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Science & Technology

JULY 1973



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Subject: Curtailing air pollution: elimination of sulfates and acidic sulfur oxides.

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TO: Dr. Ira Kukin, President

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- (1) Bulletin U-561 Cold-End Corrosion in Oil-Fired Units
- (2) Bulletin U-513 Use of Apollo Coaltrol M As a Supplementary Cold End Treatment to Control Acid Smut & Low Temperature Corrosion.
- (3) Bulletin U-527 Apollo Dual Feed For Use With Electrostatic Precipitators

Name _____ Title _____
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Reference:

THE NEW YORK TIMES, MONDAY, MARCH 12, 1973

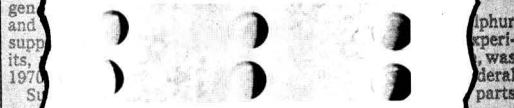
Sulphate Peril May Lead To Tighter Clean Air Law

By GLADWIN HILL
 Special to The New York Times

DURHAM, N. C.—A new villain is emerging in the air pollution picture, a situation that may in February.



Untreated air heater (Union Electric Co.) in coal-fired boiler (500 Mw, 3,290,000 lb/hr of 1000° F. steam at supercritical pressure) showing deposits from SO₃ in the stack gas.



Same air heater after 12-weeks with cold-end Apollo Coaltrol MS treatment.



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Environmental Science & Technology

Volume 7, Number 7, July 1973

ESTHAG 7 (7) 573-662 (1973)

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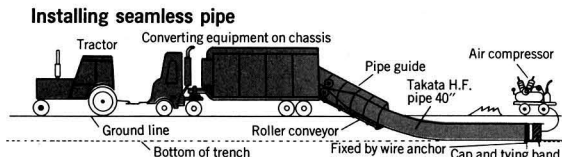
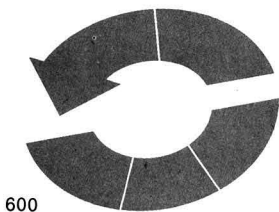
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Published monthly, with additional Pollution Control Directory in October, by the American Chemical Society, from 20th and Northampton Sts., Easton, Pa. 18042. Executive offices, Editorial Headquarters, 1155 16th St., N.W., Washington, D.C. 20036. Advertising office: 142 East Ave., Norwalk, Conn. 06851. Second-class postage paid at Washington, D.C. and at additional mailing offices.

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CURRENT RESEARCH

Rate of evaporation of low solubility contaminants from water bodies to the atmosphere. Donald Mackay and Aaron W. Wolkoff

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The transfer of contaminants from the water to air environments can occur much faster than has generally been thought. Equations are derived to predict evaporation rates of hydrocarbons and chlorinated hydrocarbons that have very low solubilities. These rates can be high even for compounds of low vapor pressure, and that "half lives" in solution can be as low as minutes or hours under laboratory or environmental conditions.

Mercury removal from waste water with a starch xanthate-cationic polymer complex. Charles L. Swanson, Robert E. Wing, William M. Doan, and Charles R. Russell

614

Sequential addition of starch xanthate and a cationic polymer to a mercury solution precipitates both polymers and the mercury as a cohesive floc that is easily removed by filtration. Some xanthate groups on the starch backbone may form mercury (II) salts while others react with the polycation to form a polyelectrolyte complex. The effectiveness of mercury removal depends on the ratios of mercury, cationic polymer, and xanthate.

Identification of cutin, a lipid biopolymer, as a significant component of sewage sludge. Pappachan E. Kolattukudy and Richard E. Purdy

619

Sewage sludge was thoroughly extracted with organic solvents, and the residue gave polyhydroxy alkanes after hydrogenolysis with LiAlH_4 . The major hydroxyalkanes were identified by means of chromatographic techniques in conjunction with mass spectrometry and found to be typical of the lipid polymer cutin.

A study of the respirable dust content in the ambient air. Ralph E. Pasceri

623

The respirable dust content in the ambient air at a single near-urban location was determined by using a high-volume sampling technique and a cyclone separator to simulate the filtering action of the upper respiratory tract. On the average, approximately half of the suspended particulate mass at the sampling location was respirable.

Benzene and toluene distribution in the atmosphere of Toronto. Saul Pilar and William F. Graydon

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The study measures nonmethane hydrocarbon concentrations at various urban locations simultaneously. Benzene and toluene were identified, and variations in their concentrations with time were compared with total hydrocarbon concentration in the same location. Results show that distinct patterns exist between concentration variations and automobile traffic.

Metal contamination of urban woody plants. William H. Smith

631

Results are presented of an attempt to establish the plant burden and the location of various metals on or in six woody plant species growing in New Haven, Conn. Cd, Cu, and Mn were present in normal amounts. Al, Cr, and Ni were present in slightly above normal amounts. Fe, Pb, Na, and Zn were present in above normal amounts.

NOTES

Extraction of dispersed oils from water for quantitative analysis by infrared spectrophotometry. Michael Gruenfeld

636

Some parameters that optimize the extraction of dispersed oils from water for quantitative analysis by infrared spectrophotometry are examined, and an improved extraction procedure is recommended. Trichlorotrifluoroethane, an essentially nonpoisonous solvent, is preferable to carbon tetrachloride.

Baseline concentrations of light hydrocarbons in Gulf of Mexico. James M. Brooks, Alan D. Fredericks, and William M. Sackett

639

A 2500-mile survey of light hydrocarbon concentrations in surface water of the Gulf of Mexico was conducted to determine "baseline" concentrations for a program to identify problems related to oceanic environmental quality. High concentrations seem to be associated solely with man's port and oil operation activities.

Identification of aliphatic amines volatilized from a cattle feedyard. Arvin R. Mosier, Charles E. Andre, and Frank G. Viets, Jr.

642

Direct gas chromatographic (gc) analysis of acid solutions and gc separation of pentafluorobenzoyl derivatives were used to determine basic organic N-compounds volatilized and collected in dilute acid from a cattle feedlot. Methyl, dimethyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and *n*-amyl amines were among the basic N-compounds found.

Ammonium nitrate in airborne particles in Los Angeles.

Robert J. Gordon and Robert J. Bryan

645

Ammonia nitrate comprised approximately 10–15% of the total airborne particles in composite samples collected in a Los Angeles study. Methanol was used to extract inorganic materials following previous extraction of benzene solubles. The methanol extraction was subjected to qualitative tests, Kjeldahl titration, 2,4-xyleneol nitrate determination, and infrared spectra.

CORRESPONDENCE

Stoichiometry of ozone-iodide reaction: significance of iodate formation. Lawrence R. Schmitz

647

Commenting upon article appearing in *ES&T*, 7, 65 (1973), correspondent claims that if the determination of iodine is carried out under proper conditions, no error will result from the formation of iodate.

Response. Edward P. Parry

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Credits: 583, USDA; 585, Du Pont; 589, A-1 Passport Studio, Inc.; 596 (left), Vernon L. Smith; 596 (center), Kaiser Graphic Arts; 596 (right), Walter H. Scott; 596 (lower), Consolidated Coal Co.; 598, Chamber of Commerce of Metropolitan St. Louis; 600 (upper left), UPI; 600 (upper right), Paul D. Steffee; 600 (lower left), U. S. Forest Service; 601, Union Carbide; 603, David Harris; 604 (upper), R. M. Kneller; 604 (lower), David Harris

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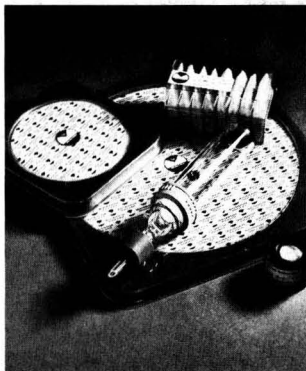
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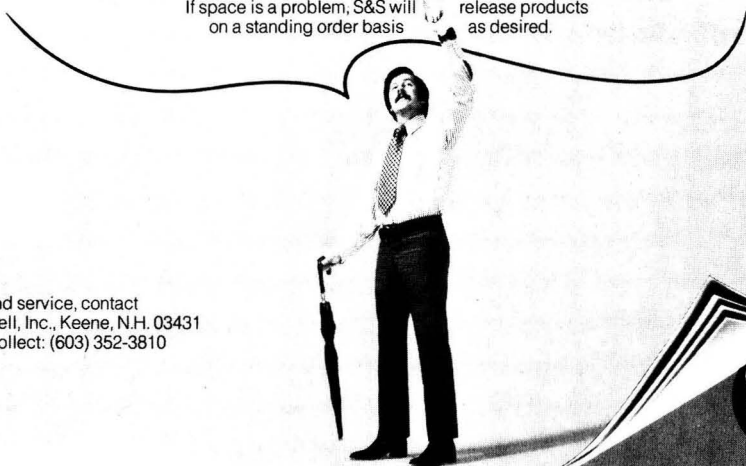
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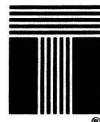
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Published by the
AMERICAN CHEMICAL SOCIETY
1155 16th Street, N.W.
Washington, D.C. 20036

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name of the author to whom inquiries should
be addressed carries a numbered footnote
reference.

When will it be safe to drink?

The water, of course! When was the last time you visited an advanced waste treatment plant, and when the operator presented you with a sample of the clean and odorless effluent you either said to yourself or out loud, "Is it safe to drink?" In his recording, "Pollution, Pollution," Tom Lehrer had no answer either but did point out that the effluent that you discharge in San Francisco in the morning you drink for lunch in San Jose.

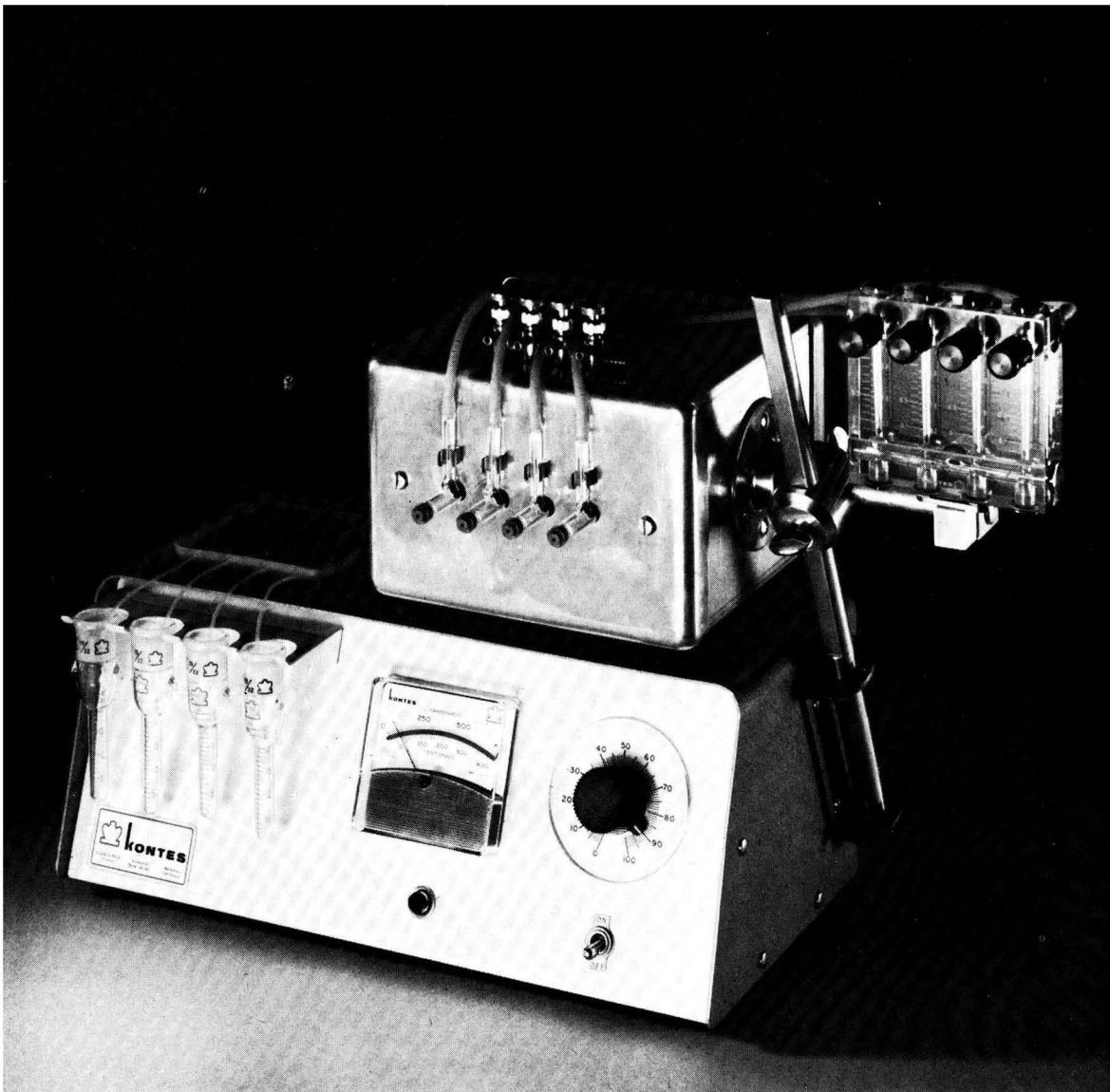
This point is borne out by more recent evidence. As this month's feature authors, Shuval and Gruener, point out, the concentration of contaminants has been shown to increase in downstream communities as water is used and reused and as the percentage of unremoved residual refractory chemicals grows. Newer pollutants are showing up in drinking water supplies, it seems, more and more frequently. The organic components in the Evansville, Ind., municipal water supply and the biorefractories in the drinking water in Louisiana have earlier received attention in *ES&T*.

Already there is some evidence that the need for water by municipalities, industries, and agriculture in certain areas is outstripping the supply of natural waters that have passed through the evaporative and precipitative phases of the hydrological cycle.

Water supply and water demand are on a collision course in the water-short country of South Africa. And there at Windhoek, as far as we are aware, is the first place in the world where renovated waste water is being used for drinking purposes and makes up 14% of the normal supply and as much as 40% of the supply during the winter months. Whether this practice is safe or not no one dares to say.

But if the demand outstrips the supply in other parts of the world, including the U.S. for that matter, then undiluted waste water in a city, including industrial wastes, may have to be processed to a point of becoming fit for human consumption. Another aspect of this health problem is the longer life span of man, which subjects him to more and more pollutants for many more years than before. Certainly his longer life aggravates, in time and concentration, the pollutional insults to which he is exposed.





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CURRENTS

WASHINGTON

A significant reduction has taken place in air pollution from automobiles produced after the 1968 federal emissions standards became effective. According to the EPA, the results come from three auto exhaust emission surveillance programs undertaken in cities across the U.S. Results showed that average emissions from the 1968-71 cars tested were 4.54 grams per mile (gpm) of hydrocarbons, as compared to 8.74 gpm from the precontrol level. Nitrogen oxides emissions were slightly higher than the precontrol level; however, the 1968-71 standards did not apply to nitrogen oxides.

If the catalytic muffler becomes the standard automobile exhaust control device, then domestic demand for platinum could triple overnight. According to a report by the Interior Department's Bureau of Mines, each device would require about a tenth of an ounce of platinum. This means that in 1976, when all newly manufactured vehicles are supposed to have antipollution equipment, almost a million and a half ounces of platinum could be needed for the manufacture of catalytic mufflers. Normally the country uses about 500,000 oz of platinum each year, three-fourths of which is recycled. The U.S. produces very little of this metal.

Final EPA regulations on waste water discharge permits are out. The regulations mean EPA can now begin to issue permits until the time that states can develop programs allowing them to issue their own permits. California is the only state at present to possess such authority. To be issued on an individual basis, the permits will control dumping into navigable waters by stating what substances and in what amounts can be discharged. They include requirements for monitoring and reporting information regarding each discharge and regulations allowing an applicant for a permit, or a private citizen, to appeal an EPA decision in a formal hearing. The regulations also require that fact sheets be

prepared by EPA on any application for a permit that involves a discharge exceeding 500,000 gal.

In the air category, EPA has proposed performance standards for a second batch of industries (a first batch covered five industries—*ES&T*, Oct. 1972, p 884). These proposed standards apply primarily to new plants or existing plants which are modified substantially to increase emissions. EPA now says nitrogen

Performance standards proposed for another seven industries

Asphalt concrete plants
Petroleum refineries
Petroleum storage tanks
Secondary brass and bronze ingot plants
Secondary lead smelters
Sewage treatment plant incinerators
Iron and Steel plants (basic oxygen furnaces)

dioxide is not as widespread an air pollutant as earlier thought, based on 1972 data derived from measurements at some 200 sites across the nation. Only two air quality control areas—Los Angeles and Chicago—definitely have nitrogen dioxide levels exceeding the national ambient air quality standard ($100 \mu\text{g}/\text{m}^3$). Originally, 47 air quality control regions were in this category.

The prospects for solar energy use in dealing with the critical energy problem forecast for the 1980's and beyond are excellent, according to Dr. Alfred J. Eggers, Jr., assistant director for research applications at the National Science Foundation. Dr. Eggers said it appears that solar heating, using present technology, can become less costly than electric heating in most areas of the U.S. He said the nation's goals in solar energy use by the next century are to provide 35% of the energy needed for building, heating, and cooling and to supply the energy equivalent of 30% of the nation's gas fuel, 10% of our liquid fuel, and 20% of our electric energy.

EPA also has published interim criteria on ocean dumping for evaluating another set of permit applications. The guidelines specify the materials absolutely prohibited from being dumped, the materials prohibited in more than trace amounts, those that may be discharged only in quantities not exceeding permissible concentrations, and materials that require special conditions for disposal. The criteria include a list of sites in the oceans for regulated dumping.

The Experimental Technology Incentives Program (ETIP) proposed by President Nixon in his fiscal 1973 budget has been funded for \$7 million. The program seeks to increase the nation's application of technological invention and innovation to such questions as productivity, unemployment, pollution, energy conservation, and unfavorable trade balances. In making the announcement of the

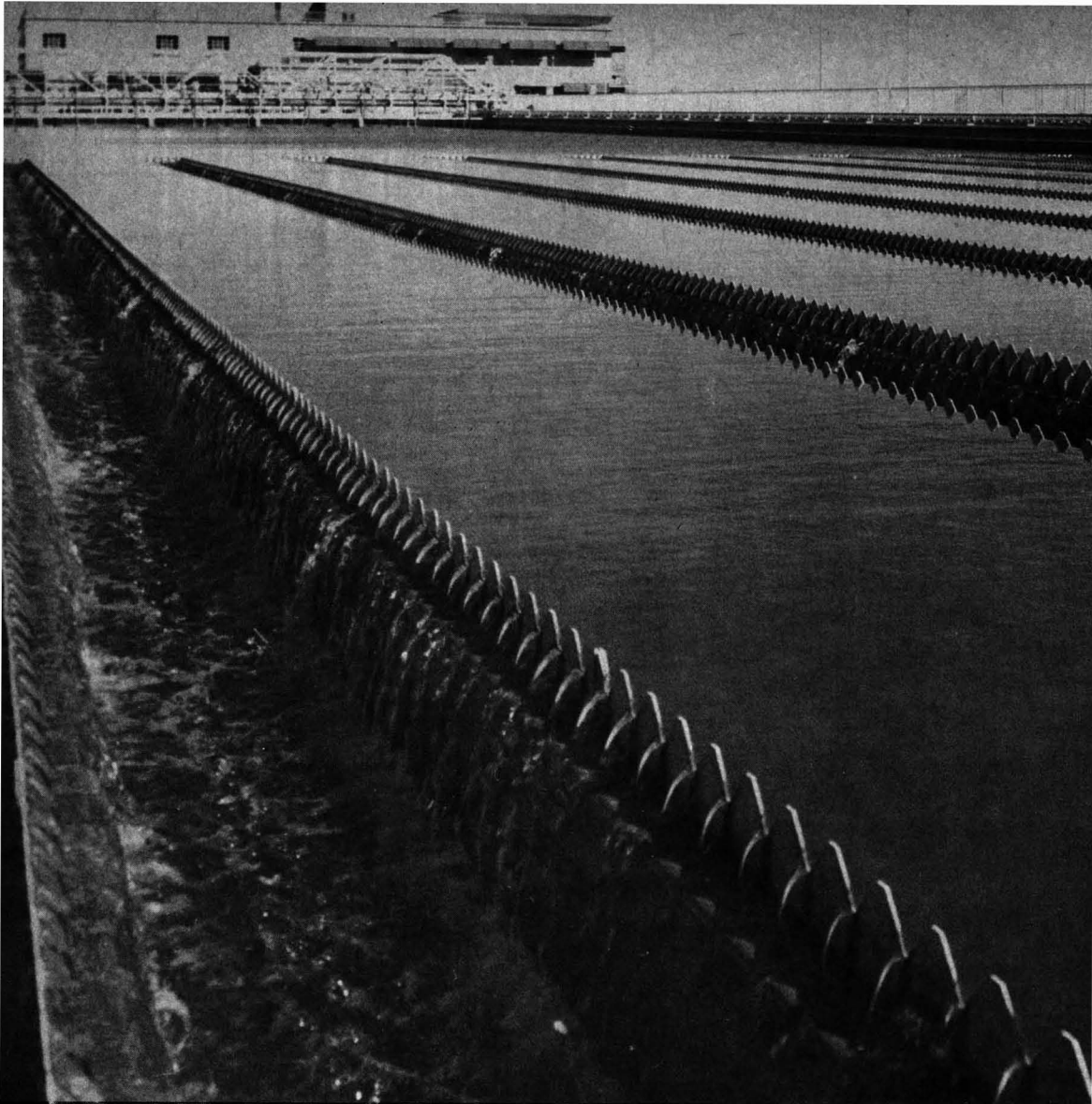


NBS director Roberts

funding, Dr. Richard W. Roberts, director of the National Bureau of Standards (Department of Commerce), said many of the experiments to be conducted under ETIP will be based on suggestions solicited from various elements of the industrial community, professional and trade organizations, educational institutions, state and local governments, and individuals.

STATES

Delaware's legislature is considering a tough environmental legislative package. One bill, already passed by the Senate, requires permits and supervision, at company expense, for dumping wastes in Delaware



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CURRENTS

waterways. Another measure regulates residential and commercial development in the state's coastal zone. One proposal levies a charge on each barrel of oil lightered or delivered in Delaware, and another bill gives the state authority to grant or deny permits for any activity in the state's wetlands.

The Maine Supreme Court ruled that a state law levying a half-cent tax per 42 gal of oil shipped through Maine waters was constitutional. The law also holds oil concerns responsible for oil spills and states that terminals would be responsible for spills once tankers enter the 12-mile limit.

Hamilton, Ohio disinfects its water supply with chlorine dioxide rather than chlorine as the usual oxidizing agent. In 1970, state agency-desired minimums of free chlorine were not being maintained in outlying areas of the water system, but increased chlorine levels caused consumer complaint. During a trial period with a chlorine dioxide generator borrowed from Herbert Chemical Co. (Cincinnati, Ohio), the chlorine residual equaled or exceeded USPHS recommendations as far as 15 miles away. City officials feel the 50% higher treatment costs are justified in maintaining the residual and satisfying customers.

Kenosha, Wis., is using biological adsorption to treat and remove pollutants from combined sewage during heavy rain storms. Activated sludge from the main dry weather plant is used to treat the extra sewage flow during rainy weather. The effluent meets all federal EPA water quality standards.

Unnecessary horn honking is now regulated in New York City. In the Environmental Protection Administration's antihorn honking campaign, motorists will be fined \$50, \$100, or \$250 for the first, second, and third offenses, respectively, for honking unnecessarily.

New York City's Environmental Control Board has ordered the Department of Air Resources to seal the incinerators of 11 persistent violators of the city's Air Pollution Control Code. This is the first instance where the Board used new powers to issue such orders.



