen dioxide, ozone, chloral, acetaldehyde, chlorine, and phosgene. The presence of hydrocarbons reduced the decomposition rates of several chloroethylenes.

The fate and effect of chloro methanes, ethanes, and ethylenes which may be discharged to the environment (2–7) are of interest from an ecological standpoint. In a previous paper (8) we showed that the major portions of several low-molecular-weight chlorohydrocarbons evaporated relatively rapidly from dilute aqueous solutions under simulated environmental conditions. We therefore undertook a study of the photodecomposition rates of several of these compounds, methylene chloride (CH_2Cl_2), 1,1,1-trichloroethane (CH_3CCl_3), trichloroethylene ($\text{CHCl}=\text{CCl}_2$), and tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$), which are important because of their current widespread use as solvents, and also of several other related chloro compounds under simulated atmospheric conditions.

A previous report indicated that CH_2Cl_2 , when irradiated under simulated atmospheric conditions, did not disappear at a significant rate (9). No specific data have been reported on the photodecomposition rates of CH_3CCl_3 under simulated atmospheric conditions. One report (10) indicated a half-life of several months for chlorine-substituted methanes and ethanes, while another report (11) stated that chlorinated saturated hydrocarbons were virtually unreactive. Considerably more work has been done on the behavior of $\text{CHCl}=\text{CCl}_2$ than on the other chlorinated compounds considered in this paper (11–17). In general, $\text{CHCl}=\text{CCl}_2$ decomposed at intermediate rates when compared with other common atmospheric contaminants; $\text{CCl}_2=\text{CCl}_2$ had a relatively low decomposition rate under simulated atmospheric conditions (11–13).

Changes in the decomposition rate of one organic compound in the presence of another have been reported (14, 16, 18, 19). Relatively little work has been reported on the effect of other compounds on the photodecomposition rates

of CH_2Cl_2 , CH_3CCl_3 , $\text{CHCl}=\text{CCl}_2$, and $\text{CCl}_2=\text{CCl}_2$ (9, 14, 16).

Experimental

Reactor and Analyses. The reactor (9.58 l.) was a water-jacketed Pyrex cylinder sealed with silicone rubber-gasketed quartz windows at each end. The reactor is shown in Figure 1 which will appear following this article in the microfilm edition of this journal. (See paragraph at end of paper about supplementary material.) The reactor temperature was maintained at $27 \pm 1^\circ\text{C}$. The ultraviolet light sources were two General Electric 275-W reflector sunlamps (20), each of which had a short wavelength cutoff of 290 nm. The ultraviolet light intensity was ~ 2.6 times that of natural sunlight at noon on a summer day in Freeport, Tex. The rates of disappearance of the organic compounds in the reactor were determined by flame ionization GC.

Materials. Ultrahigh purity air (synthetic, 20% O_2 , 80% N_2) from Matheson showed no impurities by GC. Nitric oxide (NO) and nitrogen dioxide (NO_2) from Matheson were used as received. Water, CH_2Cl_2 (uninhibited), CH_3CCl_3 (uninhibited), and $\text{CCl}_2=\text{CCl}_2$ were redistilled. $\text{CHCl}=\text{CCl}_2$ (Hi-Tri), which contained 20 ppm of diisopropyl amine, was used without purification. Other materials were either redistilled or shown to be free of impurities by GC. The ozone (O_3)–air mixtures were prepared as follows. A stream of air was passed into a flask in which was suspended a screen electrode. The electrode was charged by a small Tesla coil. The exit gas which contained a mixture of O_3 and air was collected in a 20-l. Saran plastic bag which then was used to fill the previously evacuated photochemical reactor. The O_3 concentration was determined iodometrically (21).

Example of a Typical Photolysis. After the reactor was evacuated to 0.2–0.5 mm for an hour or more, 47.9 μl of NO was added to the reactor through a silicone rubber septum to give a concentration of 5 ppm. While the reactor was still under vacuum, 94 μl of distilled water was added. Evaporation of the water with a heat gun from outside the reactor gave a calculated relative humidity of 35–40%. Air was then added from a Saran bag to the reactor until atmospheric pressure was reached. Finally, 0.34 μl of $\text{CHCl}=\text{CCl}_2$ was added to the reactor from a syringe to give a concentration of 10 ppm. All concentrations are expressed as a molar or gas volume basis. Gas samples were analyzed periodically by GC. The first samples analyzed, before the lamps were turned on, were used as standards to which subsequent samples were compared during the reaction.

All reactions were run at 35% relative humidity unless specified otherwise.

Results and Discussion

Table I shows a summary of the results of the photodecomposition rates, based on the time required for 50% disappearance of the compound, of a variety of chloro compounds, some standard hydrocarbons, and other materials. All data are from reactions run under the same conditions. The compounds are listed in order of increasing decomposition rate in the presence of NO.

¹ Environmental Sciences Research. ² Styrene Molding Polymers Research and Development. ³ Chemicals Processes Research. This is Part XIII of the series. For Part XII, see Reference 1.

Table I. Photodecomposition Rates of Chloro Compounds, Standard Hydrocarbons, and Other Materials under Simulated Atmospheric Conditions

Compound ^a	Time (h) for 50% disappearance of compound	
	With NO ^b	With NO ₂ ^c
CH ₃ CCl ₃	<i>d</i>	<i>e</i>
CH ₂ Cl ₂	<i>f</i>	<i>g</i>
<i>t</i> -Butyl alcohol	34.5 ^h	
Epichlorohydrin	16.0	
1,1,2-Trichloroethane	15.9 ⁱ	
1-Butene oxide (<i>c</i> -CH ₂ EtCH ₂ O)	15.9 ^j	15.2 ^k
Ethyl acetate (EtOAc)	14.6 ^l	
CCl ₂ =CCl ₂	14.2 ^m	8.3 ⁿ
Methyl ethyl ketone (MeCOEt)	9.8 ^o	
Nitromethane	9.2	
Chlorobenzene	8.7 ^p	
Cyclohexane (<i>c</i> -C ₆ H ₁₂)	6.9	6.5, 7.5 ^k
Toluene (PhMe)	6.8	
<i>n</i> -Butyl alcohol (<i>n</i> -BuOH)	6.5	
Ethyl benzene	5.0	
Trioxane	4.7	
Vinyl chloride (CH ₂ =CHCl)	4.3	
<i>s</i> -Butyl alcohol	4.0	
CHCl=CCl ₂	3.5	2.9
Methyl isobutyl ketone (MeCO <i>i</i> -Bu)	3.5	
Isobutyl alcohol (<i>i</i> -BuOH)	3.5	
Dioxane [<i>c</i> -O(C ₂ H ₄) ₂ O]	3.4	
1-Methoxy-2-propanol (MeOCH ₂ CHOHMe)	3.1	
<i>p</i> -Xylene ^q (<i>p</i> -Me ₂ C ₆ H ₄)	3.1	
<i>m</i> -Xylene ^q (<i>m</i> -Me ₂ C ₆ H ₄)	2.9	
<i>cis</i> -Dichloroethylene (<i>cis</i> -CHCl=CHCl)	3.0	3.0
<i>trans</i> -Dichloroethylene	2.9	2.8
Ethylene (CH ₂ =CH ₂)	2.9	2.5
Vinylidene chloride (CH ₂ =CCl ₂)	2.1	
Cyclohexene (<i>c</i> -C ₆ H ₁₀)	0.87	0.19 ^k
2,4,4-Trimethyl-1-pentene	0.60	
<i>trans</i> -2-Butene (<i>trans</i> -MeCH=CHMe)	0.30	0.17 ^k
N-Methylpyrrole	0.16	

^a All compounds at 10 ppm in air initially, unless specified otherwise. ^b All initial concentrations, 5 ppm. ^c All initial concentrations, 16.8 ppm, except as noted. ^d Reaction, <5%, in 23.5 h. ^e Reaction, <5%, in 8.0 h. With 50-ppm CH₃CCl₃ and 10-ppm NO₂: <5% reaction in 28 days. ^f Reaction, <5%, in 21.0 h. ^g Reaction, <5%, in 7.5 h. With 50-ppm CH₂Cl₂ and 10-ppm NO₂: <5% reaction in 4 days. Anomalous reactions were observed at longer times; these reactions are currently under study. ^h Extrapolated from 22% reaction in 15.2 h. ⁱ Extrapolated from 22% reaction in 7.0 h. ^j Extrapolated from 47% reaction in 14.9 h. ^k Initial NO₂ concentration, 5 ppm. ^l Extrapolated from 24% reaction in 7.0 h. ^m Extrapolated from 44% reaction in 12.5 h. ⁿ Extrapolated from 42% reaction in 7.0 h. ^o Extrapolated from 33% reaction in 6.5 h. ^p Extrapolated from 43% reaction in 7.5 h. ^q *p*-Me₂C₆H₄ and *m*-Me₂C₆H₄ measured simultaneously at initial concentrations of 2 and 8 ppm respectively.

Table II. Effect of Light Intensity on Photodecomposition Rates

Compound ^a	Relative light intensity	Time for 50% disappearance of compound	Relative reactivity
<i>trans</i> -MeCH=CHMe	1.00 ^b	11 min	1.00
	0.50	23	0.48
	0.25	40	0.26
CH ₂ =CH ₂	1.00 ^b	2.8 h	1.00
	0.50	5.2	0.52
	0.25	10.0	0.28
CHCl=CCl ₂	1.00 ^b	3.5 h	1.00
	0.50	6.3	0.56
	0.25	9.5	0.37

^a All reactions carried out with 10 ppm of the compound and 5-ppm NO. ^b Usual light intensity in this work.

Table III. Effect of Concentration on Photodecomposition Rates

Compound	Initial concentrations, ppm		Time for 50% disappearance of compound	Relative reactivity
	Compound	NO		
<i>trans</i> -MeCH=CHMe ^a	10	5	26 min	1.0
	20	10	22.5	1.2
	40	20	17	1.5
	100	50	13	2.0
CHCl=CCl ₂	10	5	3.5 h	1.0
	20	10	3.0	1.2
	40	20	1.5	2.3
	100	50	1.0	3.5
CCl ₂ =CCl ₂	10	5	11.2 ^b h	1.0
	40	20	7.0	1.6
	100	50	3.8	3.0

^a Reactions with *trans*-MeCH=CHMe carried out with 0.50 relative light intensity. ^b Extrapolated from 29% reaction in 6.5 h.

Table IV. Effect of CHCl=CCl₂:NO Ratio and Relative Humidity on Photodecomposition Rates of CHCl=CCl₂^a

Initial NO concentration, ppm	Relative humidity, %	Time, h, for 50% disappearance of CHCl=CCl ₂
0	~0	5.0
0	35	10.9 ^b
2.5	35	1.8
5	~0	2.0
5	35	2.1
5	70	3.0
10	35	2.5
20	35	2.5
40	35	2.5

^a All reactions carried out with 10 ppm of CHCl=CCl₂ initially. ^b Extrapolated from 32% reaction in 7.0 h.

Table V. Photodecomposition Rates of Chloro Compounds, Standard Hydrocarbons, and Other Materials in Combination with Other Organic Compounds Under Simulated Atmospheric Conditions
Time (h) for 50% disappearance of compound at top of column in the presence of other compound at left side of row^a

Compound	CH ₃ Cl ₃	CH ₂ Cl ₂	CHCl ₃	CH ₂ Cl ₂	CH ₃ Cl ₂	c-CH ₂ CH ₂ O	EtOAc	CCl ₂ =CCl ₂	MeCOEt	c-C ₆ H ₁₂	PhMe	n-BuOH	CH ₂ =CHCl	CHCl=CCl ₂	MeCO-t-Bu	t-BuOH	c-O(C ₂ H ₅) ₂ O	MeOCH ₂ CHOHMe	cis-CHCl=CHCl	CH ₂ =CH ₂	CH ₂ =CCl ₂	c-C ₆ H ₁₀	trans-MeCH=CHMe	MeOH	
CH ₂ Cl ₃	b									9.0 ^c				3.5							2.9				0.24
CH ₂ Cl ₂		d								6.8				7.0							4.0				0.26
c-CH ₂ CH ₂ O			15.9											6.1											
EtOAc				14.6										2.8											
CCl ₂ =CCl ₂					14.2					7.6 ^e				5.8											0.30
MeCOEt						9.8				6.9				8.7											
c-C ₆ H ₁₂		f									6.8		5.5		3.9					13.1					
PhMe												6.5		7.6											
n-BuOH										5.4		3.0	4.3	8.5							3.7				0.32
CH ₂ =CHCl										4.9	5.2			3.5	3.5	3.3	2.4	2.5			2.5				0.16
CHCl=CCl ₂										8.3				6.0											8.3 ^f
MeCO-t-Bu														10.5 ^k											
i-BuOH														7.8											
c-O(C ₂ H ₅) ₂ O														6.0											
MeOCH ₂ CHOHMe														5.4											
cis-CHCl=CHCl														5.0											
CH ₂ =CH ₂														4.8											
CH ₂ =CCl ₂														6.1											
c-C ₆ H ₁₀														8.3 ^q											
trans-MeCH=CHMe														7.0											
Methanol (MeOH)														6.8											
														4.3 ^p											
														6.1											
														3.2 ^r											
														4.1											
														3.0											
														2.9											
														3.4											
														3.1											
														2.5											
														2.1											
														0.82											
														0.73											
														0.37											
														0.37											
														0.30											

^a Initial concentrations for combination experiments: 10 ppm each of the two organic compounds and 10 ppm of NO. Initial concentrations for reactions with only one organic compound (data along the major diagonal): 10-ppm compound, 5-ppm NO (data from Table I). ^b <5% reaction in 23.5 h. ^c Extrapolated from 39% reaction in 7.0 h. ^d <5% reaction in 21.0 h. ^e Extrapolated from 43% reaction in 6.5 h. ^f 5% reaction in 7.0 h. ^g 13% reaction in 6.8 h. ^h 13% reaction in 16.9 h. ⁱ Extrapolated from 42% reaction in 7.0 h. ^j <5% reaction in 7.0 h. ^k Extrapolated from 32% reaction in 6.7 h. ^l 11% reaction in 5.8 h. ^m <5% reaction in 5.5 h. ⁿ <5% reaction in 2.0 h. ^o <5% reaction in 2.5 h. ^p Extrapolated from 34% reaction in 2.9 h. ^q Extrapolated from 30% reaction in 5.0 h. ^r Extrapolated from 31% reaction in 2.0 h.

Table VI. Effect of Organic Compound Ratio on Photodecomposition Rates of $\text{CHCl}=\text{CCl}_2$ and $c\text{-C}_6\text{H}_{12}$

Initial concentration, ppm		Ratio [$\text{CHCl}=\text{CCl}_2$] [$c\text{-C}_6\text{H}_{12}$]	Initial NO concentration, ppm	Time, h, for 50% disappearance	
$\text{CHCl}=\text{CCl}_2$	$c\text{-C}_6\text{H}_{12}$			$\text{CHCl}=\text{CCl}_2$	$c\text{-C}_6\text{H}_{12}$
10	0	∞	5	3.5	—
10	0.01	1000	5	3.3	—
10	0.1	100	5	2.7	~0.9
10	0.2	50	5	3.5	1.3
10	2	5	5	5.6	2.2
10	10	1	5	>16	5.5
2	10	0.2	5	>20	6.7
0	10	0	5	—	6.9
10	2	5	10	6.6	2.8
10	10	1	10	8.7	4.9

Table VII. Photodecomposition Rates of Organic Materials in the Presence of NO , NO_2 , and O_3

Compound ^a	Time h for 50% disappearance			Relative reactivity		
	$\text{NO}^{b,c}$	$\text{NO}_2^{b,d}$	O_3^e	NO	NO_2	O_3
$c\text{-CH}_2\text{CH}_2\text{O}$	15.9	15.2	0.83	0.23	0.19	0.51
$c\text{-C}_6\text{H}_{12}$	6.9	7.5	1.0	0.51	0.38	0.42
$\text{CHCl}=\text{CCl}_2$	3.5	2.9 ^f	0.42	1.0	1.0	1.0
$\text{CH}_2=\text{CH}_2$	2.9	2.5 ^f	—	1.2	1.2	—
$c\text{-C}_6\text{H}_{10}$	0.87	0.19	—	4.0	15.1	—
$\text{trans-MeCH}=\text{CHMe}$	0.30	0.17	—	11.7	16.9	—

^a All compounds at 10 ppm initially. ^b Data from Table I. ^c All initial concentrations, 5 ppm. ^d All initial concentrations, 5 ppm, except as noted. ^e Initial concentration, 15 ppm. ^f Initial NO_2 concentration, 16.8 ppm.

A comparison of the relative photodecomposition rates of the standard hydrocarbons ($c\text{-C}_6\text{H}_{12}$, PhMe, $\text{CH}_2=\text{CH}_2$, and $\text{trans-MeCH}=\text{CHMe}$) in Table I with those obtained by other workers, who used different types and sizes of irradiation chambers, shows a satisfactory correlation (Table X in the microfilm edition of this journal).

CH_3CCl_3 and CH_2Cl_2 did not decompose at a significant rate with either NO or NO_2 present. $\text{CCl}_2=\text{CCl}_2$ decomposed more slowly than $c\text{-C}_6\text{H}_{12}$ while the decomposition rates of the remaining chloroethylenes, including $\text{CHCl}=\text{CCl}_2$, were comparable to that of $\text{CH}_2=\text{CH}_2$. In general, the relative decomposition rates of the materials in Table I roughly parallel the known or expected reactivities of these materials with electrophilic radicals.

In several reactions, the light intensity was varied to determine its effect on the reaction rate since our reactions were carried out with a light intensity higher than that of sunlight. Table II shows a good linear correlation between decomposition rate and light intensity with the exception of $\text{CHCl}=\text{CCl}_2$ at the lowest light intensity. Estimated half-lives under bright sunlight conditions can be calculated by multiplying the half-lives given in Table I by 2.6.

For three of the olefins studied, a change in the absolute concentrations of compound and NO from 10:5 to 100:50 (ppm) resulted in a 2 to 3.5-fold increase in decomposition rate (Table III).

The maximum decomposition rate of $\text{CHCl}=\text{CCl}_2$ occurred at a ~4:1 ratio of $\text{CHCl}=\text{CCl}_2$ to NO at 35% relative humidity (Table IV). There was about a 50% decrease in the decomposition rate of $\text{CHCl}=\text{CCl}_2$ on increasing the relative humidity from 0 to 70% (Table IV).

Photodecomposition rates were determined for a number of the compounds listed in Table I, each in combination with other organic materials that had a wide range of decomposition rates. The data are shown in Table V.

$\text{CHCl}=\text{CCl}_2$ was studied more extensively than the other compounds. In all combinations, except those which involved $\text{CHCl}=\text{CCl}_2$ with $\text{CCl}_2=\text{CCl}_2$ and with CH_3CCl_3 , the photodecomposition rate of $\text{CHCl}=\text{CCl}_2$ decreased compared with the rate of $\text{CHCl}=\text{CCl}_2$ in the absence of other organic compounds. For example, in the absence of other organic compounds, $\text{CHCl}=\text{CCl}_2$ decomposed faster than $c\text{-C}_6\text{H}_{12}$ while in the mixture of $\text{CHCl}=\text{CCl}_2$ and $c\text{-C}_6\text{H}_{12}$, $c\text{-C}_6\text{H}_{12}$ decomposed faster than $\text{CHCl}=\text{CCl}_2$. More extensive data on the $\text{CHCl}=\text{CCl}_2$ - $c\text{-C}_6\text{H}_{12}$ system are presented in Table VI. In general, as the $\text{CHCl}=\text{CCl}_2$: $c\text{-C}_6\text{H}_{12}$ ratio decreased, the decomposition rate of $\text{CHCl}=\text{CCl}_2$ decreased. In contrast, as the $c\text{-C}_6\text{H}_{12}$: $\text{CHCl}=\text{CCl}_2$ ratio decreased, the decomposition rate of $c\text{-C}_6\text{H}_{12}$ increased. These results suggest that there is a reactive intermediate involved when $\text{CHCl}=\text{CCl}_2$ is present that is not involved when $c\text{-C}_6\text{H}_{12}$ is photolyzed in the absence of $\text{CHCl}=\text{CCl}_2$. These results are qualitatively consistent with the generation of chlorine atoms as the reactive intermediates. In solution, $c\text{-C}_6\text{H}_{12}$ is about five times more reactive toward chlorine atoms than is $\text{CHCl}=\text{CCl}_2$ (22). In all of the reactions which involved both $c\text{-C}_6\text{H}_{12}$ and a chloroethylene except that with $\text{CCl}_2=\text{CCl}_2$, the photodecomposition rate of $c\text{-C}_6\text{H}_{12}$ increased while the rate of the chloroethylenes decreased.

Experiments with mixtures of $\text{CHCl}=\text{CCl}_2$ and $c\text{-CH}_2\text{CH}_2\text{O}$ gave results which were similar to those observed in the $\text{CHCl}=\text{CCl}_2$ - $c\text{-C}_6\text{H}_{12}$ system (Tables XI and XII in the microfilm edition of this journal).

Experiments were carried out in an attempt to identify the reactive species present in these reactions. These studies involved the use of NO , NO_2 , O_3 , and other potentially reactive species with $\text{CHCl}=\text{CCl}_2$ and other organic materials in individual and competitive reactions.

The data in Table I indicate that in general, with materi-

Table VIII. Photodecomposition Rates of Organic Materials in Competition Reactions Which Involve NO, NO₂, and O₃

Compound pair ^a	Time, h, for 50% disappearance of compound in combination			Reactivity ratio		
	NO ^b	NO ₂ ^b	O ₃ ^b	NO	NO ₂	O ₃
c-C ₆ H ₁₂	4.9	5.0	0.73			
CHCl=CCl ₂	8.7	10.5	0.87	1.8	2.1	1.2
c-CH ₂ EtCH ₂ O	6.4	8.0	0.5			
CHCl=CCl ₂	7.0	10.5	0.5	1.1	1.3	1.0
trans-MeCH=CHMe	0.37	0.13	—			
c-C ₆ H ₁₀	0.37	0.15	—	1.0	1.1	—

^a Initial concentration, 10 ppm each. ^b Initial concentration, 10 ppm.

als which decompose slowly, both NO and NO₂ gave similar results, while with materials which decompose rapidly, such as *trans*-MeCH=CHMe and c-C₆H₁₀, NO₂ produced an increased decomposition rate over that observed when NO was used. Reactions with O₃ indicate that it causes a much faster decomposition of the organic material than either NO or NO₂ (Table VII).

In competition reactions, the ratios of the photodecomposition rates of the compound pairs were similar even though the absolute rates varied greatly as the "initiator" was changed from NO to NO₂ to O₃ (Table VIII). O₃ appeared to have a slightly greater leveling effect than did NO or NO₂.

Comparison of the data in Tables VII and VIII further suggests that CHCl=CCl₂ caused the formation of some reactive species other than NO₂ or O₃ in the photochemical reactions. Whether NO, NO₂, or O₃ was used as the "initiator", CHCl=CCl₂ decomposed faster than c-CH₂EtCH₂O and c-C₆H₁₂, whereas in competition reactions, CHCl=CCl₂ decomposed slower. The unknown reactive species appeared to be highly reactive toward CHCl=CCl₂ in individual experiments, but was even more reactive toward c-C₆H₁₂ and c-CH₂EtCH₂O when either of the latter two compounds was present. This led us to consider, as possible intermediates or their precursors, possible photochemical oxidation products of CHCl=CCl₂ such as phosgene (COCl₂), chlorine (Cl₂), chloral (CCl₃CHO) (23), dichloroacetyl chloride (CHCl₂COCl), and so forth (24). These products could lead to free radicals such as chlorine atoms, trichloromethyl radicals (·CCl₃), and acyl radicals, and so forth, under the reaction conditions. Table IX shows the photodecomposition rates of CHCl=CCl₂ with a number of these possible products and also with acetaldehyde (MeCHO) and bromotrchloromethane (CBrCl₃). CCl₃CHO significantly increased the decomposition rate of CHCl=CCl₂ in comparison with the effect of NO or NO₂. CCl₃CHO would be expected to lead to two types of radicals, trichloroacetyl and ·CCl₃. MeCHO was used to determine if the acetyl radical (25) would lead to similar results. MeCHO decreased the decomposition rate of CHCl=CCl₂ whereas CBrCl₃, in combination with NO, did increase the decomposition rate of CHCl=CCl₂. From these experiments, it is not clear why CCl₃CHO was so active. Chlorine atoms also were potential intermediates in the photochemical oxidation of CHCl=CCl₂. Indeed, CHCl=CCl₂ reacted extremely rapidly in the photochemical reaction with Cl₂, even faster than with O₃. Cl₂ in combination with NO in-

Table IX. Photodecomposition Rates of CHCl=CCl₂ in the Presence of Possible Photooxidation Products and Other Coreactants

Co-reactants (concentration in ppm) ^a	Time, h, for 50% disappearance of CHCl=CCl ₂
NO (5)	3.5
NO ₂ (16.8)	2.9
CCl ₃ CHO (2)	3.2
CCl ₃ CHO (5)	0.93
CCl ₃ CHO (10)	0.45
MeCHO (10)	15.7 ^b
MeCHO (10) + NO (5)	10.7 ^c
CBrCl ₃ (10)	5.0
CBrCl ₃ (10) + NO (10)	1.3
Cl ₂ (1)	3.1 ^d
Cl ₂ (1) + NO (5)	0.43
Cl ₂ (2)	0.18
Cl ₂ (5)	<0.05 ^e
Cl ₂ (10)	<0.05 ^f
COCl ₂ (5)	5.8
COCl ₂ (5) + NO (5)	2.3

^a Initial concentration of CHCl=CCl₂ was 10 ppm in each case. ^b Extrapolated from 15% reaction in 4.7 h. ^c Extrapolated from 30% reaction in 6.4 h. ^d Extrapolated from 28% reaction in 1.8 h. ^e Interpolated from 85% reaction in <0.08 h. ^f Interpolated from 100% reaction in <0.11 h.

creased the decomposition rate of CHCl=CCl₂ even more. Although COCl₂ was a product from the photochemical oxidation of CHCl=CCl₂ (24), COCl₂ by itself did not increase the decomposition rate of CHCl=CCl₂. A combination of COCl₂ and NO did increase the decomposition rate of CHCl=CCl₂.