Protecting the Mich. shoreline

The Michigan Natural Resources Commission recently designated 950 miles of public and private property as shoreland environmental areas under the state's Shorelands Protection Act. After designating such environmental areas, the Department will mail maps to the local units of government involved. Local governments then have until April 1974 to provide zoning safeguards to protect the area from development activities. If no action is taken, environmental areas in those locales will then come under a state system of permit controls.

If the Denver area a policy statement calling for postponement of freeway construction approval, until environmental impact statements show that air quality will not be adversely affected, has been adopted by Colorado's Air Pollution Control Commission. The Commission also resolved that construction of any complex pollution source not endanger achieving ambient air quality standards; less polluting forms of transportation, other than automobiles, be encouraged in Denver; and laws be passed to mandate land use transportation planning to achieve or maintain air quality.

In opposition to higher costs for auto emission control devices, the California Air Resources Board requests that light duty manufacturers of 1975 vehicles impose the same cost of emission control throughout the nation regardless of the types used in any state.

In a consent agreement, Owens-Corning Fiberglas Co. (Barrington, N.J.) was fined \$120,000. In action taken on behalf of the state Department of Environmental Protection, the company agreed to meet state standards for odor and smoke emissions and allowable levels of particulate matter discharges. Under the consent decree, the glass wool manufacturer is legally entitled to a rebate of up to 90% of the fine if it meets terms of the agreement by December 1, 1974.

CONSULTING

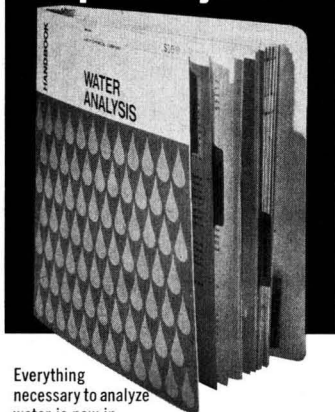
The Consulting Engineers Council (CEC) blasted EPA's regulation on design/construct (alias turn-key) construction. In a sharply worded four-page letter, CEC branded EPA's action as "unwarranted, arbitrary, inconsistent, specious, and an apparent disregard of the intent of Congress and the recommendations of virtually all segments of the sewage treatment industry." EPA's effective interim regulations were published on Feb. 28. Applications for this type of construction will be approved by the EPA regional administrator but the state agency must certify the project for priority and come forth with performance specifications. At press time, none had been approved.

TECHNOLOGY

The phosphate removal process, PhoStrip of Biospherics, Inc. (Rockville, Md.), will get a full-scale test at a 1.5-mgd plant at Seneca Falls, N.Y. Seneca Falls is under orders to remove phosphate from its sewage effluent by mid-1974. About half of the phosphate in the waste stream is detergent phosphate, and Procter & Gamble Co. has agreed to finance the evaluation of the process.

Catalytic converters can be tested in a simple and inexpensive test, according to engineers at Corning Glass Works (Corning, N.Y.). Called the "bag test," the procedure involves driving a vehicle on a chassis dynamometer through a simulated 7.5-mile-long series of accelerations, decelerations, and cruise situations lasting

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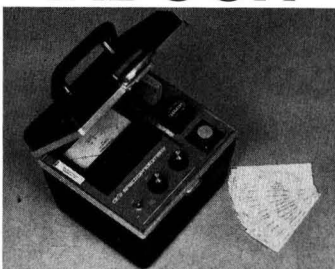
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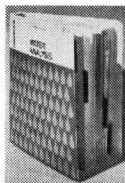
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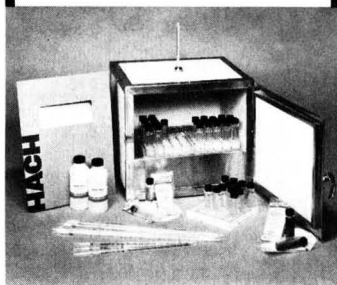
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CURRENTS

approximately 23 min. The exhaust gases are collected in the bag, and hydrocarbon and carbon monoxide emissions are determined for the complete driving cycle. The Corning test takes seven minutes and requires no driver. Corning is a supplier to the auto industry of a multicellular ceramic substrate that is used as a catalyst support in emissions control units.

Another rotary engine is vying for the automobile pollution control limelight. The Anidyne Corp. (Harrisburg, Pa.) engine relies on split cycling and is said to overcome the thermodynamic deficiencies of all other types of internal combustion engines by virtue of its split cycle principle. In conventional two- and four-stroke reciprocating piston engines, the process of induction, compression, expansion, and exhaust are the cyclic function of the same piston. The Anidyne split-cycle principle utilizes two double-ended pistons working together. One acts as the power piston for expansion and exhaust, the other acts as an air pump to suck in air and transfer it under pressure to the power piston.

Continuous, plastic pipes can be put in the ground and may one day be used in sewage collection systems, according to a Japanese firm—Takata Kojiyo Co., Ltd. (Tokyo). The pipe does not require the jointing of pipe segments together every few feet; hence, there could be no infiltration to the line. The Takata H.F. (hardened, flexible) pipe in 16- and 40-in. diameters is being used on an irrigation project at Dixon, Calif., but other diameter (8-, 12-, 16-, and 20-in.) pipes can be fabricated. The plastic materials are produced in prepared, softened condition in coils for shipment and storage and then converted at the site of its final form by a heating process.

A double alkali scrubbing system for SO₂ removal from stack gases has been announced by Envirotech. The system has been tested in pilot plant on a 3000-scfm stream for more than one year and for more than six months on a 24-hr, 5-day per week continuous basis without any evidence of scaling in the system. Removal efficiencies of 85–95% have been achieved. In the system, flue gas is initially quenched with water to saturation temperature and then passed into the bottom of a polysphere scrubber equipped with two trays of balls. Sodium hydroxide liquor is sprayed on the balls and passed through the scrubber by gravity into a splitter. Particulate and SO₂ are removed through contact with the sodium hydroxide liquor and the clean flue gas is then passed to a cyclone separator and a fan and discharged through the stack.

The oil industry has spent \$4.4 billion over the past seven years to protect the U.S. environment, according to a survey published by the American Petroleum Institute. Last year alone, the industry spent \$1.2 billion—an average of nearly \$3.3 million a day—compared to a \$271-million investment in 1966. Classification of expenditures during the seven-year period showed that \$2.6 billion, 60% of the total, went for capital improvements in the environmental field.

The future of the plastics industry can be adversely affected unless business and community leaders work together for balanced environmental legislation. Du Pont vice-president Irene du Pont, Jr., called for legislation which would be



Irene du Pont, Jr.

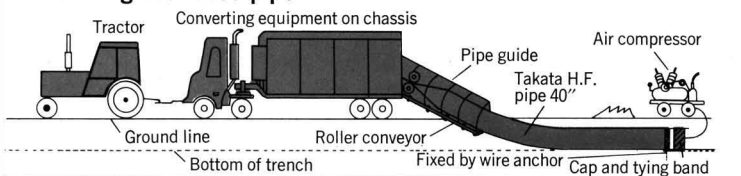
INDUSTRY

Pollution control efforts by the steel industry "lags far behind what is legally required and technologically feasible," says a study by the Council on Economic Priorities (CEP). The 500-page study by the nonprofit CEP ranks U.S. Steel, Gary, Ind., works and National Steel's Weirton, W. Va., works as the worst air polluters of the 47 mills operated by these companies. The study says only Armco Steel's Sand Springs (Okla.) works adequately controls pollutants to the 90% or better level. CEP estimates that seven major steel producers could bring their mills into compliance with air and water pollution control regulations with an annual price increase of less than 1.3% over five years. "If this were passed entirely on to the consumer, it would cause an increase of about \$5.00 in the price of a large car," says Jean Halloran, editor of the CEP study.

"fair to the consumer." Although plastics have ushered in a new era of convenience and economy to the American public, du Pont said, "the warning sign is up" because of the issue of plastics in the environment. Burning waste plastics to generate steam or electricity is "a promising secondary use" since any given amount of hydrocarbon is in essence used twice, the Du Pont executive said.

A major switch to a nuclear electric economy is the long-range solution to energy problems in the U.S., says Westinghouse Power Systems Co. president John W. Simpson. At a symposium sponsored by the Carnegie-Mellon University, Simpson charged that President Nixon's April 18 energy message to the Congress "falls short in not offering a comprehensive plan which sets forth priorities among our various energy programs aimed at reducing the use of critical fuels and expanding the use of more plentiful energy forms."

Installing seamless pipe



OUTLOOK

Upping the down sewer line repairs

Feds say no excessive infiltration or else no funds as sewer maintenance companies gear up for business

It's no joke. There is both good news and bad news in the water pollution control construction field. First, the good news—in a recent decision a federal district court judge says that the Administration must release the additional \$6 billion for waste water construction specified in the water pollution control amendments of 1972. The bad news—after July 1, the EPA administrator cannot award grants for the construction of waste treatment facilities until he is assured that there is no excessive sewer infiltration to the treatment plant.

Not only is it a requirement of the law—now, too, federal funds, for the first time ever, are available for sewer line infiltration studies and repair. In general, it is cheaper to add new plant capacity than it is to repair the line.

The federal view

EPA drafted its proposed regulation on the control of infiltration inflow in sewer systems on March 19. Basically, the regulation says that "The Federal Water Pollution Control Act Amendments of 1972 requires all applicants for a treatment works grant to demonstrate that each sewer system discharging into such treatment works is not subject to excessive infiltration/inflow."

The term "excessive" is then further defined in economic terms. When it becomes cheaper to treat the inflow than it would be to repair the line, then the option is to treat. In other words, the rehabilitation of the sewer line must be cost effective, and EPA plans to fund selective rehabilitation of sewer lines.

The way EPA determines excessive infiltration is by the process of regression analysis. By this analysis technique, first the cheaper sources to eliminate are determined; eventu-

ally a point is reached at which it is not economical to repair the line in which case treatment of that additional water is simply paid for.

The reimbursement of federal funds for rehabilitation of sewer lines will be approved or disapproved by the regional EPA administrators. Although instructions from Washington headquarters had not been sent to regional offices at press time, the rationale is to identify sources of inflow, minimize TV inspection, and take a systematic look at the subsystem of the sewer line and to perform a regression analysis to the point of cost effectiveness.

What happens

The companies clean the lines with high velocity water and/or rodding or hydraulically operated equipment. After the sewer line is cleaned, then they inspect for leaks by closed circuit TV inspection, air pressure testing, or smoke testing. For example, a closed circuit TV camera, usually mounted on a sled-type arrangement, is moved from manhole to manhole. A truck-mounted viewing station above ground charts and notes the leaks. Behind the camera comes a inflatable rubber packer which puts pressure (5-6 psia) on the joint to detect a leak. The packer can dispatch grout as the TV cameraman above ground monitors the entire repair.

Grouts can be divided into two categories, those containing suspended solids, such as cement and bentonite, and solution grouts, or chemical grouts. For example, the AM-9 chemical grout, a commercial

product of the American Cyanamid Co., is commonly used. Another widely used chemical grout is available from the 3M Co. Chemically, AM-9 is a mixture of two organic monomers—acrylamide and *N,N'*-methylenebisacrylamide—in proportions which produce a very stiff gel from dilute aqueous solutions when properly catalyzed by free radical initiators.

Military moves

Without question, the military moved well in advance of any EPA requirement on civilian communities on the repair of their sewer line collection system, and a number of examples are available here. The reason the military moved on this problem, understandably, is that most of their waste discharges are, or soon will be, connected to either municipal or regional treatment systems. Since the dischargers pay for treatment on the basis of the waste—no doubt on a volume basis—they obviously do not want to be paying for treatment of any additional storm water or groundwater that has infiltrated into their collection systems. Nor does anyone else for that matter.

The Army has promoted the idea of sewer line repairs for years. In the past, the repair funds have come from the operating and maintenance funds of the local commanding officer at the military installation. Rather than building more waste water treatment facilities, the military planners are taking a close look at TV inspection and interior grouting of existing lines at numerous facilities throughout the U.S.

The Navy's program for sewer line repair at shore facilities started as early as 1966. Then, in 1968 DOD came up with its first five-year plan for pollution control abatement which

is periodically updated each year. For example, the Navy has checked the infiltration of sewer lines at its Naval Communications Station at Stockton, Calif. About a year or so ago it started an inspection program for the sewer line; eventually the waste water from this communications command will be connected to the municipal waste treatment facility in Stockton. Within the past year, the Navy used TV cameras in an inspection and repair project at the Naval Security Group activity, Skaggs Island, Calif.

Ready for work

By now, at least a dozen companies are in the business of sewer line inspection and maintenance (see box). Basically, the leaks come from faulty joints in the lines. The use of rubber gaskets and joints in sewer lines was introduced between 1955 and 1960, depending on the geographic location. The western states were first, and the northeastern ones were last. Prior to 1955, sewer lines used either mortar or mastic to fill the joints, and it has been conservatively estimated that 70-90% of such existing joints are leaking. Of course, it is sewer line joints of the latter type which exist in virtually every major city in this country.

The big companies in the business, of course, are Penetryn, National Power Rodding, and Roto-Rooter. Each has regional offices throughout the U.S. With 12 regional offices in the U.S., Penetryn sales in 1972 hit \$6 million—\$5 million for services and products and \$1 million for restoration services. In the eastern U.S., other leaders include Southern and Underground. Perhaps, the leading areas that have had some of their lines repaired are the urban municipalities around Detroit, Chicago, and certain areas of Florida. The Gulf Coast has tremendous problems. Of course, other areas with high water tables do too. In fact, all such areas are infiltration suspect.

Sewer line inspection, repair, and equipment companies

- American Pipe Services** (Minneapolis, Minn.)
- Dolfrim** (Tampa, Fla.)
- Gelco Grouting Service** (Salem, Ore.)
- Halliburton Services** (Duncan, Okla.)
- John Bean Division, FMC Corp.** (Jonesboro, Ark.)
- Municipal & Industrial Pipe Service** (Marietta, Ga.)
- National Power Rodding Corp.** (Chicago, Ill.)
- Penetryn International Inc.** (Latham, N.Y.)
- The Penetryn System, Inc.** (Orlando, Fla.)
- Ques Inc.** (Orlando, Fla.)
- Roto-Rooter** (West Des Moines, Iowa)
- Southern Line Cleaning Co.** (Castelberry, Fla.)
- Underground TV Inspection Inc.** (Durham, N.C.)
- Video Pipe Grouting, Inc.** (Chicago, Ill.)
- W. G. Jacques Co.** (Des Moines, Iowa)

Gelco is seven years old, but its parent company, Salem Sand & Gravel Co., has been in business for 60 years. Gelco expects 100-150 jobs this year, which will correspond to a \$0.5-1.0 million volume. Gelco services include high-velocity water cleaning, closed circuit TV inspection, chemical grout sealing of leaks in sewer lines, and water control leak sealing for power and telephone companies.

Some examples of Gelco's TV inspection and grouting repair jobs include projects for the Corps of Engineers at Hickam Field, Hawaii, and at Fort Belvoir, Va. Last year, the company completed a job for the Mountain Home Air Force Base, Mountain Home, Idaho; a water line cleaning job for the Sierra Army Depot at Herlong, Calif.; and a high-

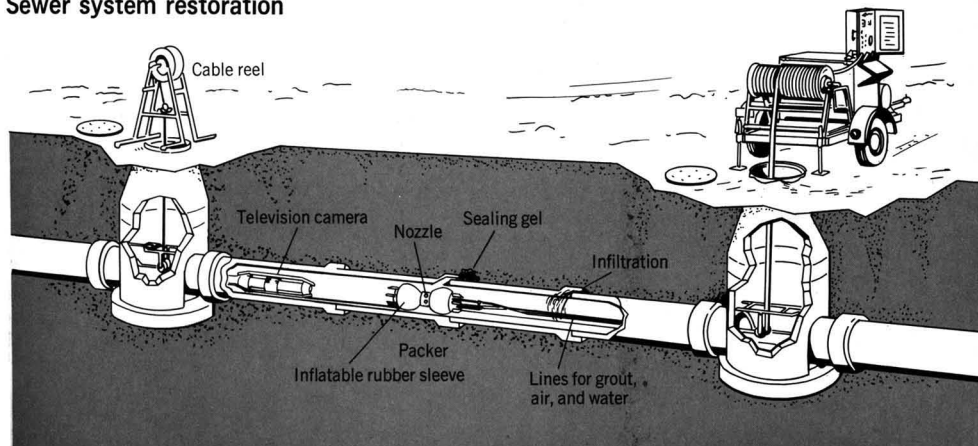
velocity water cleaning and TV inspection job at the Presidio (Army base) in San Francisco; and a job for Westinghouse Electric Corp. at the Naval Reactor Station at Arco, Idaho. In the Idaho case, Gelco sealed some leaks in tunnels under tanks carrying radioactive wastes. They have also done a chemical grouting job of sealing underground leaks down a 54-in. vertical shaft (6000 ft deep) on Amchitka Island, Alaska. Two years ago, Gelco did a TV inspection of 100 miles of earthquake-damaged sewer lines in the San Fernando Valley. The line damage stemmed from a February 9, 1971, earthquake.

Currently, Gelco is starting a TV inspection job at Fort Lewis, Wash. (between Seattle and Tacoma). On the municipal scene, Gelco is presently performing a contract for the Unified Sewer Agency of Hillsboro, Ore., and recently won a job with the city of Ashland, Ore., for TV inspection, high-velocity water cleaning, chemical grouting, and repair of its sewer lines. On the industrial scene, the company recently completed a cleaning job of a 24-in. sewer line for the Ideal Cement Co. in Seattle, Wash.

Municipal & Industrial Pipe Service (M&IPS) offers a complete line including infiltration studies on a consulting basis and contracting services for both the TV inspection and grouting of lines. M&IPS has been in the business for 10 years; what's more, it provides the same service in Canada. Its fiscal 1972 sales (which ended June 30) were forecast at \$0.5 million, but the company expects sales to triple in fiscal 1973.

Last year, the company completed 50-100 projects. Geographically, its activity is concentrated in the central and western portions of Canada and the eastern U.S. M&IPS has completed work at several military installations, including jobs for the Army at Lexington, Ky., the Navy at Norfolk, Va., and the Air Force at Eglin Air Force Base, Fla. M&IPS also

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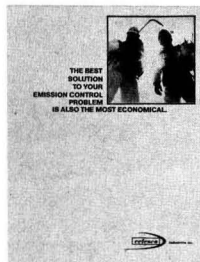
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completed a job at Dulles International Airport in Va.

Underground TV Inspection Inc. (UTVI), a relatively new company now in its third year of operation, offers a complete line of sewer line restoration and rehabilitation services. Geographically, the company does projects from Maryland to Georgia and as far west as Kentucky and Tennessee. It performs both closed circuit TV inspection and internal grouting of lines as well as sewer line cleaning services using high-velocity water, rodding equipment, or hydraulically propelled tools. Sales in 1972 (year April 1-March 31, 1973) were approximately \$0.3 million and UTVI anticipates that sales will at least double next year. It has done projects for the Navy at the Navy's guided missile school at Dam Neck, Va., and for the Air Force Base in North Carolina, as well as projects for cities including Rocky Mountain, N.C., Newport News, Va., and Clover and Dillon, S.C.

The 17-year-old W. G. Jaques Co. has been in the sewer line cleaning and repair business for the last five or six years. The company offers a complete service including cleaning, TV inspection, and pressure testing and sealing service. The Jaques Co. has completed projects in all parts of the U.S. and estimated more than 200 projects annually.

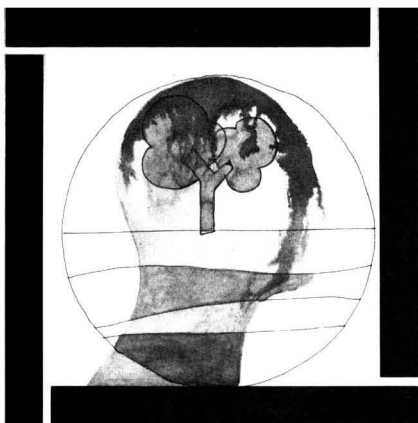
National Power Rodding Corp. started in the sewer cleaning business more than 20 years ago. They pioneered the TV inspection of sewer lines and found a subsidiary, Video Pipe Grouting, Inc., some 10 years ago.

Neither Halliburton nor FMC is in the contracting end of the business. Each manufactures equipment for the service contractors—for example, Halliburton leases or sells TV cameras and sells inflatable packers for pumping grouting chemicals into leaking joints. It also offers completely customized vans for the TV inspection and repair service. Sales in 1973 for this portion of Halliburton's business will be about \$1 million; next year they expect sales to double.

FMC's John Bean Division only manufactures hydraulic equipment of the type for high-velocity water cleaning of sewer lines. Complete units, truck-mounted, sell for about \$12-14,000 each; the FMC unit itself costs about \$9-10,000. In 1972, sales for 110 of these units totaled about \$1 million. At least a 20% increase in sales is forecast for 1973.

Meanwhile, EPA stresses the selective rehabilitation of a sewer line; these companies stand ready with inspection and repair services. Somewhere the twain shall meet. SSM

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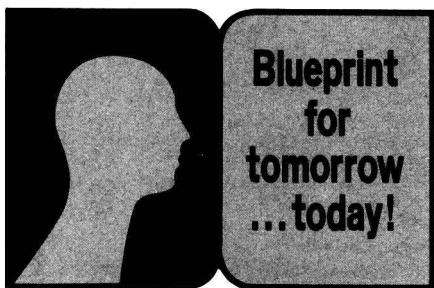
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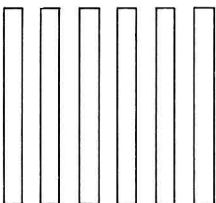
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Ford Foundation fights pollution

Philanthropic foundations entered the environmental battle with conservation gifts, but scope has greatly broadened

By 1936, Henry Ford had made his fortune on the automobile, and he and son Edsel decided to give some of the money away. They set up the Ford Foundation, an organization which made grants largely to Michigan charitable and educational institutions until 1950 when it became a national foundation.

Over the years, the Ford Foundation has given away more than \$4 billion. The Foundation's charitable umbrella covers programs in the areas of national affairs, education and research, humanities and the arts, public broadcasting, and a host of international projects. In recent years, the Foundation has launched an intensive and broadly based environmental program. Total commitments for environmental programs to date top the \$58 million mark. While the number seems small in terms of recent massive governmental spending in environmental protection, Ford's dollars have nevertheless made important inroads where government money has not generally been available.

Concern for conservation

The Ford Foundation's current involvement with environmental issues springs from an earlier program aimed at conserving nature and natural resources. In its early conservation efforts, the Ford Foundation was not unique. Several other foundations including a group of Mellon Foundations—the Avalon, Old Dominion, and Scaife Foundations—poured large sums of money into acquiring natural land preserves and in aiding in the work of various private conservation groups. Notable contributions by the Rockefeller Foundation include such magnificent wild areas as the Jackson Hole (Wyoming) Preserve and a Redwood forest.

The Ford Foundation's current environmental program is the outgrowth of an experimental organization born in the early 1950's, Resources for the Future. Resources for the Future was designed to answer questions related to the accelerating use of natural resources at a time when environmental problems were being attacked in a haphazard manner, if at all.

In the early 60's, the Ford Foundation initiated a series of training grants designed to produce multidis-

ciplinary professionals who could talk to each other about the problems encountered in environmental management. The grants supported five-year training programs in various university departments including biology, forestry, landscape architecture, engineering, and fishery. At the present time, some 375 candidates for masters or doctorate degrees are involved in the programs with slightly more than half having completed their training.

The next phase of the Foundation's environmental program was a series of workshops. The workshops aimed at bringing scientists and decision makers together, with the ultimate goal of producing a regional program which could be taken over, funded, and implemented locally. One of these workshops at the University of Vancouver (British Columbia) turned into the first of the Ford Foundation's regional environmental management (REM) projects. The Vancouver REM project focused on creating a computer simulation model to take into account land use, transportation patterns, population growth, waste generation and disposal, and various other interrelated factors affecting government officials. Soon to become operational, this model will serve as a jumping-off point for other regional environmental management projects.

In the REM project as well as other programs undertaken by the Ford Foundation, the plan has been to use Foundation money as trigger

money to attract federal funding. A REM project in San Diego for example, has attracted \$150,000 in funding from the National Science Foundation and an additional \$450,000 from the Environmental Protection Agency.

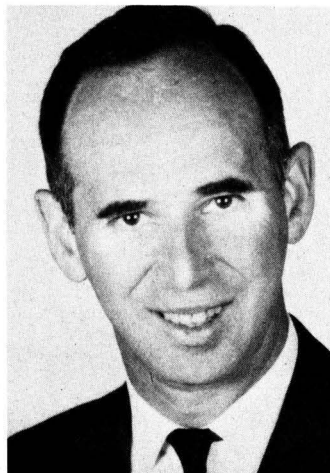
Yet another area in which the Foundation has been active is the fight for environmental protection by public interest law firms. Foundation grants for the Center for Law in the Public Interest, The Natural Resources Defense Council, Environmental Defense Fund, and the Sierra Legal Defense Fund have helped pave the way for landmark environmental decisions.

Grass roots action

One program which typifies the Foundation's philosophy in providing funds for environmental protection is the Municipal Conservation Commission program. The idea is to let citizen groups, professionals with expertise, and state administrators to join hands to combat local problems. In 1957, Massachusetts became the first state to establish Municipal Conservation Commissions by law, and several other New England states have since followed suit. The small commissions which generally consist of town citizens and a local official, may receive small grants from the Foundation with any amount over \$750 requiring matching funds from the state. The Ford Foundation has allotted more than \$150,000 in grants so far and figures that local commissions have raised an additional \$150,000.

While the Foundation has concern with aiding local programs, however, the major thrust of its grant-making philosophy continues to be an effort to define the big picture. Typical of that philosophy was the decision to begin the Energy Policy Project in May 1972. The two-year project headed by S. David Freeman, formerly with the Energy and Environment Section of the President's Office of Science & Technology, was designed to look at short- and long-term implications of energy supply and demand on the quality of American life. The grant provides some \$2 million for a program of studies to focus on the creation of a national energy policy. HMM

Energy Project's Freeman
The big picture



Ultimate disposal: no final answer

National symposium rediscovers the complex problem of waste water and residual disposal

If you can't throw it away, give it away, or sell it, what are you going to do with waste water and the residual matter left after treatment operations? Well, logically enough, you might have to keep it. But if you keep it where and how are you going to store it?

The questions, pardon the pun, keep piling up—so Region IV of the Environmental Protection Agency and the Research Triangle universities in North Carolina held a national symposium on the subject in an effort to find some of the answers.

Well, they found some. But mostly they rediscovered just how complex the problem is. The only solutions are to treat it and clean it up, or to store what cannot be cleaned. The symposium was told dumping in navigable waters eventually must be stopped in accordance with the Federal Water Pollution Control Act Amendments of 1972, and that atmosphere, ocean, and deep well disposal methods are no longer acceptable.

Paul DesRosiers, head of the applied science and technology branch of EPA's Office of Research and Development, said the agency is at work trying to find alternatives to the present practice of dumping into rivers and other waterways. Faced with the goal of "zero discharge" by 1985, he said, we must undertake the technology to bring about water reuse and by-product recovery. DesRosiers predicted that closed cycle operations in plants eventually "may not only be economically competitive with treatment for discharge, but may be less costly."

This call for waste water reuse was supported by EPA's assistant administrator for Research and Development, Stanley Greenfield. He told the symposium the EPA supports waste water reclamation in the form of reuse, recycling, and recharge as a major element in water resource management. The EPA, he added, does not currently support the direct interconnection of waste water reclamation plants with municipal water treatment facilities. He said research would have to show there were no health hazards before renovated waste waters blended with other ac-

ceptable supplies in reservoirs could be used.

Incineration ruled out

Robert Dean, head of the Ultimate Disposal Research Program at the National Environmental Research Center in Cincinnati, said capacity and air quality standards rule out incineration and burning methods in the disposal of waste residuals. He said better technology is needed before the method would be clean enough to be considered seriously.

Likewise, the oceans as ultimate sinks for waste waters and waste water residuals disposal was opposed. Richard Barber, director of oceanographic programs for the Duke University Marine Laboratory at Beaufort, N.C., said deep sea dumping off the continental shelf must be stopped until more is known of its ecological impact. He said some dumping on the continental shelf could be tolerated, but only if the quantity were not too great. James Carpenter, chairman of the Chemical Oceanography Division at the Rosensteel School of Marine and Atmospheric Science at Miami, was quick to point out, however, that disposal even on the ocean's shelf is no long-term solution. He said the coastal zone doesn't have the capacity to absorb the wastes it would be necessary to dump there by the year 2000.

Deep well injections are also being questioned as a disposal method. William Walker, director of the Virginia Water Resources Research Center at Virginia Polytechnic Institute at Blacksburg, pointed out that this method has produced some unsatisfactory results. He noted that earthquakes in some areas seem to be related to pressure from salt water injections. Walker said both legal and environmental considerations prevent deep well usage at this time.

Reclaiming land

Symposium speakers generally agreed that one acceptable alternative would be to utilize both waste water and residuals in reclaiming land. Sherwood Reed, professor in the Department of Environmental

Sciences and Engineering at the University of North Carolina, said spray irrigation has been used successfully in St. Petersburg, Fla., where secondary treatment plant waste water is sprayed on golf course and park lands. That city's public works administrator, Lloyd Dove, said the project has been a "great success" and as yet, at least, there has been no sign of "salting out" or other adverse side effects because of salts and other materials in the water.

Another disposal method that has been undertaken with some success is the direct dumping of wet sludge to improve marginal land. Dove said the method has been used successfully in the St. Petersburg area where the soil is sandy and good sod scarce. Success also has been achieved in Oregon where wet sludge dumping is credited with im-



Interim uses. *Spraying, irrigation, and recreation. Spray irrigation has been used successfully in St. Petersburg, Fla.; dumping of sludge improves marginal land and aids reclamation; secondary treatment plant effluents keep golf course and park lands green in Fla.*

proving marginal desert land. In the Oregon project, soil benefited both from the water and the humus.

The major problem with the land reclamation disposal of wet sludge is transportation, and General American Transportation Corp., Chicago, has marketed a rail tank car especially designed to meet this need. Calling it "one of tomorrow's best solutions," General American consultant Marcus Kestolich said the method is inexpensive enough for general use by most cities. It was found to cost \$2.00 per ton of sludge in a pilot project in Chicago, he said.

An example of a successful market usage for sludge came from Frank Styers, superintendent of plants for Winston-Salem, N.C. Styers said his city has a contract with Organix of Rhode Island, which

processes sludge, mixing in catalysts to aid in drying it, and sells the dried material in packages as garden humus. "It has been a good answer to our sludge problem but demand would not be great enough for this method to be universally applicable," he said.

Special storage problems

As useful as these projects are, however, they cannot utilize all the sludge accumulating country-wide. Some waste water and residuals simply will have to be stored, but storage presents its own special problem. For example, a permanent lagoon, according to Dean, can be as much a liability as an asset. He said lagoons have a way of filling up before their time because of increases in production, lower grades of raw material, of the inability of sludge to

residuals could be converted into calcium sulfate, which would be bulky but acceptable as a fill material. Another alternative would be to recover the sulfur, cast it in monoliths and store it. The volume of a ton mole of cast sulfur is less than one fifth the volume of a ton mole of gypsum, he pointed out.

Salt water treatment

Salt water is very difficult to treat for disposal since sodium chloride ions do not form insoluble precipitates at low concentrations. For this reason the dumping of brines containing sodium chloride are prohibited in many areas. At the same time, shipment to acceptable locations is expensive. Dean pointed out that the only available methods for reducing the volume of salt-contaminated water are those used in desal-

for titanium, however, are being exploited because they reduce the pollution problem, even though there are problems with equipment corroding.

Once all necessary sludge treatments have been undertaken it is sometimes feasible to reduce volume, thus reducing storage costs. For example, any ion, Dean pointed out, that can be precipitated can be concentrated further by sedimentation, filtration, or centrifugation. It then can be stored until such time as it becomes worthwhile to take steps to recover it. Dewatering precipitators such as ferric hydroxide and gypsum from the treatment of mining and manufacturing wastes is not always easy, but some water can be removed. Dean said EPA's research unit in Cincinnati presently is working on this problem.

Electroplating pollution

The volume of polluted water from electroplating processes can be reduced in several ways, according to Dean. Air blasts can return some of the dragout to the electrolyte bath as a direct saving. Likewise, counter-current rinsing in which the effluent from the last rinse is used for earlier rinses can reduce the total volume of waste water. To reduce the quantity of pollutant chemicals in the waste, chemical precipitation or electrical recovery can be incorporated in the rinsing cycle. This has the same effect as treating the rinse water to recover metals and water for reuse, and it may be easier to operate, Dean said.

Finally, some pollution problems can best be handled through improved design and operation. Dean pointed out that the cost of cleaning up dirty water used to transport logs on a pond at a saw mill or to transport vegetables in a film at a cannery can be so high that alternative transport methods may be preferred. Dean said care also should be given to water used for washing tanks, floors, clothes, or other equipment. In recent years, systems to conserve such wash water have been developed in the food, agriculture, and forest product industries to minimize the cost of purifying the waste water, he said.

So what those attending the symposium found out was that if the pollutant cannot be caught early before it has been mixed and diluted, disposal costs are going to increase, but all is not lost. Drying and removal methods still can be applied. Also, some waste water and sludge can be returned to the land to aid in reclamation. And, as a last resort, permanent storage may be utilized. WSF



de-water as much as had been expected. In addition, he said, rising land prices in urban areas are forcing many plants to look again at the potential or tax value of their lagoons on land that once was cheap. In such cases, municipalities will have to pay hauling costs to storage sites away from the actual treatment plant.

Another special problem occurs with toxic substances. Dean said many of these are too dangerous to store as they are and must be converted to less objectional forms. He noted that the sulfur in fossil fuel re-

ination processes—distillation, reverse osmosis, and freezing, which are expensive, or solar evaporation, which is useful only in areas west of Kansas City, Mo.

Soluble organic substances are less of a problem, but they still require special treatment. Larger organic molecules can be adsorbed on activated carbon and converted to carbon dioxide and water by heating to 1000°C, Dean said. Many low-molecular-weight water-soluble substances, which cannot be adsorbed efficiently on carbon, can be oxidized biologically in a trickling filter or by activated sludge.

Sulfur and sulfuric acid wastes present special treatment problems because of their caustic nature. Dean said one approach has been to use hydrochloric acid instead of sulfuric to pickle iron and steel. In this process, the resultant ferrous chloride can be cooked to recover hydrochloric acid and iron oxide. The approach, unfortunately, cannot be used to treat mine waters in cases where iron sulfide, which accompanies coal in the deposits, is oxidized to acid pollutants by the atmosphere. Chloride recovery processes



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Looking for products to manufacture?

Marketing research firm sees profits for firms
producing whole complex of antipollution products

A lot of companies won't get rich, but a lot of them should show profits. At least this is how one market research firm feels about the business potential of pollution abatement. According to Predicasts, Inc. (Cleveland, Ohio), which held a meeting for manufacturers and consultants in New York City recently, capital spending in the pollution control field will triple by 1985 as government and industry try to keep pace with federal antipollution requirements.

Predicasts predicts the following will take place during the 12-year period:

- Energy prices will rise.
- Overall productivity growth will slow.
- The less polluting sectors of the economy will grow more rapidly than the polluting sectors.
- Pollution control expenditures will expand greatly.
- Innovations will take place in regard to new low-pollution technologies.
- Efforts will be made to undertake more recycling and by-product production.

In the energy supply field, Predicasts says hydro and nuclear energy promise the greatest growth potential. While the overall energy growth rate will slow somewhat by 1985—from 4.1% annually at present to 3.7%—the hydro and nuclear energy fields will grow by a yearly rate of 13.8%. The company sees oil imports continuing to increase, but at a slower rate—decreasing from 9% in 1972 to 6% by 1985. Coal production growth will increase slightly, and natural gas and crude oil growth will decrease by about half.

Auto spending

Predicasts estimates that \$4.5 billion will be spent annually on auto pollution control devices by 1975, and \$12.7 billion by 1985. This compares with \$495 million spent in 1970. Here Detroit has decided, with EPA agreement, to achieve 1975(76) pollutant decreases through the use of catalytic converters and recycling systems. Thus, the immediate mar-

ket will be for these devices rather than for new or redesigned engines. The most pressing need, Predicasts says, is for a nitrogen oxides converter. The device presently is estimated to cost about \$150 per car, or about half the costs of positive crankcase ventilation, moisture control systems, and evaporation control systems put together.

The market for gaseous control equipment, the firm maintains, will continue. Predicasts executive vice-president, William Weiss, pointed out that there is presently a market for sulfur dioxide control devices, especially if anyone has plans for a more efficient one. And as more and more the need to burn high-sulfur dioxide coal is realized, such devices will become even more necessary. Predicasts' president, Samuel A. Wolpert, told the group, "We can handle sulfur dioxide emissions at the present, but the problem is cost." It is in marketing a device that will remove sulfur at a lower cost that Predicasts sees a market.

In terms of industrial air pollution control, Predicasts sees the need for gaseous control devices increasing faster than the need for particulate control devices. Today the spending ratio is about one third to two thirds in favor of particulate control devices, but the need is for more sophisticated gaseous control devices. By 1985 this ratio will have changed

from 46% to 54%, and gaseous control device spending will have increased from \$367 million in 1970 to \$3 billion. As to particulate removal equipment, the fastest growth will occur in developing more efficient collectors. Fabric and wet collectors will be needed more so than electrostatic precipitators and mechanical collectors since their efficiency rates are higher.

Air pollution test and measuring systems will show a rapid increase in market growth in the immediate years ahead, and will then slow up, Predicasts says. There will be a large growth in ambient and stationary source systems as well as in auto emissions measuring systems by 1975 with a slower, but steady, growth beyond that.

Total urban mass transit miles will increase some by 1985, but will still be a small part of the overall passenger transportation market. Predicasts says its effect on automotive sales will be small despite dire predictions that the energy crisis will force changes in our transportation habits.

Tertiary equipment

As to water pollution control equipment, the big growth will take place in tertiary treatment equipment. This will be brought about by the demand for a more thorough cleaning of waste water. Predicasts sees packaged systems growing more than in-

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dividual components, and monitoring and cleaning equipment growing more than movement equipment. Biological and advanced equipment, such as aeration demineralizers and dewaterizers, will grow at an annual rate of 14.8%; and combination units, sewage packages, and water treatment packages will grow at an average rate of 13.5% per year.

The water treatment chemical market by 1980 should more than double its 1970 capital spending of \$400 million. The amount is expected to reach \$950 million. Predicasts sees this market growing at a rate of 9.4% per year. The emphasis will be on polyelectrolytes rather than inorganic coagulants and oxygen techniques, on membrane usage rather than other filter media, on ion exchange resins rather than lime, and on organic chlorine compounds rather than chlorine. In the coagulant field, Predicasts sees alum getting competition from polyelectrolytes, and therefore not growing at an especially high rate. Organic coagulants, however, are expected to grow at a rate exceeding 11.1% per year. In internal water preparations, cooling towers will be in high demand, as will inorganic chlorine compounds, oxygen, and other biologically active chemicals.

Predicasts says as incineration becomes more expensive and difficult, and recycling for the most part unable to compete with cheaper forms of disposal, we will be forced to turn to landfills as a waste disposal alternative. For this reason, a lot of new transportation equipment will be needed. This equipment will include on-site compaction equipment to reduce bulk, containers to minimize collection manpower requirements, collection vehicles to transport waste to central stations, central station reduction equipment to further reduce bulk, and mass handling equipment to transport waste to remote sanitary landfill sites.

Predicasts sees a future for procedures and equipment to recycle materials, but claims the immediate prospects for economic growth gain in this field are not great. While recycling is important in conserving scarce resources, it is not a viable pollution control approach because it now is less expensive to obtain primary materials than to reprocess secondary materials. The firm points out that new technology in mining techniques has had an adverse effect in this regard. However, secondary nonferrous metals, such as copper and aluminum, will be the exceptions to the rule. Demand and high prices will bring about an annual growth rate to exceed 8% in both of these cases.

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Occupational health and safety

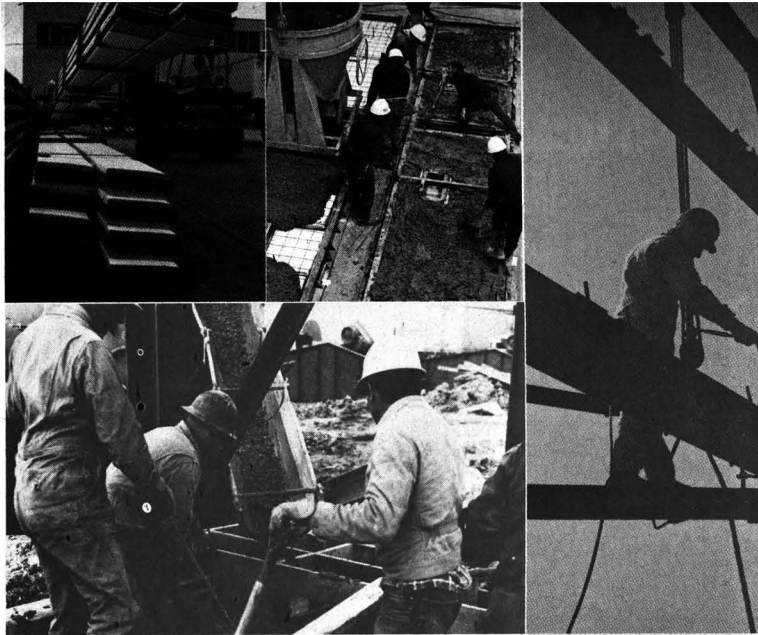
A few years ago, an obscure term, "environment," began to gain recognition; now it's a common household word used by all members of the family. Likewise the phrase occupational safety and health, which, until two years ago, was spoken only intermittently, is now the subject of a major piece of federal legislation that covers more than 60 million employees in five million workplaces. Also known as the Williams-Steiger Occupational Safety & Health Act of 1970, P.L. 91-596 is the enactment responsible for the emphasis on safety and health for U.S. workers (ES&T, August 1972, p 684).

The Act, which became effective in 1971, created the Occupational Safety & Health Administration (OSHA) in the Department of Labor to administer the Act and enforce health standards. Also created by the Act is the National Institute for Occupational Safety and Health (NIOSH) in the Department of Health, Education, and Welfare which, although one half the size of OSHA, carries on occupational safety and health-related research, develops criteria documents which serve as a basis for OSHA standards, provides hazardous evaluation services to determine dangers in the workplace, and develops manpower to carry out the Act.

Prior to the Williams-Steiger Act, there were, according to the figures most often cited, 14,000 job-related deaths, over 2 million disabling injuries, and 400,000 illnesses annually. These add up, as a national average, to 15.2 disabling injuries per million employee hours worked. However, several industries top this average—longshoring, 69.1; meat, 43.1; roof and sheet metal, 43; lumber and wood, 34.1; and transportation equipment, 33.3.

Standards

OSHA promulgates and enforces standards in three industrial categories—general industry, construction, and maritime. However, before any standards are set, OSHA receives



input from many organizations, individuals, state health and safety agencies, as well as its own personnel.

The agency may adopt standards developed by private standards-producing organizations such as the American National Standards Institute, the National Fire Protection Association, and the American Society for Testing and Materials. Furthermore, OSHA receives NIOSH criteria documents which provide detailed scientific information about specific hazards, recommend safe levels of exposure, and outline ways to protect workers from exposure. Thus far, NIOSH has submitted criteria documents on asbestos, beryllium, lead, carbon monoxide, heat stress, ultraviolet radiation, and coke oven emissions.

If OSHA desires additional information before promulgating standards, then a standards advisory committee may be formed. The members of the committee are experts in a particular field and consist of four employers, four employees, and seven state and federal representatives. Some of these committees are permanent—for example, construction and agriculture—because many standards will be needed over the years. But other committees are temporary and are disbanded after their work is completed. Director Gerald Scannel, of the OSHA Office of Standards, states that advisory committees on noise and heat stress have been assembled, and their recommendations will be forthcoming shortly.

During 1972, OSHA made more than 100 revisions to the original

standards promulgated to make them apply more directly to the workplace through clarification, updates, extensions in effective dates, or even revocation of standards. For example, one sanitary standard stated that ice used to cool drinking water should not come in contact with the water; however, in view of modern sanitary capabilities, OSHA amended it to require that ice provided for drinking water be free of contamination.

Last year OSHA limited permissible level of asbestos fibers in the air to 5 fibers/cc of air, effective last July, and to 2 fibers/cc of air, effective July 1, 1976. However, in light of additional information not considered when the standards were issued, OSHA is reopening discussions on the asbestos standards.

In April, OSHA issued temporary emergency standards covering 21 pesticides used on seven crops. These standards govern the time when an employee may reenter a crop area after it has been treated with agricultural chemicals. These temporary standards went into effect last month, and after hearings, permanent standards will be issued.

Then in May, OSHA issued emergency temporary standards to end employee exposure to 14 carcinogens used by the chemical and rubber industries, in the manufacture of dyes and pigments, and in the preparation of flame-resistant fabrics. The standards are taking effect now.

According to OSHA officials, their goal is to make the standards flexible enough to encourage employers to exercise judgment and ingenuity to meet the safety and health stan-

dards. These "performance standards" set the goal without enumerating every step to be taken. OSHA officials point out that costs in complying with standards are usually offset by gains—increased productivity and decreased health and disability costs.

The Small Business Association will grant loans for compliance costs. By April 1, 45 loans were approved that will be used to comply with OSHA standards. To assist the small businessman, OSHA will, at the employer's request, offer consultation and guidance without penalty.

Education

Besides training courses for federal and temporary state inspection officers and tailor-made programs to correct deficiencies, OSHA personnel are making courses available to educate both employers and employees about occupational safety and health. Training courses are held at the OSHA Training Institute near Chicago, Ill., and regional offices conduct seminars for both employers and employees. One course covers the major standards, hazard analysis and control, accident investigations, and record-keeping requirements. Two construction safety courses are offered through the National Audiovisual Center (Washington, D.C.) under the auspices of the General Services Administration.

A new 100-hr correspondence course is scheduled to be available this year. The course will give a broad background in occupational safety and health to those who want to enter the field professionally and also to those who want to expand their knowledge. A programmed instructional course for first-line supervisors is in the design stage. It will cover the major provisions of the Occupational Safety and Health Act. At press time, Earl Heath, director of the Office of Education and Training, indicated that additional programs are being planned.

Compliance

To ensure compliance, the Occupational Safety & Health Act has certain enforcement provisions. Through 55 area offices in 10 regions, over 500 federal compliance and safety inspectors, aided by 200 state inspectors working with the Federal Government under a temporary agreement, inspect workplaces at random and investigate catastrophes, fatalities, and employee complaints. Each OSHA inspection officer completes four weeks of intensive training at the Training Institute plus on-the-job training at field offices. The majority of OSHA inspectors have years of experience in industrial hygiene.

During the current fiscal year, more than 45,000 inspections were conducted. Thus far, two thirds of the inspections have resulted in citations for one or more violations; monetary fines have been imposed four times out of 10; and one of 20 violations is classified as serious.

OSHA schedules inspections according to the following priorities:

- **Catastrophes and fatalities.** These investigations often point out the need for special compliance or training programs, for example, a special emphasis on combating trench and excavation cave-ins which resulted in 100 fatalities last year.

- **Employee complaints.** Such complaints receive prompt attention, and those alleging any immediate danger to safety or health receive immediate attention.

- **General inspections.** These are based on a random sample of workplaces of all sizes, in all industries, and in all parts of the country.

- **Target programs.** OSHA inspectors are concentrating on workplaces covered by two special programs.