Further data, of the same type given in Table IX for CHCl=CCl₂, were obtained for c-CH₂EtCH₂O, CCl₂=CCl₂, c-C₆H₁₂, CH₂=CH₂, c-C₆H₁₀, and *trans*-MeCH=CHMe (Tables XIII–XV in the microfilm edition of this journal).

Data on oxidant formation for five of the chlorinated compounds were obtained (Appendix in the microfilm edition of this journal). Qualitatively, the amount of oxidant formed was in the order CHCl=CCl₂ ~ CH₂=CHCl > CCl₂=CCl₂ > CH₂Cl₂ ~ CH₃CCl₃.

The products of photodecomposition of CH₂Cl₂, CH₃CCl₃, CHCl=CCl₂, and CCl₂=CCl₂ will be the subject of a future publication.

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Toxicity of Organic and Inorganic Arsenicals to an Insect Herbivore

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■ Four arsenicals including organic and inorganic forms of both the trivalent and pentavalent states were tested for their potential environmental effect on a nontarget animal species. Cacodylic acid, cacodylic acid plus sodium cacodylate, arsenic trioxide, and arsenic pentoxide were evaluated in terms of formulation, exposure time, and tissue arsenic concentrations on the survival of an exposed population of meadow katydids. Tissue concentrations of elemental arsenic were higher for organic forms than for inorganic forms at similar exposure dosages. Life expectancies were reduced to <10% of unexposed populations by levels above 5 μg As/g dry weight in dosing formulations. While As concentrations in katydid tissues did not exceed those in the dosing formulations, they did exceed tissue concentrations found in unexposed populations by as much as three orders of magnitude. These results illustrate the impact of herbicidal arsenic formulations on a nontarget animal species.

The pesticidal properties of arsenical compounds have been known since 1867 when copper acetoarsenite (commonly known as Paris Green) was first used to control the Colorado potato beetle (1). Other arsenites and arsenates were then developed as "stomach" poisons for insect control (1, 2). Organic arsenicals including sodium cacodylate, cacodylic acid (CA), and methyl arsonic acid (MAA) have come into common use because of their high toxicity to plants but relatively minor effects on animals (1). These

qualities have led to large-scale production of arsenical formulations designed to thin forests, defoliate cotton, renovate turf, and serve as general postemergent weed-control agents (3, 4).

With the exception of the series of studies relating bark beetle mortality to host-tree treatment with organic arsenical thinning agents, there are few data available which may be used to evaluate long- and short-term effects of these materials upon nontarget species (5-10). In the bark beetle studies, appreciable kills of *Dendroctonus*, *Ips*, and *Pseudohylesinus* spp. were obtained with precommercial forestry thinning procedures, but it is not known if brood destruction and adult mortality were due to the production of arsine gas or desiccation of woody tissue (5). Concern has been voiced over the need to adequately assess the environmental impact of organic arsenicals used as defoliant for crop destruction under the code name "Blue" in the Republic of Vietnam and as commercially available, nonselective herbicides in the United States (11-17). "Blue", manufactured as Phytar 560-G, contained sodium cacodylate and free CA in concentrations to produce a total elemental arsenic content of 15.8% (14, 15). Phytar 560 Herbicide (trade named compounds produced by the Ansul Co., 1 Stanton St., Marinette, Wis. 54149) is sold in this country for use in noncrop areas and contains CA and its sodium salt in amounts to produce a total arsenic concentration of 12.7%.

Recent papers by C. R. Malone (18, 19) have evaluated the ecological impact of arsenical herbicide applications in

a grassland ecosystem by determining the fate and direct effects of cacodylic acid on the system's vegetational components. The experiments included in the present study were initiated in conjunction with Malone's study to assess the secondary effects of parent compound and possible degradation products on natural animal populations.

Experimental

Fourth instar nymphs of *Conocephalus fasciatus* (De Greer) were obtained by sweep-net sampling in the grassland area on the ERDA-Oak Ridge Reservation, Oak Ridge, Tenn. Ten individuals were placed in each of three experimental cages previously provisioned with fresh fescue (*Festuca arundinacea* Schreb.) clippings and drinking water containing an arsenical compound in solution. The range of treatment doses for each of the four test compounds is given in Table I. The entire experiment was performed in a growth chamber at 27 °C, 50% relative humidity, and a 14-h light/10-h dark photoperiod. Fresh clippings and dosing solution were provided when required.

Mortality observations were made and recorded every other day. Data accumulated after 7 and 14 days were subjected to probit analysis (20) to arrive at LD₅₀ values.

To correlate mortality statistics with accumulated arsenic from dosing solution, whole-body determinations of arsenic were performed. The carcasses of individuals dead after 14 days' exposure were dried at 100 °C for 24 h and then again at 70 °C for 24 h before being crushed with a mortar and pestle. Volatilization of arsenic is negligible at these temperatures (21). To prevent cross-contamination, the mortar and pestle were washed between samples with 4 N HCl and then rinsed twice with demineralized water. Arsenic concentrations were determined by neutron activation analysis in the High Flux Isotope Reactor at Oak Ridge National Laboratory, Oak Ridge, Tenn., at a flux of 10¹⁵ cm⁻² sec⁻¹. Background arsenic concentrations in fescue clippings used as food averaged 0.05 ppm.

Results and Discussion

Finney's Probit analysis (20) of the 7- and 14-day mortality data generated the LD₅₀ values presented in Tables II and III. When only the compound dose is considered, inorganic arsenical formulations are more toxic than organic preparations, with the trivalent inorganic form being the most lethal. This result is consistent with the general pattern of mammalian arsenical toxicity discussed at length in review papers by Schroeder and Balassa (21) and Frost (1). Arsenites (As³⁺) are more toxic than arsenates (As⁵⁺), and inorganic compounds are more toxic than organic formulations. However, if an examination of the elemental arsenic content of the test compounds is made, an altogether different pattern emerges (last column, Tables II and III). After 7 days' exposure, the mortality response of *C. fasciatus* to 1.3 ppm of elemental arsenic in the form of Phytar 560 was not different from the mortality response elicited by exposure to either 3.1 ppm of arsenic as As₂O₃ or 4.5 ppm of arsenic as As₂O₅. After 14 days' exposure, there was no difference in the elemental arsenic dose required to produce the LD₅₀, regardless of formulation.

It appeared that the meadow katydid's dose response was due to digestive assimilation of arsenic and not differential toxicity due to compound. To further test this hypothesis, all carcasses of individuals dead after the 14-day mortality experiment were pooled according to treatment and analyzed for elemental arsenic by the neutron activation (Figure 1). From these plots it is possible to estimate the amount of elemental arsenic present in *C. fasciatus* tissue at the 14-day LD₅₀ dose for each compound. These data are presented in Table IV with their corresponding

Table I. Experimental Design

Test compound	Formulation	Treatment doses ppm compound
Organic		
Cacodylic acid (CA)	65% Formulation of dimethyl arsenic acid; 35% elemental arsenic (Matheson, Coleman and Bell)	1.5, 15, 150, 1500, 15 000
Phytar 560R	4% Free cacodylic acid +23% sodium cacodylate + 73.5% inert ingredients; 12.7% elemental arsenic (The Ansul Co.)	0.15, 15, 150 1500
Inorganic		
Arsenic trioxide	99% Assay of As ₂ O ₃ ; 76% elemental arsenic (J. T. Baker Chemical Co.)	0.015, 0.15, 1.5, 15, 150
Arsenic pentoxide	99% Assay of As ₂ O ₅ ; 65% elemental arsenic (J. T. Baker Chemical Co.)	0.015, 0.15, 1.5, 15, 150, 1500

Table II. Chronic Oral Toxicity (LD₅₀) of Arsenicals to *Conocephalus* spp. Nymphs After a Seven-Day Exposure (n = 30)

Test compound ^a	LD ₅₀ dose, ppm	
	Compound dose ^b	Elemental arsenic ^b dose in formulation
Organic		
Cacodylic acid (35.3%)	34.4 [17.5-58.5]	12.1 [6.2-20.7]
Phytar 560 (12.7%)	10.0 [3.8-21.3]	1.3 [0.5-2.7]
Inorganic		
Arsenic trioxide (75.7%)	4.1 [1.6-8.5]	3.1 [1.2-6.4]
Arsenic pentoxide (64.6%)	6.9 [0.9-25.6]	4.5 [0.6-16.5]

^a Values in parentheses refer to proportion of elemental arsenic present in compound. ^b Values in brackets refer to 95% confidence limits. Note: LD₅₀ values calculated from mortality data of Finney (20).

Table III. Chronic Oral Toxicity (LD₅₀) of Arsenicals in *Conocephalus* spp. Nymphs After a 14-Day Exposure (n = 30)

Test compound ^a	LD ₅₀ dose, ppm	
	Compound dose ^b	Elemental arsenic, ^b dose
Organic		
Cacodylic acid (35.3%)	7.5 [1.8-16.5]	2.6 [0.6-5.8]
Phytar 560 (12.7%)	3.5 [0.6-10.6]	0.4 [0.1-1.3]
Inorganic		
Arsenic trioxide (75.7%)	1.6 [0.7-3.5]	1.2 [0.5-2.6]
Arsenic pentoxide (64.6%)	2.8 [1.0-5.5]	1.5 [0.5-3.0]

^a Values in parentheses refer to proportion of elemental arsenic present in compound. ^b Values in brackets refer to 95% confidence limits. Note: LD₅₀ values calculated from mortality data of Finney (20).

LD₅₀'s. The toxicity ranking based on arsenic content of parent compound previously noted is also observed in this case—i.e., *C. fasciatus* exposed to Phytar 560 incorporates an amount of elemental arsenic that is not different from the amount incorporated upon exposure to As₂O₃. Arsenic trioxide has long been used as a slow-acting poison and is a common constituent of rodenticides and insecticides registered for household use. Our findings demonstrate that in-

Table IV. Fourteen-Day LD₅₀ Values Compared with Whole-Body Elemental Arsenic Concentrations

Test compound	LD ₅₀ dose, ppm		Incorporated ppm (dry wt basis) arsenic
	Compound	Elemental arsenic	
Organic			
Cacodylic acid	7.5	2.6	65.0
Phytar 560	3.5	0.4	5.0
Inorganic			
Arsenic trioxide	1.6	1.2	9.0
Arsenic pentoxide	2.8	1.5	27.0

LD₅₀ doses in columns 2 and 3 are those included in Table III and are calculated values (20). The values in column 4 above have been read off the y-axis of each of the four graphs in Figure 1 according to compound. The arrows on these graphs represent the 14-day LD₅₀ in ppm-dosing compound. Each point represents a mean of 30 observations.

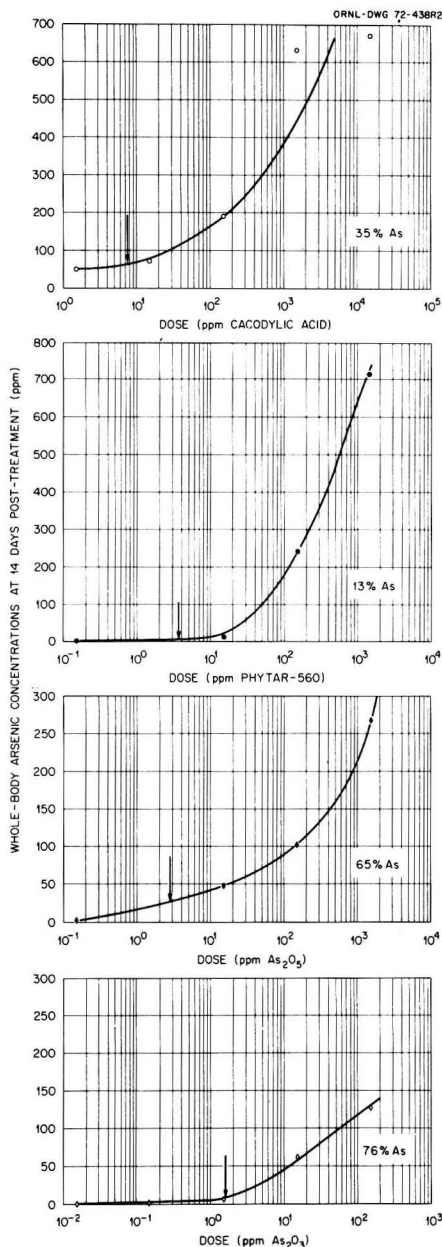


Figure 1. Whole-body elemental arsenic concentrations in meadow katydids following 14-day chronic ingestion of cacodylic acid, Phytar-560, As₂O₅, and As₂O₃. Arrows indicate the 14-day LD₅₀. Note that scales for the abscissa differ between graphs

gestion of arsenic as a commercially available organic herbicide is at least as toxic to *C. fasciatus* as ingestion of the trioxide. However, neither the valence state nor chemical form of arsenic present within insect tissue was determined.

The manufacturer's recommended application rate of Phytar 560 is 1–2 gal of liquid/100 gal of water. At this rate (9900–19 600 ppm herbicide or 2500–5400 ppm CA, nontarget organisms such as herbivorous insects would likely ingest the herbicide and be adversely affected. The insect species utilized in these toxicity tests account for a substantial proportion of the herbivore population in grassland communities (22). In such systems, detrimental effects on these insects could alter the structure of the existing food web. In associations where animals exert a controlling influence on community structure, an insult such as food-web alteration could prove to be a major factor in alteration of system stability.

The results of this study also indicate that appreciable quantities of arsenic could be introduced into food chains via ingestion of contaminated vegetation by herbivores. A 14-day chronic dose of 1500 ppm herbicide gave rise to an arsenic concentration of 715 ppm in the analyzed carcasses (Figure 1). At recommended application rates, it is highly probable that such transfer can and does occur.

Conocephalus fasciatus (De Greer) is a nontarget species, a primary consumer, and relatively innocuous. Yet exposure of this species to an organic arsenical herbicide produced a toxic response equal to that of arsenic trioxide, a common biocide. It is apparent that the environmental impact of the widespread use of arsenical herbicides on a nontarget animal is inadequately known. This is especially true in view of the fact that the greatest use of these materials to date has been on Vietnamese rice fields at rates exceeding those recommended for domestic use on noncrop land (17).

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Analysis of Carbonaceous Materials in Southern California Atmospheric Aerosols

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■ A technique is described for estimating the contributions of elemental carbon and primary organic and secondary organic materials to atmospheric particulate matter collected in California's South Coast Air Basin. The technique employs a combination of solvent extractions and carbon determinations; primary organics are estimated from the carbon solubilized in cyclohexane and secondary organics by the carbon solubilized by successive extraction with benzene and methanol-chloroform minus the primary organics. At the same time an upper limit estimate of the elemental carbon is obtained from the carbon remaining insoluble after the two-step extraction. Support for this technique is provided for samples collected at four locations.

The carbonaceous material present in atmospheric aerosols is a combination of elemental carbon, organic (including polymeric), and inorganic compounds (e.g., carbonate salts). When considering the origins of atmospheric aerosols, the organic fraction may be further divided into "primary" and "secondary" materials (1). The former term indicates material introduced into the atmosphere directly in the particle state. Materials which, because of their low vapor pressure, condense shortly after introduction into the atmosphere from an elevated temperature source are also considered "primary". Secondary refers to particles formed as the result of homogeneous or heterogeneous reactions in the atmosphere.

While considerable research effort has been devoted to determining the concentrations and origins of organic particulate constituents known to be hazardous (e.g., polynuclear aromatics), less effort has been devoted to characterizing the nature and origins of carbonaceous material more generally. Even the proportion of the elemental carbon present remains a matter of speculation. Previous studies of carbonaceous matter have primarily examined organic solvent-soluble fractions and include the work of Mader et al. (2), Dubois et al. (3), Ciaccio et al. (4), and Cukor et al. (5). The latter group analyzed solvent extracts from suspended particulate matter collected near a major intersection in New York City. They concluded that the organics strongly resembled used automobile lubricating oils (i.e., were "primary" in origin).

Mueller et al. reported a technique for determining carbonate and noncarbonate carbon (6). Their work in analyzing aerosols from Pasadena, Calif., demonstrated that carbonate carbon was consistently less than 5% of the total carbon present and that noncarbonate carbon (including both elemental and organic carbon) represented from 18-44% of the total suspended particulate matter.

Recent work includes studies by Grosjean and Friedlander (7) and Grosjean (8). Grosjean compared the ability of various solvents and solvent mixtures to extract organic carbon. For atmospheric particulate matter collected in Pasadena, Calif., the extraction efficiency of the polar solvents, ethanol and acetone, increased with the ozone concentration measured during the time of particle collection while, for the solvents isooctane and methylene chloride, no change was observed. Although Grosjean did not use these results to quantitate primary and secondary organics, it is

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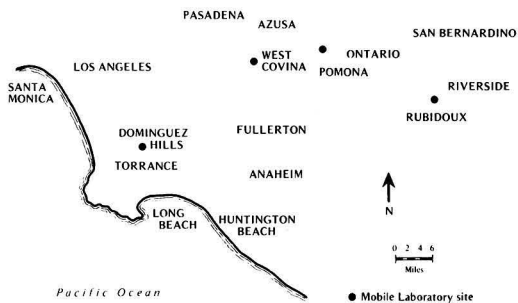


Figure 1. Sampling sites for the ACHEX

clear from these results that solvent extraction might be so used.

As part of the work sponsored by the California Air Resources Board in the Aerosol Characterization Experiment (ACHEX), we have sought methods to determine ambient air concentrations of elemental carbon as well as primary and secondary organics. As in Reference 6, carbonates were again shown to represent less than 5% of the total carbon present and have, therefore, been ignored. Numerous techniques were explored, including column chromatography, high resolution mass spectroscopy, thermal analysis, and multiple solvent extraction with total carbon analyses of the various solvent extracts. We present here a discussion of the latter technique since, thus far, it has proved to be the most useful.

The basis of this technique is to equate primary organics in atmospheric aerosols to those organics soluble in cyclohexane and total organics, to those solubilized by successive extraction with benzene followed by methanol-chloroform. An upper limit estimate to the elemental carbon present is obtained from the carbon remaining insoluble after the two-step extraction. The secondary organics are obtained by difference between total and primary organics. All determinations are based upon carbon analyses rather than total weight to avoid errors resulting from solubilization of inorganic salts (e.g., NH_4NO_3).

The techniques for estimating primary and secondary organics will be supported by comparisons with ozone data obtained during sample collection and used to indicate the extent of photochemical (i.e., secondary) organic particle production expected.

The technique was applied to samples collected on filters at four locations within California's South Coast Air Basin. Sampling locations for the study are shown in Figure 1. These include a site adjacent to a complex of chemical plants and refineries, Dominguez Hills (DH), and three receptor sites with respect to photochemical smog, West Covina (WC), Pomona (PO), and Rubidoux (RB). As indicators of levels of air pollution on the days sampled, Table I lists maximum values observed for ozone and the light-scattering coefficient (b_{scat}) (9), as well as the total suspended particulate matter and particulate carbon averaged over the sampling period shown. The episodes include days of light, intermediate, and heavy photochemical smog.

Experimental

Materials. Cyclohexane, benzene, and 1:2 v/v methanol-chloroform were Eastman Spectrograde having a nonvolatile residue less than 0.001%. For the 85 ml of each solvent used for extractions, this represents <0.8 mg.

Particulate Sample Collection. Gelman Type A 8 × 10

in glass fiber filters were used after pre-extraction for 18 h in refluxing ethanol to reduce the carbon blank. The extractable carbon from a precleaned filter amounted to 2–7% of the weight of the total organic carbon extracted from a loaded filter including the solvent residue. The carbon blank by combustion (6) of a 1-in. disk of the filter was 4 μg and represented about 1% of the carbon found with a similar section from a loaded filter. Filter samples were collected for the time periods shown in Table I employing a high volume sampler equipped with a cyclone for removal of particles greater than 3.5 μm (10). Comparing total carbon determinations for the resulting refined samples with those for low-volume glass fiber filters simultaneously sampling 0–20- μm particles, the mean ratio refined/total particulate carbon was 1.04 ± 0.09 . Thus, on average, all of the carbonaceous material was present in the refined particle samples. Immediately following collection, the filter samples were stored at dry ice temperature with protection from atmospheric moisture, and were brought to room temperature just prior to analysis.

Solvent Extraction. The filters were cut in half and one-half extracted with cyclohexane. The other half was extracted first with benzene and then with 1:2 v/v methanol-chloroform. The extraction period was from 6–8 h with each solvent using a Soxhlet extractor. Solvent was removed at steam bath temperature under a stream of nitrogen. An independent experiment employing a Du Pont Thermal Evolution Analyzer demonstrated, for about 400 samples from the same locations, <0.5% volatilization of carbon up to 100 °C relative to the total evolved at up to about 500 °C. Thus, steam bath treatment of organic extracts is not expected to produce significant loss of organic aerosol constituents. Following solvent removal, the residue was dried to constant weight over silica gel and the weight of the extract determined with a precision of ± 0.1 mg in 25-ml Erlenmeyer flasks. By weighing empty flasks as controls, variations in weight due to changes in buoyancy effects or other factors were used to obtain corrected extract weights.

Carbon Analysis. Aliquots (100–600 μg) of each solvent extract were weighed into disposable aluminum sample boats with a Cahn Model 4100 electrobalance with a precision of ± 1 μg . The sample was combusted to CO_2 and determined by gas chromatography using the technique detailed by Mueller et al. (6). The blank correction for the boats was 8.3 ± 1.9 μg C. The resulting carbon determination was compared to that on a section of the original filter prior to extraction (the total carbon). The difference permitted calculation of the carbon remaining insoluble in the extracting solvent.

Ozone Determination. Ozone was monitored continuously throughout the sampling periods by a REM chemiluminescent analyzer calibrated against buffered 2% KI (11). Recent work has demonstrated this calibration procedure to yield values, high by about 29% relative to ozone values determined by the reference method, uv absorption (12).

b_{scat} Determination. The light-scattering coefficient was obtained continuously with an integrating nephelometer (13) calibrated against Freon 12 and particle-free air.

Results and Discussion

Comparison of Solvent Extraction Efficiencies. Table II summarizes the results of the extractions with cyclohexane and by successive extractions with benzene and methanol-chloroform. The results are expressed as $\mu\text{g}/\text{m}^3$. Also shown for comparison are the weight percent carbon contents of each extract.

On the average, the benzene/cyclohexane solubles weight

Table I. Sampling Episodes in the South Coast Air Basin

Sampling site (date)	Sampling time, PST	Max. O ₃ , ppm	Max. b _{scat} × 10 ⁻⁴ m ⁻¹	Total suspended particulate, μg/m ³	Carbon ^a % of TSP	
West Covina (WC)	(7/11-7/12/73)	2100-2100	0.197	7.0	137	10.5
	(7/23-7/24/73)	2100-2110	0.542	16.0	211	11.4
	(7/24-7/25/73)	2300-1605	0.449	10.2	241	9.50
	(7/26/73)	0500-1826	0.230	8.38	194	6.60
	(8/8-8/9/73)	2100-2100	0.177	9.51	123	8.70
Pomona (PO)	(8/16-8/17/73)	2100-2100	0.321	7.75	180	9.11
	(8/22-8/23/73)	2100-2100	0.194	3.47	148	7.36
Rubidoux (RB)	(9/5-9/6/73)	2300-2300	0.239	11.0	262	5.76
	(9/18-9/19/73)	2300-2300	0.256	21.8	284	5.39
	(9/24-9/25/73)	2300-1800	0.188	8.49	211	3.8
Dominguez Hills (DH)	(10/4-10/5/73)	2100-2105	0.141	7.35	148	7.16
	(10/10-10/11/73)	2100-2100	0.119	5.38	114	12.2

^a Carbon obtained by analysis of a refined filter sample, expressed as a percent of the total suspended particulate matter obtained in simultaneous sampling with a conventional high-volume sampler (i.e., without size segregation).

Table II. Solvent Extraction of Refined^a Particulate Matter Samples^b

Sampling site (date)	Cyclohexane extractables		Benzene extractables		CH ₃ OH-CHCl ₃ extractables (after benzene extraction)	
	μg/m ³	% Carbon ^c	μg/m ³	% Carbon ^c	μg/m ³	% Carbon ^c
WC (7/11-7/12/73)	4.9	— ^d	11.0	62.6	12.0	39.3
	—	—	16.6	61.7	16.4	33.0
	8.8	55.0	18.1	65.8	23.8	43.7
	6.6	60.4	10.9	67.4	16.3	34.5
	7.4	61.4	7.6	65.2	10.0	32.3
PO (8/16-8/17/73)	5.4	67.8	11.0	72.2	13.3	38.3
	6.1	61.0	9.0	62.0	11.0	29.6
RB (9/5-9/6/73)	7.9	59.3	13.7	61.5	60.0	9.3
	5.3	56.9	10.5	60.2	52.2	6.6
	3.8	62.9	5.3	59.8	15.8	17.0
DH (10/4-10/5/73)	3.8	50.9	7.8	43.6	7.8	36.6
	9.0	58.5	11.5	60.5	9.0	18.2
Means:	6.3 ± 1.8	59.4 ± 4.6	11.1 ± 3.7	61.9 ± 6.8	20.6 ± 17.2	28.2 ± 12.3

^a Indicates particles ≤ 3.5 μm. ^b Coefficient of variations for all determinations range from 4-12% except for WC (7/11-7/12/73) for which the range was 9-23%. ^c Weight percent carbon in the solvent extract. ^d Not determined.

ratio was 1.8 which compares to the values 1.6 and 1.2 reported by Gordon (14) and by Grosjean (8) respectively. The methanol-chloroform solvent mixture extracted an additional amount nearly equal, on a mass basis, to the prior benzene extraction except for the episodes at RB where the second extraction yielded from three to five times the mass extracted in benzene. In all cases the cyclohexane and benzene extracts had the texture of a tacky gum while the methanol-chloroform solubles were brittle and, in the cases of the RB episodes, had a definite crystalline appearance. The latter was subsequently identified by infrared spectroscopy and x-ray diffraction to be predominantly ammonium nitrate.