The Target Industry Program was undertaken to improve safety in the five industries with high accident rates—longshoring, roofing and sheet metal, meat and meat products, lumber and wood products, and miscellaneous transportation equipment such as mobile homes and recreational vehicles. The Target Health Hazards Program is geared to reduce worker exposure to five substances

—asbestos, carbon monoxide, cotton dust, lead, and silica.

In following the above priorities, one half of OSHA inspections took place in the manufacturing industries, one fifth in construction, one fifth in maritime, and one tenth in retail and wholesale trade, services, and transportation industries. Little action has occurred in the agricultural industry, but OSHA officials predict more activity this year.

Despite the federal powers of enforcement, Congress specifically decreed that development and enforcement of safety and health standards should not rest solely with the Federal Government. States may "work as partners" when they are willing to provide programs "as effective as" federal programs. Before states have control over any occupational safety and health programs, they must create OSHA-approved plans and also write legislation to back and carry out the plans.

Four states—North Carolina, South Carolina, Utah, and Washington—have both approved plans and the necessary legislation. Five states have approved plans but no enabling legislation, and 14 states have drawn up the required legislation but do not have approved plans. All but eight states—Georgia, Kansas, Louisiana, Nebraska, New Mexico, Ohio, Pennsylvania, and South Dakota—have either plans or legislation approved or under consideration. By December, OSHA expects at least 25 states to be running their own programs. OSHA does not completely relinquish authority to enforce federal standards in any state until the state program has been operating for three years, although OSHA will adjust its authority as states assume responsibility.

Through fiscal year 1973, the Williams-Steiger Act authorized the Federal Government to fund 90% of the cost of developing new state plans. States can also apply for grants up to 90% of the cost of conducting experimentation and demonstration programs in conjunction with occupational safety and health. States may also receive grants up to 50% of the cost of operating their own occupational safety and health programs. The first such grant was \$300,000 awarded to Montana last December to aid the state in building its safety and health program and hiring 15 compliance officers.

In the future, OSHA aims to publish more standards, increase training and education of employers and employees, and reexamine inspection procedures in order to increase the number of inspections. In fact, OSHA hopes to conduct four times as many inspections within the next 12 months. CKL

Besides maintaining the inspection and training programs, last year OSHA:

- answered 1.2 million inquiries about occupational safety and health
- sent officials to speak to some 500 organizations about the Act
- distributed public service messages to radio and television stations nation-wide
- presented OSHA exhibits at trade centers, conventions, and fairs
- published numerous printed materials to help explain the various facets of the law
- conducted 1500 seminars for more than 100,000 employers and employees
- issued updated sets of standards for general industry, construction, and maritime
- published a "General Industry Guide for Applying Safety and Health Standards" to help users determine the standards applying to their operations, and began preparing standards guides for 50 industry groups

The Regional Air Pollution Study (RAPS) is the largest air monitoring program the federal EPA has ever undertaken. (The largest water monitoring program was described earlier—*ES&T*, March 1973, page 198.) RAPS is a five-year program and it has been estimated to cost \$5 million each year. The first two years will be spent in setting up the monitoring network and the next three in data collection.

"The central purpose of this program is to produce for a single urban area enough information on all the processes that determine the concentrations of air pollutants so that they can be described in a system of mathematical models," says Philip Allen, RAPS director.

RAPS has been referred to as an air pollution modeler's model. Models have been developed for emissions, transport processes, photochemical reactions, aerosol formation, removal processes, and so on. Each of the completed submodels has been checked individually but never have enough data been available to validate them on a real time basis. "One of the key parts of this program will be the collection of a data base on which this system of models can be tested and upon which the submodels can be validated," he adds.

Ultimately, the model will permit air pollution control agencies to test and compare control strategies before approving such strategies. It is important that control agencies have confidence in the model; it is also important that the general public and industry learn what modeling can do and to have confidence in it.

In general, there are two control strategies. According to one, which is used today, all pollution sources are treated alike and in operation each of them is ordered to reduce emissions by some arbitrary amount, for example 50%. According to the other strategy, there could be a reduction of selective sources. For example, during a certain type of meteorological condition, it might be possible to release more of a certain pollutant than another type. Ideally, information from the RAPS program would be able not only to suggest the sources to cut back on but more importantly to substantiate and validate such operational policy decisions.

Modeling in St. Louis

St. Louis was chosen as the test site for a number of reasons, a basic



EPA's Office of Research and Development takes the wraps off its RAPS program, the largest air-monitoring program ever, in St. Louis in order to answer . . .

How good and useful are air pollution models?

one being that other air pollution studies and data were collected there. Additional reasons include:

- A number of air pollution control agencies are in operation there.

- The terrain is flat; there are no hills or valleys of more than 100-200 ft vertical dimension in the test area and no large bodies of water.

- The area is sufficiently large and representative of a large number of urban areas in the interior of the U.S. Hence, the information should be translatable to other regions of the country.

In all, RAPS will place 25 monitoring stations around St. Louis in addition to the 10 local agency stations in operation today. Having a radius of 25 miles, the area for the monitoring study involves parts of Illinois and Missouri, the city of St. Louis (800,000 population), and St. Louis county which includes 97 municipalities. On the Missouri side of the Mississippi River, there are two air pollution control agencies. Charles Copley heads the city agency, and Donald Pecsok the county agency. On the other side of the river, the Illinois state air pollution control agency in Springfield is headed by John Roberts; the district agency is headed by Walter Franke; and smaller air pollution control agencies are operational in Granite City and East St. Louis.

There are some models which have not as yet been tested. Others have been checked individually but not in relation to other submodels. There are yet other models which are only now being developed. For example, the photochemical models have been developed but not sufficiently tested. Aerosol dynamics are not yet in model form. A very complex process, aerosol dynamics involves the going from gases to solids and the grouping of solid or liquid particles into larger particles. Eventually, many of the particles become large enough to fall out.

Understandably, before all the submodels can be put together into a system, sufficient data must be available to test all of them. The network will provide meteorological data, and concentrations for all of the chemical species for the same period of time and for the same city to be used for the future of modeling.

The first two years alone will be consumed in building the monitoring network, which alone is estimated to cost \$3.5 million. The actual building of the facility, operating the network, and data handling facility will be performed by a prime contractor, Rockwell International Science Center (RISC), in Thousand Oaks, Calif. RISC will be assisted by a team of firms, including McDonnell-Douglas and Ryckman, Edgerley Tomlinson and Associates, both of St. Louis, Meteorology Research, Inc. (Altadena, Calif.), and Xonics (Van Nuys, Calif.).

Each of the 25 RAPS stations will contain analytical equipment to measure all of the half-dozen pollutants specified in the national air quality

standards. The appropriate meteorological variables include measurement of wind, temperature, humidity, and four bands of solar radiation (for the photochemical submodel).

Building the network

RAPS is big environmental science funding at its best. After taking the EPA three months to write the specifications for the contract, the request for proposal (RFP) went out last November. By the end of January 1973, six responses had been received.

The prime contractor will build and operate the 25-station network. Understandably, the subcontractors will be responsible for portions of the work such as fabrication of the stations, maintenance, and data management. The prime contractor and its team will also support the RAPS research program itself and contribute to the process of atmospheric sampling, data analysis, sample analysis, and data processing. Additionally, the network will be supplemented by at least two instrumented helicopters, several mobile van monitoring stations, and at least four atmospheric sounding stations. The latter will periodically send up balloons with instrument packages to measure wind, temperature, humidity, and pressure.

There are two kinds of data collection. The first, a so-called continuing data collection process, involves the routine measurements of a large number of variables—meteorological variables, chemical variables, and even some economic variables, on a day-in, day-out basis. These data are needed for tying the various submodels together. Another aspect involves the development of individual submodels, such as the one for aerosol dynamics. In this sense, the RAPS program will involve "expeditionary" studies to learn more about aerosol dynamics and chemical changes. Other expeditionary studies will use tracers to study diffusion processes in the atmosphere; they too are used to identify emissions from different sources.

Some good questions on the RAPS have been asked in advance:

- What will you do with all that data?
- Do you need all that data?
- Will any data be wasted?

At this juncture Allen points out that EPA does not have some of the submodels that it wishes to evaluate

using the data. Candidly, RAPS director Allen says: "It's entirely possible that EPA will collect data that will never be used. We can't predict that in advance. We are attempting to get the information we think will be needed. I'm hoping that most of it will be used."

With respect to staffing, RAPS will require only seven EPA personnel full-time. The prime contractor will have a variable number of people, perhaps about 15-20 on a permanent and continuing basis. On occasion,



RAPS director Allen
Validation of submodels

of course, it will be necessary to bring together certain teams from other parts of the program, as well as from the universities. At any one time during the life span of the program, RAPS may have as many as 100 people involved in a project.

Not the only study

RAPS is not the only air pollution study being conducted in the St. Louis area. A number of other studies are either under way or being planned which relate in varying degrees to RAPS. A program directly related is being considered by the U.S. Department of Transportation. Interested in emissions from transportation sources, DOT may be monitoring the emissions from highways, different types of automotive vehicles, airports, railyards, and even tugboat traffic on the Mississippi River. DOT does not expect to have funding for its study until fiscal 1974.

Other studies in St. Louis have been going on for a number of years. METROMEX, for Metropolitan Meteorological Experiment, began several years ago. It is funded at the level of \$1.5 million/year and involves AEC, EPA, NSF, and the state of Illinois.

The CHES program (ES&T, March 1973, page 204), a companion to RAPS, is studying two communities in St. Louis now and may add another two to four communities. The funding for the St. Louis portion alone is about \$0.5 million/year.

FAPS, the Fate of Atmospheric Pollutants Study, an NSF program at the National Center for Atmospheric Research (Boulder, Colo.), is concerned with the removal of pollutants by processes other than precipitation at distances greater than those of interest to the RAPS program. For example, FAPS is interested in pollution carried over from one urban center to another, and eventually into the global area. NSF funding here has been on the order of \$200,000/year.

B-CAPS, Biological Components Study, is the only program not actively funded at this time. The interest here lies in the effects of pollution on the biosphere.

Coordination of results from RAPS as well as the above studies, is the responsibility of ICAS, the Interdepartmental Committee on Atmospheric Science. It's a federal advisory committee with representatives from a dozen agencies that require meteorological services including Agriculture, Commerce, EPA, and Interior. In fact, it was ICAS that asked EPA to serve as the lead agency in the RAPS study in St. Louis.

Checking the data

In the agreement between the U.S. and the U.S.S.R. that was signed last year by Nixon and Podgorny is an item of cooperation on environmental matters. St. Louis has been paired with Leningrad as areas on which scientists from the two countries will compare air pollution modeling efforts and air pollution control strategies and experiences. Periodically, during the next few years, U.S. scientists will be looking forward to visiting Leningrad. A delegation from the U.S.S.R. recently visited the U.S. and toured St. Louis in mid-May. Both visits, of course, are to check and validate air monitoring data and air pollution control strategies. SSM



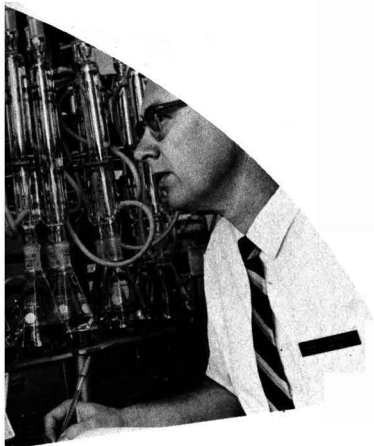
Health considerations in renovating waste

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Hebrew University, Jerusalem, Israel

In water-short and heavily polluted areas, complete water reuse may be close at hand; however, countless precautions and safeguards are necessary

The development of advanced waste water treatment technology has in recent years brought the possibility of waste water reuse for domestic consumption under active consideration in a number of water-short areas. In the process of developing waste water treatment trains capable of removing much of the incremental inorganic and organic contaminants which might have deleterious effects on water courses, it has become apparent that in certain cases the effluent produced could be of a quality comparable to recognized drinking water standards.

In Windhoek, South West Africa, waste water processed by such advanced treatment trains has actually served as a source of municipal water supply, and the



Water for domestic use



of which serve as absolute grounds for rejecting a supply as unsafe for human consumption. The World Health Organization (WHO) Drinking Water Standards contain a few more chemical parameters which may serve as grounds for rejecting a supply. Neither of these widely known and accepted standards lists more than a few synthetic organic compounds despite the fact that hundreds of such chemicals may find their way into municipal and industrial waste water, and many of them are known for their potential deleterious effects on human health. For that matter, neither do these standards exhaust the list of potential inorganic toxicants that may be found in industrial wastes.

Conventional drinking water standards were originally based on the assumption that water for human consumption would generally be drawn from groundwater sources or protected uncontaminated surface water sources, and that the limited number of chemical parameters included were adequate for most situations, then considered feasible. This assumption is rarely true for most surface supplies of today.

The unbridled increase in the use of hundreds of new and often structurally complex synthetic compounds in industry and agriculture has led to intensive study of their toxic effects. In addition to acute toxic effects, some of these chemicals have chronic effects which can be detected only after long-term exposure. Among them are chemicals whose effects have been found to be carcinogenic, mutagenic, and teratogenic as well as causing other deleterious health effects. Several hundred threshold limit values for such industrial substances in air have been established in the field of industrial hygiene, while some 100 maximum allowable concentrations for pesticides and other toxic chemicals have been established under food regulations.

The drinking water standards of the USSR were the first to recognize the scope of the problem and now include some 300 chemical parameters with more under study. Certainly not everyone of the 300 or so chemical standards for drinking water established by the USSR health authorities is of toxicological importance, since many were established on organoleptic grounds alone. Nevertheless, the differences among the large number of standards on the USSR list and the very limited number of standards presently considered adequate in the USA and many other countries indicate the extent of problems that will have to be faced when the undiluted waste water of a city, including industrial wastes, has to be processed to the point of becoming fit for human consumption.

adequacy of treatment has been justified by comparing the effluent quality with drinking water standards. A number of other cities, including Denver, Colo., and Tel-Aviv, Israel, are in the preparatory stages for such planned reuse for domestic purposes.

At this point it is appropriate to ask whether man's knowledge of the toxicological and epidemiological implications of waste water renovation for domestic consumption is sufficient.

Adequacy of drinking water standards

The U.S. Public Health Service (USPHS) Drinking Water Standards list 20 chemical parameters, only nine

The mere comparison of the quality of the final effluent against those standards currently listed in USPHS or WHO drinking water standards leaves too many questions unanswered to be accepted as adequate evidence that such an effluent is completely safe from the public health point of view. While some of the complex, nonbiodegradable synthetic compounds under discussion may be harmful to health at concentrations at the parts-per-billion level, advanced waste water renovation technology still cannot reduce COD or TOC to an absolute zero concentration, and except under unusual circumstances must be satisfied with residual concentrations of such organics at about the 10-ppm level. Not enough is known about the true identification of the residual microchemical pollutants, both inorganic and organic, which vary widely from one situation to the next depending on the nature of the industrial wastes which enter the sewerage system.

Microchemical pollutants in waste water

Numerous efforts have been made to gain a better understanding of toxic hazards of modern synthetic chemicals that find their way into waste water and ultimately into drinking water sources. However, there are many difficult problems in concentrating, extracting, and identifying such compounds, many of which still may be unknown breakdown products of more complex chemicals that have undergone partial biodegradation. In 1960, researchers at the Taft Sanitary Engineering Center were able to identify fewer than 40% of the soluble organics remaining in biologically treated sewage, and these were described only in general terms such as either extractable matter, protein, tannin, lignin, or alkyl benzene sulfonate.

DDT, aldrin, orthochloronitrobenzene, tetralin, naphthalene chloroethyl ether, acetophenone, diphenyl ether, pyridine, phenols, nitriles, acidic materials, and miscellaneous hydrocarbons including substituted benzene compounds, kerosine, synthetic detergents, aldehydes, ketones, and alcohols have also been identified in polluted river water. Some of these substances are known to be toxic. Many other compounds, undoubtedly present, remain unidentified. The application of chromatographic and spectrophotometric methods as well as mass spectrometry has now made analysis easier.

The conventional methods of waste water treatment leave many potentially hazardous dissolved chemicals unchanged. The concentration of contaminants has been shown to increase in downstream communities as water is used and reused and as the percentage of unremoved residual refractory chemicals grows.

Carcinogens in waste water

Petroleum products and refinery wastes are among the possible mutagenic and carcinogenic substances that may appear in municipal waste water. Various polynuclear aromatic hydrocarbons have been recovered from sewage sludge, among them the known carcinogens, 3,4-benzopyrene and 1,2-benzanthracene. Carcinogenic aromatic amino compounds, such as betanaphthylamine and benzidine, originate in dye and rubber works and may be released to sewer systems together with nitroanalogs used in the production of amino compounds, such as aminoazodyes, amino stilbenes, and tri- and diphenylmethane dyes. Pharmaceutical factories, textile dyeing plants, plastic production, and similar industries are



Drinking water. Industrial wastes discharged into streams could eventually be withdrawn for municipal water supplies

sources of these organics. Some of the intermediates, such as orthochloronitrobenzene, have been found in the Mississippi River in appreciable quantities and appear to be quite stable. Chloronitrobenzene, for example, discharged to the Mississippi at St. Louis, Mo., was still demonstrable in the drinking water drawn at New Orleans, La., hundreds of miles and many days' flow downstream.

New Orleans has been shown to have a cancer of the bladder rate three times higher than two other southern cities supplied with less polluted water. It has been hypothesized that there may be some association between cancer of the bladder in New Orleans and the contaminants in the water. This possibility must, however, raise the question as to whether potentially hazardous organics are removed adequately by activated carbon treatment which is probably the most effective treatment process available at this time. Polynuclear aromatic hydrocarbons, potentially dangerous carcinogens found in waste water, are poorly removed by activated carbon filtration if flow rates are low enough.

Microbiological problems

While most bacterial pathogens can be effectively inactivated by chlorination and other conventional disinfection procedures, there is ample evidence that some of the enteroviruses are manifold times more resistant than bacteria to the same disinfection processes. Infectious hepatitis has been transmitted by sewage-contaminated water on many occasions, and in some cases the virus appears to have passed through conventional water treatment plants which have included disinfection by chlorine.

Enteric virus levels in raw sewage have been shown to be about 1-10 per ml while their concentration in heavily contaminated river water, which may lead to epidemics of infectious hepatitis may be 1 per 10 liters or even less. Laboratory techniques for detecting such low levels of viruses in water are still in the developmental stage and present one of the major obstacles in studying the efficiency of waste water renovation processes as to virus removal. Another problem arises from the fact that it may take five days or more before the results of a virus assay of water can be completed. Effective methods of assuring virus inactivation in waste water treatment still leave something to be desired although there is growing evidence that adequate concentrations of free available chlorine (HOCl) with sufficient contact time can be highly effective in reducing enteric virus levels. Ozone is particularly promising as a virucidal agent for water and waste water treatment.

Nevertheless the effectiveness of any proposed waste water renovation treatment train must be fully evaluated as to its virus removal efficiency and ways must be found to monitor routinely such plants to assure their continued effectiveness in removing viruses.

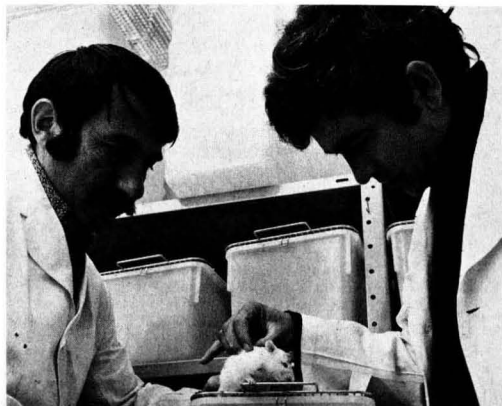
Toxicological evaluation of renovated waste water

There are two possible approaches to the toxicological evaluation of renovated waste water to be used as drinking water. The first would require establishment of maximum allowable concentrations or limits for each of the potentially hazardous chemicals that may be found in renovated waste water. The approach that has been developed by toxicologists in setting tolerance limits for food additives and chemical contaminants in food has been to establish acceptable daily intake (ADI) levels for man. These ADI are based on all relevant toxicological data available at the time of evaluation including data from cases of human exposure which are usually limited. After the "no effect" level is determined and a certain safety factor is introduced, the ADI can be established. Such figures can then provide the toxicological basis for establishing tolerance levels or maximum allowable concentrations in food, water, and air based on known consumption patterns and realistic levels of contamination which is unavoidable. To establish such figures for water, due consideration must be given to the total body burden from all environmental sources.

The toxicological evaluation of chemicals in the environment cannot be simplified to take into account acute or subacute effects alone. Today such evaluation must include effects from long-term exposure and studies for carcinogenicity, mutagenicity, teratogenicity, and various biochemical and physiological effects. Even if the specific toxicity of defined industrial and agricultural chemicals is established, the possible toxic effects of their breakdown products may be more difficult to determine. Natural biodegradation or specific waste treatment processes may lead to the development of new compounds having toxic properties quite different from those of the parent compound. Work to identify these breakdown products and to study their toxic effects is required.

Another factor complicating the toxicological evaluation of heavily polluted water or renovated waste water is the combined and possible synergistic effect resulting from the exposure to a mixture of toxic and nontoxic chemicals. Increased toxic impact of such combinations is known to occur under certain circumstances, and the case of renovated waste water must take into account

Testing. *Before renovated waste water is used as a water supply source, health effects must be thoroughly evaluated*



such possibilities. Although much is to be gained by establishing proper tolerance levels for many of the known toxicants that might appear in renovated water, this approach will take a long time to develop and even then will not cover all possible toxic effects.

For these reasons a second approach is required. A full toxicological evaluation should be carried out on the water intended for human consumption with its real mixture of known and unknown residual chemicals remaining after treatment.

Long-term feeding experiments with more than one species of experimental animal should be required as well as other toxicological tests. Such studies should preferably include feeding concentrates of the residual chemicals in the final processed water as well as the normal unconcentrated effluent. Concentration techniques used must avoid being selective as is the case with activated carbon and must not lead to the breakdown of the chemicals involved by overly harsh treatment such as high-temperature distillation. Low-temperature vacuum distillation, reverse osmosis, or lyophilization might be possible approaches.

Most governments require the full toxicological evaluation of any new drug or food additive before allowing its commercial use. The requirements for evaluating renovated waste water with its many and often complex unknowns should be at least as rigorous.

Epidemiological evaluation

No matter how thoroughly a toxicological evaluation is made, the problem of extrapolating the findings with laboratory animals to fit the human situation always remains. With drugs of potentially great medical importance, human trials are held after completion of the toxicological evaluation. In the case of new food additives which are usually less essential to human welfare than drugs, negative findings in the toxicological evaluation do not automatically mean that the new chemical will be allowed for use in human food. It must be demonstrated that the chemical will make a significant contribution to improving the quality or preservation of the foods in which it will be used and that there is no reasonable non-chemical alternative. In water-short areas, total water renovation can often be justified as being of potentially great importance to human welfare as well, particularly when no alternative water sources are available. As with other intentional exposure to chemicals in the environment, the benefits must be considered in light of any possible risks involved, if human exposure is to be allowed.

A considerable body of information has been built up concerning the effect on human health of many of the environmental contaminants discussed in this paper as a result of direct exposure of humans under various industrial situations. Further information has been gained by the accidental exposure of humans to certain toxic materials.

If waste water renovation for domestic consumption is to become widely accepted, there will be a need at some stage to carry out a full-scale epidemiological evaluation of the impact of such reuse on the health of the population exposed. It may be difficult to choose an appropriate population group for such a study, but to the extent that certain communities in water-short areas have already gone ahead with waste water reuse for drinking water, every effort should be made to carry out a thorough

epidemiological evaluation. Such a study should include baseline health evaluation of a sample population before the introduction of renovated water and then a follow-up of the same group, as a panel study, over a five- or 10-year period. Such opportunities will be few and far between, and every effort should be made to gain as much data from each case as is possible. The study should include details on potential water-borne infectious diseases, particularly of virus etiology as well as long-term health effects of chemicals.

A promising alternative to such a study with a population exposed to planned waste water reuse would be a series of studies of populations exposed to indirect or unintentional waste water reuse. Such population groups are easier to identify than might be imagined since many millions of people throughout the world are, in fact, consuming some form of renovated waste water every day and have been doing so for years. Some 15% of the flow of the Ohio River is fully or partially treated municipal or industrial waste water. Millions of people in the Rhine River Basin consume water from the river which at times of low flow may contain as much as 40% of industrial and municipal waste water.

Unintentional, and in many respects, uncontrolled reuse of waste water is now very widely practiced and provides a basis for evaluating the health impact of such use as well as the expected impact of fully engineered and carefully controlled direct waste water reuse of the type under discussion in this paper.

Monitoring waste water reuse programs

The nature of a monitoring or quality control program for products produced for human consumption should vary according to the degree of risk to health involved. Conventional water supply monitoring programs have in the past assumed that the product is basically a safe one and that it can be supplied to the consumer directly after processing without waiting for the results of quality control tests. Bacteriological test results are usually available 24-48 hr after sampling, while routine tests for toxic chemicals, when they are made, may be available only after many days. The water tested has usually been consumed by the population by that time.

In the case of a plant for renovating waste water for human consumption, it would appear necessary to require a more rigorous monitoring and quality control regime than that currently practiced by the water supply industry. Technical breakdowns and human failures at such a plant might lead to major health hazards. It would not be illogical to require that renovated water be fully tested and certified as safe before its release to the general water supply system. With improved bacteriological techniques, results can be obtained within 24 hr, as can the results of most of the important chemical tests, many of which can be automated. Ways of carrying out rapid toxicological evaluation of the finished water with bioassay techniques should be developed. For the moment, virus assays require at least three days for completion, but here too, more rapid assay techniques are under study and may become available.

Renovated water could be produced and held in batches until completion of the quality control tests, before being released. This will add additional costs to waste water renovation plants, but the additional safety obtained would justify the expenditure. Certainly such precautions should be practiced in all early plants until it can be demonstrated that less stringent quality control measures are adequate.

The approach presented in this article may appear to be overly cautious and place too heavy a burden on future waste water renovation programs. In answer, we must say that our criticism of current drinking water stan-

dards applies to any case where polluted surface water serves as a source of drinking water no less than to the special case of waste water renovation. In fact, indirect, unplanned waste water reuse of the former class may well be a greater risk than planned reuse which would include treatment processes better capable of coping with the organic pollutants found in waste water. Unplanned waste water reuse is far too widely practiced today, with too few controls, to allow one to feel complacent.

However, planned waste water reuse carries a heavy responsibility with it, since it involves the full engineering and health responsibility from the beginning to the end without the intervening hand of "nature." In such a project, the designers, operators, and health authorities who must give their approval, must carry the full responsibility of any adverse health effects which may result even if it can be shown that communities consuming polluted surface water are exposed to equal or greater risks.

We tend to agree that such communities are indeed exposed to undesirable health risks and would propose an equal tightening up of standards, treatment procedures, and quality control for all cases of waste water reuse whether direct or indirect.

Additional reading

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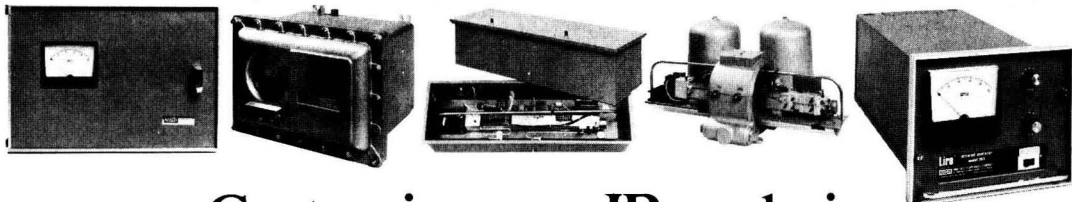


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Nachman Gruener is lecturer in Environmental Health and head of Environmental Toxicology at the Environmental Health Laboratory. Dr. Gruener is currently heading a multidisciplinary research project evaluating the toxicological effects of nitrates and nitrites in drinking water, sponsored by the U.S. Environmental Protection Agency.

Some of the material presented in this article is based on unpublished reports of the World Health Organization, their expert consultants, and advisory groups.



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Using concentrated metal-containing additives in oil-fired furnaces is common practice today, particularly with boilers having high superheat and reheat temperatures and high heat release. Such additives improve boiler cleanliness, reduce corrosion of the firesides and air heaters, and reduce stack emissions and plumes.

In general, fuel additives should provide boiler cleanliness, high-temperature vanadium corrosion protection, prevention of loss of operating capacity by maintaining design steam temperatures, cold end (air heater) corrosion protection, reduction of stack emissions from hydrocarbon particulate matter and SO₃, and improvement in the handling characteristics of ash in the flue gas in oil-fired boilers equipped with precipitators and stack collectors. The significant fuel additives in use today usually contain MgO (with or without small amounts of aluminum oxide or hydrate), manganese, and MgO with manganese.

The application of additives to solve particular boiler requirements hopefully has evolved from an art to almost a science. Utility managers today will no longer consider seriously any fireside additive that does not contain a high metallic concentration. The choice of additive, however, depends upon the needs of the particular boiler, as well as environmental requirements.

Heavy duty additives: MgO vs. Mn

The addition of MgO-based products to the fuel oil or furnace will raise the fusion point of the fuel oil ash from an initial 950–1050°F to approximately 1350–1450°F at a Mg:V weight ratio of 1.5:1. A weight ratio of 1.5:1 is equal to a 3:1 molar ratio of Mg:V which corresponds to a dilution rate with an MgO slurry containing 50% MgO of approximately 1:2000 with a fuel oil having a vanadium content of 200 ppm. The fuel oil ash, consisting generally of magnesium vanadates, magnesium sodium vanadates, and magnesium sodium vanadyl sulfates, is less adherent to the superheat surface.

Depending upon the ratio of Mg:V used, the ash will range in texture from a soft but voluminous powder at high Mg:V ratios to a somewhat brittle "popcorn" configuration or even to a dense, layered, amorphous coating as the ratio of Mg:V is lowered. The "treated" slags are generally easier to remove by manual or air lancing; also, they are more water soluble which allows easier water or steam lancing, or preferably high-pressure "steam blasting" for maximum cleaning. The treated slags also have a higher pH, by 1–2 pH units.

There are several disadvantages, however, in using MgO-based products. Deposits are highly susceptible to rapid bridging of the superheater tubes because of the increased boiler ash loading (Figure 1 which compares a furnace treated with MgO to one treated with manganese).

With fuels of 1% sulfur, or less, and a vanadium content of less than 100 ppm, high-temperature superheat fouling and corrosion of tube supports are less likely to occur than with fuels of 2.0% sulfur with 200–300 or higher ppm vanadium. With the lower sulfur fuels, it has been possible to eliminate completely any interim boiler clean-

FEATURE

Additives can clean up oil-fired furnaces

Metal-containing additives improve boiler cleanliness, cut corrosion of firesides and air heaters, and reduce stack emissions and plumes

Ira Kukin

Apollo Chemical Corp., Clifton, N.J. 07014





ings between annual outages and frequently also to eliminate even annual boiler cleanings by using manganese at low treatment rates.

With today's low-ash fuels, the use of MgO is simply not justified. However, manganese additives can result in a realizable net gain in boiler efficiency. Manganese-containing products are available commercially in economical, concentrated, liquid slurries. They can be stored and metered into the fuel inlet system of power station boilers. The treating costs with manganese are competitive and generally lower than comparable costs with MgO slurries.

Boiler problems solved by additives

Many boilers now firing fuel oil were originally designed for coal firing, and many of these boilers now suffer from too much furnace heat absorption which results in low final steam temperatures. The boiler will not reach design superheat temperatures. However, MgO-based additives foul the furnace and will often raise final steam temperatures. Unfortunately, the MgO also fouls the convection passes which results in frequent forced outages for boiler cleaning. When furnace coating is not required, the use of MgO will result in an additional requirement to use the furnace wall blowers and/or attemperating water.

The best solution for the boiler that suffers a decrease in final steam temperature after a coal-to-oil conversion is furnace modification. If it is not possible to modify the furnace, a magnesium/manganese-based additive approach gives adequate furnace fouling with a minimum of convection pass fouling.

One Apollo Chemical product, containing a stabilized slurry of magnesium oxide and manganese, at a Mg:Mn ratio of 6.5:1, has been found to be a good compromise in increasing superheat temperatures with minimum boiler fouling and minimum increase in stack emissions. This combination of magnesium oxide with manganese will frequently reduce the total amount of stack emissions, and the manganese reduces carbon emissions by 50-80%. With the use of MgO-type slurries, there is an increased ash input of 100-150% (Figure 2).

Fuel oils containing sulfur, vanadium, nickel, and sodium can produce high-temperature corrosion which is caused by the fuel oil ash forming a liquid phase which coats the boiler tubes allowing liquid phase corrosion. These compounds all having melting points in the range of 1000-1300°F will be molten at the metal temperatures of a modern utility boiler, and form tenacious slag deposits.

To prevent high-temperature corrosion and slagging, it is necessary to raise the melting point of the troublesome

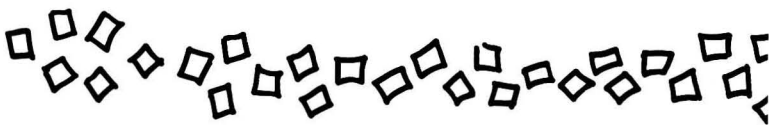
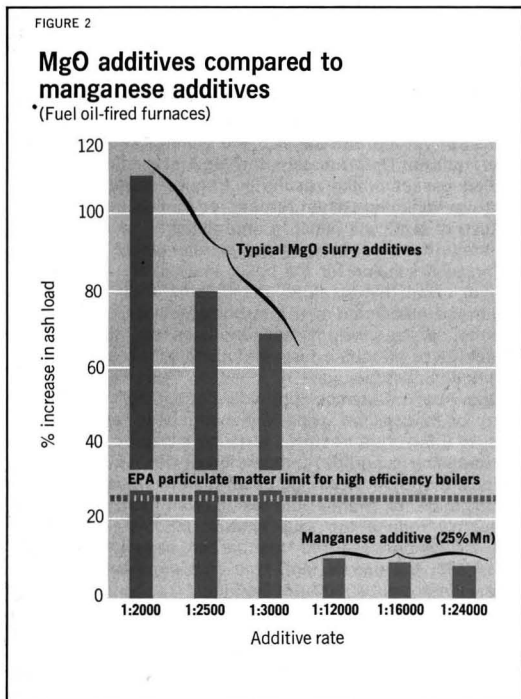




Figure 1. The superheater section of a boiler using 2.3% sulfur fuel treated with MgO (top) shows deterioration while manganese-treated fuel has little effect (bottom)



ash constituents to prevent formation of the corrosive liquid phase. This action produces a friable ash that normally responds to soot blowing. An alternate solution is to burn premium fuels containing low vanadium, sodium, nickel, and sulfur concentrations—i.e., a total ash content of 0.01–0.02%, or less.

Manganese-based additives will raise the fusion point of fuel oil ash. Where only a moderate increase in the ash fusion point is required, manganese treatment has the advantage because much less additive is required. The lower treatment rate possible with manganese results in improved boiler cleanliness which minimizes and often eliminates forced outages for boiler cleaning. Field experience has shown that manganese is superior to magnesium in maintaining boiler cleanliness, particularly with fuels of low ash content. Unlike MgO, manganese acts as a combustion improver and provides the potential for lower excess air firing.

Another problem is cold end corrosion, the result of SO₃ condensation, as sulfuric acid (H₂SO₄), on the air heater and gas duct surfaces. When the gas dew point is reached, a very sticky mist of sulfuric acid is formed and is extremely corrosive at the temperature conditions present in this boiler region.

This acidic stack fallout will also occur with fuels of lower sulfur content in the range of 2–3% and in many cases even with fuels having a sulfur content of 1 ± 0.5%. The most troublesome acid fallout problems occur under the following conditions:

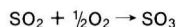
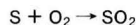
- High excess air is required to obtain steam temperatures.
- Coal-fired furnace converted to oil-fired—generally such a furnace will require a high excess air to help maintain steam temperatures. Also, the exit duct work in these furnaces, whether or not the utility continues to use the precipitators present in coal firing (mechanical or electrostatic), often presents individual problems. In these systems, there generally occurs a high SO₃ concentration in the flue gas, and a tendency exists for the SO₃ to precipitate out with a rise in dew point temperature. The surfaces of the duct work cool rapidly because of the longer path lengths that must be traversed before the flue gases enter the atmosphere. Rapid corrosion of the air heaters, the fans, and the duct work will occur.

It is virtually impossible to experience low-temperature corrosion without cold end fouling. The sulfuric acid mist traps much of the particulate matter and fly ash carbon passing through the dew point area. Normally the cold end deposits are high in carbon which absorbs SO₃ and intensifies corrosive attack.

Use of excessive amounts of magnesium oxide slurries can actually accentuate the fouling and corrosion problem. The MgO resulting from use of the MgO additive slurries is dead burned as it passes through the boiler's flame zone, significantly reducing the reactivity of the MgO. This less reactive MgO then contributes to air heater fouling.

An alternate solution is to raise the unit's exit gas temperature. However, each 50°F increase in exit gas temperature costs 1% in fuel economy. With today's fuels costing in excess of \$4.00 per barrel, it is usually more economical to control cold end problems with an additive program.

Generally, when a reduction of SO₃ of 25–40% is obtained by using fairly substantial quantities of MgO, it results from the MgO coating the iron tubes in the furnace so that the iron surfaces are no longer exposed. Otherwise, the iron acts as a catalyst to increase the percentage conversion of sulfur to sulfur trioxide:



(Reaction catalyzed by iron and/or vanadium; extent of reaction controlled by high excess air.)

With the use of magnesium oxide, successive layers of this oxide and $MgSO_4$ build up on the heaters. As a consequence, air heaters must be water-washed at frequent outages to remove the insulating deposits.

Regarding air heater cleanliness, manganese is far superior to MgO slurries. Not only does the lower dosage rate with manganese reduce the unit ash loading, but the combustion catalytic activity of the manganese reduces the amount of unburned carbon and fuel oil residue by as much as 50–70%. Although this carbon residue represents only 0.2–0.4% of the fuel oil, it acts as a binder for air heater fouling and as an absorbing agent for acidic SO_3 . Most boilers treated with manganese have required approximately one third the air heater washing frequency that they required when treated with MgO -based products.

Preventing cold end corrosion and stack fallout

Generally, application of MgO to reduce SO_3 is restricted to boilers that operate with excess air of 3% or less, but certainly no more than 5% excess air. Where it is not possible to restrict the amount of excess air to below 3–5%, then the use of MgO added to the fuel oil or furnace can actually increase the SO_3 content in the flue gas. A preferred method to reduce low-temperature corrosion and SO_3 emissions is the use of a supplementary cold end neutralizing additive.

English researchers, reporting on work carried out in England at the Marshwood generating station with boilers firing fuel oil in which back end injection with ammonia was attempted for reducing SO_3 in the flue gas, found that addition of ammonia at 20–33 lb/hr was required to control SO_3 attack in a boiler producing 550,000 lb of steam per hour at 915°F superheat temperature with a fuel containing 4.2% sulfur. At this feed rate, an increase of 3 in. of draft loss in the air heater occurred within 11 days. Further, the resultant deposits were coke-like mixtures of fused ammonium bisulfate and carbon, which were still acidic.

The economic losses to a utility because of corrosion of the air heaters can be substantial, particularly when a boiler is load-limited because of insufficient air. This situation occurs when the air heaters are plugged with iron sulfate deposits or have become corroded. In addition, utility managers report a worsening of the stack plume as air heaters become plugged or inoperative. Frequent outages to water-wash the air heaters then become necessary.

One leading process utilizing back end feed of a neutralizing complex, either as a solid or liquid injection, is offered to the utility industry by Apollo Chemical Corp. Worldwide patents have been applied for detailing this process which overcomes the problem where it occurs—for example, in the flue gas.

Summarizing, the preferred method to eliminate cold end corrosion in oil-fired furnaces is the use of a manganese, carbon-destroying catalyst in the fuel oil. This procedure often allows lower excess air firing, modifying the vanadium ash, coating the furnace iron tubes thus preventing the catalytic action of iron and vanadium in converting SO_2 to SO_3 , and significantly reducing the flue gas carbon grain loading. Then, if air heater corrosion and fouling persists, or if the stack plume indicates SO_3 (acid) fallout as evidenced by a deep blue attached or detached plume, a supplemental flue gas-neutralizing treatment can be used, one that is injected into the economizer outlet.

At Union Electric Co.'s (St. Louis, Mo.) 500-MW coal-fired plant producing 3,290,000 lb/hr of 1000°F steam at supercritical pressures, there was a persistent buildup of deposits of iron sulfate in the tubular air heaters in the

Utilities That Have Tested Additives

Gainesville Electric & Water Authority
Gainesville, Fla.

Jacksonville Electric Authority
Jacksonville, Fla.

Narragansett Electric Co.
Providence, R.I.

Northeast Utilities Service Co.
Hartford, Conn.

Public Service Electric & Gas Co.
Newark, N.J.

Union Electric Co.
St. Louis, Mo.

Note: List not exhaustive; these utilities have carried out extensive, competitive test programs.

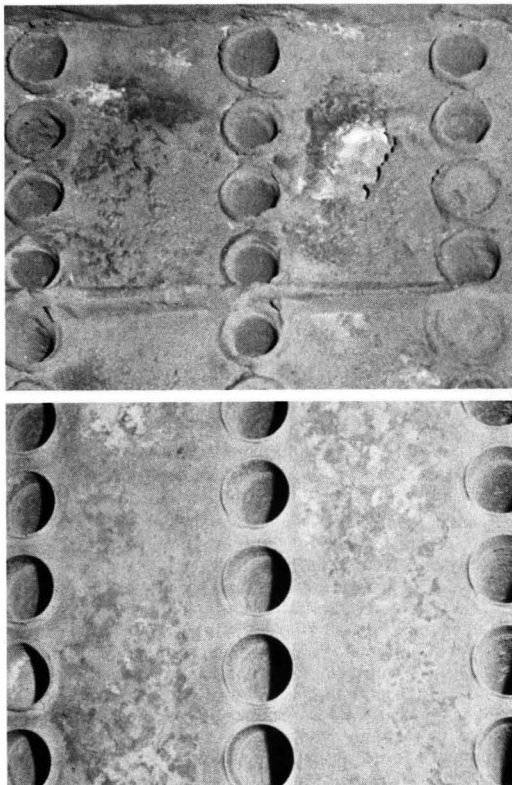


Figure 3. Untreated air heater (above) shows fouling, but back-end neutralizing additive decreases damage (below)

bypass section. This bypass section, accounting for 10% of the exit flue gas, required forced outages at almost bi-monthly intervals to water-wash and manually remove the deposits in the tubular air heaters.

Attempts to improve this condition by raising the steam temperatures through installing heating coils around the tubular air heaters were tried but were unsuccessful or otherwise economically prohibitive.

One of the twin tubular air heaters then was treated by tail end injection of a specially processed alkaline-containing 15–30- μ size complex. This product was over 90% active for removing SO₃ within a residence time of 4 sec. As shown in Figure 3, this method resulted in a dramatic improvement in the air heaters. No cleaning was required during the 12-week test trial. The untreated section had to be water-washed at monthly intervals.

Handling characteristics and air emissions

Flue gas supplemental feed has proved superior to the use of fuel oil treated with MgO with regard to electrostatic precipitator performance in oil-fired furnaces. The problem of cracking the porcelain insulators and shorting out the emitting wires can often be reduced by supplementary air cooling of the insulators, but this action will not entirely eliminate the problem.

TABLE 1

Reduction of carbon particulate matter by manganese

Test period	Additive		Flue gas particulate matter, av concn. (mg/SCF)	Av % carbon (in particulate matter)
	Slurry of:	ppm Mn		
IA	None		0.17	72
IB	Manganese	45	0.04	31
IIA	None		0.14	58
IIB	Manganese	45	0.03	32

The problem, it is thought, originates because of the accumulation on the insulators of carbon and acidic flue gas by-products. When subjected to high temperatures, these products destroy the insulation material.

This tail end neutralization has been useful not only for improving the overall efficiency of the precipitators, but it also often permits ash hoppers to be operated without interruption. The additive dries up the fuel ash in the back end by virtue of the acid-neutralizing properties of the injected additive. The ash no longer tends to clump, but rather flows freely. Indeed, this tail end feed will often eliminate the necessity to revert to the more expensive method of water sluicing of the ash to remove it from the hopper collectors.

Manganese reduces particulate matter

The use of manganese will result in significantly less particulate stack emissions, as much as 80% less (Table 1). In this situation carried out at an oil company in the U.S., the fuel consisted of heavy asphaltic bottoms. This pitch was burned in a package boiler producing 200,000 lb of steam/hr at 900°F superheat temperatures of 900 psi. Measurement of the flue gas particulate matter showed a decrease from 0.17 to 0.04 Mg/SCF, with a reduction of carbon content of the emitting particulate matter from 72 to 31%.

Manganese also shows a significant effect in reducing particulate emissions when burning waste oils and bottoms in petrochemical and refinery heaters. In one exam-

ple, a Canadian refinery was burning a petrochemical waste pitch in a boiler. Because of the appearance of the stack, which exceeded a Ringelmann 2 value, the refinery could burn only 100 barrels per day of the pitch, rather than the 800 barrels produced daily and for which the heater originally was designed. Otherwise, the smoke number exceeded the local regulations that prohibited the stack having a Ringelmann value in excess of 1. Therefore, the refinery had to burn natural gas which was extremely limited in availability.

It was economically prohibitive to modify the furnace to meet the regulations. A quick solution was found in the use of an oxide slurry (25% by weight of manganese) at a feed rate of 1 gal/75 barrels of pitch. The required feed rate of manganese was determined with an in-line Bailey meter. From a visual point of view, the manganese kept the Ringelmann number below 1, permitting the refinery to burn all 800 barrels/day of pitch.

A chemical refinery on the Gulf Coast of the U.S. had a severe smoking problem since resultant plume opacity was not meeting local air pollution regulations. Three Combustion Engineering boilers, each rated for 460,000 lb of steam to be produced per hour, burned a mixture of natural gas and pitch (produced from the cracking of middle distillate fuel) which was used as feed stock to produce ethylene. The pitch had a low sulfur content (below 0.2%). Unfortunately, the stacks showed a noticeable carbon emissions plume having a Ringelmann 2+ value.

Manganese, in the form of a manganese oxide slurry containing 25% Mn was fed into one of the three units. The initial feed rate was 1 gal per 4000 gal of oil. The response was immediate and dramatic. The plume was reduced to essentially zero visibility, noted both by visible observation and recordings on a Shell Oil Co. light transmission meter which monitors stack plume.

The additive rate was reduced gradually to 1 gal per 8000 gal while still maintaining stack plume improvement. The exact feed rate required depended upon the amount of pitch burned and the excess air used. This relationship is not linear, but is easily controlled by the operators, resulting in minimum treatment costs. The use of the additive then was extended to the other two boilers. All three units are being treated at the above rate and maintain a stack plume reading below a Ringelmann 1. This dramatic response with the manganese was accomplished with a refinery pitch, one of the most troublesome fuels to burn.

Additional reading

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Ira Kukin is president and founder of Apollo Chemical Corp. where he has pioneered the field of scientific application of chemical fuel additives. As a member of technical committees in the power industry, he has advanced the practical usefulness of chemical additives, and while employed by Gulf Research and Development Co. for six years, Dr. Kukin was in charge of research on fuel oils and fuel oil additives.