The carbon content of both the cyclohexane and benzene extracts was about 60%. As expected from the solubilization of inorganics and the prior extraction with benzene, the methanol-chloroform extracts exhibited much lower carbon contents, especially for samples collected at Rubidoux; the overall mean percent carbon with the mixed solvent extract was about half the value for cyclohexane and benzene.

Elemental Carbon Estimation. To demonstrate the technique employed to estimate elemental carbon, Table III compares the efficiency of cyclohexane, benzene, and benzene plus 1:2 v/v methanol-chloroform for extraction of carbon from the particulate samples expressed as a percent of the total carbon present in the original filter sample.

Clearly, with the use of the nonpolar solvents cyclohexane and benzene, on the average more than 50% of the carbon remained unextracted. By extraction with methanol-chloroform, about half of the carbon remaining after benzene extraction is solubilized and is, therefore, not in elemental form. These results are quite similar to those of Grosjean and Friedlander (7) who found up to 40% additional organics solubilized by a polar solvent following nonpolar solvent extraction.

If the remainder after successive benzene and methanol-chloroform extraction is equated to elemental C, then, on the average, only 22% of the total carbon present exists in this form. Since all of this insoluble fraction need not be elemental carbon, this technique provides only an upper limit to the level of elemental carbon present.

Estimation of Primary and Secondary Organics. Based in part on the work of Cukor et al. (5), we believed that primary organic particulate matter in urban areas has as its principal source partially oxidized lubricating oils. To further demonstrate this, a comparison was made of the cyclohexane soluble organics in atmospheric particles collected at 12 locations throughout California with cyclohexane extracts from automobile exhaust particulate matter. The exhaust sample was collected on a glass fiber filter by the staff of the California Air Resources Board's Vehicle Emission Control Division, El Monte, Calif., using a 1970 Chevrolet equipped with a 350-in.³ displacement V-8 engine and

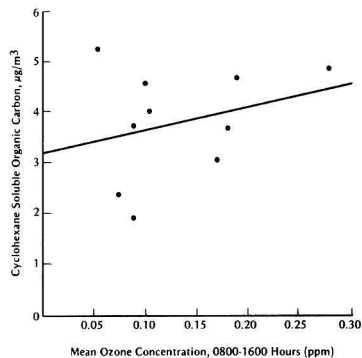


Figure 2. Cyclohexane-soluble organic carbon vs. mean ozone concentration for sampling sites in the Los Angeles Basin

driven over a 300-mile route. Employing column chromatography over silica gel and successive elution with isooctane, benzene, and 1:1 v/v methanol-chloroform to obtain an aliphatics, aromatics, and polar organics ("polars") fraction, we found that cyclohexane extracts from 46 ambient air samples yielded an average composition of 24% aliphatics, 15% aromatics, and 61% polars. This compares to the values 31% aliphatics, 8% aromatics, and 61% polars found for the organics extracted from the exhaust aerosol suggesting a similar composition. In these cases, therefore, the cyclohexane-soluble organics appeared to be primary in origin.

The demonstration that cyclohexane-soluble organics from the South Coast Air Basin are not secondary products would provide more direct support for the use of cyclohexane-soluble carbon to estimate primary organic carbon. To this end we assume that photochemical reactions are the principal sources of secondary organics in the South Coast Air Basin, and that such reactions occur predominately during daylight hours, but the resulting secondary (aerosol) products are collectable throughout longer periods. Accordingly, Figure 2 plots cyclohexane-soluble carbon for 10 sampling episodes against the mean daytime ozone level. The resulting scatter diagram, with least squares slope not significantly different from 0 at the 95% confidence level, and the large intercept suggest the lack of dependence of cyclohexane-soluble organics on photochemical reactions leading to secondary organics.

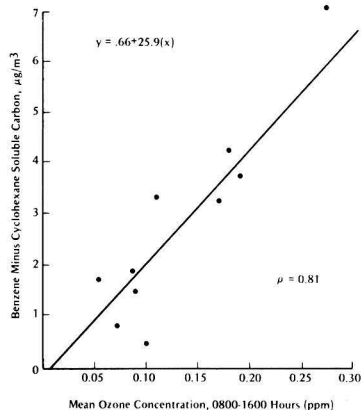


Figure 3. Benzene minus cyclohexane-soluble organic carbon vs. mean ozone concentration for sampling sites in the Los Angeles Basin

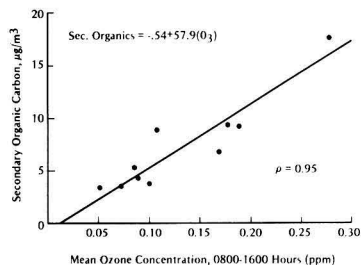


Figure 4. Calculated secondary organic carbon vs. mean ozone concentration for sampling sites in the Los Angeles Basin

We next examine the organic carbon solubilized by benzene which does not dissolve in cyclohexane. If cyclohexane solubilizes all the primary organics, then the additional soluble organics should be secondary reaction products. Figure 3 plots the difference in carbon solubilized by the two solvents vs. mean daytime O_3 . In contrast to the cyclohexane solubles, a correlation is obtained with Spearman's $\rho = 0.81$ and intercept near zero, thus supporting our hypothesis that cyclohexane solubilizes principally primary organics.

Table III. Comparison of Extraction Efficiency of Cyclohexane, Benzene, and Benzene Plus $CH_3OH-HClCl_3$ (% of Total Carbon)

Sampling site (date)	Cyclohexane-extracted C	Benzene-extracted C	Benzene + ($CH_3OH-HClCl_3$) extracted C
WC (7/11-7/12/73)	—	41	81
(7/23-7/24/73)	—	43	65
(7/24-7/25/73)	21	52	97
(7/26/73)	31	57	100
(8/8-8/9/73)	43	46	77
PO (8/16-8/17/73)	22	48	79
(8/22-8/23/73)	34	51	82
RB (9/5-9/6/73)	31	56	93
(9/18-9/19/73)	20	41	63
(9/24-9/25/73)	30	40	74
DH (10/4-10/5/73)	18	32	59
(10/10-10/11/73)	38	50	62
Mean:	28.8 ± 8.3	46.4 ± 7.3	77.7 ± 13.9

Table IV. Composition of Carbonaceous Material

Sampling site (date)	% Secondary organic C ^a	% Ele- mental C ^b	% Primary organic C ^c
WC (7/11-7/12/73)	—	19	—
(7/23-7/24/73)	—	34	—
(7/24-7/25/73)	76	3	21
(7/26/73)	70	0	30
(8/8-8/9/73)	34	23	43
PO (8/16-8/17/73)	57	21	22
(8/22-8/23/73)	48	18	34
RB (9/5-9/6/73)	62	7.3	31
(9/18-9/19/73)	44	37	19
(9/24-9/25/73)	44	26	30
DH (10/4-10/5/73)	41	41	18
(10/10-10/11/73)	24	38	38
^a (C ₆ H ₆ + MeOH-CHCl ₃) sol C - C ₆ H ₁₂ sol C × 100.			
^b Total C - (C ₆ H ₆ + MeOH-CHCl ₃) sol C total C. This is probably			
^c C ₆ H ₁₂ sol C total C × 100.			

Finally, the correlation of mean O₃ against total secondary organic carbon, defined as the total soluble C less cyclohexane soluble C, is shown in Figure 4. The correlation coefficient, $\rho = 0.95$ and the near zero intercept for the least squares fit regression line suggests that it can account for nearly all of the photochemically related secondary organics.

We rationalize the difference in solubility behavior of primary and secondary organics by noting the importance of relatively low-molecular-weight difunctional compounds as likely secondary aerosol constituents (15, 16). The substantial dipolar and hydrogen bonding interactions possible between such molecules and other insoluble aerosol constituents suggest the requirement for solvents of higher polarity to solubilize secondary organics. It should be emphasized, however, that the observed correlations between solubility behavior and aerosol origin may only be valid for the Southern California area.

Using this approach and approximating elemental carbon by insoluble carbon as discussed above, we summarize in Table IV the composition of the carbonaceous material at the four Southern California locations. By this approach, secondary organics dominated at all of the photochemical

smog receptor sites while elemental carbon and primary organics were of greater importance at Dominguez Hills.

Further work is planned to verify the analytical approaches used here and to refine these techniques to permit analysis of samples collected over shorter time periods. Hopefully, conducting such analyses with better time resolutions will provide more information on sources, formation mechanisms, and transport for suspended carbonaceous material. Such information is a necessary prerequisite to a successful control strategy.

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Reverse Osmosis Separation of Polar Organic Compounds in Aqueous Solution

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■ The reverse osmosis separation of polar organic compounds from water was examined. A total of 12 different reverse osmosis membranes were tested with 13 polar low-molecular-weight organic compounds consisting of various functional groups. Experimental data indicated that the separations of these compounds were not as effective as those of inorganic salts for all the membranes tested. The aromatic-polyamide-(AP)- and NS-type membranes gave respectively an overall of 50 and 75% separation of polar organic compounds, whereas the cellulose acetate base showed an overall separation ranging from 13–27%. The separation of a given organic compound with a given membrane depends on the chemical nature of the molecule as well as the characteristics of the membrane. In addition, the separation of compounds having the same functional group increases with the increase in the size and branching of the molecules.

A number of new reverse osmosis membranes have been developed in the last few years (1, 2). Separation of inorganic salts has been investigated for most of these membranes, but little work has been done on the study of their separation of polar organic chemicals commonly found in the wastewaters. The objective of this study was to examine the effectiveness of various reverse osmosis membranes for the separation of polar organic chemicals in water. The tested membranes included eight different types of flat-sheet membranes made of various materials, as well as four types of modules manufactured in either tubular or hollow fiber form.

It has been reported (1, 3–5) that the separation of a specific polar organic compound by a given reverse osmosis membrane depends largely on the functional group of the compound, whereas the separation of compounds having the same functional group depends on the size and branching of the molecules. Accordingly, in this study only the low-molecular-weight compounds were selected for membrane testing from each functional group, including acid, aldehyde, amide, amine, ester, ether, ketone, and phenol. Three alcoholic compounds—i.e., methanol, ethanol, and *i*-propanol—were tested by each membrane for the examination of the steric effect of the solute.

Experimental

Testing was performed using the system illustrated in Figure 1. The temperature of the test solution was controlled by a thermoregulator. With sufficient circulation of the solution, the temperature was maintained at 25 ± 0.1 °C. A Yarway (Blue Bell, Pa.) Cyclo-Phram metering pump was employed for delivering the pressure of the test solution. The flow rate of the solution was controlled by adjusting the stroke displacement. The pressure, on the other hand, was adjusted through a pressure regulator placed downstream of the test unit. Pressure pulsations were dampened effectively by a bladder-type accumulator. Pressure gauges and flowmeters were installed at both the up-

stream and downstream of the test unit. All the wetted parts under high pressure were constructed of 316 stainless steel.

The membranes tested in this study, their abbreviations, configurations, and suppliers are shown in Table I. Flat-sheet membranes were tested at 600 lb/in.² (psig) and a flow rate of 0.30 gal/min (gpm) using stainless steel test cells based upon Manjikian's design (6). As suggested by the suppliers, the tubular modules made of CA and NS-100 membranes were tested at 600 psig and 1.5 gpm while the hollow fiber B-9 and B-10 modules were tested at 400 psig and 2.5 gpm, and 750 psig and 4.0 gpm, respectively.

Each membrane was first characterized with a 5000-parts-per-million-(ppm) sodium chloride solution followed by testing with 13 solutions each containing a single organic compound at a constant concentration of 1000 ppm at zero product water recovery. However, with the B-9 and B-10 permeators, a product water recovery of 75% was employed. No pH adjustment was made for these test solutions. At the end of each series of testings, the membrane was again tested with a 5000-ppm sodium chloride solution. By comparing both tests against sodium chloride, the deterioration of a membrane, if any, could be identified. The organic compounds selected for membrane testing, their chemical classifications, and toxicities (7) are shown in Table II.

A Yellow Springs Conductivity Bridge, Model 1485 (Yellow Springs, Ohio), was used to measure the concentration of sodium chloride. At dilute concentration (<100 ppm), the conductivity is proportional to the concentration of the salt solution. A Beckman Total Carbon Analyzer, Model

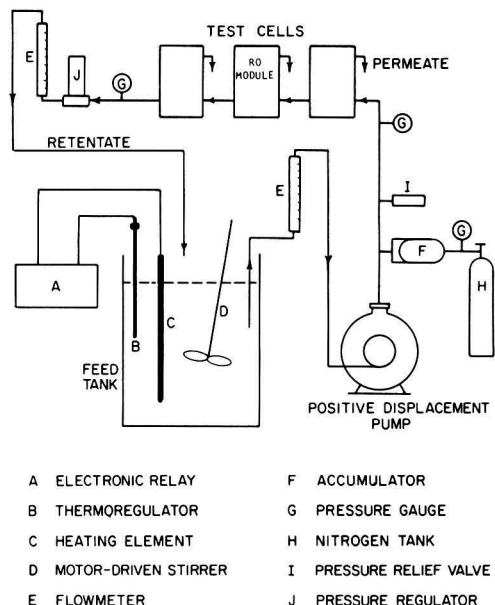


Figure 1. Flow diagram of membrane-testing facility

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Table I. Reverse Osmosis Membranes, Their Abbreviations, Configurations, and Suppliers

Membrane material	Abbreviation	Configuration	Supplier
Cellulose acetate	CA	Flat sheet	University of Illinois
Cellulose acetate	CA-T	Tube	Universal Oil Products
Cellulose acetate butyrate	CAB	Flat sheet	Universal Water
Cellulose triacetate	CA3	Flat sheet	Envirogenics
Cross-linked polyethylenimine	NS-100	Flat sheet	University of Illinois
Cross-linked polyethylenimine	NS-100-T	Tube	Universal Oil Products
NS-200	NS-200	Flat sheet	North Star
Poly-2,2'-(<i>m</i> -phenylene)-5,5'-bibenzimidazole	PBI	Flat sheet	Celanese
Sulfonated polyphenylene oxide	SPPO	Flat sheet	General Electric
Aromatic polyamide	AP	Flat sheet	Chemstrand
Aromatic polyamide	B-9	Hollow fiber	Du Pont
Aromatic polyamide	B-10	Hollow fiber	Du Pont

Table II. Organic Compounds for Membrane Testing

Compound	Chemical classification	Toxicity ^a
Methanol	Alcohol	3
Ethanol	Alcohol	2
<i>i</i> -Propanol	Alcohol	3
Acetic acid	Acid	—
Formaldehyde	Aldehyde	3,4
Acetone	Ketone	3
Ethyl ether	Ether	3
Urea	Amide	—
Glycerol	Polyhydric alcohol	1
Phenol	Phenol	4
Hydroquinone	Dihydric phenol	4
Aniline	Amine	4
Methyl acetate	Ester	—

^a Toxicity scale is from 1, relatively nontoxic, to 6, highly toxic (ref. 7).

915 (Fullerton, Calif.), was used to measure the concentration of organic solutes. The carbon content of a dilute solution (total organic carbon <100 ppm) was proportional to the peak height shown in the recorder of the analyzer. Three to five injections were made for each sample to confirm the reproducibility of the analysis. The accuracy of the analysis was ±1 ppm of organic carbon content, when diluted to a concentration of less than 100 ppm for analysis.

The solute separation by each membrane is defined as follows:

$$\text{Solute separation} = \left[1 - \frac{\text{solute concentration in permeate solution}}{\text{solute concentration in test solution}} \right] \times 100\%$$

Results and Discussion

Figure 2 illustrates the separation of sodium chloride with all of the membranes tested. Most of the membranes gave better than 93% separation of salt with the exception of PBI and SPPO, which separated less than 75% of salt. The latter two membranes did not perform as well as their respective suppliers (8, 9) claimed. However, comparisons of the salt separations of each membrane before and after each series of tests indicated that none of the tested membranes yielded any sign of deterioration during the testing period.

Figures 3-8 illustrate respectively the separations of methanol, ethanol, and *i*-propanol; acetic acid and formal-

Table III. Average Permeate Fluxes and Overall Solute Separations of Reverse Osmosis membranes

Membrane	Average flux, gfd	Overall separation of ^a 13 model compounds, %
CA	7.66	12.82
CA-T	10.17	17.84
CAB	1.37	21.81
CA3	4.89	26.61
NS-100	9.71	69.83
NS-100-T	6.50	73.65
NS-200	6.69	78.92
PBI	36.03	16.12
SPPO	17.39	19.36
AP	2.45	63.48
B-9 (2' × 5" diam.)	1,250 gpd ^b	50.00
B-10 (4' × 5" diam.)	4,500 gpd ^b	50.81
B-10 (4' × 5" diam.)	4,500 gpd ^b	52.11 ^c

^a The overall separation of solutes shown here indicates that the anticipated separation of a mixture having a concentration of 1000 ppm of TOC contributed on equal weight basis by each of the thirteen test compounds.

^b Since the total surface area of hollow-fiber module is unknown, the permeate capacity, in terms of gallons/day, is shown. ^c Actual separation of mixture of solutes on equal weight basis having a final TOC of 1000 ppm.

dehyde; acetone and ethyl ether; urea and glycerol; phenol and hydroquinone; as well as aniline and methyl acetate. The permeate flux was insensitive to the type of organic solute present in the test concentration at a level of 1000 ppm. The average permeate flux and the overall separation of the 13 polar organic compounds (see definition in Table III) with each membrane are shown in Table III. Although the overall separation of solute is meaningless while relating to the separation of other unknown organic compounds, it, however, provides a basis for the comparison of the overall effectiveness of each membrane toward the separation of these thirteen compounds tested in this study.

In general, the specific PBI and SPPO membranes evaluated in this study showed poor separation toward both or-

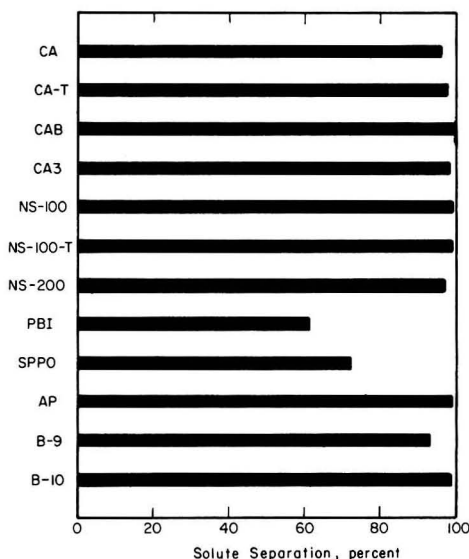


Figure 2. Separation of sodium chloride

ganic and inorganic compounds. Membranes made of cellulose acetate and its derivatives, including CA, CA-T, CAB, and CA3, separated inorganic salt between 97 and 99.5%, but yielded a very low degree of separation for the polar organic compounds. In the cases of methanol, phenol, hydroquinone, and aniline, these membranes yielded negative

separation—i.e., the solute concentration was higher in the permeate than that in the test solution. The concentration of such highly polar compounds in the permeate is due to the high polarity of cellulose acetate (4). Efforts have been made by various investigators (2) to reduce the polarity of the cellulose acetate membrane material by substituting a free hydroxyl group of cellulose acetate with additional acetyl group—e.g., CA3—or with a butyl group—e.g., CAB. However, membranes made of CA derivative performed only slightly better than the CA and CA-T in their separation of polar organic compounds. For instance, all of these membranes—i.e., CA, CA-T, CAB, and CA3—yielded good separation of *i*-propanol and glycerol; on the other hand, all yielded negative separation of methanol. Besides, the relatively nonpolar nature of CAB and CA3 greatly reduces the affinity of these membranes to water; as such, both CAB and CA3 showed a drastic reduction in permeate flux (see Table III) as compared to CA and CA-T.

The NS membranes were originally developed by the North Star R & D Institute (Minneapolis, Minn.) and subsequently studied extensively by Fang and Chian (3, 10) and Chian and Fang (1, 11, 12). Although they were prepared in different laboratories, the NS-100, NS-100-T, and NS-200 yielded comparable membrane performances. At the same level of permeate flux, these membranes yielded 98–99.5% separation of salt as compared to 96–98% by CA. Table III shows that the overall separation of polar organic compounds by NS membranes is much higher than that of CA.

Three membranes made of aromatic polyamide, including AP, B-9, and B-10, also yielded similar separation of these model compounds. They separated better than 90% of salt and 50% of the test compounds. Although the permeate flux of membranes made of polyamide is low, the capacity of permeation flow can be increased by increasing the active membrane surface area per unit module volume, such as the hollow fiber module of B-9 and B-10. For all the

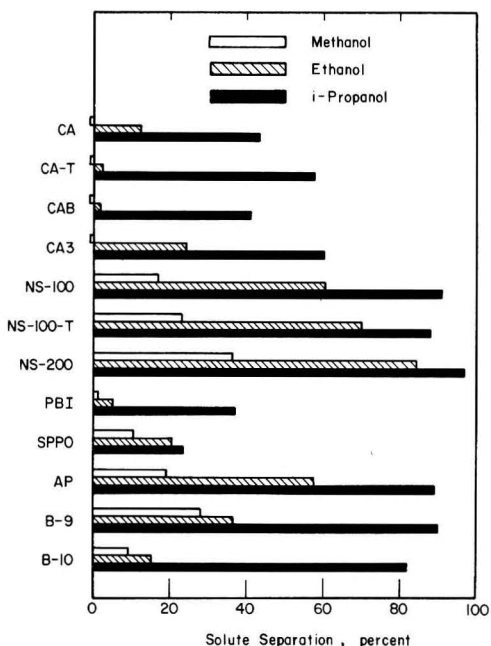


Figure 3. Separation of methanol, ethanol, and *i*-propanol

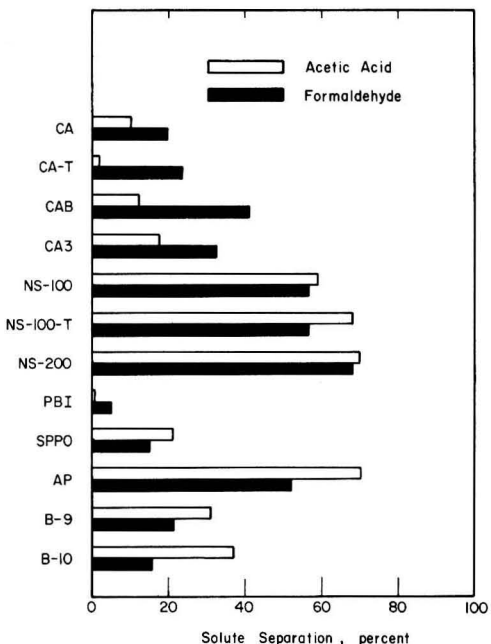


Figure 4. Separation of acetic acid and formaldehyde

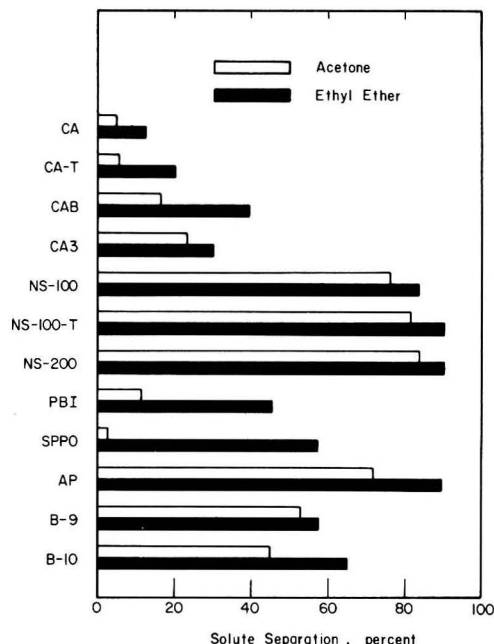


Figure 5. Separation of acetone and ethyl ether

compounds tested, the AP membrane gave better separation than B-9 and B-10. This is due to the higher average feed concentration as well as the polarization effect at the membrane surface encountered with the hollow fibers in both B-9 and B-10. These effects were reduced by the invariant feed concentration and the existence of highly turbulent flow near the flat-sheet AP membrane surface. The B-10 yielded 3-4 times higher permeate rate than the B-9 (see Table III), because it has a larger active surface area (approximately twice) and higher operating pressure.

Solute Separation

Although the mechanism by which the membrane separates solutes from solutions is still a subject of much controversy, and theory of separation mechanism is, however, intimately concerned with the physicochemical properties of both the membrane and the solutes under study. The most widely accepted theory on reverse osmosis separation of solutes so far is the preferential sorption-capillary flow mechanism proposed by Sourirajan (13). It states that an appropriate chemical nature of the membrane surface in contact with the solution, together with the existence of pores of appropriate size on the skin layer at the interface, is an indispensable twin requirement for the success of solute separation.