CURRENT RESEARCH

Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere

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■ Equations are derived to predict the rate of evaporation from aqueous solutions of compounds such as hydrocarbons and chlorinated hydrocarbons which are of low solubility. The rate of evaporation can be high even for compounds of low vapor pressure and "half lives" in solution can be as low as minutes or hours under laboratory or environmental conditions. The rate may be limited by diffusion or desorption. Transfer of contaminants from the water to air environments may thus occur much faster than has been generally appreciated.

Chlorinated hydrocarbons, such as pesticides and polychlorinated biphenyls (PCBs), have been transported widely throughout the global environment, even to remote Arctic and Antarctic regions. The mechanism of transport and accumulation in food chains of various species have received considerable recent attention (Woodwell et al., 1971; Frost, 1969; Risebrough and Brodine, 1970).

The major route by which these contaminants are transported is apparently through the atmosphere. Analysis of rainwater in England has shown concentrations of total pesticide residues of 104–229 ppt (parts per trillion) (Frost, 1969), DDT concentrations of 40 ppt have been reported in meltwater from Antarctic ice (Peterle, 1969). The residues are presumably either vapor or are adsorbed on dust particles and may be carried many thousands of miles from the original source. Some of these materials are applied by spraying techniques with the possibility of direct evaporation; however, most are used as solids, liquids, or wettable powders in which transport to the atmosphere can take place only by natural evaporative processes when exposed to the atmosphere.

There is an apparent contradiction in that these compounds are usually of high molecular weight and low vapor pressure, and thus evaporation should be slow. A factor which is often overlooked is the remarkably high activity coefficients of these compounds in water which cause unexpectedly high equilibrium vapor partial pressures and thus high rates of evaporation.

An attempt is made here to quantify the rates of evaporation of these materials from aqueous solution or suspension.

The approach taken is to calculate from equilibrium thermodynamic considerations the composition of vapor in equilibrium with the water solution. Generally the ratio of contaminant to water in the vapor is greater than the ratio in the liquid, thus evaporation causes the liquid concentration of contaminant to fall. The integrated mass balance differential equation gives a relationship between

the contaminant concentration in the liquid and the mass of water evaporated. If an actual water evaporation rate is available the aqueous contaminant concentration can then be expressed as a function of time. Such evaporation rates for rivers and lakes are well documented in texts on meteorology and hydrology. The rate of loss of contaminant is thus calculated from a rate of water evaporation (which is available from these other sources) and the ratio of the contaminant to water in the vapor.

Since the evaporation rates predicted here cannot be easily confirmed by experiment under environmental conditions, the underlying assumptions should be clearly recognized. These assumptions will often be violated. First, the contaminant concentration is that truly in solution, not in suspended, colloidal, ionic, complexed, or adsorbed form. The analysis can be applied to contaminant in these other forms provided it can be converted to dissolved form as evaporation proceeds. Second, it is assumed that the vapor formed is in equilibrium with the liquid at the interface. This is generally accepted (Treybal, 1968) as applying to phase change mass transfer processes such as distillation. Third is the assumption that the water diffusion or mixing is sufficiently fast that the concentration at the interface is close to that of the bulk of the water. The validity of this depends on the relative rates of evaporation and diffusion or mixing. The slower rate of these two will tend to control the overall rate. Here we estimate only the evaporation rate, which can be shown to control in some environmental conditions and in others to be unimportant, the overall rate being diffusion or mixing controlled. This is more fully discussed later. A fourth assumption is that the water evaporation rate is negligibly affected by the presence of the contaminant. This will be valid for low concentrations of nonsurface-active compounds as are considered here.

The validity of these assumptions can only be confirmed by comparison with experimental data, of which few are presently available.

We believe these equations represent with reasonable accuracy some of the physical processes involved in evaporation and are thus valuable in predicting rates of loss of such compounds from water bodies such as rivers, lakes, and oceans.

Thermodynamic Basis

If we consider G grams of water containing m_i grams of the compound i which may be present either as a solution or as a separate phase (possibly colloidal), the equilibrium mole ratio of " i " in the vapor above the water is P_i/P_w where P_i and P_w are the partial vapor pressures of compound i and water, respectively. The mass ratio is thus: $P_i M_i / 18 P_w$ where M_i and 18 are the molecular weights of

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i and water, respectively. If E g/day of water evaporates from this solution, the rate of evaporation of *i* is $EP_iM_i/(18 P_w)$ ($18 P_w$). This may be equated to the change of mass of *i* in the solution with time:

$$\frac{dm_i}{dt} = -EP_iM_i/(18 P_w) \quad (1)$$

If the concentration C_i (mg/l.) is small then,

$$m_i = GC_i10^{-6}$$

If we consider processes in which G changes only by a few percent, then any change in m_i will be attributable to changes in C_i . It will be shown later that C_i undergoes a very much greater relative change than does G , and

$$\frac{dm_i}{dt} = \left\{ G \frac{dC_i}{dt} + C_i \frac{dG}{dt} \right\} 10^{-6} \doteq G \frac{dC_i}{dt} 10^{-6} \quad (2)$$

and thus

$$\frac{dC_i}{dt} = -EP_iM_i10^6/(18 GP_w) \quad (3)$$

The partial pressure of *i* and its concentration in the aqueous solution may be linked by equating the fugacities in both phases. It can be assumed throughout that vapor phase fugacity coefficients are unity, thus equating the fugacity to the partial pressure P_i . The liquid phase fugacity is related to the concentration by Equation 4 below in which x_i the mole fraction is typically about 10^{-7} , γ_i the activity coefficient is about 10^7 and f^R the reference fugacity is the fugacity of pure liquid *i* at the same temperature and pressure.

$$P_i = x_i\gamma_i f_i^R \quad (4)$$

In the case where pure *i* is a liquid at the system temperature and pressure, the reference fugacity can be equated to the saturation vapor pressure. If, as is the case with most pesticides, *i* is a solid, then the appropriate reference fugacity is the vapor pressure of the hypothetical supercooled liquid. Prausnitz (1969) and Tsionopoulos and Prausnitz (1971) have discussed this problem and methods of estimating the reference fugacity and activity coefficients in such cases.

Fortunately in this instance we do not require to know γ_i and f_i^R individually; only their product need be known. If we consider the case of pure *i* (solid or liquid) in equilibrium with water, then the fugacity of *i* in the aqueous phase will be the vapor pressure P_{is} of pure solid or liquid *i*. If the solubility x_{is} is known, then the product $\gamma_i f_i^R$ must be equal to P_{is}/x_{is} . Since γ_i usually varies in such systems in proportion to the square of the mole fraction of water, it can be assumed constant. Thus Equation 4 may be rewritten for both solid and liquid *i* to express P_i as a function of concentration x_i or C_i and accessible properties P_{is} and x_{is} (mg/l.).

$$P_i = x_i P_{is} / x_{is} = C_i P_{is} / C_{is} \quad (5)$$

Evaporation Rates

Two cases can now be considered: first, evaporation from a saturated solution of *i* containing excess *i* as a separate phase. This would be colloidal, emulsion, or a wettable powder. The existence of such colloidal systems for hydrocarbon-water mixtures has been described by Peake and Hodgson (1966). Here P_i equals P_{is} and x_i equals x_{is} and C_i equals C_{is} . Substituting in Equation 3 and integrating from $t = 0$ to $t = t$ and $C_i = C_{i0}$ to $C_i = C_i$ give

$$C_{i0} - C_i = EP_{is}M_i t 10^6 / (G 18 P_w) \quad (6)$$

A half-life, τ , may be defined as the time required for the concentration of *i* to drop to one half its initial value—that is,

$$\tau = C_{i0} G 18 P_w / (2 EP_{is}M_i 10^6) \quad (7)$$

In the second case, evaporation takes place from a true solution in which *i* is present at a concentration less than saturation. Substituting Equation 5 in Equation 3 and integrating as before give Equation 8 from which a "half-life" may be estimated as in Equation 9.

$$\ln (C_{i0}/C_i) = EP_{is}M_i 10^6 t / (18 GP_w C_{is}) \quad (8)$$

$$\tau = 12.48 GP_w C_{is} / (EP_{is}M_i 10^6) \quad (9)$$

In summary, if *i* is present in water at a concentration above its saturation value and the solution remains satu-

Table I. Evaporation Parameters and Rates for Various Compounds at 25°C

Compounds	Solubility, mg/l.	Vapor pressure, mm Hg	$\tau E/G$	F, %	τ for $L = 1$ meter
Alkanes					
<i>n</i> -Octane	0.66	14.1	1.2×10^{-7}	>99	3.8 sec
2,2,4-Trimethylpentane	2.44	49.3	1.3×10^{-7}	>99	4.1 sec
Aromatics					
Benzene	1780	95.2	7.0×10^{-5}	62	37.3 min
Toluene	515	28.4	5.8×10^{-5}	70	30.6 min
<i>o</i> -Xylene	175	6.6	7.4×10^{-5}	61	38.8 min
Cumene	50	4.6	2.7×10^{-5}	92	14.2 min
Naphthalene	33	0.23	3.3×10^{-4}	19	2.9 hr
Biphenyl	7.48	0.057	2.5×10^{-4}	24	2.2 hr
Pesticides					
DDT	1.2×10^{-3}	1×10^{-7}	1.0×10^{-2}	0.7	3.7 days
Lindane	7.3	9.4×10^{-6}	7.9×10^{-1}	0.009	289 days
Dieldrin	0.25	1×10^{-7}	2.0	0.004	723 days
Aldrin	0.2	6×10^{-6}	2.8×10^{-2}	0.3	10.1 days
PCB's					
Aroclor 1242 (C ₁₂ H ₇ Cl ₃)	0.24(6)	4.06×10^{-4}	6.8×10^{-4}	9.7	5.96 hr
Aroclor 1248 (C ₁₂ H ₆ Cl ₄)	5.4×10^{-2}	4.94×10^{-4}	1.1×10^{-4}	46	58.3 min
Aroclor 1254 (C ₁₂ H ₅ Cl ₅)	1.2×10^{-2}	7.71×10^{-5}	1.4×10^{-4}	39	1.2 min
Aroclor 1260 (C ₁₂ H ₄ Cl ₆)	2.7×10^{-3}	4.05×10^{-5}	5.5×10^{-5}	72	28.8 min
Other					
Mercury	3×10^{-2}	1.3×10^{-3}	3.4×10^{-5}	87	17.9 min

rated, its rate of evaporation will be described by Equation 6 until its concentration equals the saturation value. The rate will then be described by Equation 8.

Discussion

These equations represent situations in which perfect mixing and equilibration of the liquid phase occurs—that is, as the compound evaporates from the upper layers no concentration gradients appear. This situation may or may not be approached in practice, and in many cases the rate of evaporation will be substantially reduced by the delay in transferring material from the bulk of the liquid to the depleted interfacial area. It should be possible to estimate a mixing time or diffusion time characteristic of the time required to transport material to the interface. This could be obtained from eddy or molecular diffusivities or flow velocities. Comparison of the evaporation time and the mixing time will permit an order of magnitude estimation of which resistance controls the overall rate. Evaporation from a deep quiescent lake and a fast flowing shallow river represent two extremes of mixing time from months to seconds.

It is apparent from Equation 5 that the partial pressure of i although tending to be reduced by the low values of P_{is} is greatly enhanced by the low values of C_{is} . Essentially the decrease in vapor pressure expected by dilution (Raoult's law) is compensated by exceptionally high activity coefficients. This has been recognized previously by Rassow and Schultzky (1931) who derived an equation which has been used to estimate "co-distillation" rates of DDT with water for example by Acree et al. (1963). Although the ratio of i to water in the vapor formed on evaporation is small, it is very much greater than the ratio in the liquid. The "relative volatility" is not the small ratio P_{is}/P_w but rather $\gamma_i P_{is}/P_w$ which is of the order of unity. As a result the loss of even a small amount of liquid by evaporation results in a marked drop in the liquid phase concentration of i .

The half-lives, τ , may now be calculated from Equation 9 by use of known solubility and vapor pressure data. This equation is probably more frequently applicable to real situations since hopefully unsaturated solutions of these materials are in the environment. It is instructive to tabulate values of the dimensionless quantity, $\tau E/G$, which is a measure of the time required for evaporation for each compound and then relate these values to particular situations. Also tabulated is F , fraction of the mass of i present which is evaporated when 0.01% of the water is evaporated—i.e., tE/G is 10^{-4} in Equation 8.

The solubility data in Table I were obtained for hydrocarbons from McAuliffe (1966), for pesticides from Gunther et al. (1968), for PCBs from the correlation of Tsionopoulos and Prausnitz (1971) and for mercury from Stock et al. (1934). Vapor pressure data were obtained for hydrocarbons from API Project 44 data compiled by Wilhoit and Zwolinski (1971) and from the "Handbook of Chemistry and Physics" (51st Edition), for pesticides from Edwards (1966), and for PCBs by extrapolation of Monsanto (1967) data using an Antoine equation with a C parameter of 200°K, the A and B parameters being fitted from data in the temperature range 150–300°C.

Hydrocarbons and PCBs evaporate quickly but the pesticides rather more slowly mainly because of their low vapor pressures.

Few experimental data are available to confirm these equations. Acree et al. (1963) evaporated aqueous solution of DDT and showed in three experiments at 25°C that an initial mass of 250 grams of water containing 0.36, 0.60, and 0.84 ppb DDT lost 5.4, 5.0, and 5.2% of the water in

24 hr and 77.7, 80.0, and 71.5% of the DDT initially present. The water was unmixed and the surface placid. The constancy of the percent evaporated is expected from Equation 8 as is DDT's greater relative volatility than water despite its very low vapor pressure. Since the water was unmixed, the interface would be depleted in DDT and the slow diffusion of DDT from the bulk would tend to reduce the rate of DDT evaporation to a value lower than that predicted by Equation 8. This lower rate is observed, since Equation 8 predicts that when 5.2% of the water is evaporated, 97% of the DDT initially present will evaporate. This difference between the predicted 97% and the average experimental figure of 76.4% corresponds to a factor of 2.5 decrease in rate which is reasonable and can be explained mainly by the mixing rate and possibly by some uncertainty in the solubility and hence activity coefficient of DDT.

In an extreme case, if a solution of octane in water is allowed to evaporate under similar conditions, τ would be 0.4 sec.

These surprisingly small half-lives must be considered when analyzing solutions of hydrocarbons and pesticides in water since significant amounts may evaporate during analysis.

Environmental Applications

The equations may be applied to environmental conditions. One difficulty is that mixing or diffusion in a large lake or in surface water on a field may be slow so the above equations will represent maximum rates of evaporation achievable. Reasonable estimates of these rates (and certainly relative rates) can be obtained and may indicate that diffusion is the rate-controlling mechanism.

It is convenient to consider 1 m² of water of depth L meters and derive an equation similar to Equation 9. Since $G = 10^6 L$, then,

$$\tau = 12.48 LP_w C_{is} / (EP_{is} M_i) \quad (10)$$

Rates of evaporation from lakes have been discussed by Sellers (1965). Typically in the middle latitudes of the Northern Hemisphere evaporation rates from lakes vary from about 1.5 mm/day to 4.5 mm/day depending on the season, with a yearly evaporation ranging from 800–2200 mm. The Atlantic Ocean loses 1040 mm/year by evaporation. The rate of evaporation from land masses depends on the precipitation and for North America is about 400 mm/year. If a value of 1000 mm/year evaporation is assumed, this corresponds to a value of E of about 2740 g/m² day. This value is used in calculating values of τ in Table I for a depth of water L of 1 meter.

The rates calculated may be conservative since the presence of atmospheric water vapor reduces the evaporation rate of water but not that of the contaminant, thus increasing the ratio of contaminant to water in the material evaporated.

In a fast-flowing shallow river of depth 1 meter (where good mixing is probable), values of τ are quite low. For DDT, τ is 3.7 days. Even shorter half-lives occur for Aroclor 1242 (5.9 hr) and Aroclor 1260 (0.5 hr). An interesting consequence of these short half-lives is the difficulty introduced in monitoring effluents from industrial and municipal sources. If a monitoring station is located 1 hr downstream from a source of, say Aroclor 1242, into the river, then by the time the water reaches the station, potentially about one tenth may already have evaporated.

Mercury, a widespread contaminant, has also a surprisingly short half-life. The half-life in a lake of depth 10 meters is about 3.0 hr. This suggests that mixing or diffusion is the controlling mechanism and the upper layers of

water exposed to the atmosphere will be rapidly freed of dissolved metallic mercury. Ionic or adsorbed mercury will not evaporate at these rates.

In applying these equations to pesticides on soil, certain difficulties are encountered and certain additional factors must be considered (Edwards, 1966). Among these are the adsorption of pesticides on different soil types by leaching, microbial population of the soil, and the formulation of the pesticide.

Conclusion

Because of their high activity coefficients in water, hydrocarbons and chlorinated hydrocarbons potentially will evaporate at high rates and have short half-lives in water bodies. Evaporation from rivers and lakes may thus represent a major mechanism of the transport of pollutants through the environment. The equations presented here provide a method of calculating this potential rate of evaporation for compounds whose vapor pressure and water solubility are known. The actual rate of evaporation under environmental conditions may of course be substantially slower owing to diffusion or desorption rates.

The approach developed here may be of value in calculations of the environmental behavior of hydrocarbons and chlorinated hydrocarbons in rivers, lakes, and lagoons arising from industrial emissions, spills, and discharges of gasoline and lubricating oil from outboard motors. The data for pesticides may be useful in calculations of the retention time in water or in moist soils.

Mercury Removal from Waste Water with Starch Xanthate-Cationic Polymer Complex

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■ Sequential addition of starch xanthate and a cationic polymer [e.g., poly(vinylbenzyltrimethylammonium chloride) or polyethylenimine] to a mercury(II) solution precipitates both polymers and the mercury as a cohesive floc that is easily removed by filtration. Some xanthate groups on the starch backbone may form mercury(II) salts while others react with the polycation to form a polyelectrolyte complex. The amount of xanthate required to precipitate the cationic polymer and mercury is determined by streaming current measurement. Effectiveness of mercury removal depends on the ratios of mercury, cationic polymer, and xanthate. Residual mercury concentrations were as low as 3.8 $\mu\text{g}/\text{l}$. after single treatment of solutions that had initial mercury(II) concentrations of $1.0 \times 10^5 \mu\text{g}/\text{l}$.

Removal of mercury(II) ion from waste water by treatment with xanthates of simple alcohols has been proposed by Nanjo et al. (1971). They found that $(\text{ROCS}_2)_2^- \text{Hg}^{2+}$ precipitates when the mercury(II) concentration is less than that of the xanthate, but if the mercury(II) concentration is greater, the soluble $[(\text{ROCS}_2)^- \text{Hg}^{2+}]^+$ species is formed. Starch xanthate is known to precipitate zinc(II) and other heavy metals (Russell et al., 1962).

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Received for review May 19, 1972. Accepted March 21, 1973. Work supported by the National Research Council of Canada and the Institute of Environmental Sciences and Engineering of the University of Toronto.

Jellinek and Luh (1969) coprecipitated ions of many heavy metals, other than mercury, in polyelectrolyte complexes (PEC) (Michaels and Bixler, 1968) of polycarboxylic acids and polyethylenimine (PEI). However, the formation constants of the acid-metal complexes were so small that appreciable amounts of the metals remained in solution. Replacement of the polycarboxylic acids in their process by starch xanthate could increase its efficiency since mercury(II) xanthates are very insoluble [K_{sp} Hg(II) ethyl xanthate is 1.7×10^{-38} (Kakovsky, 1957)] and since starch xanthate can also form insoluble PEC by reaction with a polymeric amine (Carr et al., 1973).

Materials

Reagents. All solutions and dispersions were prepared with distilled water that had no detectable mercury.

Starch xanthates having degrees of substitution (DS, average number of substituent groups per glucose unit) in the range 0.11-0.40 were prepared in a high shear mixer as described by Swanson et al. (1964), diluted to about 10% concentration (w/v, starch basis), and stored at 34°F. Portions of these stock dispersions were diluted to 1% (w/v, starch basis) daily for performing all titrations and precipitations.

The cationic polymers poly(vinylbenzyltrimethylammonium chloride) (PVBTMAC, experimental resin QX-2611.7, The Dow Chemical Co.) and PEI (Montrek 1000, The Dow Chemical Co.) were received and stored as aque-

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ous dispersions (about 33%, w/w). Each was diluted to 1% concentration (w/v) for use.

Mercury(II) chloride (2.707 g) and concentrated hydrochloric acid (1 ml) were dissolved in a small amount of water and the solution was diluted to 1 liter. Portions of this stock solution (2000 mg/l. or 0.01M) were used to prepare test samples as well as analytical standards containing 1, 5, 10, or 15 μg of mercury per liter.

Cadmium(II) carbonate (0.1724 gram), zinc(II) chloride (0.1363 gram), calcium(II) chloride (0.1109 gram), and iron(II) sulfate heptahydrate (0.2780 gram) were weighed into separate containers. Each was dissolved in 100 ml water containing 1 ml concentrated hydrochloric acid.

For sequestrant solutions (0.5%, w/v), individual 0.50-gram samples of citric acid, diglycolic acid, sodium tripolyphosphate $[(\text{PO}_4)_n]$, and nitrilotriacetic acid (NTA) trisodium salt monohydrate were dissolved in water (100 ml). The pH of each sequestrant solution was adjusted to 9.0 by addition of 1N sodium hydroxide or 1N hydrochloric acid, as needed.

Apparatus. Concentrations of residual mercury were measured at the 253.6 nm mercury line by flameless atomic absorption (AA) in a Varian Techtron AA120 spectrophotometer. The mercury vapor train used in analysis was similar to that of The Dow Chemical Co. (1970) but included a drying tube loosely filled with glass wool immediately downstream from the magnesium perchlorate bottle.

A streaming current detector (SCD) (Waters Associates, Inc., Framingham, Mass.) indicated the state of balanced charge when titrating one polyelectrolyte with another having an opposite charge. In the SCD an alternating streaming current is generated when the test solution flows across two silver electrodes as it alternately is displaced from a cavity on the downstroke of a reciprocating piston and returns to the cavity on the upstroke. This current is rectified and amplified to drive a microammeter. The meter's scale is arbitrarily divided into 20 equal units ascending from -10 to $+10$. Scale expansion electronics permit full-scale readings of ± 5 to ± 200 scale units.

Methods

Titration. A desired volume of polyelectrolyte dispersion (0.5–10 ml) was added to 50 ml of water or other test solution and titrated with counterionic polyelectrolyte. At arbitrary intervals the solution's SCD reading was determined. Graphs of these SCD readings as a function of titrant volume are sigmoid and resemble acid-base titration curves. The more vertical segment of the curve crosses the zero-SCD-reading axis and coincides with precipitation of the PEC. Titration was discontinued on evidence of leveling of the curve after precipitate had formed. From each curve, as will be described later, the amount of titrant required for each precipitation was selected.

Precipitation. In 150-ml beakers were prepared 50-ml samples of each test solution, which (unless otherwise noted) had mercury(II) concentrations of $1.0 \times 10^5 \mu\text{g/l.}$ and pH values of about 3.2. When precipitations had two polyelectrolytes, the desired amount of one was run into each sample from a buret and the requisite amount of counterionic polymer (as determined by SCD titration) was added dropwise from a second buret. The concentration of cationic polyelectrolyte in the test solutions was 0.2 g/l. (0.948 meq/l. of nitrogen), unless otherwise noted. If xanthate was used alone to precipitate mercury(II), it was added dropwise. The usual addition rate was 0.6 ml/min.

During addition of the precipitant polyelectrolyte and for 10 min thereafter, unless otherwise noted, each sample

was stirred with a magnetic stirrer at a rate that produced a vortex about 1.2-cm deep. Samples were filtered through medium porosity 60-ml sintered glass funnels into 125-ml graduated Erlenmeyer flasks. Each beaker was rinsed with about 10 ml of water that was also collected. The contents of each flask were diluted to the 100-ml mark before analysis.

Analysis. Residual mercury was determined by a modified version of the AA spectrophotometric method of The Dow Chemical Co. (1970). Our procedure differed as we used 1 ml of 5% potassium persulfate in addition to 1 ml H_2SO_4 (1:4) and 1 ml KMnO_4 (4%, w/v) for digestion of the samples. Organic matter or sulfides were oxidized with persulfate under less favorable test conditions. Also, we digested samples on a steam bath for $\frac{1}{2}$ hr rather than boiling them for a few seconds on a hot plate. Heating on the steam bath avoided bumping during digestion without apparent detriment to the accuracy of analysis. Aeration was identical with the Dow procedure except that we aerated 100-ml samples directly in the 125-ml sample flasks.

Combined relative standard error for the precipitation and analysis was 16.7% (8 degrees of freedom) at the 8.0 $\mu\text{g/l.}$ residual mercury level.

Oxygen demands, BOD_5 [Alsterberg (azide) modification of Winkler's method] and COD, were estimated as recommended by the American Public Health Association (1960).

Results and Discussion

SCD Titration. To provide reproducible means of selecting the amount of polyelectrolyte required to precipitate a mixture of mercury(II) and counterionic polyelectrolyte, SCD titrations were run each day on each sample to be precipitated. This procedure was necessitated by the slow decomposition of starch xanthate over a period of weeks and by the narrow latitude for end-point error in achieving maximum removal of mercury. The validity of SCD titrations for determining these end points was established by evaluation of their reproducibility on replicate samples and on samples having different NaCl, mercury(II), and PVBTMAC concentrations.

These tests indicated that the volume of titrant required to produce zero SCD reading is nearly constant for replicate samples but that the volume required for other SCD readings varies somewhat from titration to titration. Increasing the salt concentration progressively attenuates the SCD readings and also reduces the volume of xanthate required to attain a zero SCD reading. Precipitation of the mercury(II)-xanthate-PVBTMAC mixture occurs at or near zero SCD reading in each titration.

Relation of SCD Readings to Residual Mercury. Correlations between SCD titration curves and residual mercury concentrations were investigated to select effective reagent combinations directly from titration curves. The relationship between residual mercury concentration and volume of xanthate titrant is illustrated in Figure 1.

Residual mercury concentrations were low at -11 – 0 SCD readings, but they increased for SCD readings above or below this range. On the titration curve this range corresponds to the negative segment of the approximately linear portion that passes through zero SCD reading. The increase in residual mercury concentration with deviation from this range is probably related to solubility of electrostatically unbalanced mixtures of polyelectrolytes as reported by Michaels and Bixler (1968). The range of effective titrant volume spans 0.15 ml, which is only about 3.3% of the amount added.

Since the range of SCD readings on the effective segment of the curve varies from sample to sample, no one SCD reading (other than zero) is usable as an end point for all precipitations. In this work end points were selected at SCD readings one-third to one-half way from zero to the beginning of curvature for the plateau of excess xanthate (between -0.4 and -4 SCD reading). This selection assured maximum effectiveness in precipitation of mercury(II) if concentrations of mercury, cationic polymer, or xanthate varied slightly from sample to sample.

Xanthate Degree of Substitution. The concentration of residual mercury was influenced little by the DS of the precipitant xanthate over the range 0.11-0.40. Residual mercury concentrations fell within the range 11-20 $\mu\text{g/l}$.

Order of Polyelectrolyte Addition. Residual mercury concentrations in samples having PVBTMAC added before the xanthate were compared with those in samples having xanthate added first. When PVBTMAC was added first, residual mercury concentration was 6 $\mu\text{g/l}$.; whereas when xanthate was added first, the residual mercury level was 20 $\mu\text{g/l}$. Initial mercury concentration each time was $1.0 \times 10^5 \mu\text{g/l}$.

Cationic Polymer Concentration. The effect on residual mercury concentration due to varying the dosage of PVBTMAC over the range 0.004-1.0 g/l. (0.019-4.74 meq nitrogen/l.) was evaluated for initial mercury concentrations of 4×10^3 - $1.0 \times 10^5 \mu\text{g/l}$. At each initial mercury level, the concentration of residual mercury is least at some critical dosage of PVBTMAC.

A typical relationship between residual mercury concentration [initial concentration was $1.0 \times 10^5 \mu\text{g/l}$. (0.5 mM/l.)] and dosage of PVBTMAC [0.1-1.0 g/l. (0.47-4.74 meq nitrogen/l.)] is shown in Figure 2. Precipitation required 3.2-11.5 ml of xanthate dispersion (0.91-3.25 meq of 0.23 DS xanthate). At the critical PVBTMAC concentration (for minimum residual mercury, 0.45 g/l.), the residual mercury concentration was about 7.5 $\mu\text{g/l}$. Residual mercury levels of 10 $\mu\text{g/l}$. or less was obtained with PVBTMAC dosages of 0.3-0.63 g/l. In contrast to the polyelectrolyte complexes reported by Michaels and Bixler (1968), these complexes do not precipitate with constant proportions of reactant groups. If concentration of PVBTMAC is low, the tendency is toward $X \text{ Hg}^{2+}$ and Y amine groups reacting with $(X + Y)$ xanthate groups, as at the 0.1 g/l. level in Figure 2 where the proportion is 1 Hg^{2+} : 0.94 N:1.82 xanthate. However, as PVBTMAC concentration increases, the sum $X + Y$ becomes increas-

ingly larger than the number of xanthate groups required for precipitate formation. If each mercury is combined with at least one xanthate group, there must be increasing occlusion of amine (not associated with xanthate group) as PVBTMAC concentration increases. The ratio mercury(II):xanthate group tends toward 1:1 in the more dilute solution which suggests the presence of $(\text{ROCS}_2)^-$ - Hg^{2+} in the precipitate.

Critical dosage of PVBTMAC is a nonlinear function of initial mercury(II) concentration (Figure 3). The critical amount of PVBTMAC is 2.5 times the weight of the mercury at $2.0 \times 10^4 \mu\text{g/l}$. initial mercury(II) concentration but increases to 4.5 times the weight of mercury at $1.0 \times 10^5 \mu\text{g/l}$. Increasing ratios of amine to mercury at high mercury levels may result from increasing occlusion of the amine.

Initial Mercury(II) Concentration. The residual mercury concentration after treatment of test solutions with PVBTMAC and starch xanthate (3.2-5 ml, 0.23 DS) is shown as a function of initial mercury(II) concentration (0.1-100 mg/l.) in Figure 4. For this combination of precipitants, the residual mercury level is within the tentative U.S. Public Health Service drinking water standard (5 $\mu\text{g/l}$.) when the initial mercury(II) concentration is 50-80 mg/l. As initial mercury levels recede from this range, the residual mercury concentration increases toward a maximum of about 50 $\mu\text{g/l}$., which occurs at an initial mercury concentration of 12 mg/l. The increase in residual mercury may result from reduction of the percentage of total mercury associated with the xanthate as mercury(II) level and, consequently, xanthate levels are reduced. As the xanthate concentration stabilizes near its lower limit (the amount required to react with the constant amount of PVBTMAC in the solutions), the decrease in initial mercury(II) level becomes greater than the decrease in association of the mercury with the xanthate, and the residual mercury concentration again declines. Even at the lowest initial mercury concentration more than 90% of the mercury was removed.

Rate of Xanthate Addition. The effect on residual mercury concentration due to changing the rate of adding xanthate dispersion (8.12 ml, 0.12 DS) to the test solutions [PEI and mercury(II)] is shown in Figure 5. The residual mercury concentration is a linear function of rate of addition over the range of conditions studied (0.7-29 ml/min). Furthermore, slow addition favors low residual mercury concentrations. Thus precipitation of mercury(II) by

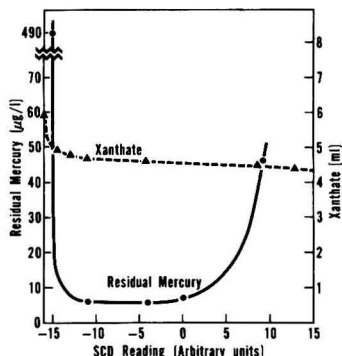


Figure 1. Relationships between volume of starch xanthate added, SCD reading, and residual mercury concentration

Fifty-milliliter samples containing mercury(II) (5 mg) and PVBTMAC (10 mg) were treated with starch xanthate [0.23 DS, 1% (w/v)]

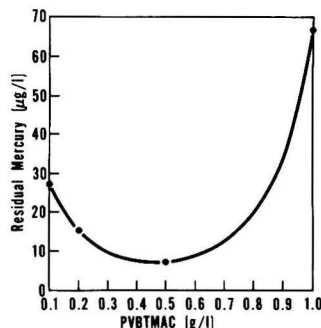


Figure 2. PVBTMAC concentration vs. residual mercury concentration

Initial mercury(II) concentration was $1.0 \times 10^5 \mu\text{g/l}$. Dosages of starch xanthate (0.23 DS) were [concentration of PVBTMAC (g/l), xanthate added (g/l)]: 0.100, 0.640; 0.200, 0.830; 0.500, 1.390; and 1.000, 2.290

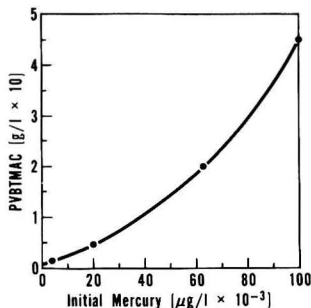


Figure 3. Relationship between initial mercury(II) concentration and dosage of PVBTMAC required for minimum residual mercury concentration

Dosages of starch xanthate (0.23 DS) were [initial mercury concentration ($\mu\text{g/l} \times 10^3$), xanthate added (g/l.)]: 4, 0.072; 20, 0.225; 63, 0.84; 100, 1.30

these systems is not an instantaneous chemical reaction. Slow precipitation presumably produces fewer and larger (more filterable) particles of precipitate than are formed by rapid precipitation. Postprecipitation stirring for up to 120 min did not affect residual mercury concentrations. Although PEI was used as the cationic polymer in this experiment, residual mercury levels were similar to those obtained when PVBTMAC was the cationic polymer.

Initial pH of Mercury(II) Solution. There was little effect of initial pH of the test solutions over the range 3-11 on the effectiveness of precipitation of mercury(II) in the starch xanthate-PVBTMAC complex. The solubility of the mercury(II) xanthate is so small relative to the degree of ionization of xanthic acid that pH changes probably have little effect on the equilibrium.

Sodium Chloride Concentration. Sodium chloride concentrations in the test solutions that are lower than about 2.6% have little effect on completeness of mercury removal. Higher salt concentrations increase the concentration of unprecipitated mercury severalfold and may reflect increased solubility of the polyelectrolyte complex in salt solutions as has been reported by Michaels and Bixler (1968). In addition, high concentrations of salt hinder identification of the end point by SCD titration.

Starch Xanthate Compared with Starch Xanthate-PVBTMAC Complex for Precipitating Mercury(II). Starch xanthate can react with mercury(II) in the absence of cationic polyelectrolyte to form a precipitate. The effectiveness of this precipitate for removal of mercury(II) from solution was compared with that of starch xanthate-PVBTMAC complex over a DS range of 0.15-0.40 and an initial mercury(II) concentration range of 4-100 mg/l. The lowest residual mercury concentration observed in the absence of cationic polyelectrolyte was 100 $\mu\text{g/l}$. This level was achieved with 0.4 DS xanthate and 100 mg/l. initial mercury concentration. Residual mercury levels increased as either initial mercury(II) concentration or DS of the xanthate was reduced. With 4 mg/l. initial mercury concentration there was no evidence of mercury removal with 0.23 DS xanthate alone. However, when PVBTMAC was included in a similar test solution more than 99% of the mercury was precipitated. In this instance, it is probable that there was insufficient mercury to precipitate starch xanthate, although the two probably reacted. When PVBTMAC was included, both the starch and its associated mercury were precipitated. Residual mercury levels were always 5-100 times greater when cationic polymer

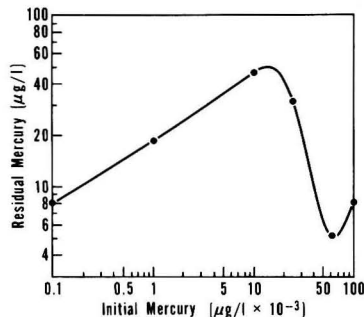


Figure 4. Effect of initial mercury(II) concentration on residual mercury concentration

Dosage of PVBTMAC was 0.200 g/l. Dosages of starch xanthate (0.23 DS) were [initial mercury concentration ($\mu\text{g/l} \times 10^3$), xanthate added (g/l.)]: 0.100, 0.623; 1.00, 0.630; 10.0, 0.655; 25.0, 0.680; 50.0, 0.758; and 100, 1.006

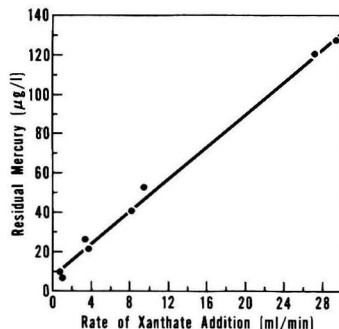


Figure 5. Rate of xanthate addition vs. residual mercury concentration

Fifty-milliliter samples containing mercury(II) ($1.0 \times 10^5 \mu\text{g/l}$) and polyethylenimine (0.200 g/l.) were each treated with 8.12 ml of starch xanthate dispersions [0.12 DS, 1% (w/v)]

was omitted than when it was present during precipitation.

Effect of Sequestrants. Test solutions containing 0.1 g/l. of the sodium salt of citric, diglycolic, nitrilotriacetic, or tripolyphosphoric acid, in addition to the mercury, were treated with starch xanthate (0.23 DS) and PVBTMAC. The residual mercury concentrations and meq of xanthate required to precipitate the mercury from each 50-ml sample are listed in Table I.

Presence of sequestrants at the test level does not greatly affect the residual mercury concentration. Residual mercury concentrations were near the control value (6.1 $\mu\text{g/l}$.) within the range 3.8-10.3 $\mu\text{g/l}$. However, the amount of xanthate required for precipitation depends on the type and amount of sequestrant present in the test solution. Inclusion of polyphosphate reduced the xanthate requirement by almost one half. This result suggests that polyphosphate and other sequestrants can replace xanthate groups in interactions with cationic polymers since strong interaction of the sequestrants with the mercury(II) should have increased the residual mercury concentration appreciably. If it is true that the PVBTMAC polymer was partially neutralized by the sequestrants without detriment to its effectiveness as a coprecipitant, less highly charged cationic polymers, which are usually less expen-

Table I. Effect of Sequestrants on Residual Mercury Level and Starch Xanthate Requirement^a

Sequestrant ^b	Residual mercury, $\mu\text{g/l.}$	Xanthate requirement, $\text{meq} \times 10^2$
Diglycolate	4.37	5.61
Nitrilotriacetic acid	3.86	5.19
Polyphosphate	10.3	3.36
Citrate	10.33	4.36
Control	6.1	6.53

^a Meq of starch xanthate [1% w/v, 0.23 DS] required to precipitate 2.5×10^{-2} mM (5 mg) mercury(II) and 4.74×10^{-2} meq poly(vinylbenzyltrimethylammonium chloride) (PVBTMAC) from 50 ml of solution.

^b In each 50-ml test solution 5 mg of sequestrant was used. The control contained none.

Table II. Effect of Selected Cations on Residual Mercury Level and Starch Xanthate Requirement^a

Cation ^b	Residual mercury, $\mu\text{g/l.}$	Xanthate requirement, $\text{meq} \times 10^2$	K_{sp} ^c
Cadmium(II)	9.29	10.14	2.6×10^{-14}
Zinc(II)	11.65	7.45	4.9×10^{-9}
Iron(II)	13.65	6.59	8.0×10^{-8}
Calcium(II)	14.6	6.48	...
Control	6.1	6.52	...

^a Meq of starch xanthate (1% w/v, 0.23 DS) required to precipitate 2.5×10^{-2} mM (5 mg) mercury(II), 4.74×10^{-2} meq PVBTMAC, and the cation from 50 ml of solution.

^b Each test solution, except the control, contained 0.5 mM of the listed cation.

^c Solubility products for ethyl xanthate salts, as reported by (Kakovsky, 1957).

sive, may be nearly as effective as PEI or PVBTMAC for these precipitations.

Selected Divalent Cations. The effectiveness of starch xanthate-PVBTMAC complex for precipitation of mercury(II) was evaluated with solutions that were 0.01M in cadmium(II), calcium(II), iron(II), or zinc(II) ion. The residual mercury concentrations and meq of xanthate (0.23 DS) required for the precipitations are given in Table II. The solubility products for the ethyl xanthate salts of cadmium(II), zinc(II), and iron(II) are included in the table. These data indicate that inclusion of any of these ions at the 0.01M level interferes somewhat with precipitation of the mercury(II) but that ions whose xanthates have lowest solubility interfere least.

When cadmium(II) and zinc(II) are present, more xanthate is required for precipitation than is required in their absence. Since the xanthate requirement increases as the K_{sp} of the metal ethyl-xanthate salts decreases, the metals may be reacting with the xanthate and precipitating. Zinc(II) ion is known to precipitate starch xanthate (Russell et al., 1962). Effectiveness of starch xanthate-cationic polymer complexes for precipitating other metals is being investigated.

Residual Contaminants. Any process for removing noxious substances from water should not add others. Contaminants that might be introduced by treatment of water with starch xanthate and a cationic polymer include: small ionic species (Cl^- from these cationic polymers; Na^+ , OH^- , and CS_3^{2-} from the xanthate), small nonionic species (CS_2 and COS from the xanthate), and the polyelectrolytes themselves.

Samples for analysis of the residue from the treatment were prepared by precipitating mercury(II) (100 mg/l.) with PVBTMAC (200 mg/l.) and starch xanthate (0.23 DS, 890 mg/l.; starch basis). Hydroxide from the xanthate dispersion normally raises the pH during treatment. If neutralization is accomplished with hydrochloric acid, sodium chloride will be formed at a concentration of less than 200 mg/l. (based on the initial concentration of sodium in the xanthate). Sulfur (reported as sulfate) was 36 mg/l. These concentrations of chloride and sulfate are below the 250 mg/l. upper limit for each in waters being discharged into public and food processing waters in Illinois [Illinois Pollution Control Board (IPCB), 1972]. BOD_5 was 0-12.5 mg/l. compared with 168.6-169.7 mg/l. for both starch and starch xanthate, and COD was 80-82 mg/l. compared with 327 mg/l. for glucose (standards at concentrations of 0.3 g/l.). Effluents having BOD in this range may be discharged into many Illinois streams since IPCB has established maximum BOD_5 levels of 4-30 mg/l. Hence, precipitation of mercury(II) with starch xan-

thate and cationic polyelectrolytes does not appear, in itself, to produce legally unacceptable concentrations of these residual contaminants for which limits have been established.

Commercial Potential. Treating solutions containing mercury(II) ion with starch xanthate-polycation complex reduces residual mercury(II) content to extremely low levels (3.8 $\mu\text{g/l.}$) without introducing large amounts of other contaminants. Organic mercury is precipitated poorly by this system (0-98% removal of 1×10^5 $\mu\text{g/l.}$ initial mercury) and should be converted to mercury(II) ion before treatment with the polymers. The physical state of the precipitate depends to a great degree on the particular cationic polymer used. However with PVBTMAC and PEI 1000, the precipitate first appears as a fine floc that coagulates and settles rapidly to less than 10% of the solution volume when stirring is stopped. The supernatant liquid filters like water, and in favorable circumstances, the precipitate dewaterers almost immediately on the filter.

Effective precipitation of mercury(II) requires accurate control of the polyelectrolyte balance in the system, addition of cationic polymer before xanthate, selection of an efficient ratio of cationic polymer and mercury(II), and slow addition of the xanthate. Inclusion of less than 2.6% NaCl, 0.1 g/l. sequestrant, or 0.1 molar divalent ions [Ca(II), Cd(II), Fe(II), or Zn(II)] has little effect on residual mercury level but does influence the amount of xanthate required. Many of these factors depend on the composition of the waste solution, so costs of precipitating mercury by this method can be evaluated accurately only after optimizing treatment in each proposed application.

Our method seems amenable to continuous treatment of effluents in a process where cationic polymer and starch xanthate dispersions are pumped sequentially into the effluent stream and where the mercury-bearing precipitate is removed by filtration or centrifugation. A settling stage, after addition of the precipitants, could reduce the load on the filter bed or centrifuge. The method's effectiveness for precipitation of mercury(II) and apparent suitability for continuous treatment of waste water warrant further evaluation using actual industrial effluents and less expensive cationic polymers.

Acknowledgment

We gratefully acknowledge the efforts of M. I. Schulte (determination of BOD's and analysis of xanthates), W. L. Williams and L. D. Miller (preparation of the starch xanthate), and L. T. Black (assistance in operation of the AA spectrophotometer). We also express our sincere appreciation to W. T. Sullivan of the Illinois State Water Survey for his helpful advice on the determination of mercury.

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Received for review August 22, 1972. Accepted March 21, 1973. Northern Regional Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture. The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

Identification of Cutin, a Lipid Biopolymer, as Significant Component of Sewage Sludge

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■ Sewage sludge, the end product of digestion in a domestic waste treatment plant, was thoroughly extracted with organic solvents. The residue on hydrogenolysis with LiAlH_4 gave polyhydroxy alkanes which accounted for 12-28% of the organic matter in the sludge. The major hydroxy alkanes were identified by means of chromatographic techniques in conjunction with mass spectrometry to be 1,18-dihydroxyoctadecene, 1,9,18-trihydroxy- and 1,10,18-trihydroxyoctadecane, 1,9,18-trihydroxy- and 1,10,18-trihydroxyoctadecene, 1,9,10,18-tetrahydroxyoctadecane, 1,9,10,18-tetrahydroxyoctadecene, 1,7,16-trihydroxyhexadecane, and 1,8,16-trihydroxyhexadecane. The structure and distributions of these components are unique and typical of the lipid polymer cutin.

Sewage sludge is one of the most abundant substances in sewage treatment plants. Disposal or utilization of this material is a challenging problem of modern society. A knowledge of the chemical composition of the sludge is essential to the development of potential avenues of utilization or disposal of this material. However, very little is known about the chemistry of sludge.

Polysaccharides contained in activated sludge (Tenney and Stumm, 1965; Nishikawa and Kuriyama, 1968; Wallen and Davis, 1972) and those produced by microorganisms isolated from activated sludge (Anderson and McCoy, 1963; Dias and Bhat, 1964; Friedman et al., 1968) have been studied particularly with regard to their possible role in the flocculation process. In this regard poly- β -hydroxybutyrate, produced by the bacterial population contained in the sludge, has also attracted attention (Crabtree et al., 1965). Other polymeric materials, such as deoxyribonucleic acid, have been extracted from activated sludge (Nishikawa and Kuriyama, 1968). However, very little information is available regarding the nature of the polymeric materials of sludge. Identification is reported of a lipid biopolymer, cutin, in sludge with the use of a novel hydrogenolysis technique coupled to gas-liquid chromatography and mass spectrometry. This polymer constitutes the outer layer of all plants and therefore it is pres-

ent in most foodstuffs derived from plants. It is essentially a polyester formed from hydroxy fatty acids although some ether bonds and peroxide bridges may be found in the polymer (Kolattukudy and Walton, 1972). This polymer is rather resistant to biological degradation as indicated by its recovery in ancient sediments (Eglinton et al., 1968).

Procedure

The sample of sludge suspension was obtained from a 450,000-gal anaerobic digestion tank operated by the city of Moscow, Idaho. In this final treatment of sewage a 20-day digestion period is used and our samples represent the end product of the treatment.