In this study, the pore size of each membrane evaluated was controlled by its separation of sodium chloride tested under standard conditions as given in the previous section. With the exception of PBI and SPPO membranes, all other membranes studied here yielded the most optimal separation of sodium chloride and flux under the standard testing conditions as shown in Figure 2. The lower than the desired level of separation of sodium chloride with the PBI and SPPO membranes (see Figure 2) may account for their poor separation of the test compounds as shown in Table III. Based on the mechanism of capillary flow (14), for a given solute, any degree of reverse osmosis separation is

possible with a given membrane material, if the porous structure of the surface of the membrane is allowed to vary. Therefore, the separation of these test compounds with both PBI and SPPO membranes can be improved appreciably, if the surface porosities of these membranes were brought to a point which would separate sodium chloride

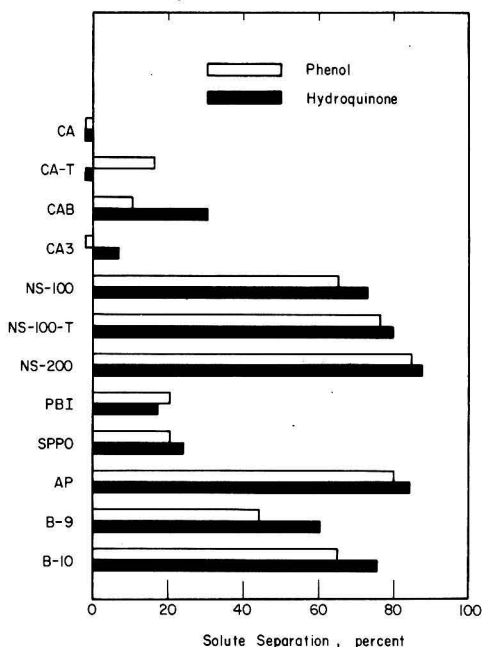


Figure 7. Separation of phenol and hydroquinone

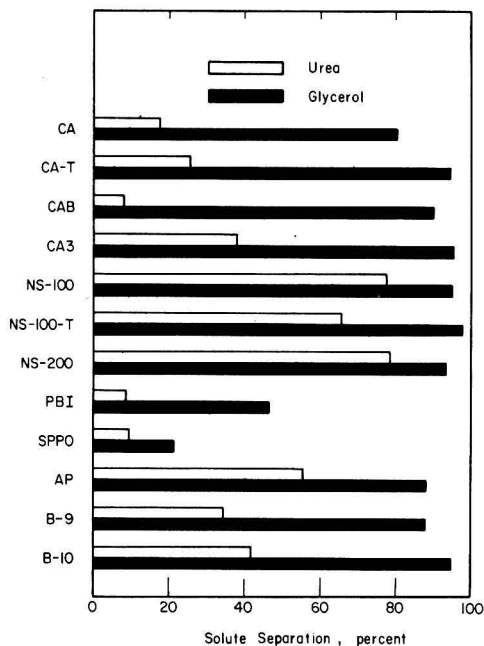


Figure 6. Separation of urea and glycerol

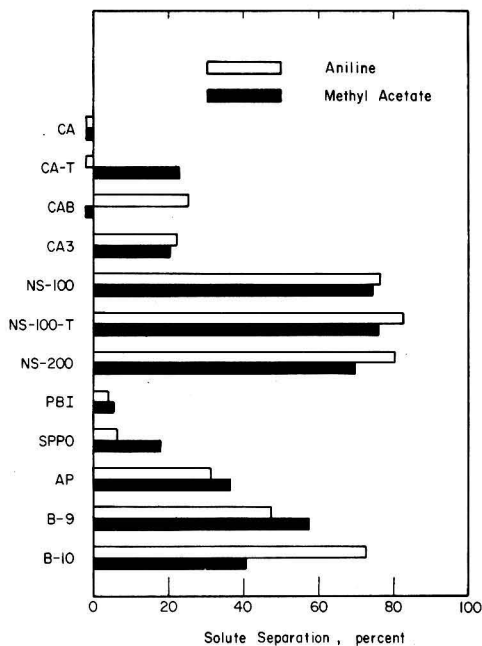


Figure 8. Separation of aniline and methyl acetate

comparable to those obtained with the other membranes tested—i.e., 95–99% (see Figure 2).

Once the physical properties of the membrane, such as the surface structure and porosity, are determined as characterized by their separation of sodium chloride (see Figure 2) and fluxes (see Table III), the relationship between the physicochemical properties of solute in aqueous solutions and the chemical nature of the membrane materials can then be established to interpret the separation data of these organic compounds with various membranes tested.

According to the analysis of Matsuura and Sourirajan (4), for a given membrane material and structure, one of the most important physicochemical criteria governing reverse osmosis separation of organic solute in aqueous solution is the "Polar Effect" of the solute molecule which includes both the functional group and the substituent groups. Both acidity and basicity of the functional groups are considered to be the relevant expression of polar effect. A measure of acidity and basicity is given by the ease of hydrogen bond formation and/or degree of dissociation of the molecule in aqueous solution. The former can be quantitatively expressed by the shift of the OH— and OD— band maximum in the ir spectra, and the latter by the dissociation constant, pK_a , with both carboxylic acids and amines. A measure of the effect of the substituent groups on the polar effect of the molecule can be quantitatively expressed by Taft and Hammett numbers. Other less quantitative measures of solute separation include the use of solubility parameters between the organic solutes and the membrane materials (14) and the steric effect of the molecule (3, 5).

Whereas the quantitative analysis of separation data of a large number of organic compounds with a limited number of membranes, such as CA and NS-100, has been reported by Matsuura and Sourirajan (4) and Fang and Chian (3), respectively, only qualitative analysis is given here in relating the solute separation data of polar organic compounds with the chemical nature of a large number of membrane materials.

Many investigators (3–5) have reported that the separation of aqueous solution of organic compounds with membranes depends greatly on their degree of ionization. For instance, the separation of formic acid by the NS-100 membrane varied from approximately 6% when partially undissociated to 98% when dissociated completely (3). In the case of inorganic salts, it has also been reported that the separation of an ion with a given membrane depends on its enthalpy of hydration (10); the larger the extent of the enthalpy of hydration of the ion, the higher the degree of separation resulted. This is due to the formation of hydrated complex of the dissociated ion which is bulky in size and hence is difficult to diffuse through the membrane. Comparisons of Figures 2–8 indicate that the separations of the low-molecular-weight polar organic compounds were not so effective as those of sodium chloride for all the membranes tested. This is attributable to the lesser degrees of dissociation of organic molecules under the pH of testing as compared to the bulkier hydrated inorganic ion as well as the lesser degree of electrostatic repulsion between the solutes and the membrane materials.

According to the preferential-sorption mechanism (13), solute molecule is first adsorbed on the membrane surface and then transported through the membrane because of the gradient of its chemical activity. Therefore, in addition to the steric effect as discussed above, the solute separation is also dependent on the characteristics of the membrane and the functional group of the molecule to be separated. Figures 3–8 show results of solutes separation with different membrane materials.

Salome (15) has developed a molecular parameter, per-

Table IV. Separation Soluble Organics^a In Sewage and Secondary Effluents by Reverse Osmosis (18)

	TOC, mg/l, feed	TOC, mg/l, RO effluent ^b	Percent separation
Sewage	32.8	9.8	70.1
High-loading secondary effluent (F/M = 0.69 day ⁻¹)	18.0	3.1	82.8
Low-loading secondary effluent (F/M = 0.33 day ⁻¹)	11.1	0.7	93.7

^a Soluble organics in the filtrate of the 0.45- μ Millipore Membrane (Bedford, Mass.). ^b B-10 Permeator (Du Pont, Wilmington Del.) operating conditions: product water recovery, 80%; pressure, 800 psig; feed flow rate, 4 gal/min; temperature, 25°C.

machor, from the study of permeability of organic vapors through polyethylene film. The parameter permachor increases with increasing size, branch, and polarity of the molecule. A molecule having a high permachor, has a lesser degree of permeability through the polyethylene film. However, it is commonly known that the nonpolar hydrocarbons have a lower degree of permeability through the reverse osmosis membranes when compared to those molecules having more polar functional groups (13). This is due to the nature of the membranes selected, for the reverse osmosis membrane differs from that of polyethylene film. Certain degrees of polar characteristics are required in order to have affinity to water molecules and thus good water permeation flow. Hence it is not a surprise to find that the experimental results of this study indicate that permachor parameter was not applicable to the solute separation of reverse osmosis. Nor was a quantitative relationship found between the solute separation and any single molecular parameter of organic solute, such as dipole moment or solubility parameter.

Fang and Chian (3), and Duvel and Helfgott (5) have reported that the separations of solutes having a same functional group depends on the size and shape of the solutes. Those solutes having a longer chain and/or more branches yield a higher degree of separation. This general rule is confirmed from the tests of three alcoholic compounds using different membrane materials as shown in Figure 3. All the membranes tested, without a single exception, separated a greater extent of *i*-propanol than ethanol, which in turn separated better than methanol. This can be attributed to the steric effect of the solute while diffusing through the membrane and the polar effect of the solute.

Application to Wastewater Treatment

The ultimate goal of this study is to assess the effectiveness of various reverse osmosis membranes for the separation of organic contaminants in wastes. However, in the real world of waste treatment, the membrane process is to be applied to separate complex mixtures of molecules rather than single solute solutions. Therefore, the possible effect of solute interaction on its separation in mixtures, along with results of actual reverse osmosis separation of various wastewaters, is discussed here.

Since the organic compounds selected for this study consist of some of the lowest molecular-weight homologs in each of the functional groups, results of solute separation with various membrane materials represent the most conservative data as compared with the actual organic contaminants in wastewaters based on the mechanism of the steric and polar effect of the solute as discussed previously. Whereas the individual effect of solute interaction between

each pair of the test compounds is unknown, a limited experiment of the combined effect of solute interaction among all the test compounds has been conducted with the B-10 module. A slightly higher separation of total solutes in a mixture of these 13 test compounds was observed as shown in the bottom line of Table III. This discrepancy is well within the combined experimental errors of both the reverse osmosis runs and the analytical procedures. This slight increase in the separation of a mixture of test compounds can be also explained by the neutralization effect of the acid and the basic molecules in the test compounds, resulting in somewhat higher dissociable neutral compounds. However, in the case of separating dissociable compounds, solute separation is closely related to the concentration of solutes and pH and ionic strength of the solutions. For a mixture consisting of dissociable compounds from the same functional group, such as the carboxylic group, the solute separation of mixtures was found to be lower than that calculated from data obtained from single solute solutions (16). This is due to the depression of solute dissociation.

Fortunately, in waste treatment, the organic compounds present in wastewaters were found to have higher molecular weight, and thus lower polarity, than those tested in this study (17). Chian et al. (18) have studied the effect of biological treatment of municipal sewage on the removal of organics with the reverse osmosis process. Table IV shows that membrane separation of TOC increases with the increase in the degree of treatment of sewage with the activated sludge system. It is seen from Table IV that membrane separation of soluble TOC increases from 70.1% for raw sewage to 82.8 and 93.7% respectively for effluents from the high- and the low-loading units. The decrease in loading implies that sewage is treated more intensively. As such, a higher percentage of biologically refractory materials is expected in the treated effluent from a low-loading system (19). These materials are mainly high-molecular-weight humic substances formed as a result of biological activities.

The specific membrane studied by Chian et al. (18) is a B-10 permeator which has an overall separation of 50% for the test compounds (see Table III). This is much lower than that obtained with the worst case while separating soluble organics from raw sewage. Therefore, the overall separation of solutes with various membranes as given in Table III can be considered to be the lowest limit that one can expect while treating sewage wastewaters.

Conclusion

With the exception of PBI and SSPO, most of the twelve membranes evaluated showed a high degree of separating sodium chloride. When tested, of 13 low-molecular-weight polar organic compounds consisting of various functional groups, the NS series membranes yielded the highest over-

all separation of 75% of these compounds, while the AP and the CA series membranes yielded somewhat better than 50 and 15% respectively. The overall separation of these compounds with various membranes can be considered to be the lowest possible ones while applying reverse osmosis to treatment of wastewaters, especially sewage.

Acknowledgment

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Distribution of Airborne Polycyclic Aromatic Hydrocarbons Throughout Los Angeles

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■ High-volume air samplers were used to collect samples of airborne particulate matter on an intermittent schedule at 39 locations throughout Los Angeles County for a full year. Composites were extracted and analyzed for 14 polycyclic aromatic hydrocarbons (PAH). Major PAH show high seasonal correlations (negative) with median early morning atmospheric inversion heights. PAH are highest during the November–January quarter but ranges for different PAH vary by factors 4–10 during the year. Comparison of relative PAH concentration patterns for different areas suggests that PAH in the better ventilated coastal areas arise primarily from automobiles, while in the areas farthest inland additional smaller amounts of PAH arise from nonautomobile sources. Benzo(a)pyrene averaged 0.46 ng/m^3 , but no composite concentration was higher than 2.0 ng/m^3 .

In a large-volume air sampling program in Los Angeles, differences in concentrations of polycyclic aromatic hydrocarbons (PAH) were found among four locations (1). The patterns of relative concentrations of various PAH were similar and resembled that of auto exhaust except when affected by nearby localized sources. Observations of lung cancer rate excesses in one area of the county (2) led to a further brief survey in that area to define current PAH levels (3). This was then extended to the entire County in a detailed year-long air sampling survey described here.

Experimental

Conventional "high volume" samplers as described by the Intersociety Committee (4) were used. The samplers

were located at fire stations (all but two were on one or two story roofs) and were serviced as before (3). Thirteen areas had been selected along census tract boundaries to divide the basin (2). In each area three collection sites (A, B, and C) were chosen. During one month all 13 A sites were sampled, next month the B sites, the third month the C sites, and then back to A, and so on for the full year. In one month the A series, for example, was sampled for seven days spread through the month (including each day of the week once only), then the samplers were moved to the B sites for a similar sequence. Site locations and areas are shown in Figure 1. The filters were equilibrated at constant humidity and weighed before and after exposure. For the first quarter the seven filters for any one month and area were combined and extracted with benzene. Since no striking differences in PAH patterns were seen among the A, B, and C sites within any area, thereafter the three sites were made into quarterly composites for extraction, to reduce the amount of analytical work. There were therefore 13 composites of seven filters for each of the first three months and 13 composites of 21 filters for each of the last three quarters. Sampling went from February 1974 through January 1975. Extractions and PAH analyses by chromatography and ultraviolet spectrophotometry were done as before (1, 3).

From reports of the Los Angeles Air Pollution Control District the inversion heights for 0600 h at Los Angeles Airport for each sampling day were obtained. Since there are numerous low-level inversions recorded as 100 ft and no heights above 9900 ft are listed, median rather than mean values were used to compare different periods. Average morning (0600–1200) wind speeds and the medians of the maximum calculated inversion heights for downtown Los Angeles during the sample periods were also derived from APCD reports.

Table I. Sample Yields, $\mu\text{g/m}^3$

Area	1	2	3	4	5	6	7	8	9	10	11	12	13
	Automobile Traffic Density (ATD), $10^{-5} \text{ Mi/Da/Mi}^2$ (5)												
	0.75	1.2	1.5	1.5	2.0	1.2	0.65	0.4	0.8	1.05	0.95	0.95	0.9
	Suspended Particulate Matter (SPM), Quarterly Geometric Means												
Quarter													
1	59.1	75.6	75.4	92.2	84.7	94.1	113.5	101.6	106.0	106.1	71.9	92.2	82.1
2	101.9	84.7	69.4	83.2	90.4	108.8	116.1	123.5	100.4	84.7	68.8	76.7	72.0
3	109.0	97.3	73.5	82.4	83.2	116.8	156.1	130.7	112.0	74.7	57.3	84.1	82.0
4	76.6	93.2	80.2	84.5	85.1	120.1	130.4	121.4	109.3	68.8	67.4	83.5	80.4
Geom. mean, year	84.2	87.2	74.5	85.5	85.8	109.5	128.0	118.8	106.8	82.4	66.1	83.9	79.0
	Benzene-soluble Particulate Matter (BSPM), Composites Except 1st Quarter ^a												
Quarter													
1 ^a	5.9	10.0	9.0	11.0	10.0	11.1	11.5	9.0	9.4	11.6	7.9	8.4	7.0
2	7.4	7.2	3.9	6.7	7.5	8.6	7.4	7.5	4.4	5.0	3.7	4.2	4.2
3	9.1	8.4	4.3	5.9	5.3	10.0	10.9	8.8	7.1	5.9	3.0	4.4	4.0
4	8.7	14.0	11.8	15.1	12.6	17.0	14.6	12.0	13.0	8.4	8.6	14.1	10.0
Geom. mean, year	7.7	9.6	6.5	9.0	8.4	11.3	10.8	9.2	7.9	7.3	5.3	6.8	5.9

^a Geometric mean of A, B, and C composites (see text).

Results

Traffic Densities (ATD). The ATD values given in Table I are averages for the three sample sites in each area, derived as before (1) from data of Roberts et al. (5).

Suspended Particulate Matter (SPM). Geometric means of SPM by quarters and for the year for each area are given in Table I. The highest concentrations are found at inland areas 6-9, where the levels may sometimes be more than twice those at coastal locations. The means for the whole year vary among areas by less than twofold (areas 7 and 11) and do not relate to ATD. Variation by quarter is only 30-40% except for area 1.

Benzene-Soluble Particulate Matter (BSPM). Extract yields of BSPM are also shown in Table I. Highest

yearly means are found at areas 6, 7, and 8. The range among areas and by quarters is about threefold at most. The highest levels are uniformly in the first and fourth quarters (except for area 1). (This is unlike the case for SPM, where quarterly variation is smaller and highest levels are sometimes in the third quarter.) The BSPM fraction of the SPM annual means by area is fairly uniform (7.4-11.0%) but by quarters the fraction ranges 6.4-13.3%, highest in winter. BSPM does not correlate with ATD.

Polycyclic Aromatic Hydrocarbons (PAH). Concentrations of 14 PAH are shown as quarterly geometric means for all sites combined in Table II. All PAH are highest in the fourth and first quarters. This is parallel to BSPM levels, but the quarterly PAH ranges are wider, up to tenfold in some areas. The PAH concentrations are listed by area in Table III; the upper figure in each pair is the geometric mean of the observed values over the full year. The lowest observed levels are found at the coastal areas 11 and 13, and the highest at inland areas 6 and 7. The ranges vary

Table II. PAH Concentrations, ng/m³
Quarterly geometric means of all areas

PAH ^a	Quarter				Year, geom. mean
	1	2	3	4	
PYR	0.58	0.23	0.25	1.24	0.45
FLT	0.38	0.15	0.24	0.68	0.31
BAA	0.30	0.06	0.10	0.59	0.18
CHY	0.70	0.26	0.44	1.57	0.60
BEP	1.30	0.42	0.62	1.96	0.90
BAP	0.77	0.17	0.26	1.27	0.46
BBF		0.24	0.33	1.30	(0.54) ^b
BJF	0.26	0.06	0.12	0.43	0.17
BKF	0.27	0.07	0.15	0.52	0.20
PER			0.06	0.22	(0.10) ^b
ANT	0.33	0.08	0.14	0.79	0.23
GEE	3.80	1.35	2.71	8.25	3.27
INP	1.79	0.68	1.00	2.64	1.34
COR	2.49	1.13	1.66	4.44	2.13

^a PAH identities are given in Nomenclature section.
^b Based on incomplete data.

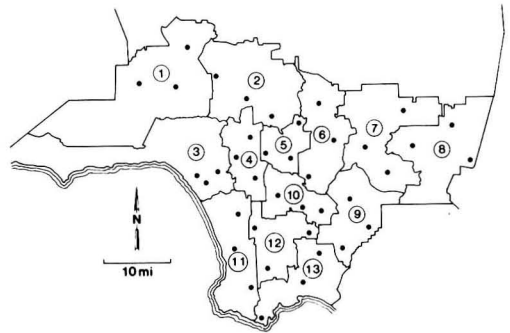


Figure 1. Los Angeles County divided into 13 areas (excluding sparsely populated northern portion)
Dots denote air sampling sites

Table III. Observed PAH Annual Geometric Mean Concentrations, ng/m³ and Calculated Based on Patterns in Coastal Areas^a

PAH	Area												
	1	2	3	4	5	6	7	8	9	10	11	12	13
PYR	0.41	0.46	0.37	0.49	0.47	0.76 ^b	0.84	0.67	0.34	0.34	0.33	0.42	0.29
FLT	0.36	0.50	0.40	0.60	0.48	0.61	0.46	0.33	0.39	0.38	0.30	0.44	0.30
BAA	0.28	0.32	0.20	0.33	0.30	0.50	0.61	0.55	0.25	0.27	0.21	0.30	0.22
CHY	0.23	0.32	0.26	0.39	0.31	0.40	0.30	0.21	0.25	0.25	0.19	0.28	0.19
BEP	0.18	0.18	0.15	0.26	0.21	0.44	0.23	0.24	0.10	0.12	0.11	0.17	0.11
BAP	0.13	0.18	0.15	0.22	0.18	0.23	0.17	0.12	0.15	0.14	0.11	0.16	0.11
BBF	0.62	0.68	0.36	0.65	0.76	0.92	1.02	0.68	0.53	0.42	0.38	0.66	0.45
BJF	0.44	0.60	0.49	0.72	0.59	0.75	0.57	0.40	0.48	0.46	0.36	0.53	0.37
BKF	0.81	1.01	0.73	1.06	1.00	1.34	1.22	0.88	0.92	0.77	0.65	0.89	0.70
PER	0.75	1.04	0.85	1.26	1.02	1.30	0.98	0.69	0.83	0.80	0.63	0.92	0.63
ANT	0.47	0.63	0.41	0.56	0.54	0.77	0.76	0.53	0.41	0.35	0.24	0.38	0.27
GEE	0.32	0.45	0.36	0.54	0.44	0.56	0.42	0.30	0.36	0.35	0.27	0.40	0.27
INP	0.17	0.25	0.17	0.18	0.23	0.28	0.26	0.14	0.14	0.14	0.10	0.15	0.11
COR	0.13	0.19	0.15	0.22	0.18	0.23	0.17	0.12	0.15	0.14	0.11	0.16	0.11
PYR	0.16	0.26	0.16	0.21	0.23	0.27	0.29	0.25	0.14	0.16	0.11	0.19	0.11
FLT	0.14	0.19	0.15	0.23	0.18	0.23	0.18	0.13	0.15	0.14	0.11	0.17	0.11
BAA	0.25	0.35	0.28	0.29	0.26	0.42	0.38	0.25	0.18	0.15	0.13	0.17	0.12
CHY	0.18	0.25	0.21	0.31	0.25	0.32	0.24	0.17	0.20	0.20	0.15	0.22	0.15
BEP	2.86	3.78	3.02	4.33	3.84	5.01	4.02	2.67	2.99	3.05	2.31	3.41	2.32
BAP	2.73	3.79	3.08	4.57	3.69	4.72	3.56	2.52	3.02	2.91	2.29	3.35	2.30
BBF	1.10	1.22	1.11	1.89	1.55	2.05	1.96	1.18	1.33	1.18	0.90	1.48	1.01
BJF	1.09	1.51	1.22	1.82	1.47	1.88	1.41	1.00	1.20	1.16	0.91	1.33	0.91
BKF	1.83	2.54	2.06	3.06	2.47	3.16	2.38	1.69	2.02	1.95	1.53	2.24	1.54

^a Upper value in each pair = observed; lower value calculated using the average PAH/COR ratio for areas 3, 11, and 13.
^b Italicized observed values exceed calculated values by at least three times the coefficient of variance among 3, 11, and 13.

Table IV. Correlation Between Air Concentration, *C*, and Median Inversion Height, *H*
 $\log C = a + bH$

Variable	<i>a</i>	<i>b</i>	<i>r</i>	<i>P</i>
SPM	1.951	3.9×10^{-6}	0.28	
BSPM	1.069	-1.568×10^{-4}	-0.97	<0.05
COR	0.600	-2.776×10^{-4}	-0.96	<0.05
GEE	0.857	-3.515×10^{-4}	-0.95	~0.05
BAP	0.104	-4.567×10^{-4}	-0.99	<0.01

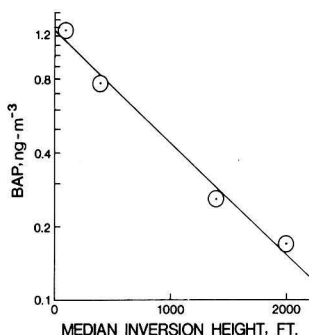


Figure 2. BAP, 13-area geometric means, against median inversion heights, by quarters

from two- to fourfold among various PAH. The lower figure in each pair in Table III is the calculated contribution from auto exhaust, based on coronene content and using the average patterns for the coastal areas, as described below.

Discussion

Meteorological Effects. SPM, BSPM, COR, GEE, and BAP log concentrations (quarterly for all sites combined) were tested for correlation with median quarterly inversion heights during sampling periods. As shown in Table IV, all but SPM show high negative correlation coefficients. The regression line for BAP is shown in Figure 2. The early morning inversion heights at the airport cannot be precisely related to concentrations since the inversion heights vary during the day and from place to place and may even break completely, but they obviously influence the PAH concentrations very strongly. SPM basinwide means, on the other hand, vary only slightly by season and do not correlate with inversion height. SPM contains some larger and denser particles which settle rapidly, hence would not be diluted much by an increase in inversion height. The PAH are mostly associated with small particles which do not settle rapidly (6, 7).

Average morning wind speeds and calculated maximum inversion heights did not correlate with concentrations.

Seasonal Effects. It is evident in Table II that all PAH concentrations are lowest in the May–October period and highest November–April. Earlier it was shown that COR correlates well with traffic density (1). It is also one of the PAH most stable toward degradation in air (8, 9). Ratios of the high 4th quarter PAH concentrations to those in the low 2nd quarter range from 3.9 for COR and INP to 7.5 for BAP and 9.8 for BAA. The PAH with wider ranges, such as BAA, may arise to a larger degree from nonautomobile sources such as boiler furnaces during the winter, and may

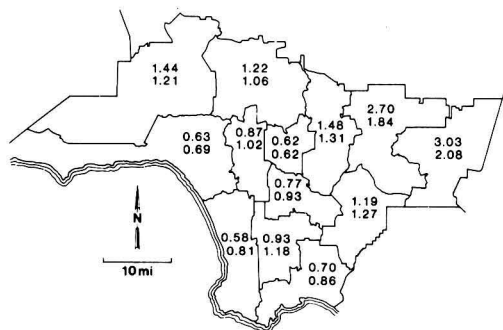


Figure 3. Ratios, normalized to 13-area geometric means; upper values in each pair: BAP/ATD; lower values: COR/ATD

be degraded more rapidly during the summer because of increased temperature, sunlight, and ozone.

Location Effects. In Figure 3 are shown the ratios of BAP and COR concentrations to automobile traffic densities (ATD) for the 13 areas, after normalization to the 13-area mean. Both ratios increase inland and are highest in areas 7 and 8. The prevailing winds are strongly onshore during the afternoon and more weakly offshore at night, so that the net long-term air movement is onshore. As a result, areas 7 and 8 with low ATD (Table I) nevertheless have higher PAH levels due to transport from areas to the west. (Areas 1 and 2 are bordered on the south by a range of hills up to about 600 m which shelter them from onshore winds.) Among other PAH, GEE, and INP concentrations parallel COR, while 10 other PAH are more like BAP.

For areas near the coast $COR/ATD > BAP/ATD$; for inland areas the converse is true. One possible reason for this is that COR decomposes or settles out more rapidly than BAP and most other PAH. The chemical stability of COR is very high, however, and it seems unlikely that the behavior shown in Figure 3 is due to preferential decomposition of COR. Since it seems to be associated with the same sized particles as other PAH (6, 7), there is no reason to expect COR to settle out more rapidly, either.

Another possibility is that there is nonautomobile emission of PAH. There is auto traffic in all directions around every sampling site. Nonauto point sources are not so uniformly distributed. The probability of there being one or more upwind of a sampling site during sample collection increases as the site is moved inland, since there are no sources offshore and the main air movement is onshore. Therefore, the PAH patterns at coastal sites should most

Table V. PAH Pattern Comparisons

PAH	PAH/COR		PAH	PAH/COR	
	Ref 1 ^a	Mean, areas 3, 11, 13		Ref 1 ^a	Mean, areas 3, 11, 13
PYR	0.38	0.19	BJF	0.09	0.07
FLT	0.27	0.13	BKF	0.11	0.07
BAA	0.21	0.07	PER	0.09	0.06 ^c
CHY	0.45	0.24	ANT	0.06	0.10
BEP	0.52	0.41	GEE	1.38	1.49
BAP	0.16	0.18	INP	0.16	0.59
BBF	0.27	0.21 ^b			

^a Reference 1, Table III. ^b Areas 11 and 13 only. ^c Areas 3 and 11 only.

nearly resemble that of auto exhaust. Let us average the very similar patterns (ratios of each PAH to COR) for the three coastal areas 3, 11, and 13, on the assumption that their PAH have no important sources except auto traffic. By using the average of these patterns (Table V) it is possible to estimate from the COR concentration in each area the approximate contribution of auto traffic to the other PAH. This is shown as the lower figure of each pair in Table III. The coefficients of variation (CV) for the patterns of the three coastal areas were also calculated. The observed values which exceed the calculated by more than 3 CV times the basin mean, are italicized in Table III. Most of these italicized values are found in areas 6-8. In Table V the PAH/COR pattern from previous work (1) is shown for comparison with the average of areas 3, 11, and 13. The previous results were obtained with a different type of sampler. Nevertheless, except for the tetracyclic PAH (where volatility losses may differ) INP is the only PAH in serious disagreement.

Even at their highest (area 7), the calculated nonauto PAH are less than those related to auto traffic. No individual quarterly sample showed total BAP levels above 2.0 ng/m³. The maximum calculated concentration of "non-auto" BAP is about 40% of this (0.8 out of 2.0 ng/m³ total BAP in area 7 during the fourth quarter). It appears that the automobile is not a rich source of BAP, and other sources in Los Angeles contribute even less on an area-wide basis. A recent report from the Environmental Protection Agency (10) of BAP concentration data from the National Air Sampling Network shows that the mean for 32 urban sites had declined from about 3 ng/m³ in 1966 to about 2 ng/m³ in 1970. The curve, if extrapolated to 1974, would indicate an average of about 1 ng/m³, roughly twice the average Los Angeles value of 0.46 ng/m³.

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Nomenclature

PAH = polycyclic aromatic hydrocarbon
SPM = suspended particulate matter

BSPM = benzene-soluble particulate matter
ATD = automobile traffic density
PYR = pyrene
FLT = fluoranthene
BAA = benz(a)anthracene
CHY = chrysene
BEP = benzo(e)pyrene
BAP = benzo(a)pyrene
BBF = benzo(b)fluoranthene
BJF = benzo(j)fluoranthene
BKF = benzo(k)fluoranthene
PER = perylene
ANT = anthanthrene
GEE = benzo(ghi)perylene
INP = indeno (1,2,3-cd) pyrene
COR = coronene

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PAN and Oxidant Measurement in Ambient Atmospheres

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■ PAN and ozone or oxidant measurements were made at four different sites. Three of these sites were urban locations, the other was rural. PAN and corresponding ozone and oxidant measurements were compared. The maximum O_3/PAN or O_x/PAN ratios varied at each sampling site thus preventing the prediction of PAN concentrations estimates from ambient ozone concentration alone. Generally high ozone concentrations were observed when corresponding high PAN concentrations were measured. However, high ozone was observed when PAN concentrations were low. These observations concur with simulated chamber irradiations and modeling predictions of ozone and PAN concentrations.

Precursors to photochemical smog, namely, the hydrocarbon and oxides of nitrogen, are measured routinely by a network of state, federal, and other governmental laboratories throughout the United States. Information of detailed hydrocarbon composition in ambient atmosphere has also been reported (1-7). With the exception of ozone, little information is available on ambient concentrations of the secondary products of photochemical smog such as peroxyacetyl nitrate (PAN). PAN formation has been reported in several simulated sunlight irradiations of hydrocarbon and nitrogen oxides mixtures (8-13) and by sunlight irradiations of ambient air samples in plastic bags (5, 14, 15). In these plastic bag studies, PAN was observed as a major nitrogen-containing photochemical product accounting for a sizable percentage of the reacted oxides of nitrogen.

PAN is the most abundant member of a homologous series of peroxy acyl nitrates. This is due to relative abundance of PAN precursors in the ambient atmosphere as compared to other PAN-type compounds. PAN has been identified as strong phytotoxicant at ambient concentrations (16) and has been related to physiological interference (17, 18), but at concentrations above normal ambient maximums.

Ambient levels of PAN have been well documented for Los Angeles and Riverside, Calif., (19-21). This paper presents results from PAN measurements of metropolitan areas of Los Angeles; Hoboken, N.J.; St. Louis; and in the rural areas of Wilmington, Ohio. Also, PAN measurements are compared to oxidant (ozone) measurements made at similar sample times.

Experimental

PAN measurements were made by a gas chromatograph equipped with an electron capture detector. The GC columns used were prepared from 120 cm \times 3.2 mm o.d. and 240 cm \times 3.2 mm o.d. glass tubing packed with 10% Carbowax 600 on Gas Chrom Z. The column was maintained at 23 °C. Two Ni^{63} electron capture detectors were used in these experiments (Microtek and Loenco). A 5-ml air sample injection was adequate for subpart per billion sensitivity. In St. Louis and Wilmington, air samples were injected

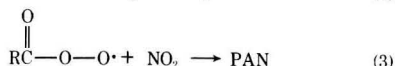
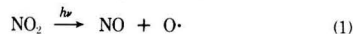
every 30 min with an automated valve. In Los Angeles and Hoboken, air samples were manually injected.

The GC analysis was calibrated by dilution of PAN samples prepared by the photolysis of ethyl nitrite in air (22) and calibrated by its absorptivities (23). When possible the standard PAN sample was calibrated in the field at the ambient air-sampling location. However, on occasion, the PAN standard was calibrated at the Environmental Research Center, Research Triangle Park (ERC-RTP) facility and transported to the field unit. This method proved to be adequate for GC calibration since PAN stored quite well (less than 10% loss over a five-day storage period) in Tedlar bags. The reliable storage of PAN in Tedlar-type containers were observed by other experimenters (24).

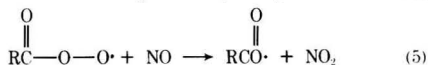
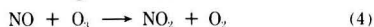
Continuous ozone measurements were made in Hoboken, N.J., using a rhodamine b chemiluminescent analyzer. Continuous ozone measurements were made in Wilmington, Ohio, using a Bendix ethylene-ozone chemiluminescent analyzer. Oxides of nitrogen were measured in Wilmington with a TECO model 14B chemiluminescent system. PAN samples were collected at the Los Angeles APCD (downtown facility) and at the EPA-CAMP station in St. Louis, Mo. Therefore, oxidant and oxides of nitrogen data were obtained from these networks. The procedures used by both networks were wet chemical. The EPA-CAMP station in St. Louis used neutral buffered KI for oxidant determinations, whereas the Los Angeles APCD employs neutral unbuffered KI. Recent studies have shown as much as 40% differences between these two KI solutions (25-27). These differences are important if one chooses to compare O_x/PAN ratios between cities; however, these types of comparison were not made in this paper. Both stations used Saltzman solution for NO_x determinations.

Results and Discussion

Photochemical Production of PAN and Ozone. In simulated sunlight, irradiations of hydrocarbon and nitrogen oxides mixtures, the PAN and ozone formation occur at approximately the same time (5, 8-15) thus suggesting that, at least for some systems, there is a close relationship in the mechanism for the formation of these two species. The simplified general mechanism for ozone and PAN formation are given by the following reactions:



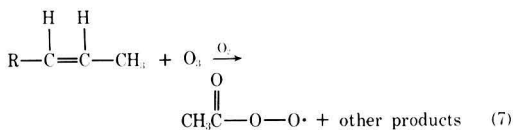
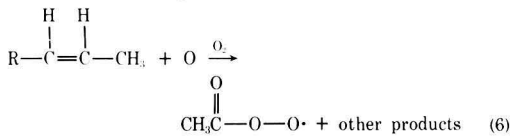
Excess nitric oxide will inhibit the formation of both O_3 and PAN by the following reactions:



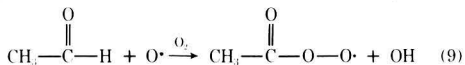
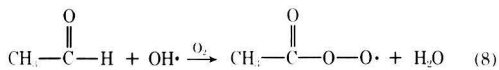
Since both of these reactions are fast, it is apparent that production of PAN and O_3 will not start until the NO_2/NO ratio is favorable for Reactions 1 through 3 to predominate.

The formation of the peroxyacetyl radical occurs by the following reactions:

Fragmentation Reactions:



Hydrogen abstraction reactions:



From rates of reaction considerations Reactions 7 and 8 are expected to predominate the formation of the peroxyacetyl radical.

From Reactions 1 through 3, it is expected that the production of ozone in the ambient atmosphere is a function of NO_2 photolysis. The NO produced in Reaction 1 would be rapidly converted back to NO_2 by RO_2 and RCO_3 radicals arising from the photochemical chain thus resulting in a continuous generation of ozone as long as NO_2 remains or is regenerated in the system. PAN formation, however, is only a function of NO_2 and hydrocarbon precursor concen-

trations and is chain-terminating. Thus PAN precursors are removed from the reaction chain when PAN is produced unlike the chain involved in the production of ozone. Also, ozone can be expected to be produced only during the daylight hours while PAN can be expected to be produced during the nighttime hours as long as hydrocarbon precursors, NO_2 , and O_3 are available (via Reactions 7 and 3).

Effect of Dilution on PAN and Ozone Formation. Niki et al. (28) have shown the effect of dilution on photochemical product formation using a photochemical model developed for the propylene-nitrogen oxide system. In a simulation run employing a tenfold dilution of initial reactant concentrations, maximum ozone concentration was decreased by only 50%, whereas maximum PAN concentration, although not specified, was indicated to be an order of magnitude lower. Other reactivity parameters, such as propylene half-life, NO_2 consumption rate, time to ozone maximum were also effected by this tenfold dilution. The principal concern, however, is the net effect of dilution on the O_3/PAN ratio.

To demonstrate the effect of dilution on PAN and ozone formation, a computer simulation study was performed using a photochemical model developed by Hecht et al. (29) for a mixture of *n*-butane-propylene- NO_x . PAN and ozone isopleths for 300-min irradiations are given in Figure 1. Interpretations of these isopleths agree that dilution has its greatest effect on PAN production. For example, for an initial mixture of 0.16 ppm of hydrocarbon and 0.16 ppm of nitrogen oxides, 300-min values of PAN and ozone are approximately 17 and 200 ppb, respectively. When the mixture is diluted by a factor of four to 0.04 ppm, as the initial conditions for both hydrocarbon and nitrogen oxides, 300-min values of PAN and ozone are approximately 2.5 and 50 ppb, respectively. In other words, a fourfold dilution of initial reactants resulted in a seven-fold decrease in PAN and

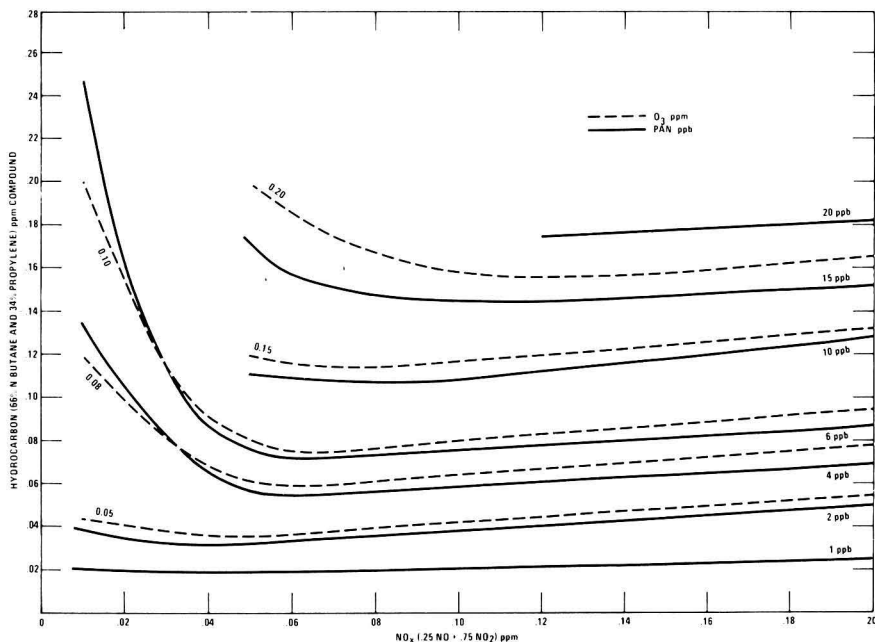


Figure 1. O_3 and PAN isopleths for *n*-butane-propylene-nitrogen oxides mixtures after 300-min irradiation from computer K_1 for NO_2 photolysis is 0.30 min^{-1}

a fourfold decrease in ozone. The model also shows that with longer irradiations, the O_3 /PAN ratio increases.

The hydrocarbon mixture used in this model is not suggested to be representative of any real ambient atmosphere but merely to demonstrate the effect of dilution. In reality, the urban and rural atmospheres also contain aromatic hydrocarbons.

Effect of HC/NO_x on PAN and Ozone Formation. Computer simulation studies (29) have demonstrated the importance of HC/NO_x on ozone formation but have not dealt with predicted concentration of PAN. Using the limited information in Figure 1, no conclusive effect of HC/NO_x on the O_3 /PAN ratio can be seen. Chamber studies of simple hydrocarbon-NO_x mixtures (9) and diluted auto exhaust-NO_x (30) mixtures have not shown any conclusive effect of HC/NO_x on the O_3 /PAN ratio. These studies, however, were performed using short-term (360 min) irradiation times and HC/NO_x ratios ranging from 1-12. Long-term multiday irradiations and high HC/NO_x ratios such as those conditions considered in long-range transport processes may result in different conclusions.

Effect of Hydrocarbon Composition on PAN and Ozone Formation. It is clear that varying hydrocarbon composition will also affect PAN and ozone formation. As the paraffin content increases, PAN maximum is expected to decrease since paraffinic hydrocarbons have been shown to produce much lower PAN concentrations via reaction (8). However, chamber studies also suggest that paraffins under prolonged irradiation—such as multiday exposure to sunlight, during long-range pollutant transport—produce high concentrations of ozone with very little PAN formation. The aromatic hydrocarbons react to a greater extent resulting in higher PAN concentration; however, the PAN yields are much lower than those observed for the olefin-PAN precursors (11).

The hydrocarbon composition of most urban atmospheres is similar to diluted auto exhaust with additional sources of natural background of methane as well as industrial and automotive evaporative sources of hydrocarbons. The hydrocarbon composition of a particular atmosphere would vary as a function of industrial and automotive activity. These activities, however, are usually consistent in a particular atmosphere. Therefore, variation of the O_3 /PAN

ratio due to hydrocarbon compositional variations may be minimal.

Effect of Other Meteorological Parameters on PAN and Ozone Formation. The effect of light intensity on PAN and ozone formation was reported for simple hydrocarbon-NO_x mixtures (9) and for typical ambient hydrocarbon-NO_x mixtures (5). These studies report a predictable slowdown of photochemical process with reduced light intensities, but do not suggest any significant change in the O_3 /PAN ratio. Temperature effects have not been reported.

Ambient Measurements of PAN and Ozone. Results of ozone and PAN measurements made in Los Angeles are reported in Table I. The measurements were assembled and averaged during the 10:00 a.m. to 4:00 p.m. period of maximum photochemical activity. These measurements were collected at random times over a three-month period of September through November 1968. The daily PAN maximum was generally in the 10-30-ppb range with the average PAN maximum for the entire sampling period of 18.4 ppb. These measurements compare favorably to those reported by Mayrsohn (19).

Corresponding oxidant measurements made at similar sampling times are also reported in Table I. It is to be noted that when PAN concentrations are high, the corresponding oxidant concentrations are also high. The converse, however, is not true. Even at low PAN concentrations high oxidant concentrations were observed. These observations are consistent with the effects of dilution and hydrocarbon compositional changes; however, the possibility of other meteorological variations must also be considered.

Results of a similar sampling program in Hoboken, N.J., in 1970 are reported in Table II. Fewer PAN samples were collected during this study; however, the sampling period represents photochemical activity extending from the months of June through August. It is to be noted that PAN concentrations in Hoboken are much lower than those observed in Los Angeles. The average PAN concentration observed during the 10:00 a.m. to 4:00 p.m. time interval was 3.7 ppb. The contrast of the PAN concentration found between Los Angeles and Hoboken is probably the result of higher precursor concentrations found in Los Angeles due

Table I. PAN and Oxidant Measurements (10:00 a.m.—4:00 p.m.), Los Angeles, Calif., 1968

Samples	Range PAN concn, ppb	Av PAN concn, ppb	Range oxidant concn, ppb	Av oxidant concn, ppb	Ratio av. O _x /av PAN	Range of obsvd O _x /PAN
19	0-10	8.65	30-190	79.	9.13	5.1-24.4
59	10-20	13.0	44-220	97.	7.58	3.3-18.3
27	20-30	24.0	70-290	144.	6.04	2.8-13.0
6	30-40	32.6	100-400	168.	5.23	3.0-9.7
5	40-50	47.1	160-285	209.	4.49	3.2-6.1
2	50 higher	65.5	243-410	327.	4.94	3.9-6.0

Table II. PAN and Ozone Measurements (10:00 a.m.—4:00 p.m.) Hoboken, N.J., 1970

Samples	Range PAN, ppb	Av PAN concn, ppb	Range ozone, ppb	Av ozone concn, ppb	Ratio av O ₃ /av PAN	Range of obsvd O ₃ /PAN
14	0-2	1.5	15.0-112.0	42.0	28.0	5.6-77.5
15	2-4	2.8	22.0-150.0	71.0	25.3	10.1-62.5
4	4-6	4.7	100.0-135.0	113.0	24.0	22.9-25.0
8	6-8	7.1	97.0-219.0	162.0	22.8	12.6-34.1
2	8-10	9.9	214.0-278.0	246.0	25.1	20.7-29.6

Table III. PAN, Oxidant, and Ozone Measurements (10:00 a.m.–4:00 p.m.), St. Louis, Mo., 1973

Samples	PAN concn range, ppb	Av PAN concn, ppb	Range oxidant concn, ppb	Av oxidant concn, ppb	Ratio av O _x /av PAN	Range ozone concn, ppb	Av ozone concn, ppb	Ratio av O ₃ /av PAN
3	0–2	1.7	46–100	80.6	47.5	10–40	28.6	16.3
31	2–4	3.0	46–216	84.6	28.3	24–116	48.1	16.2
60	4–6	5.0	30–260	67.3	13.4	10–140	50.2	10.0
31	6–8	6.8	39–224	68.7	10.1	20–120	50.3	7.4
14	8–10	9.3	40–180	84.6	8.1	10–96	50.2	5.4
5	10–12	10.8	30–90	73.4	6.8	30–85	54.0	5.0
10	12 higher	18.6	52–100	85.6	4.6	32–80	59.5	3.2

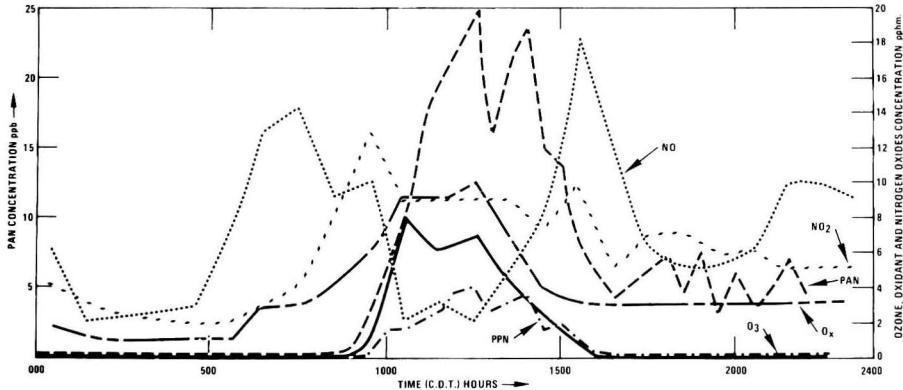


Figure 2. Diurnal pattern of PAN and other aerometric data at St. Louis CAMP station on August 10, 1973

to the poor ventilation characteristics of the basin area. The lower precursor concentrations in Hoboken appears to have greater effect on maximum PAN concentration than it has on maximum ozone. The observations again concur with photochemical model and chamber predictions.

Results of PAN and ozone sampling in the St. Louis, Mo., area are reported in Table III. These measurements were made at the EPA-CAMP station during the months of June through August 1973. Twelve days of complete PAN and CAMP station aerometric data were used to prepare Table III. The usual PAN concentration was observed to fall in the 2–8-ppb range with the average concentration for the entire study approximately 6.3 ppb. This average PAN concentration was 50% higher than that observed in Hoboken. This would suggest that the PAN precursor concentrations were greater in St. Louis than in Hoboken.

Both ozone and total oxidant measurements were available at the St. Louis CAMP station and are shown in Table III. The comparison of these two measurements during our sampling period were not comparable. This could be the result of either equipment malfunction or pollutant interference. The ethylene-ozone chemiluminescent method is specific for ozone. However, the neutral KI procedure is affected by other pollutants in the atmosphere.

Ozone and oxidant measurement in St. Louis were in general lower than those measured in either Hoboken or Los Angeles. This may be the result of instrument malfunction, although it is unlikely that both instruments are simultaneously malfunctioning. The probable cause of low ozone readings is the sampling site location. The St. Louis-CAMP station is located near a major downtown roadway. Influxes of freshly emitted nitric oxide from automotive sources may titrate ozone resulting in lower ozone and ox-

idant measurements. Even with the apparent problem of ozone and oxidant measurements, the same general trends of high oxidant-low PAN and decreasing ozone/PAN or oxidant/PAN ratios with increasing PAN concentration observed in Los Angeles and Hoboken were observed in St. Louis.

Diurnal variations of PAN were measured in St. Louis. The 24-h pattern of PAN and other pollutants for one sample day (August 10, 1973) is illustrated in Figure 2. The highest rates of formation of both ozone and PAN occur at the same time, approximately an hour after the NO₂/NO ratio becomes favorable for photochemical oxidant production. Both PAN and ozone curves reach two maximums during the afternoon hours approximately 1½ h apart. The second peak maximums may be the result of intermittent cloud coverage or transport of ozone and PAN from upwind locations. It is interesting to note the difference in peak maximum times between ozone and PAN. For the first afternoon peak, maximum ozone appears to peak out 2 h before PAN. At the second afternoon peak maximum, the time lag between ozone and PAN maximum decreases to about 75 min. Lag times between maximum ozone and maximum PAN were observed in bag irradiation of ambient air samples in Los Angeles (5). Ozone-forming reactions occur early in the photooxidation process, while PAN forming reaction are operative in the latter stages of the reaction.

Relatively high concentrations of the nitrogen oxides are observed throughout the day. Significant interference of freshly emitted nitric oxide with ozone can be speculated particularly at 1600 h when ozone drops to 0-ppb concentration due to a corresponding influx of nitric oxide. A diurnal plot of PPN (peroxypropyl nitrate) is also included

Table IV. Aerometric Measurements of PAN and Other Pollutants at 6–9 a.m. and at Maximum PAN Concentration, St. Louis, Mo., 1973

Date	6–9 a.m. av concn			Early morning crossover time (CDT) NO ₂ /NO > 1	PAN and other pollutant concentrations at PAN max				
	PAN, ppb	NO _x , ppb	NO ₂ , ppb		PAN, ppb	Ozone, ppb	Oxidant, ppb	NO _x , ppb	NO ₂ , ppb
June 30	2.5	190.0	110.0	7:10 a.m.	8.5	140.0	260.0	20.0	20.0
July 14	1.5	65.0	55.0	<i>a</i>	6.3	50.0	110.0	10.0	10.0
July 22	2.0	10.0	10.0	<i>a</i>	12.0	44.0	80.0	86.0	56.0
July 24	—	140.0	20.0	1:30 p.m.	7.5	14.0	50.0	145.0	70.0
August 4	3.2	108.0	60.0	<i>a</i>	12.5	55.0	75.0	50.0	30.0
August 10	0.0	173.0	52.0	8:40 a.m.	25.0	70.0	100.0	110.0	90.0
August 11	2.0	88.0	30.0	8:20 a.m.	11.5	20.0	50.0	40.0	30.0
August 12	—	37.0	17.0	7:40 a.m.	11.8	75.0	80.0	30.0	20.0
August 24	3.5	210.0	50.0	11:30 a.m.	10.5	55.0	60.0	70.0	50.0
August 25	3.4	80.0	48.0	<i>a</i>	8.8	80.0	72.0	30.0	20.0
August 26	4.5	54.0	39.0	<i>a</i>	7.5	100.0	90.0	30.0	20.0
August 27	2.5	310.0	80.0	9:30 a.m.	5.5	35.0	50.0	50.0	40.0

^aNo clear crossover point for NO–NO₂.

in Figure 2. A maximum concentration of approximately 5 ppb was observed. Trace concentrations of PPN were observed on other sampling days.

Early morning nitrogen oxides concentrations and composition (NO₂/NO ratio) were compared to afternoon PAN and ozone maximums for St. Louis. The results are given in Table IV. Neither NO₂ nor NO appears to have significant effects on the maximum concentration of these photochemical products. This is at variance with chamber investigations; however, the ambient atmosphere is not a controlled system. Meteorological variations are inconsistent and have complicating effects on the photochemical process. On

many of the days, the afternoon concentrations of NO_x are similar or, at times, higher than morning levels. Total hydrocarbon concentrations were not included; however, they are expected to follow a pattern similar to the nitrogen oxides because of similar sources.

Early morning PAN concentrations were included to indicate that on many of the sampling days, nighttime and early morning samples contained PAN probably from the previous day's photochemical activity. PAN concentrations as high as 7.5 ppb were observed at midnight. Nighttime and early morning PAN measurements were seldom taken in either Los Angeles or Hoboken. On occasion, however,

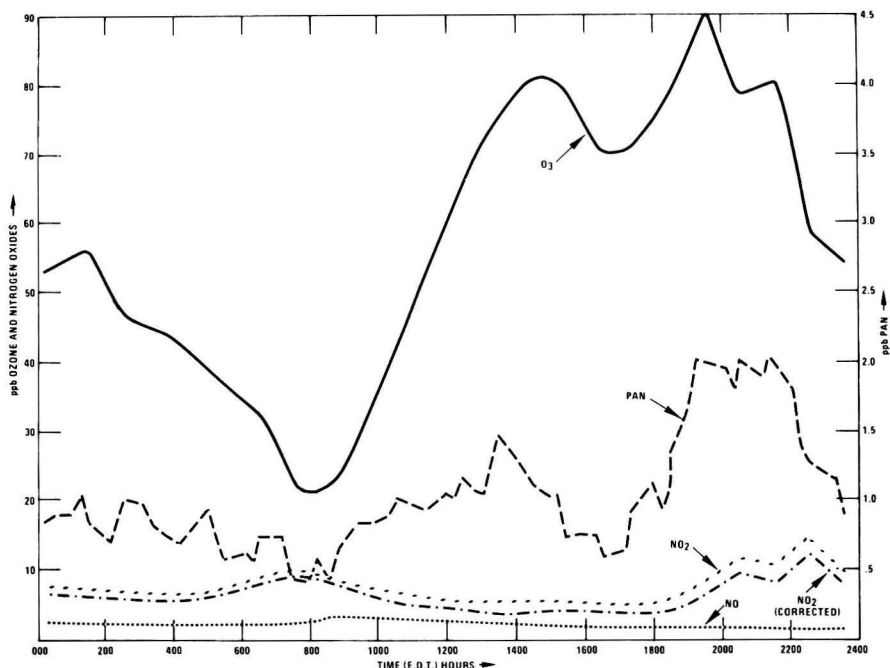


Figure 3. Diurnal pattern of PAN and other aerometric data at Wilmington, Ohio, on August 21, 1974

samples were taken at times other than those listed in either Tables I or II. At midnight on July 24 in Hoboken, 1.4 ppb was observed. No nighttime measurements were made in Los Angeles; however, 11 ppb PAN was observed at 9:00 a.m. on September 22, 1968. Nighttime concentrations of PAN of 10 ppb have been reported for Riverside, Calif. (20), 60 mi east of Los Angeles.

A continuous sampling program was performed in Wilmington, Ohio, during the summer of 1974 as part of a Midwest oxidant transport study. More than 1500 samples were collected during the month of August. Since low concentrations were generally observed in this rural area, a table similar to Tables I, II, and III was difficult to establish. The maximum concentration of PAN observed during this sampling period was 4.1 ppb. The daily PAN maximum rarely exceeded 3.0 ppb, even though the oxidant standard of 80 ppb was frequently exceeded. As in St. Louis, nighttime PAN concentrations were observed. In fact, some traces of PAN were observed in practically every sample taken. Typical diurnal patterns of PAN and other pollutants are given in Figures 3 and 4.

The diurnal patterns of ozone and PAN on the two days appear to contrast with each other. Ozone and PAN taken on August 21 (Figure 3) appear to follow similar curve patterns much like those observed in urban locations. Curve patterns for the two species were very much different on August 19 (Figure 4). PAN levels on August 21 were approximately four times greater than those observed on August 19, while corresponding ozone maximum showed only a 25% increase. The observations are probably due to both HC/NO_x ratio and PAN precursor concentrations differences. Apparently the PAN precursor concentrations on August 19 were much lower than those observed on August 21. This is reflected in the comparison of NO₂ measurements; however, these levels of nitrogen oxides are practically at the baseline sensitivity of our chemiluminescent instrument. The curve patterns for ozone and PAN in Figure 3 suggest that the formation of both compounds are similarly affected by atmospheric variations. These results indicate clearly that the measured ozone was the result of

tropospheric photochemistry and is not the result of stratospheric transport.

Ozone formation appears to start at approximately 8:30 a.m. on both days. The possibility of some of this ozone buildup resulting from fumigation by stratified layers of high ozone aloft appears to be unlikely as indicated by the August 19 data (Figure 4). If fumigation processes were occurring, a corresponding increase in the PAN curve would be expected unless ozone is more stable aloft than PAN. Fumigation processes probably occur; however, their effect upon the air quality at ground level is a function of the magnitude and pollutant concentration in these stratified layers.

The ozone/PAN ratios varied from 10/1 to over 150/1 in the Wilmington atmosphere. High ratios were expected since PAN precursor concentration were generally low; however, HC/NO_x ratios were sufficient for producing high levels of ozone. PAN and ozone maximum were not necessarily observed at the same time in Wilmington. Table V contains results indicating both maximums. On some occasions the ozone maximum occurred after the PAN maximum; however, on several days the ozone maximum occurred earlier.

One other important feature of the PAN measurement is its interference with the accurate measurement of NO₂. PAN interference of 100% was reported (30) for each of the presently available converters used in the nitrogen oxides chemiluminescent instruments. These results confirm similar findings observed in our laboratories. Nitrogen dioxide measurements made in Wilmington for the most part were below 10 ppb and oftentimes below 5 ppb. In most cases, maximum PAN was obtained when NO₂ was at its minimum concentration (although the nitrogen oxides did not show the usual diurnal patterns). PAN interference at these times would be at a maximum. In Figure 3, the lower NO₂ curve represents the NO₂ curve corrected for PAN interference. A maximum of 10% interference was observed. Table V contains results of PAN maximum with corresponding NO₂ measurements. In each case the NO₂ measurement was not corrected for the PAN concentration. In

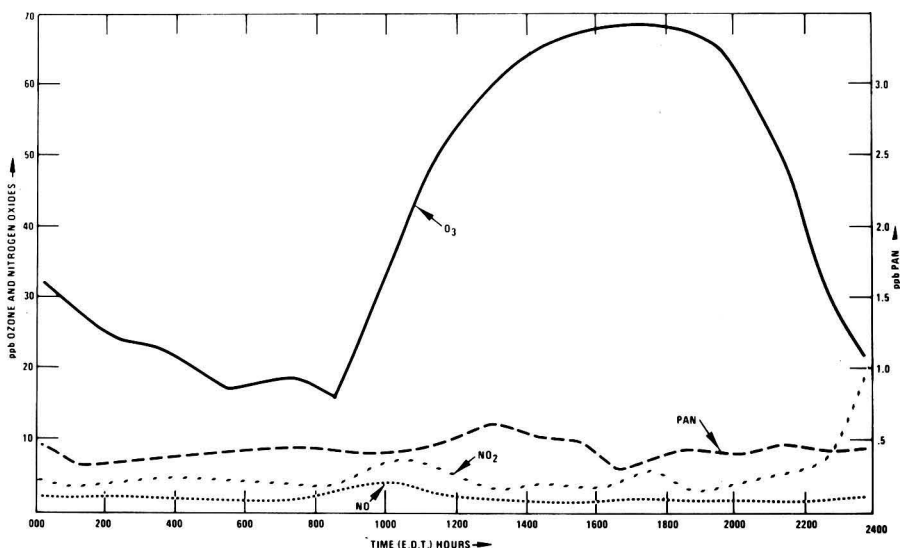


Figure 4. Diurnal pattern of PAN and other aerometric data at Wilmington, Ohio, on August 19, 1974

Table V. Maximum PAN and Other Aerometric Measurements, Wilmington, Ohio, August 1974

Date	PAN max, ppb	Corresponding O ₃ , ppb	Corresponding NO ₂ , ppb	O ₃ max, ppb
8/3	1.4	55.0	3.0	55.0
8/4	1.4	45.0	4.0	53.0
8/5	2.7	55.0	2.5	63.0
8/7	1.8	42.0	6.0	64.0
8/8	1.4	55.0	7.0	63.0
8/9	1.4	74.0	4.0	75.0
8/10	1.6	60.0	8.0	70.0
8/13	4.1	100.8	10.0	107.0
8/14	1.6	52.0	11.0	76.0
8/15	1.7	86.0	7.5	90.0
8/16	1.8	75.0	5.0	84.0
8/17	1.7	76.0	5.5	76.0
8/18	0.8	52.0	4.5	58.0
8/20	1.4	80.0	8.0	92.6
8/22	1.5	48.0	6.5	82.0
8/23	2.3	91.2	7.0	91.2
8/24	2.6	94.0	7.5	94.0
8/25	2.3	93.0	7.0	93.0
8/26	3.2	55.0	9.0	55.0
8/27	2.3	93.2	11.0	96.2
8/30	2.7	97.0	9.0	97.0

each case we observe that PAN represents a significant percent of the NO₂ response. The worst case is August 5 where apparently the entire NO₂ response can be attributed to PAN.

Conclusions

Photochemical activity will occur anytime during the daylight hour as long as hydrocarbons and NO_x are present. PAN would be expected as a photochemical product, provided the precursor concentrations are sufficient for PAN production. PAN formation like ozone is a function of HC/NO_x ratios; however, PAN maximums cannot be estimated from ozone measurements. High ozone measurements were observed when low PAN concentrations were observed. This is expected since the production of ozone is not chain terminating. Low concentrations of pollutants—i.e., HC and NO_x can produce significant concentrations of ozone as long as NO₂ can be regenerated. PAN formation is limited to precursor concentration since its formation is chain terminating. Once RCO₃ radicals combine with NO₂, the reactants are removed from the system. Therefore, high ozone levels can exist with corresponding low levels of PAN-type compounds.

The aerometric data and modeling results suggest that hydrocarbon controls should not only control oxidant formation but also control PAN formation.

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Adsorption of Polychlorinated Biphenyls from Aqueous Solutions and Sewage

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■ The adsorption of PCB's from synthetic aqueous solutions and raw sewage has been studied on a variety of adsorbents, including activated carbons, polymeric resins, polyvinyl chloride, and polyurethane foams. The carbons, foams, and XAD-2 strongly adsorbed the PCB's from aqueous solutions but were much less effective in raw sewage. The PVC, however, was very effective in raw sewage. A small-scale treatment unit was designed to demonstrate the feasibility of removing PCB's from sewage by this method.

Polychlorinated biphenyls, PCBs (tradename "Aroclor" in North America), are ubiquitous persistent pollutants of the environment with adverse ecological and toxicological effects (1). Since first being introduced in 1929, they have had widespread application in the electrical, paint, paper, and plastics industries (2) and have seen extensive use as hydraulic fluids and pesticide additives. It has been estimated that the total world production during the past 45 years has exceeded one million tons, of which about 400 000 tons have been released to the environment (3). Concerned for environmental quality, the Monsanto Co., the only North American producer of PCBs, restricted sales in 1971 to closed-system applications such as electrical capacitors and transformers; however, it is not known how many PCB-containing items are imported. Even with these restrictions, significant quantities of PCBs are still released into the environment.

For reasons that are not fully understood, raw municipal sewage often contains appreciable amounts of PCBs. For example, raw sewage entering the Hamilton Sewage Treatment plant contains on the order of 10 ppb PCB [mainly Aroclor 1254 and 1260 (4)]. Considering Hamilton's flow rate of 230×10^6 l/day (52 mgd), this influent concentration corresponds to approximately one metric ton entering the plant annually. Concentrations of PCBs in sewage from other cities in southern Ontario, while not as high as that from Hamilton, are nevertheless still significant.

The physical chemical properties of PCBs—i.e., low vapor pressure, low aqueous solubility, and chemical inertness to water, acid, alkali, and heat make them extremely persistent environmental contaminants. There are 210 possible combinations of chlorine substitutions on the biphenyl nucleus but only about half that number are sterically possible. The number of PCBs occurring in the environment is of the order of 30–40 (1). The main contributors are the various isomers of pentachlorobiphenyl (Aroclor 1254), hexachlorobiphenyl (Aroclor 1260) and, to a lesser extent, trichlorobiphenyl (Aroclor 1242). However, some lower chlorinated isomers are present as a result of limited degradation. Degradation usually proceeds via successive dechlorination prior to breaking of the stable aromatic biphenyl structure (5).

The low solubility and hydrophobic nature of the chlorinated biphenyls make them relatively easy to adsorb from aqueous solution (6–8). The purpose of this work was to study the feasibility of extracting PCBs from raw sewage

by adsorption onto various media. However, because of the varying nature of raw sewage, the adsorption was first studied using synthetic aqueous solutions of Aroclor 1254 and 1242 and then this was followed by measurements on raw sewage collected from the Hamilton Sewage Treatment plant.

Experimental

The two stock solutions of Aroclor 1242 and 1254 were prepared by vigorously mixing an excess of each Aroclor (Monsanto Co.) with water for 8 h, allowing the solutions to stand overnight and carefully decanting off the true aqueous phase. The water used was double distilled, the second distillation being from an all-glass system. The concentration of these solutions determined by gas chromatography was 45 ± 10 ppb, which is consistent with the published solubility for Aroclor 1254 of 56 ppb (6).

All solvents used were glass-distilled pesticide grade (Caledon Laboratories Inc.). The activated carbons employed were lignite-based Hydrodarco 400 (Atlas Chemical Industries) and anthracite-based Filtrasorb 400 (Calgon Corp.). These were pretreated by heating to 300 °C for 12 h, cooling, and twice extracting each 500 g with 2 l. of hexane. The extracted carbon was then filtered and air dried. The polyurethane foams used were DiSPo plugs (Canlab Supplies Ltd.) and Foams 1115 and 2328 (B. F. Goodrich Ltd.). The first two digits relate to the density—i.e., 1.1 and 2.3 lb/ft³ and the second two to the hardness. The foams were shredded and successively washed with *n*-hexane (several times), acetone, and distilled water. They were then air dried. The pretreatment was developed to remove trace organic contaminants from the surface of the foams. The macroreticular polystyrene resins Amberlite XAD-2 and XAD-4 (Rohm and Haas Co.) were pretreated by successively washing each 500 g of resin with 1-l. batches of water, methanol, and water. The cleaned resins were stored in sealed glass containers under methanol to prevent them from drying out. Polyvinyl chloride chips (Monsanto Co.) were washed several times with *n*-hexane and air dried.

To determine the adsorption characteristics, 100-ml aliquots of stock Aroclor solutions were stirred vigorously with 8–10 weighed amounts of adsorbent for 30 min. The quantities of adsorbent were chosen to cover the range from 1 mg to approximately 1 g. After contacting, the adsorbent was removed by filtration through a prefilter pad (Millipore Ltd.). Five milliliters of *n*-hexane were then vigorously stirred with the filtrate for 45 min and the organic extract was withdrawn. These extracts were analyzed with a gas chromatograph (Varian series) equipped with an electron-capture detector (Ni⁶³). The gas column (1.8 m × 1.5 mm i.d.) was packed with 4% OV-101 and 6% OV-210 on Chromosorb W HP 80/100 mesh. Nitrogen was used as a carrier gas at 50 ml/min. The injection port, column, and detector temperatures were 250, 200, and 300 °C respectively. The amount of PCB adsorbed per unit weight of adsorbent was then calculated and plotted as a function of the equilibrium concentration of PCB remaining in solution.

Wastewater was collected from the Hamilton Sewage Treatment plant at the raw sewage inlet pipe. Sampling

was carried out using all-glass containers to ensure against adsorption onto container walls. The samples were stored at a constant temperature of 3 °C and in all cases were treated and/or extracted within 24 h of collection. The concentration of PCBs in the raw sewage ranged from 1–25 ppb but was usually between 5 and 13 ppb. In the evaluation of PCB adsorption from sewage, the procedure described previously for pure Aroclor solutions was followed except that 100-ml samples of raw sewage were stirred vigorously with the weighed adsorbent for 1 h and the adsorbent was separated by filtration through a 60-mesh, stainless steel screen. After washing, the screen did not retain any raw sewage and, with the exception of activated carbon, 100% separation of adsorbent was achieved. The samples were then twice extracted with 50 ml of *n*-hexane in 500-ml separator funnels. The aqueous portion was discarded and the organic phase, after being dried through 15 g of Na₂SO₄, was reduced to about 3 ml, using a rotary evaporator. The sample was purified by liquid-solid chromatography on a florisil support column using petroleum ether to elute the PCB fraction and then the eluate was evaporated to 3 ml (9). Prior to injection of the sample into the gas chromatograph, it was shaken with 0.2 ml mercury to remove residual sulfur compounds.

The PCBs in the samples were identified by comparison with chromatograms of standard Aroclors (Figure 1). Concentrations were determined from the peak height ratios of peaks A, B, C, and D for Aroclor 1254 and peaks of E, F, and G for Aroclor 1260. The minimum amount of PCB that could be detected with confidence by the GC was 22 p/g in a 10- μ l injection. When we allowed for the increase in concentrations during extraction from the aqueous phase, the limit of detection in the aqueous samples was estimated as 0.5 ppb with an accuracy of ± 0.1 ppb.

Results and Discussion

Adsorption data for Aroclor 1254 and 1242 on activated lignite carbon, anthracite carbon, two polyurethane foams, Amberlite XAD-2 and XAD-4 and PVC are shown in log-log form in Figure 2. The weight of PCB adsorbed per unit weight of adsorbent is expressed as a function of the equilibrium concentration of PCB remaining in solution. The error bars have not been drawn on Figure 2 as they distract from the clarity of the data: In the worst cases, the diameter of the error circles corresponds to about two-and-one-half times the diameter of the marked points. These are insufficient to linearize the isotherms. The sets of data do not follow any of the common isotherm expressions—e.g., Langmuir, Freundlich, BET, and so forth, and consequently a theoretical interpretation of the results has not been attempted. It is evident that the two carbons and XAD-2 have the greatest adsorption capacities but a residual concentration of less than 3 ppb could not be obtained with lignite carbon. Both polyurethane foams appear to be good adsorbents with relatively high adsorption capacities and low residual levels. The sets of data for XAD-2 and XAD-4 are very similar. The lower efficiency of PVC can be explained by the lower surface area of this adsorbent. The surface area per unit weight is reported as 500–2000 m² g⁻¹ for carbon; 750 m² g⁻¹ for XAD-4 and 330 m² g⁻¹ for XAD-2¹⁰ but only 2×10^{-3} m² g⁻¹ for PVC chips, there being no macroreticular structure in PVC. This gives an area ratio XAD-2/PVC of about 10⁵.

There are two complicating conditions associated with adsorbing PCBs from raw sewage rather than synthetic

aqueous solution: Sewage contains other hydrophobic organic matter that competes for the active sites on the adsorbent and much of the PCB has already adsorbed onto the suspended solids by the time the sewage reaches the treatment plant. The second condition can easily be demonstrated by filtering raw sewage and monitoring the change in PCB concentration. With typical raw sewage containing 10 ppb PCB, vacuum filtration through a Millipore prefilter pad resulted in the removal of about 75%. It is therefore necessary to find an adsorbent that is not only relatively specific to PCBs, but that also has sufficient af-

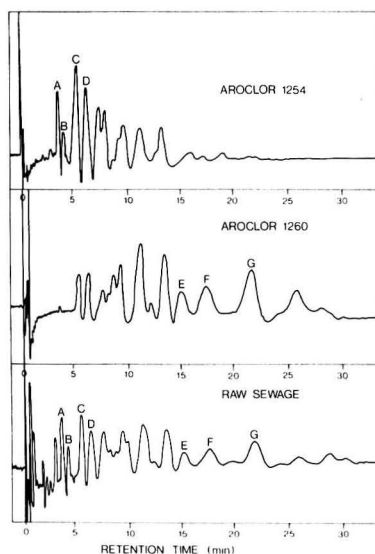


Figure 1. Gas chromatograms of Aroclor 1254, Aroclor 1260, and raw sewage

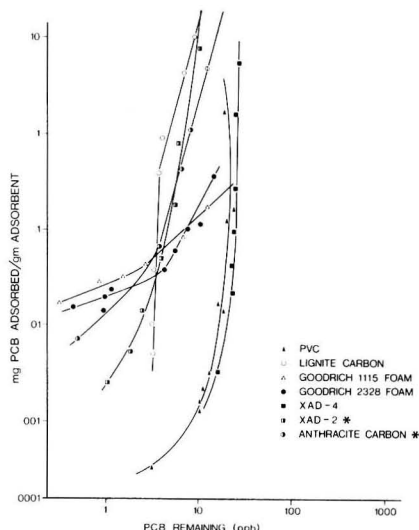
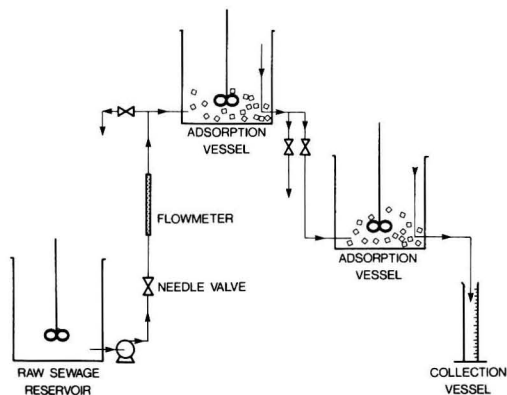
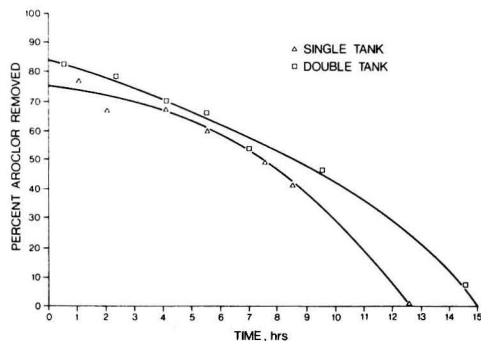


Figure 2. Adsorption of Aroclor 1254 on PVC lignite carbon, anthracite carbon, polyurethane foams, and Amberlite XAD-2 and XAD-4. Asterisk indicates adsorption of Aroclor 1242 rather than 1254

Table 1. Adsorption of PCBs from Raw Sewage

Adsorbent	% PCB adsorbed*
Lignite carbon	46 ± 3
Polyurethane foam	35 ± 3
Amberlite XAD-2	23 ± 2
Amberlite XAD-4	60 ± 3
PVC	73 ± 4

* Includes both Aroclors 1254 and 1260. Data are averaged over several determinations to minimize the variations in raw sewage.

**Figure 3. Apparatus used for tank adsorption experiments****Figure 4. Percentage of Aroclor removed as function of time for tank tests**

finity for the PCBs such that the PCB-suspended solid equilibrium is reversed.

Table I shows the percentage of PCB (including both Aroclor 1254 and 1260) adsorbed from raw sewage by five different media. With the exception of the PVC, approximately 1 g of each media was stirred with 200 ml of raw sewage for 45 min; approximately 10 g of PVC were used because of the lower surface area. To minimize the inconsistency of raw sewage, the data have been averaged over several determinations on different days and with different samples of sewage. The data indicate that PVC and XAD-4 are more effective than carbon or polyurethane foams in terms of percentage of PCB removed from raw sewage. This is somewhat surprising since the graphs for PCB adsorption for pure Aroclor solutions (Figure 2) would predict the opposite to be true. The likely reasons for this apparent anomaly are: The active sites on carbon are preferentially occupied by hydrophobic species in sewage other than

PCBs and suspended solids adhere to the surface of carbon and foam acting as a barrier to further adsorption.

The above results indicate that PVC is superior to the other media for removing PCBs from sewage. To demonstrate the feasibility of a sewage treatment method based on PVC adsorption, a small-scale flow-through unit was designed, capable of treating about 3 l. of sewage per hour. The unit is shown in Figure 3. Each tank had a capacity of approximately 4.5 l. and was equipped with a paddle and baffle to ensure thorough agitation of the chips. Seven hundred grams of washed PVC were placed in each tank. The flow through the entire system was governed by the feed rate and this could be maintained at 50–60 ml/min (3 l./h) by adjustment of the needle valve on the inlet line. Effluent samples from both tanks were collected for analysis every 30 min.

The 50–60 ml/min flow rate was calculated on the basis of a 1-h retention time in each tank. Earlier batch equilibrium experiments with PVC and sewage had indicated that the adsorption equilibrium was established within the first 15 min of contact if sufficient agitation was employed. An arbitrary factor of four was then selected as a margin in the transfer from batch to flow through conditions.

Data from the flow through system are shown in graphical form in Figure 4. The efficiency of the single tank unit dropped from 75 to 47% during the first 8 h of operation while that of the twin tanks dropped from 84 to 53% over the same period. Although the second tank resulted in a 4–9% better removal of the PCBs, the extra cost involved with the two-stage process would probably not be justified in a large-scale application. Regeneration of the spent PVC was easily accomplished by successively flushing the chips with *n*-hexane, acetone, and water. The acetone and water rinses were to remove all traces of hexane from the surface of the PVC. The PVC was then ready for reuse.

In conclusion, PVC is very effective for adsorbing PCBs from raw sewage. A small-scale unit has been used to demonstrate the feasibility of the method but more engineering design research is required to optimize the technique. A system incorporating continual addition of fresh chips and removal of spent adsorbent would probably yield more uniform results than those illustrated in Figure 4. Further research into the regeneration of spent PVC and degradation of the recovered PCBs is currently under way in this laboratory. The PVC adsorption process should be equally as effective for treating concentrated industrial effluents as municipal sewage. Where a point source of PCB-containing effluent can be located, there would be obvious economic advantages to locating it prior to discharge into the sewer system.

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Apparent Ionization Constant of Hypochlorous Acid in Seawater

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■ Hypochlorous acid is the first product formed when chlorine gas is added to water. Both its toxicity to aquatic organisms and the rate at which it forms subsequent reaction products are influenced by the degree to which it ionizes in the receiving water. Based on potentiometric titrations with a glass electrode, the apparent ionization constant in artificial seawater is described by the following equation: $pK'_c = 937.7 T^{-1} - 0.149 Cl^{1/3} + 4.433$, where T is absolute temperature and Cl is chlorinity in g/kg. Under the pH and temperature conditions prevailing in typical estuaries, the less toxic, nonprotonated form predominates. There is evidence that this form participates in ion-pair formation to a small degree in seawater. The equilibrium concentration of the protonated form, HOCl, is enhanced by low pH, low temperature, and low salinity.

Chlorine is widely used as a disinfectant and biocide, and large quantities of its reaction products are being discharged to estuarine and coastal waters by wastewater treatment plants and electric power plants. Figures compiled by the U.S. Bureau of Mines (C. L. Klingman, private communication) suggest that consumption of chlorine in the United States for sanitation more than doubled between 1965 and 1973. Recent reviews of the toxicity of chlorine to aquatic organisms have established that concentrations which are 10–100 times lower than the Cl_2 doses typically applied to discharges are still lethal (1, 2). These facts have sparked interest on the part of ecologists in the fate of chlorine reaction products in receiving waters.

When chlorine gas is applied to water in the usual doses (0.1–10 mg/l.), it disproportionates and hydrolyzes almost instantly to form dilute hydrochloric acid plus hypochlorous acid (3). The natural alkalinity of most waters is adequate to neutralize the hydrochloric acid. Therefore the toxicity of chlorine derives either from the hypochlorous acid or from its subsequent ionization and reaction products.

Knowledge of the degree of ionization of hypochlorous acid in the receiving water is important for two reasons. First, there is evidence that the nonionized form, HOCl, is much more toxic to bacteria than the ionized form, OCl^- (3). It has been suggested that this is due to a greater rate of permeation of the uncharged form through cell membranes. Second, studies of the kinetics of formation of toxic secondary products, such as inorganic and organic chloramines and hypobromite, suggest that HOCl is much more reactive than OCl^- (4, 5). This paper presents the data needed to predict the relative proportions of HOCl and OCl^- in marine and estuarine waters.

Theory

The apparent ionization constant of hypochlorous acid is defined:

$$K'_c = \frac{OCl^-}{HOCl} \bar{a}_H \quad (1)$$

where OCl^- and HOCl are, respectively, the concentrations of total hypochlorite and hypochlorous acid, and \bar{a}_H is the operational hydrogen ion activity which is that obtained

from an ordinary pH measurement made with a glass electrode and a reference electrode having a liquid junction. Hawley and Pytkowicz (6) showed that the operational hydrogen ion activity can be related to the conventional hydrogen ion activity a_H , by a constant, j , which depends primarily upon the difference in the liquid junction potential between the measurement of the buffer and the measurement of the test solution:

$$\bar{a}_H = ja_H \quad (2)$$

It should be noted that K'_c is defined in terms of concentrations of the chlorine species, rather than activities, and therefore it is a function of ionic strength or salinity. Furthermore, the term OCl^-_f does not represent simply the concentration of free hypochlorite ion, which we shall designate OCl^-_f , but rather it includes the concentrations of any ion-pairs, such as $MgOCl^+$, $CaOCl^+$, and $NaOCl^0$, that react with hydrogen ions to form hypochlorous acid during a titration with acid.

If a_{OCl^-} is the activity of the free hypochlorite ion, then the stoichiometric activity coefficient, γ_{OCl^-} , and the free ion activity coefficient, f_{OCl^-} , may be defined as follows (7):

$$a_{OCl^-} = \gamma_{OCl^-} OCl^-_f = f_{OCl^-} OCl^-_f \quad (3)$$

and

$$\alpha = \frac{OCl^-_f}{OCl^-_t} = \frac{\gamma_{OCl^-}}{f_{OCl^-}} \quad (4)$$

where α is the fraction of the nonprotonated hypochlorite which is free (i.e., not associated with cations). If K^0 is the thermodynamic constant of hypochlorous acid at infinite dilution, represented by:

$$K^0 = \frac{a_{OCl^-}}{a_{HOCl}} a_H \quad (5)$$

Then from the preceding equations:

$$\frac{K'_c}{K^0} = \frac{j f_{HOCl}}{\gamma_{OCl^-}} \quad (6)$$

$$\alpha = \frac{j f_{HOCl} K^0}{f_{OCl^-} K'_c} \quad (7)$$

Thus if values for j , f_{HOCl} , and f_{OCl^-} can be obtained, α can be evaluated at any salinity and temperature from the appropriate measured values of K'_c and K^0 . The two activity coefficients may be estimated with reasonable confidence from data in the literature, but j is more difficult to obtain. Bates (8) has reviewed the procedure by which liquid junction potentials may be approximated using the Henderson equation. In Figure 1, the value of $\log j$ calculated from this equation for two commonly used reference electrode filling solutions vs. seawater is presented as a function of chlorinity. $\log j$ is obtained from:

$$\log j = -(E_{jt} - E_{jb}) F/2.303 RT \quad (8)$$

E_{jt} is the calculated liquid junction potential in the seawater test solution and E_{jb} is the calculated liquid junction potential in the standard phosphate buffer solution. Limiting equivalent conductances were taken from Robinson and Stokes (9) except for $H_2PO_4^-$ ($33 \text{ cm}^2 \Omega^{-1}$) from Mason (10) and HPO_4^{2-} ($54 \text{ cm}^2 \Omega^{-1}$) from Prideaux (11). Hawley and Pytkowicz (6) found that by calculating j from the

Henderson equation, they obtained good agreement with the value which they measured in 0.725 m NaCl solution. On the other hand, Finkelstein and Verdier (12) found that errors in $\log j$ of ± 0.03 could be expected when the Henderson equation was used to calculate liquid junction potentials of KCl-KNO₃ salt bridges.

Procedure

A simplified, bromide- and carbonate-free synthetic seawater was made from reagent grade chemicals to have the following composition: 0.4224 m NaCl, 0.0280 m Na₂SO₄, 0.05405 m MgCl₂, and 0.01001 m CaCl₂. The formal ionic strength of this solution was 0.70 m, and the true ionic strength, corrected for sulfate ion-pairing (13) was 0.65 m. From this solution, a second solution having a formal ionic strength of 0.10 m was prepared by dilution. A commercial laundry bleach was added to these solutions to produce 0.003 m NaOCl. The bleach consists of essentially an equimolar solution of NaOCl and NaCl. The amount of acid required to reach the hypochlorite end point in our experiments agreed, within experimental error (2%), with the amount expected based on an iodometric determination of the concentration of hypochlorite, indicating that the concentration of weak acid contaminants such as CO₃²⁻ and HCO₃⁻ was negligible.

In a thermostated reaction vessel, the NaOCl solutions were titrated with standardized HCl from an initial pH above 9 to a final pH near 5. Approximately 25 pH measurements were made in each experiment and pK'_c was determined by locating the inflection point on the titration curve. The titrations were conducted in a semidark laboratory to prevent photodecomposition of the hypochlorite. The pH measurements were made with a glass electrode and an Orion double-junction reference electrode with 10% KNO₃ outer filling solution. The calculations presented in Figure 1 suggest that 10% KNO₃ filling solution is preferable to saturated KCl for studies in variable salinity marine waters because $\log j$ varies by a fairly small amount over a broad salinity range. Commercial pH buffers were used to calibrate the electrodes.

Results and Discussion

The measurements are presented in Table I. The precision of the pK'_c values, as judged by the reproducibility at any particular salinity and temperature, is ± 0.02 . The following empirical equation describes all the data within this tolerance:

$$pK'_c = 937.7 T^{-1} - 0.149 Cl^{1/3} + 4.433 \quad (9)$$

Here T is absolute temperature and Cl is the chlorinity in g/kg. Our choice for the form of Equation 9, especially the use of a $Cl^{1/3}$ term, was influenced by the experience of previous workers (14, 15) with apparent ionization constants for H₂CO₃ and H₂S in seawater. This equation was found to fit the data better than a similar equation in which the $Cl^{1/3}$ term was replaced by a $Cl^{1/2}$ term.

In Figure 2, the fields of predominance of HOCl and OCl₂⁻, based on Equation 9 are shown as a function of pH and chlorinity. Two isotherms, bracketing normal estuarine temperatures, are presented. In general, natural pH values fall in the region where OCl₂⁻ predominates. However in river waters and in those regions of estuaries where the chlorinity is low, HOCl can predominate. For a given pH, the amount of HOCl relative to OCl₂⁻ will be greater at lower temperature and at lower chlorinity.

In view of the previously cited evidence that HOCl and OCl₂⁻ differ greatly in their toxicity to bacteria, these re-

sults are relevant to the design and reporting of experiments on the toxicity of "free chlorine" (HOCl + OCl₂⁻) to estuarine organisms. Too often, when such experiments are reported, only the chlorine dose and temperature are mentioned. If the degree of ionization is as important for other organisms, as it is for bacteria, then in addition to these parameters, salinity and pH must be specified before the results will be fully interpretable.

The extent to which pK'_c decreases with increasing chlorinity suggests that the hypochlorite ion may be slightly associated with cations in seawater. We can obtain some approximate information regarding this possibility by use of Equation 7. To do this, we approximated j using the Henderson equation (Figure 1). We also assumed that $f_{OCl_2^-}$ was equal to $\gamma_{\pm KCl}$ which we obtained from Robinson and Wood (16). The activity coefficient for HOCl was obtained from data reported by de Valera (17) and K^0 was taken from Morris (18). It should be noted that K^0 is not equal to K'_c at zero chlorinity because j does not approach unity in dilute solutions. For seawater (19 g/kg Cl⁻), the computation is as follows:

$$\alpha = \frac{j f_{HOCl} K^0}{f_{OCl_2^-} K'_c} = \frac{(1.18)(1.06)(10^{-7.54})}{(0.64)(10^{-7.17})} = 0.83 \quad (10)$$

The uncertainty in this value for α is primarily due to the uncertainty in j as calculated from the Henderson equation. The error may be 10% or more. Nevertheless, the

Table I. Experimental Data

		Chlorinity, g/kg					
0.11 ^a		2.73		19.14			
<i>T</i> , (°C)	<i>pK'</i>	<i>T</i> , (°C)	<i>pK'</i>	<i>T</i> , (°C)	<i>pK'</i>	<i>T</i> , (°C)	<i>pK'</i>
25.2	7.51	12.7	7.52	10.7	7.34		
		18.8	7.43	17.8	7.26		
		25.2	7.34	25.2	7.17		
		34.5	7.26	34.2	7.09		
		39.5	7.24	39.5	7.04		

^a No "seasalt" present; ionic strength = 0.006 due to the presence of NaOCl and an equivalent amount of NaCl.

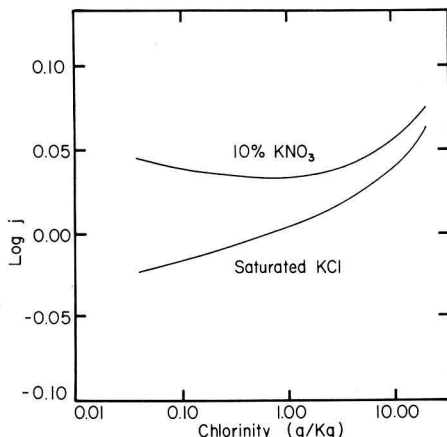


Figure 1. Calculated difference in liquid junction potentials in seawater and standard pH 6.86 phosphate buffer solution for two different reference electrode filling solutions

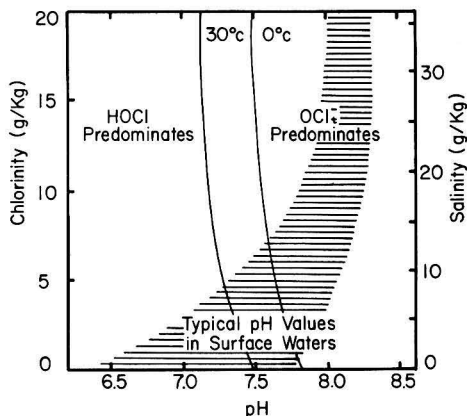


Figure 2. Fields of predominance of HOCl and OCl⁻ based on Equation 9

Hatched area represents field of typical estuarine pH values

result suggests that some ion pairing is occurring between OCl⁻ and cations in seawater. For comparison, the recent work of Pytkowicz and Hawley (19) indicates that $\alpha = 0.81$ for HCO₃⁻ and = 0.51 for F⁻ in seawater.

Ion pairing probably affects the diffusivity of OCl⁻ and consequently its toxicity to organisms, but the degree of association is so small that if this effect is observable, it will appear only at chlorinities approaching that of seawater.

Summary

At constant temperature, the apparent ionization constant of hypochlorous acid decreases with increasing chlorinity, the amount of this shift being large enough to suggest that the hypochlorite ion is partly associated with cations in seawater. In most normal marine and estuarine waters the OCl⁻ ion will predominate over HOCl and over OCl⁻ ion pairs. Our data permit the relative concentrations of HOCl and OCl⁻ to be calculated in marine waters in terms of the readily measurable parameters pH, *T*, and chlorinity. In such calculations it is unnecessary to make

any assumptions about activity coefficients or liquid junction potentials as would be necessary if the thermodynamic ionization constant were used. Our results should prove useful in interpreting biotoxicity data obtained in estuarine waters and in modeling the kinetics of chlorine degradation in estuarine and marine waters.

Acknowledgment

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NOTES

Some Relationships Between Exchangeable Copper and Lead and Particulate Matter in a Sample of Hudson River Water

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In any natural water system, copper and lead occur in solution, on the surface of particles, and inside particles. Most analyses of trace metals in natural waters are concerned with quantities in solution (i.e., <0.45 μ), within solids (which are dissolved in the analysis), or both. Some analyses are concerned with "leachable" quantities of these elements, usually at various acid strengths.

In the present study an isotope dilution technique was used which measured the "exchangeable" copper and lead in slightly acidified aliquots of a sample of Hudson River water from which various sizes of particulate matter had been removed. The "exchangeable" copper and lead is that which equilibrates with the introduced "spike" copper and

lead in solution. In addition to the "size" test, a study was made of the change in "exchanged" copper and lead with time for a series of unfiltered aliquots.

Sample Collection and Preparation

The sample was collected in an acid-washed 6½-gal polyethylene bottle, by hand-dipping the bottle into the Hudson River off the Alpine (N.J.) boat dock. The salinity of the water was 1½‰. The sample was transported to the "clean lab" of the Lamont-Doherty Geological Observatory (Palisades, N.Y.) in 15 min, and then aliquoted into a number of 500-ml and 1-l. Teflon bottles each of which con-

■ Aliquots of a sample of Hudson River water were analyzed for copper and lead by isotope dilution. The "exchangeable" copper and lead—i.e., that which equilibrated with the spikes, ranged from an average of 7.26 ppb Cu and 11.72 ppb Pb for unfiltered aliquots, to 2.82 ppb Cu and 4.39 ppb Pb for aliquots filtered through 2- μ filter paper. More than 60% of the copper and lead is associated with particles > 2 μ in size. The measured metal contents of the

unfiltered aliquots increased with time; with the copper apparently reaching equilibrium after about 20 days, and the lead never reaching equilibrium during the 30-day time period of the tests. The lead results for the unfiltered aliquots are much more variable than the copper results, suggesting the presence of relatively large (>8 μ) lead-rich particles in the water, possibly originating from atmospheric fallout of aerosols derived from auto exhausts of leaded gasolines.

tained 1 ml (500-ml bottles) or 2 ml (1-l. bottles) of ultrapure HNO₃ and 4 μ g of an enriched ²⁰⁶Pb spike and 20 μ g of an enriched ⁶⁵Cu spike. Five aliquots were unfiltered, and duplicate aliquots were filtered through Whatman No. 41 (20–25 μ), No. 40 (8 μ), and No. 42 (2 μ) filter paper. The pH of the original sample was ~6.5; that of the acidified aliquots was ~1.5.

Analytical Technique

The analytical technique has been previously described (1, 2). In brief, an electrolytic cell is formed by suspending two 50-ml platinum wires in the sample and impressing a 1.9-V potential across the wires. Metallic copper plates out on the cathode and PbO₂ on the anode. The cell is run overnight at a current of ~20 mA. The copper is stripped from the cathode by dipping it in 1/2 ml of a 50% HNO₃ solution, and the PbO₂ is stripped from the anode by dipping it in 1/2 ml of a 99:1 2% HNO₃:35% H₂O₂ solution.

The entire chemical procedure was performed in a positively pressurized, filtered air, double-doored clean lab. All reagents were ultrapurified and only FEP Teflon containers were used (except for the 6 1/2-gal polyethylene collecting bottle). Total procedure blanks were on the order of 0.02 and 0.01 μ g for copper and lead, respectively.

Isotopic ratios were measured on a single-focusing, 12-in. radius of curvature mass spectrometer with expanded-scale recorder. Copper analyses were made on a single-filament platinum ribbon source at a temperature of ~1100 °C; lead analyses were made on a single-filament rhenium ribbon source at a temperature of ~1300 °C.

Results

The analytical results are listed in Table I. For copper, the average values for each group of aliquots are (ppb):

Unfiltered = 7.26 (7.69, see text)
 <25 μ = 3.88
 <8 μ = 3.04
 <2 μ = 2.82

Figure 1 is a plot of exchangeable copper in the unfiltered aliquots vs. time after spiking. (All plotted aliquots were spiked at the same time, on the day the sample was collected.) The amount of sample copper mixing with the spike copper increases with time. All of the filtered aliquots were analyzed after the unfiltered aliquots. Since the last two unfiltered aliquots (1d and 1e) and the duplicate analyses of the filtered aliquots show no significant change with time, equilibrium may have been achieved after approximately 20 days. In any case, it is probably more meaningful to compare the averages of the filtered aliquots with an average of the last two unfiltered aliquots (7.69 ppb) rather than the average of all the unfiltered aliquots (7.26 ppb).

Aliquot 5 I.C. (Table I) was taken from the collecting bottle 71 days after the sample was collected. The aliquot

(1 l.) was acidified with 2 ml of HNO₃ and spiked with 10 μ g of ⁶⁵Cu; no ²⁰⁶Pb spike was added because this aliquot was used to determine the isotopic composition of the lead in the sample. The aliquot was analyzed 12 days after spiking. The result (7.75 ppb) agrees well with those of the last two unfiltered aliquots (7.63 and 7.73 ppb).

For aliquots analyzed after 20 days, duplicate analyses show good precision. Statistical analysis of these and some previous duplicate analyses (2) yield a standard deviation (σ) of 1.8% per analysis and a 95% confidence limit ($t\sigma$) of 4.3% for a single analysis (based on seven degrees of freedom).

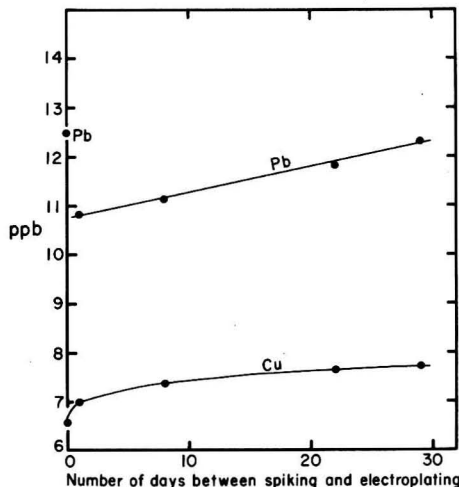


Figure 1. Variations of measured copper and lead with time (unfiltered aliquots)

Table I. Analytical Data

Aliquot no.	Filtering	Copper, ppb	Lead, ppb
1a	None	6.58	12.48
b	None	6.98	10.84
c	None	7.37	11.14
d	None	7.65	11.81
e	None	7.73	12.31
2a	≤ 25 μ g	3.94	5.40
b	≤ 25 μ g	3.83	8.20
8a	≤ 8 μ g	2.99	5.16
b	≤ 8 μ g	3.09	4.87
4a	≤ 2 μ g ^a	2.82	4.38
b	≤ 2 μ g	2.82	4.40
5 I.C. ^b	None	7.75	—

^a Sample accidentally lost. ^b Aliquot taken 71 days after sample collection.

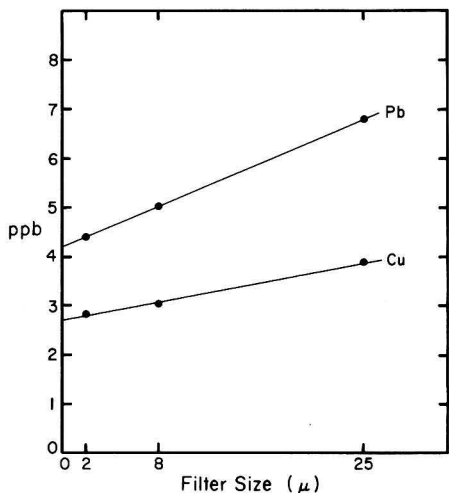


Figure 2. Variations of copper and lead content with filter size

The lead results are more variable than the copper results. The average values for each size group are (ppb):

Unfiltered = 11.72
 $<25 \mu = 6.80$
 $<8 \mu = 5.02$
 $<2 \mu = 4.39$

A plot of exchangeable lead vs. time after spiking (Figure 1) for the unfiltered aliquots shows a maximum on the first day, a minimum after one day, and a straight-line increase with time thereafter. The rather high variability of the results, even on the coarse-filtered aliquots, precludes a statistical error analysis. Only on the fine-filtered aliquots ($<2 \mu$) does the reproducibility fall within the estimated analytical uncertainty ($\pm 2\%$).

Discussion

The results show quite clearly that most of the copper and lead carried by this sample of Hudson River water is associated with particulate matter, with $>60\%$ associated with particles $>2 \mu$ in size. Figure 2 is a plot of exchangeable copper and lead vs. filtered particle size. A simple extrapolation of the straight lines to zero particle size suggests soluble copper and lead contents of 2.7 ppb and 4.2 ppb, respectively. Although such an extrapolation may not be correct, the soluble copper and lead values must, of course, be less than the values obtained in the $2\text{-}\mu$ filtered samples (2.82 and 4.39, respectively).

The results of the unfiltered aliquots show that the amounts of copper and lead mixing with the spikes increase with time—i.e., all of the atoms of sample copper and lead ultimately exchangeable with the spike copper and lead under the experimental conditions are not released instantaneously. If the copper has reached equilibrium after about 20 days (Figure 1), then approximately 85% is released immediately and 15% is released more slowly. The agreement between aliquot 5 I.C. and aliquots 1d and 1e suggests that this "recalcitrant" copper is organically chelated and is released only after decomposition of the organisms. These assumptions allow a very preliminary estimate

of the exchangeable copper contents of the various phases in the sample: 35% in solution (a maximum); 50% adsorbed on inorganic particles; and 15% chelated with organic matter (a minimum).

For lead, the anomalously high initial value and subsequent straight line increase for the other unfiltered aliquots (Figure 1) precludes estimates of the relative amounts of rapidly and slowly released atoms. The anomalous result is most likely due to natural variations in the aliquots [i.e., lead-rich particle(s) in 1a]. Such variations would also explain the poor agreement between 3a and 3b (Table I), and have been noted before (2). It is particularly interesting to note that the precision of the copper analyses decreases for the fine-filtered samples, because the mass spectrometrically measured $^{65}\text{Cu}/^{63}\text{Cu}$ ratio becomes large (~ 10) causing a decrease in measurement precision, while the reproducibility of duplicate lead analyses (mass spectrometer $^{206}\text{Pb}/^{208}\text{Pb}$ ratio between 1 and 2) gets better, probably because any large lead-rich particles present in the original sample are filtered out.

The obvious differences between the behavior of copper and lead, principally the time-release patterns (Figure 1) and the poor reproducibility of the lead results (Table I), may be explained by a difference in the ways these elements enter the aqueous system. Although both enter naturally through rock erosion, and by man's pollution through sewers and drain lines, lead also enters the system through atmospheric fallout of aerosols principally derived from automotive exhausts of leaded gasolines (3).

Once in the water, some of the copper and lead is apparently adsorbed onto, or chelated with, the surface mucilage of algae and some is adsorbed on the surfaces of inorganic particles. In these manners, the copper and some of the lead may be homogeneously distributed on particulate matter and in solution.

Although the organisms in the aliquots should have been killed immediately by the acidification ($\text{pH} \sim 1.5$), the release of chelated copper and lead, or the exchange of such with spike copper and lead, is apparently not instantaneous. Presumably, any copper and lead adsorbed on inorganic surfaces would rapidly mix with the spike components.

The straight-line release of the lead (Figure 1) and its variability even in some filtered aliquots suggest another phenomenon. Perhaps these effects are the results of the presence of inhomogeneously distributed (with respect to 1-l. volumes) lead-rich particles that enter the water from the atmosphere and dissolve only slowly in the weakly acidified sample. Lead-rich aerosol particles $>30 \mu$ in size are not uncommon close to highways (4).

In summary, it is rather difficult to propose concrete conclusions on the basis of the small amount of data presented here, but the results do support the tentative conclusions reached in the discussion and certainly suggest that differential analysis of the components of river water will prove fruitful for the study of trace metal cycles.

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INDUSTRY TRENDS

Alsld, Snowden & Associates was formed at Bellevue, Wash., to specialize in ambient and source evaluations, environmental impact assessments, and business consulting services.

Aluminum Corp. of America (Alcoa) has commenced operations at its new magnesium plant at Addy, Wash. More than 15% of investment in the plant went for environmental controls.

Air Resources, Inc. has received contracts to upgrade water treatment facilities at refineries of Quaker State Oil Refining Corp., Farmers Valley and Emmenton, Pa., and St. Mary's and Newell, W. Va., to meet 1977 and 1983 requirements.

The Bendix Corp. (Southfield, Mich.) has completed work on the Laser Geodynamic Satellite (LAGEOS). To be launched this month, LAGEOS will help with earthquake prediction, and determine other geological factors. It will be in polar orbit.

Beukers Laboratories, Inc. (Bohemia, N.Y.) has received a \$150,000 contract from the U.S. Air Force Eastern Test Range (Patrick AFB, Fla.) for three upper air meteorological sounding systems.

The Beverage Industry Recycling Program (BIRP, Phoenix, Ariz.) bought almost 13.5 million lb of used non-returnable containers for almost \$1.03 million during 1975, a record. BIRP is also constructing a solar-heated office building in Tucson.

The Boeing Aerospace Co. will act as management support contractor in a program aimed at stimulating widespread solar energy use. The Dept. of Housing and Urban Development (HUD) is lead agency.

Camp Dresser & McKee has completed expansion of its laboratory in downtown Boston, Mass.

The Carborundum Co. (Niagara Falls, N.Y.) has a worldwide license from Chemfix Inc. to practice the Chemfix process for treatment of hazardous and toxic wastes.

Chemical Data Systems (Oxford, Pa.), a firm manufacturing monitoring equipment for organics and bacteria in water, announced that Leon Industries, Inc. (St. Louis, Mo.) has bought a significant stock position in Chemical Data Systems.

Chemical Separations Corp. (Oak Ridge, Tenn.) received a \$6.1 million contract for condensate demineralizers for proposed TVA nuclear plants. This contract, involving ion exchange, is the largest such contract in the world.

Combustion Engineering, Inc.'s Power Systems Group has an order for a 675-MW coal-fired steam generator from Iowa Southern Utilities Co. Three other Iowa utilities will benefit.

Dorr-Oliver Inc. received an order from the Miami-Dade (Fla.) Water and Sewer Authority to replace existing Dorr-Oliver clarifiers, installed in 1928 and 1936, with new ones.

Du Pont's Instrument Products Division has started up its new plant to produce chemical reagent test packs at Jonesboro, Ark. The packs are used to test blood serum and other body fluids.

The Electric Power Research Institute (EPRI, Palo Alto, Calif.) has allocated \$50 million for 44 new, and 26 on-going projects. Some of these projects will involve cleaner uses of coal.

Fluitek Corp. has started operations at Cookeville, Tenn., to market top performance-rated products of the filtration industry under its own brand identity. Specialized filtration products, made all over the world, will be available from one supply source.

Enviroplan, Inc. (Rutherford, N.J.) was awarded a contract to do detailed air pollution prediction modeling studies for Wisconsin Power and Light Co., at Sheboygan, Wis. Contract value is more than \$200,000.

Environmental Research & Technology, Inc. (Concord, Mass.) will provide operation, maintenance, reporting, and other environmental services for Detroit Edison Co., at Port Huron and Monroe, Mich.

General Signal Corp. (New York, N.Y.) reported net income of \$24.5 million for 1975, as compared to \$20.6 million for 1974. Increased 1975 sales were ascribed largely to record performance by the firm's environmental and industrial process controls group.

Grumman Corp. (Bethpage, N.Y.) has a \$6.8 million contract for software for a ground-based satellite attack warning system for the Air Force's Space and Missile System Organization.

Hercules Inc. has begun construction of a new nitroglycerine facility at its dynamite plant at Bessemer, Ala., in which personnel exposure to the product will be minimal.

Honeywell's Process Control Division has a \$1.5 million order for analog controls with computer-based acquisition systems for the Springfield, Mo., Southwest wastewater treatment plant.

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NEW PRODUCTS

Peristaltic pump

The variable speed pump features pumping rates from 0.006–20.90 ml/min. Two-channel pumping is possible. The unit is self-priming. Spectroderm International, Inc. 110

Siphon clarifier

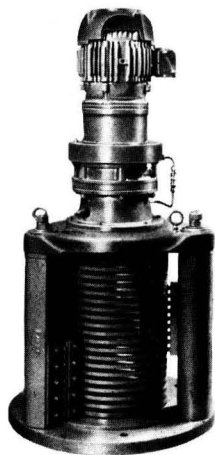
It finds application for water clarification, in secondary treatment of wastewater and as a clarifier of scrubber wastes. It withdraws sludge at a uniform rate despite changes in sludge concentration and water level in the clarifier. Neptune Microfloc, Inc. 101

Liquid membrane electrodes

The calcium, chloride, fluoroborate, nitrate, perchlorate, potassium and water hardness electrodes feature rapid and reproducible response and are insensitive to air bubbles and static electricity. Orion Research Inc. 102

Closed loop flush toilet

The waterless, no discharge system uses an oil-based flushing fluid that is purified and recycled for reuse. It is intended for residential and public use applications. Sar Industries, Inc. 103



Comminutor

The unit continuously reduces large solids found in sewage to a size that allows the pieces to pass through the mechanical equipment installed in sewage treatment plants. It has a capacity of up to 8 mgd. G.E.T. Industries, Inc. 104

Screen filtration systems

Designed for system flow capacities up to 5000 gpm. Units are available with manual or automatic flush and a choice of screen mesh. The screening elements are corrosion resistant. Rain Bird Sprinkler Manufacturing Corp. 105

Sludge density analyzer

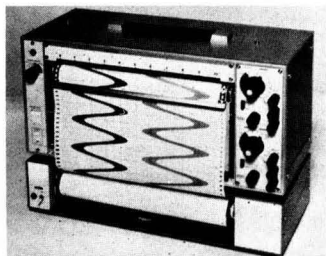
The unit is designed for use in activated sludge and other suspended solids processes. It will measure concentrations up to 70 000 ppm. The analyzer has no moving parts. Keene Corp. 106

Dissolved oxygen analyzer

Will accurately measure dissolved oxygen in a range of 0–150 or 0–15 ppb ($\mu\text{g/l}$) depending on the model. It finds application in boiler feedwater loops or in food and beverage processing industries. Rexnord Inc. 107

Plastic fan

The high pressure, plastic fan is able to handle any acid gas. Standard models can operate with capacities to 1000 cfm. Each blower is equipped with a line cord and an on/off switch. Heat Systems-Ultrasonics, Inc. 108



Inkless 2-color recorder

Because the recorder is heat-sensitive and requires no ink or felt-tip pens, the manufacturer claims minimum maintenance and servicing. The standard recorder includes 16 input ranges (1 mV–100 V), and 6-chart speeds, and may be left unattended for extended periods. Soltec Corp. 109

Strip chart recorders

Three and four pen strip recorders have a full 10-in. recording span with each pen covering the total chart width. Writing distance between channels is 2 mm; full-scale response is 0.25 s, and 16 chart speeds can be selected. Bausch & Lomb/Houston Instrument 111

Level Indicator

Liquid levels in irregularly shaped storage tanks may be converted to a digital display with this instrument. Accuracy is $\pm 0.25\%$. Digilin, Inc. 135

Incineration system

The fluid bed catalytic incineration system destroys halogenated organic material such as vinyl chloride monomer. The system operates at temperatures below 700 °F, and requires a residence time of one-quarter second. Air Resources, Inc. 113



Pre-cleaner/scrubber

A multi-cyclone bank collects and returns large granular particles from the air to the process. The wet gas scrubber washes the air to remove the dusty fines. The slurry is handled by a sludge or dewatering tank. Cleaned water is recycled back to the scrubber for reuse. W. W. Sly Manufacturing Co. 114

Boundary layer measurement system

The portable tethered balloon radio sonde system measures temperature, humidity, altitude, wind direction and wind speed in the lower atmosphere. The complete system also includes a portable receiving station and an electric power winch. Contel Corp. 115

Amplifier-power supply

The unit is an infrared transmitter, receiver and power supply modular for use with the company's sensor heads. Scientific Technology, Inc. 116

Flow totalizers

Designed for turbine-type flowmeter applications. The flow total is displayed in gal, ft³ or lb by conditioning the output signal of the flow meter in an integrated circuit counter. Olympic Controls, Inc. 117

pH/ORP tester

The instrument will measure and calibrate pH and oxidation-reduction potential instrumentation in the field when used with any millivolt potentiometer. James G. Biddle Co. 119



Electrostatic printer/plotter

Instrument produces clean, density images and smooth line contours from computer-generated graphics and alphanumeric. It plots graphics at 3 in./s, and prints 264 alphanumeric characters per line at a speed of 1200 lines/min. Gould Inc. 121

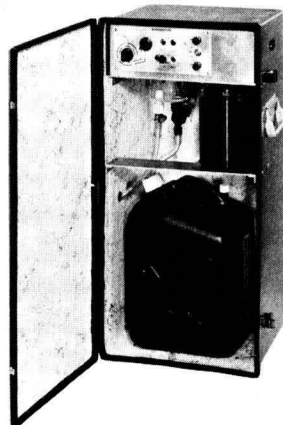
Water quality monitor

The portable unit measures and displays salinity and temperature or conductivity and temperature. INSTRO Co. 123



Sound level meter kit

Designed to monitor vehicle noise. The kit consists of a calibrator, wind meter and wind screen. The meter measures noise in a fast-response mode for moving vehicle measurements and a slow-response mode for stationary vehicle, OSHA and other measurements. Quest Electronics 124



Liquid samplers

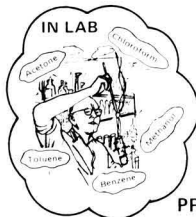
Eight different high-velocity systems are available to sample fluid streams containing high concentrations of suspended solids. The sample is collected into a composite jug or into one of 24 bottles. Sigmamotor, Inc. 130

AA spectrophotometer

The atomic absorption spectrophotometer combines microcomputer electronics with a high-resolution, double-beam optical system. The unit automatically calibrates with up to three standards and provides automatic curve correction in absorption or emission for flame or flameless sampling. Perkin-Elmer Corp. 133

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- Microbiocide.** Bulletin F.14377 describes Microbiocide 40, containing organosulfur compounds and an amine, used to inhibit algae, bacteria, and fungus growth. Oakite Products, Inc. **152**
- Cooling water treatment.** Bulletin CT-1 tells how cooling water treatment programs can save energy, reduce pollution, and extend equipment life. Flow diagrams and graphs are included. The Mogul Corp. **153**
- Equipment rental.** Catalog lists more than 5000 test instruments, some useful for monitoring, available for short- or long-term rental. General Electric Co. **154**
- Pressure gauges.** Pressure Gauge Catalog 525 is the first to list such gauges to cover metric scales and kilopascal units. 1976 edition. Weksler Instruments Corp. **155**
- Milling without solvents.** Case history tells how company devised a new chemical milling process using no solvents or other ecologically harmful materials. Koltron Corp. **156**
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- Sludge estimates.** Company offers "Nomographs for Estimating Sludge Production" for wastewater treatment plant designers and engineers. Can-Tex Industries **158**
- PCB/pesticide analysis.** Price list outlines costs for analysis for varying pesticides and PCB's by proprietary techniques. Analytical Bio Chemistry Laboratories, Inc. **159**
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- OSHA compliance.** Brochure discusses a complete line of portable and continuous monitoring infrared analyzers for OSHA compliance testing of toxic vapors and gases. Wilks Scientific Corp. **161**
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- Refrigerated chambers.** Bulletin MC-1 lists, and provides a guide for chambers which can store samples, and perform other functions at -20°C to -130°C . FTS Systems, Inc. **163**
- Methane monitoring.** Data Sheet 08-01-10 describes system for continuous monitoring of methane gas in underground mining operations. Mine Safety Appliances, Inc. **164**
- Smoke and odor control.** "Poly-Stage Precipitators" catalog outlines ways to control stack and duct smoke emissions with high efficiency at low cost ($2\text{¢}/\text{h}/10\,000\text{ cfm}$). Beltran Associates, Inc. **165**
- Meteorological data.** Tethered balloon sounding system can provide weather data, including air pollution data, in the boundary layer below 1000 m. Brochure gives full description. Ambient Analysis, Inc. **166**
- Line voltage regulators.** Bulletin 388 covers sizes, specifications, and operating parameters of POWERTRONIC line voltage regulators, and output load voltage control. Cyberex Inc. **167**
- Microbiocide.** Bulletin 7224 describes DEARCIDE 714, which controls bacteria and fungal slimes, and meets federal standards. Feed methods and dosages are given. Dearborn Chemical (U.S.) **168**
- Cyanide control.** Booklet describes system for electrochemical oxidation to cut cyanide/cyanates and nitrates from salt-bath quenches and rinse tank water to below 1 ppm. Ajax Electric Co. **169**
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- Chromate removal.** Brochure U 2000 describes patented chromate removal system for cooling towers and other applications. Chromates can continue to be used in cooling towers with this method. Andco Inc. **173**
- Pollution monitoring.** Brochure announces list of pollution monitoring instruments and laboratory products for air, water, and noise. Research Appliance Co. **199**
- Pesticides laws.** Brochure, "What You Should Know About the Pesticide Law", is available. Single copies. Public Information Office, EPA Region VI, 1600 Patterson St., Dallas, TX 75201 (write direct).
- Noise Control Update.** Quarterly publication concerning noise control technology. Otto W. Vathke, Director of Communications, Industrial Acoustics Co., 1160 Commerce Ave., Bronx, NY 10462 (write direct).
- State nuclear control laws legal?** Study raises this question, and calls state restrictions a case of express preemption. Scott Peters, Atomic Industrial Forum, 7101 Wisconsin Ave., Bethesda, MD 20014 (write direct).
- "The Recycler in America."** Describes recycling 1976-1976. National Association of Recycling Industries, 330 Madison Ave., New York, NY 10017 (write direct).
- Environmental Town Crier.** Describes environmental activities in the State of Washington. Public Affairs Office, Department of Ecology, Olympia, WA 98504 (write direct).
- "Control Of Aircraft Noise and Air Pollution; Meetings Between FAA And The Public".** RED-75-384. Comptroller General of the United States, Washington, DC 20548 (write direct).
- "The Identification and Measurement of Refinery Odours" and "The Sulphur Grid Method".** Stichting CONCAWE, 60 Van Hogenhoucklaan, The Hague 2018, The Netherlands (write direct).

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BOOKS

Solar Energy Handbook, First Edition, Revised. Paul A. Fleck, Ed. 92 pages. Time-Wise Publications, P.O. Box 4140, Pasadena, CA 91106. 1975. \$3.95, paper (add \$0.50 for handling; California residents add 6% sales tax).

In order to utilize solar energy, one needs to know basic facts about the sun and its contribution to the earth, scientific and engineering definitions and units, cost equivalents, and who is involved. This handy book provides this information in easily understandable "capsule fact" form, and provides many contacts to organizations in this discipline.

Analytical Methods for Carbon Rod Atomizers. Varian Instrument Division Service Center, 670 E. Arques Ave., Sunnyvale, CA 94086. 1976. \$25 (add \$0.75 shipping charge), loose-leaf binder.

This manual is the most complete compilation specially for those working with atomic absorption (AA) spectrophotometry with carbon rod atomizers. It gives more than 80 analytical methods applicable to air and water pollution, metallurgy, geochemistry, petrochemicals, food, and other industries, and explains flameless AA. Its "cook book" format is very helpful.

Managing Livestock Wastes. viii + 631 pages. American Society of Agricultural Engineers, Box 410, St. Joseph, MI 48085. 1976. \$32.50, hard cover.

In April 1975, a symposium on livestock wastes was held at the University of Illinois. This volume contains 180 papers presented there, which covered state-of-the-art and literature reviews, major research studies, and case studies of livestock farms with complete waste management systems. Runoff control, nutrient value use, waste properties, composting, legal matters, and other relevant topics were discussed.

Handbook on Aerosols. Richard Dennis, Ed. v + 142 pages. National Technical Information Service, U.S. Department of Commerce, Springfield, VA 22161. 1976. \$6, paper.

How do aerosols behave? Of what do they consist? What is their fate? This book, developed under U.S. ERDA auspices, discusses aerosol particulate behavior, stack monitoring, high-efficiency control system development, compliance with ever more stringent emission standards, and related topics.

Graphs and tables are provided to assist with computations.

Petroleum and the Continental Shelf of North-West Europe, Vol. 2 Environmental Protection. H. A. Cole, Ed. 126 pages. Halsted Press, 605 Third Ave., New York, NY 10016. 1975. \$24.50, hard cover.

Albuskjell. Ekofisk. Forties. Ninian. These are some of the oilfields in the North Sea, Europe's possible oil bonanza. The development of this petroleum must have potential environmental implications. This book is a collection of papers that explain the approach to cushioning the environmental shock, with emphasis on Great Britain and Norway.

Structure and Function of Tundra Ecosystems. T. Rosswall and O. W. Heal, Eds. 450 pages. Statens naturvetenskapliga forskningsråd (Swedish Natural Science Research Council), Box 23136, S-10435 Stockholm, Sweden. 1975. 50 SKr. (about \$12), paper.

The northern tundra is a fragile ecosystem (*ES&T*, November 1973, p 998). This book treats that ecosystem as an integrated unit, and is directed at zoologists, botanists, microbiologists, and soil scientists. Areas of northern Canada, Scandinavia and Finland, and the USSR are covered.

Dyes from Your Garden. Berenice Gillette Conner. 128 pages. E. A. Seemann Publishing, Inc., 8770 S.W. 131st St., Miami, FL 33156. 1975. \$7.95, spiral-bound.

Would you like to have dyes not made with "artificial" chemicals? Environmental resources, particularly many well-known garden and wild plants are fine sources of dyes. Well-supplied with photographs, this colorful book gives precise recipes for the home manufacture and application of these dyes for mordanting and dyeing.

Low-Cost, Energy-Efficient Shelter for the Owner and Builder. Eugene Eccli, Ed. viii + 408 pages. Rodale Press Inc., Emmaus, PA 18049. 1976. \$10.95, hard cover.

There are still ways to beat the high cost of home building, heating, and cooling. This book fulfills the task of explaining how these goals can be achieved. Better home insulation, use of solar energy, rational use of a greenhouse for winter heat and food, and co-

operation with nature are among many topics emphasized for home building and remodeling.

How to Build A Solar Heater. Ted Lucas. xi + 236 pages. The Ward Ritchie Press, 474 S. Arroyo Parkway, Pasadena, CA 91105. 1975. \$4.95, paper.

Lifetime hot water for \$400. Have space heating and hot water for upwards of \$2500. The author says that these figures are realistic, especially if one is a "do-it-yourselfer." He takes the futuristic mystique out of solar energy use, and tells what materials one needs, and how to put them together. For the non-"do-it-yourselfer", he lists solar energy companies. Retrofitting solar energy into existing homes is also covered.

Trace Element Analysis. Vlado Valković. x + 229 pages. Halsted Press, 605 Third Ave., New York, NY 10016. 1975. \$22.50, hard cover.

How does one analyze for elements in concentrations of one ppm or less? The author explains how this is done, and emphasizes environmental pollution, biology and medicine, and analysis techniques. Effects of trace elements, their distribution, radioactivity (where applicable), and other relevant topics are fully discussed. The author is with Rice University (Houston, TX), and "Ruder Bošković" Institute, Zagreb, Yugoslavia.

Garbage Housing. Martin Pawley. 120 pages. Halsted Press, 605 Third Ave., New York, NY 10016. 1975. \$16.50, hard cover.

It is a paradox that with a growing shortage of world resources, so much is still made to be used once and then thrown away. Perhaps this trend might be reversed through encouragement of secondary use of materials—in home building, for example. This book explains how that objective might be met without detracting from the illusion of affluence that many societies still hold dear.

Municipal Solid Waste Management. David Rimberg. xiii + 381 pages. Noyes Data Corp., Mill Rd. at Grand Ave., Park Ridge, NJ 07656. 1975. \$24, hard cover.

This work is No. 26 of the Pollution Technology Review series. Its purpose is to provide sufficient technological and administrative guidance for designing practical and economical solid waste management systems in keeping with the Federal Solid Waste Disposal and Resource Recovery Acts. Equipment and systems, economic and labor aspects, and selected city systems are fully discussed.

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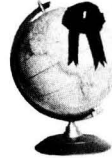
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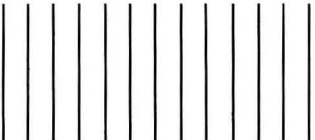
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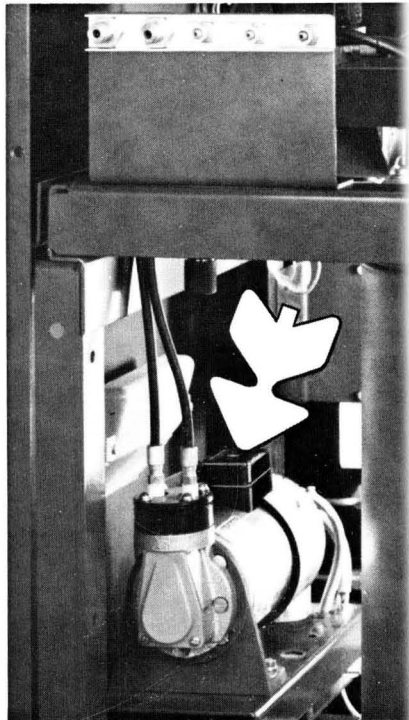
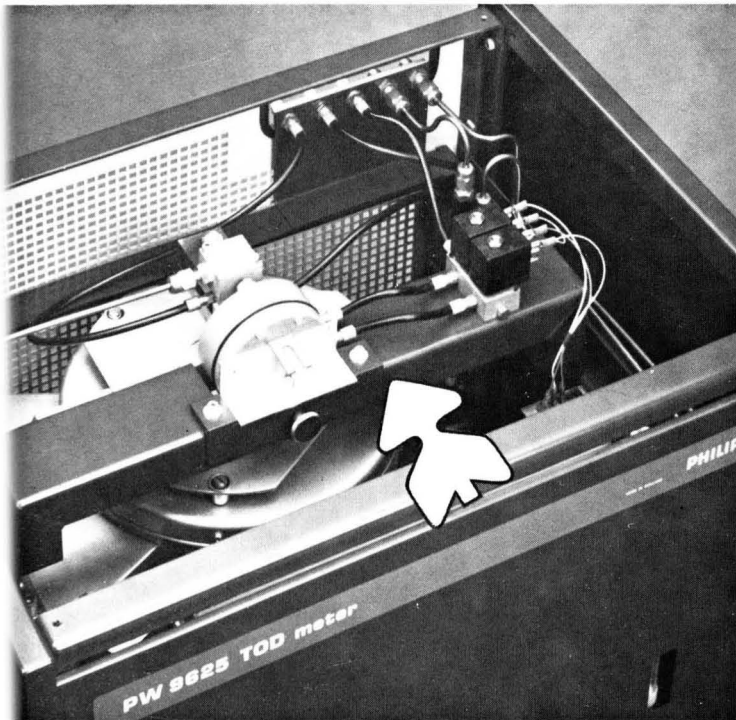
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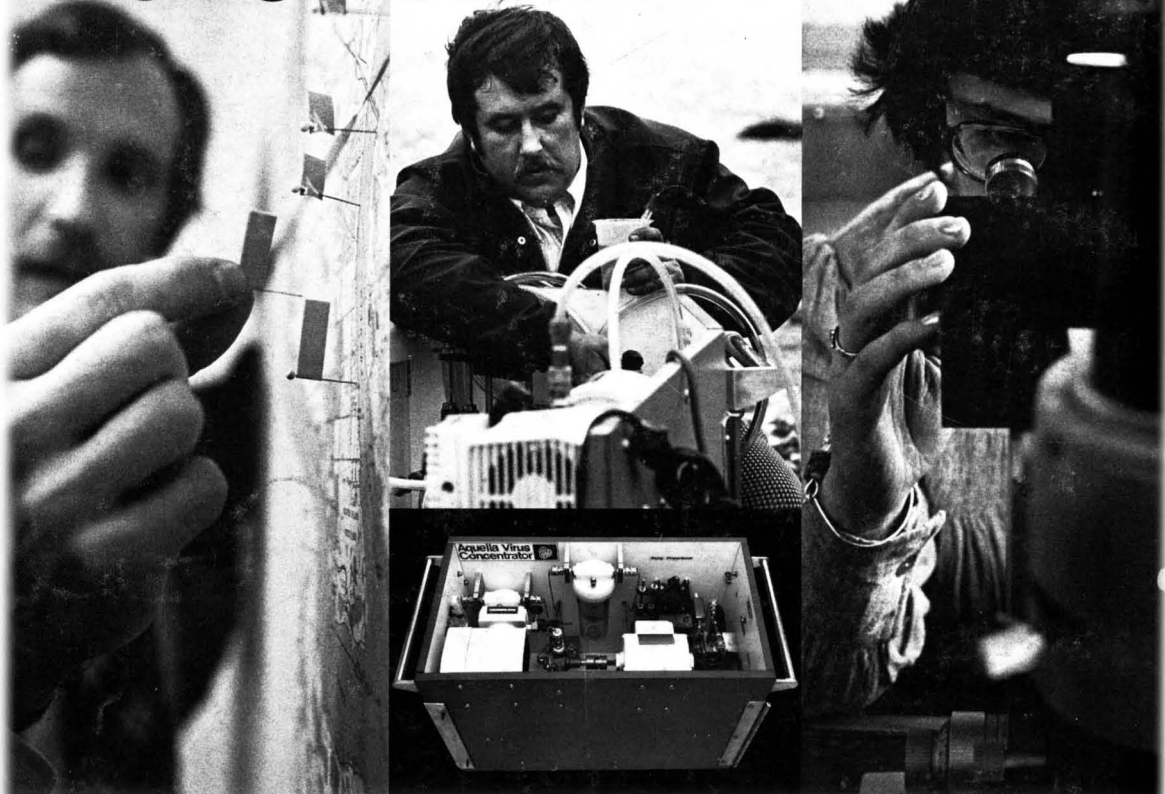


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