The sludge suspension was centrifuged at $10,000 \times g$ for 30 min and the resulting solid was dispersed in an excess (20:1 v/v) of a 2:1 mixture of chloroform and methanol. The solid residue was recovered by filtration after about 2 hr, and this washing procedure was repeated three times. When the sample contained clumps, it was treated with the same organic solvent mixture in a Waring Blender at maximum speed for 3 min and then filtered. The recovered solid was extracted with chloroform in a Soxhlet extractor overnight. The solid residue containing 45-50% organic matter was dried, and a weighed sample was subjected to exhaustive hydrogenolysis with LiAlH_4 in tetrahydrofuran for 24-48 hr (Kolattukudy, 1970).

After the excess of LiAlH_4 was carefully decomposed, the reaction mixture was acidified with HCl, and the ether-soluble products were isolated by repeated extraction with ethyl ether. The ether extract was dried over anhydrous sodium sulfate and evaporated to dryness. The resulting waxy solid was dissolved in a small volume (usually 0.5 ml) of chloroform and subjected to thin-layer chromatography on silica gel G plates (20×20 cm 0.5-mm layer) with ethyl ether-hexane-methanol (8:2:1) as the solvent system. Pear cutin hydrogenolyzate was similarly analyzed for comparison. The components were visualized with either 2',7'-dichlorofluoresceine or sulfuric acid-dichromate charring method.

The thin-layer chromatographically isolated fractions as well as total hydrogenolyzate were analyzed by a combination of gas-liquid chromatography and mass spectrometry.

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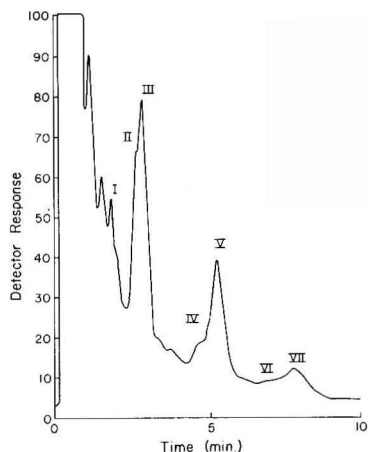


Figure 1. Gas-liquid chromatogram of trimethylsilyl ethers of the hydrogenolysis products of sewage sludge

Coiled glass column (147 cm \times 0.30 cm o.d.) packed with 3% OV-1 on 80-100 mesh Gas-Chrom Q at 235°C, and 60 ml/min carrier gas He were used

try as trimethylsilyl ethers prepared by heating the sample with *N,O*-bis(trimethylsilyl)acetamide for 20 min at 90°C. A Varian Aerograph Model 328 gas chromatograph attached to Perkin-Elmer Hitachi RMU6D mass spectrometer with a Bieman separator interphase was used. Other experimental conditions are described under the appropriate figures.

Results and Discussion

The lipid products obtained by exhaustive hydrogenolysis of the solvent-extracted sewage sludge amounted to 6-14% of the sludge as determined gravimetrically. Since the organic matter was about 50% of the sludge, the lipid material solubilized by hydrogenolysis represents 12-28% of the organic matter in the sludge. Thin-layer chromatographic analysis of the waxy material showed that the products from sludge were very similar to those from cutin. The components of the sludge product had R_f values identical to those of fatty alcohol, alkane diol, hexadecane triol, octadecane triol, and alkane tetraol fractions of cutin (Walton and Kolattukudy, 1972). This distribution of components is very typical of cutin. Although there were some nonpolar unidentified compo-

nents, we concentrated our efforts on determining the structures of the polar components so that the presence of cutin in the sludge could be proved.

Gas-liquid chromatograms of trimethylsilyl ethers of the total hydrogenolysate of sludge is shown in Figure 1.

The mass spectrum of component VII (figure 2) showed that this component was octadecane-1,9,10,18-tetraol. It showed a very weak molecular ion at m/e 606 and fragment ions at m/e 591, 516, and 501 corresponding to $M^+ - CH_3$, $M^+ - (CH_3)_3SiOH$ and $M^+ - CH_3 - (CH_3)_3SiOH$, respectively. The major peak in the high mass region was at m/e 303 which corresponds to the fragment obtained by cleavage between the two adjacent carbon atoms carrying the trimethylsilyl ether function. The weak ion expected from the cleavage of the other bond α to the in-chain substituent was found at m/e 405. Loss of trimethylsilyl from the two α -cleavage ions was observed at m/e 213 [$303 - (CH_3)_3SiOH$] and at m/e 315 [$405 - (CH_3)_3SiOH$]. These ions together with the expected ions at the low mass range showed that component VII was 1,9,10,18-tetrahydroxyoctadecane. In a similar manner, component VI was identified to be 1,9,10,18-tetrahydroxyoctadecene. In this case the fragmentation pattern was slightly different because of the unsaturation as previously observed in the case of a similar component isolated from plant cutin (Walton and Kolattukudy, 1972).

The mass spectrum of component V had a weak molecular ion at m/e 518 (Figure 3). The major ions at the high mass region showed loss of CH_3 (m/e 503, trimethylsilyl alcohol (m/e 428) and both (m/e 413). The formation of these ions is consistent with our identification of this component as 1,9,18-trihydroxyoctadecane. Intense ions at 303 and 317 representing α -cleavage on either side of the trimethylsilyl ether function together with the expected ions at the lower mass region confirmed the identification. To determine whether the octadecane triol identified in the hydrogenolysate of sludge originated from 18-hydroxy-9,10-epoxyoctadecanoic acid or 9 and/or 10,18-dihydroxyoctadecanoic acid, the sludge was hydrogenolyzed with $LiAlD_4$ and the octadecane triol fraction obtained from this treatment subjected to mass spectrometry. During deuterolysis two deuterium atoms would be incorporated into the carboxyl carbon, and one deuterium into one of the carbons involved in the oxirane ring of the epoxy acid. Therefore, α -cleavage of the trimethylsilyl ether of the resulting triol should give ions containing one deuterium and three deuterium atoms in addition to the ions with two deuterium atoms. The spectrum of the octadecane triol obtained by deuterolysis of sludge contained intense ions at m/e 318 and m/e 320 showing that cutin in sludge

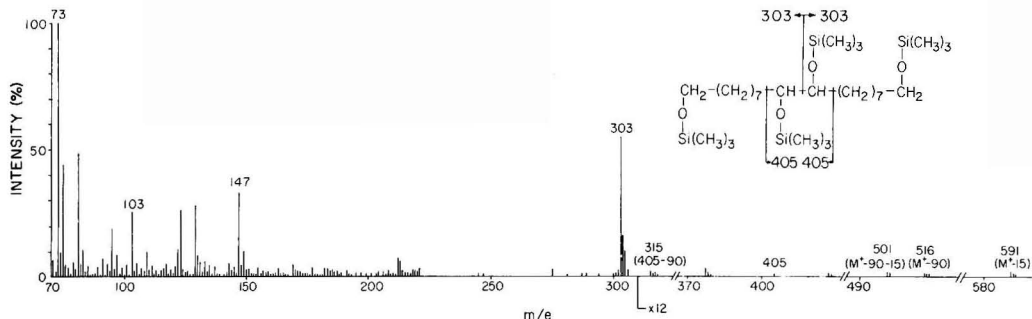


Figure 2. Mass spectrum of component VII shown in Figure 1

Spectrum was recorded at the top of the peak with 70-eV ionizing voltage

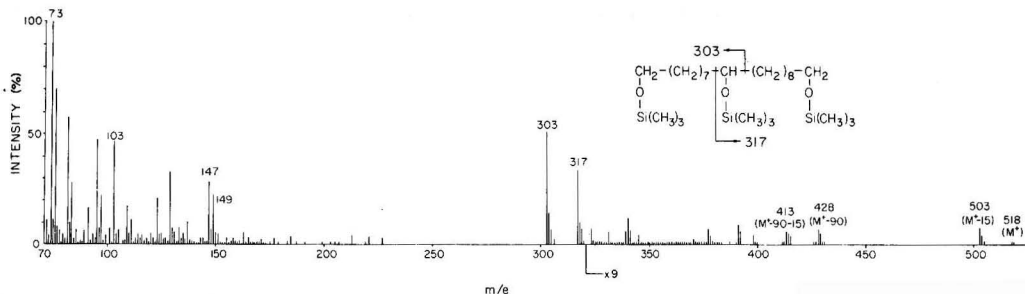


Figure 3. Mass spectrum of component V of Figure 1

Spectrum was recorded as in Figure 2

did indeed contain 18-hydroxy-9,10-epoxyoctadecanoic acid, recently identified as a major component of many plant cutins (Breskorn and Boss, 1964; Kolattukudy et al. 1971).

Component IV, although not completely resolved from component V, showed a retention time identical to that of 1,9,18-trihydroxyoctadecene. The mass spectrum of this component showed the expected molecular ion at m/e 516 and the ions formed by the loss of CH_3 (m/e 501), trimethylsilanol (m/e 426) and both (m/e 411). In the α -cleavage region the pattern was different from that of the saturated counterpart in that the ion at m/e 317 was very intense while ions at m/e 301, 303, and 315 were weak. This pattern and the relative intensities of these α -cleavage ions are identical to those obtained with the triol derived from 18-hydroxy-9,10-epoxyoctadecenoic acid of plant cutin (Walton and Kolattukudy, 1972). Therefore, it is concluded that component IV originated from 18-hydroxy-9,10-epoxyoctadecenoic acid of cutin present in the sludge.

Component III had a retention time identical to that of 1,7,16-trihydroxyhexadecane isolated from plant cutins. The mass spectrum of this component showed a weak molecular ion at m/e 490 and ions formed by the loss of a CH_3 (m/e 475), trimethylsilanol (m/e 400) and both m/e 385) as in the case of the triol of plant cutin previously reported (Walton and Kolattukudy, 1972). However, unlike the spectrum previously presented, in the α -cleavage region of the spectrum, intense ions were observed at m/e 275, 289, 303, and 317; all four ions had approximately equal intensity (Figure 4). This pattern shows that com-

ponent III is a 1:1 mixture of 1,7,16-trihydroxyhexadecane and 1,8,16-trihydroxyhexadecane. Although 10,16-dihydroxypalmitic acid had been considered to be the major dihydroxy C_{16} acid of plant cutins, recent work indicated that in some plants 9,16-dihydroxy acid or other positional isomers predominate (Holloway and Deas, 1971; Walton and Kolattukudy, 1972). Since cutin in the sludge represents many plant species, our findings indicate that positional isomers of the dihydroxyhexadecanoic acid are of widespread occurrence.

Component II showed a retention time identical to that of 1,18-dihydroxyoctadecene previously isolated from plant cutin. The mass spectrum showed a rather prominent molecular ion at m/e 428 and a significant ion at m/e 413 indicating loss of CH_3 group. Ions at m/e 338 and 323 indicating loss of trimethylsilanol and methyl + trimethylsilanol were observed. This pattern is quite typical of unsaturated diol (Walton and Kolattukudy, 1972). Confirming our identification, a major doubly charged ion was observed at m/e 199 accompanied by an ion at m/e 199.5 which shows that component II is 1,18-dihydroxyoctadecene (Figure 5). Very little saturated counterpart could be found in the sludge hydrogenolyzate. This finding is reminiscent of cutin from plants such as apple and pear where the major C_{18} diol was the unsaturated one. Component I was identified in a manner similar to that described above as 1,16-dihydroxyhexadecane. Smaller amounts of C_{16} and C_{18} alcohols were also observed.

The results described in this paper show that hydrogenolyzates of sludge contain the components characteristic of cutin. The possibility that the compounds observed

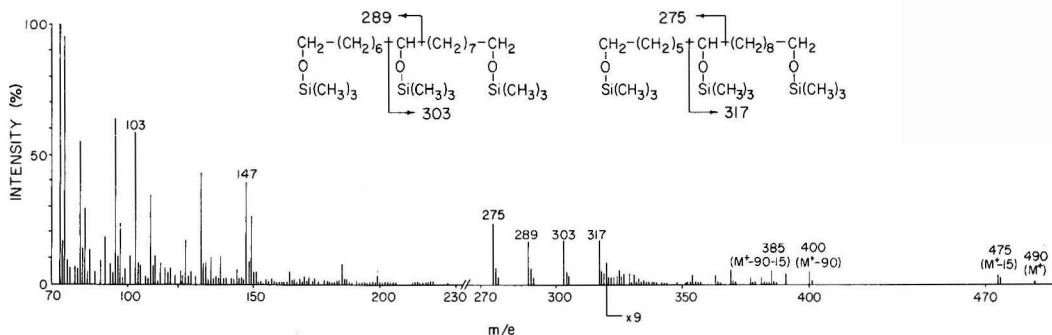


Figure 4. Mass spectrum of component III of Figure 1

Spectrum was recorded as in Figure 2

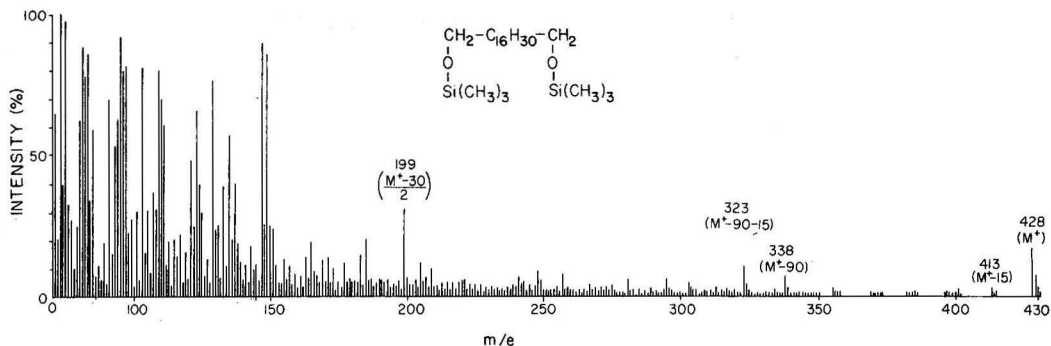


Figure 5. Mass spectrum of component II of Figure 1

Spectrum was recorded as in Figure 2

originated from a source other than cutin is highly unlikely because the structure and composition of the components are unique to cutin. The sludge used here came from typical domestic sewage waste and did not contain any industrial waste. Therefore, our results suggest that the cutin may represent a significant component of the usual sludge obtained from any sewage treatment plant. The amount of cutin found in the several samples of sludge collected at different times of the year, ranged from 12 to 28% of the organic matter. Although we have not made extensive surveys regarding the quantitative variations, our results clearly show that sludge from typical domestic sewage waste contains substantial amounts of the hydroxy fatty acid polymer, cutin. Since cutin is an insoluble polymer it would be difficult to identify it and measure it without an effective depolymerization method such as the newly developed technique used in this study.

We have obtained bacteria (Hankin and Kolattukudy, 1971) and fungi (Purdy and Kolattukudy, 1972) that can grow on cutin as the sole source of carbon. The fungi grow rather rapidly and produce stable extracellular enzymes that hydrolyze cutin. These fungi also grow on the insoluble residue obtained from sewage sludge after thorough solvent extractions as the sole source of carbon (Purdy and Kolattukudy, 1972). The observations that cutin constitutes about one fourth of the organic matter of sludge, that the hydrolytic enzymes excreted by the organisms are stable, and that the hydroxy acids released are unique and potentially useful raise the possibility that such organisms or the extracellular enzymes can be used to produce useful products from sewage sludge.

Acknowledgment

We thank Linda Brown for technical assistance and James Brown for the sludge samples.

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Received for review November 10, 1972. Accepted April 5, 1973. Supported in part by a grant, GB 23081, from National Science Foundation. College of Agriculture Research Center Scientific Paper No. 3861, Project 3001.

Respirable Dust Content in Ambient Air

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■ The respirable dust content in the ambient air at a single near-urban location was determined by using a high-volume sampling technique and a cyclone separator to simulate the filtering action of the upper respiratory tract. The cyclone's performance curve for unit density spheres closely matched an existing model for the filtering action of the nasal-pharynx and tracheo-bronchial regions. The differences between this model and other definitions of respirable dust were noted. The high-volume samplers were housed in converted light standards which allowed sampling at a height of 13 ft. This represented a departure from the normal cabinet-type high-volume configuration. The experimentally determined ratio of the respirable dust weight to the total suspended particulate weight followed a normal distribution curve with a linear correlation coefficient of 0.989 and an arithmetic average ratio of 0.56. Thus, on the average, approximately half of the suspended particulate mass at the sampling location used in this study was respirable.

The suspended particulate level in the ambient air is monitored extensively using the high-volume or spot sampler techniques. These methods, however, have not provided a measure of the respirable dust content since they do not differentiate between the smaller respirable and the larger nonrespirable particulates.

In this study a cyclone separator was used, in conjunction with high-volume samplers, to differentiate between respirable and nonrespirable particulates in the air. A new configuration was employed to obtain samples at a lower level (13 ft above ground) than usually used for high-volume sampling. The samplers were installed in modified light standards, one of which was also equipped with the cyclone separator.

Respirable dust is an important, but often ignored, air pollutant. In the determination of air quality and in routine air-monitoring measurements, for example, the total suspended particulate content has been considered a sufficient measure of particulate levels. Because the respirable portion is obviously fundamental if health effects are being considered, this study has been undertaken to relate the respirable to the total dust content of the atmosphere and to evaluate the utility of the sampling technique.

Also, it is felt that the respirable dust content should be examined now in anticipation of a curious dilemma which may arise in the approaching days of tighter air pollution controls. Since particulate emissions control equipment generally is more effective in removing larger, heavier particulates, future measurements may indicate the total suspended particulate levels are, indeed, being reduced because of better control while the amount of respirable particulates may be on the increase. Because of this anomaly, an air pollution control strategist of the future could become complacent with the stabilized, or slowly decreasing, suspended particulate levels while, in actuality, his region of control is becoming increasingly unhealthy since respirable levels are increasing.

Respirable Dust—Its Meaning

Generally, the term respirable dust is applied to particulate matter which can be deposited in the *lung* to a significant extent. It appears there has been overwhelming acceptance of this broad definition among health hygienists and governmental agencies.

The principal difficulties involved in refining the definition of respirable dust arise because the actual deposition or retention characteristics of the respiratory system are extremely difficult to evaluate quantitatively or statistically and because it is often difficult to determine whether a deposition rate is significant. To be more precise, the above definition could be altered to include deposition in the complete respiratory tract, although, for example, deposition of extremely large particles in the nasal regions is generally ignored in respiratory studies.

The general subject of respirable dust sampling has been extensively reviewed recently by Lippmann (1970) to provide supplementary information to the "Guide for Respirable Mass Sampling," a publication prepared by the American Industrial Hygiene Association (1970). Concerning dust deposition, clearance, and the various models of the respiratory system, Lippmann concludes: "... that the data are far from consistent and that the available models are at best crude approximations. Furthermore, as recent studies have demonstrated, there are very large variations in both regional deposition efficiencies and clearance rates among normal populations." Lippmann's critical remarks indicate the need for further exacting work in this difficult area of study.

Model of Dust Deposition in Respiratory Tract by Task Group on Lung Dynamics

The definition or modeling of dust deposition in the respiratory tract has been attempted by several interested investigators or agencies. Recently the U.S. Department of Health, Education and Welfare (HEW) (1969) presented a review of particulate interactions with the respiratory system and chose the deposition and retention models of the Task Group on Lung Dynamics of the International Radiological Protection Commission (1966) as being most important when considering air pollution problems.

The Task Group recommends that the respiratory tract model should consist of three compartments, the nasopharynx (N-P), trachea and bronchial tree (T-B), and pulmonary region (P).

The pulmonary region was regarded as "the functional area (exchange space) of the lungs." Only nose breathing was included in the model.

The Task Group utilized the data and models of several investigators to construct their model and computational procedure. The final result can be considered to be the most complete, overall model of particulate deposition and retention available, although the criticisms of Lippmann (1970), mentioned previously, apply to the Task Group model as well as to the lesser models which have been reviewed by the U.S. Department of HEW (1969) and Lippmann.

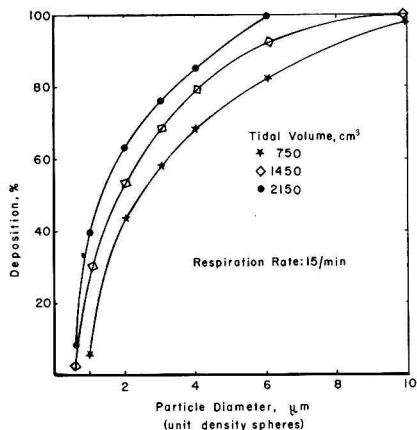


Figure 1. Deposition in N-P and T-B regions from task group model

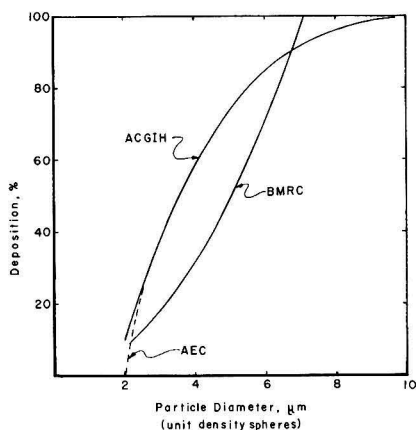


Figure 2. Recommended performance curves for respirable dust samplers

The total deposition of unit density spheres in the N-P and T-B regions is shown in Figure 1 for three tidal volumes and a respiration rate of 15/min. The data correspond to the Task Group's Table I. The 750-cm³ volume corresponds to a mild to moderately active state of energy expenditure. According to the respirable dust definition stated previously, any particulates not deposited in the N-P or T-B regions can be considered respirable since they will enter the lung.

Recommended Performance Curves for Respirable Dust Samplers

Three performance curves currently of interest in the literature, the American Conference of Governmental Industrial Hygienists (ACGIH), the British Medical Research Council (BMRC), and the Los Alamos or Atomic Energy Commission (AEC) curves have been reviewed by the American Industrial Hygiene Association (AIHA) (1970) and Lippmann (1970) (Figure 2). The AIHA recommends either the ACGIH or the BMRC curves as performance criteria for respirable dust samplers. The differences between the BMRC and the other curves occur because the BMRC curve is based on the theoretical performance of a horizontal elutriator while the other curves are based, to a close approximation, on the early lung deposition data of Brown et al. (1950).

Performance of UOP Design 2 Cyclone

The performance of the UOP cyclone used in this study was evaluated by Dennis et al. (1952) for quartz, Al₂O₃, and Fe dusts having specific gravities of 2.65, 4, and 7.86, respectively. These data can be scaled to predict performance for unit density particulates using the classical performance curve for cyclones as given by Lapple (1950) and Loeffler (1970). For this case:

$$\eta \sim d(\rho)^{1/2} \quad (1)$$

where η is collection efficiency, d is particle size, and ρ is particle density.

The resulting predictions of performance are shown in Figure 3 for unit density particles. The curves predicted from the Al₂O₃ and Fe dust data are quite similar while the quartz curve is consistently to the right of the others.

The cause of this difference is unknown, although particle shape may contribute. For example, consider that the Al₂O₃ and Fe particles were spheres (shape factor $\phi = 1$)

Table I. Statistical Parameters of Data for Regular and Respirable High-Volume Tests

	Linear correlation coefficient		Normal distribution		"F" values for sets I and II	
	Normal	Log-normal	Arith. mean	Arith. std dev	Exptl	95% confidence limit
Regular						
Set I ^a	0.982	0.981	72.3	23.8		
II	0.929	0.963	73.1	24.7		
I & II	0.971	0.985	73.7	24.2	1.05	1.97
Respirable						
Set I	0.960	0.986	40.9	16.4		
II	0.976	0.973	40.2	13.1		
I & II	0.971	0.991	41.4	15.6	1.75	2.19
Ratio Respirable/Regular						
Set I	0.973	0.935	0.561	0.099		
II	0.971	0.982	0.546	0.108		
I & II	0.989	0.967	0.559	0.101	1.02	2.19

^a Set I consists of 33, continuous 24-hr tests. Set II consists of 17, 24-hour tests, obtained by operating during three consecutive 8-hr intervals. Set I and II is combined data of Sets I and II.

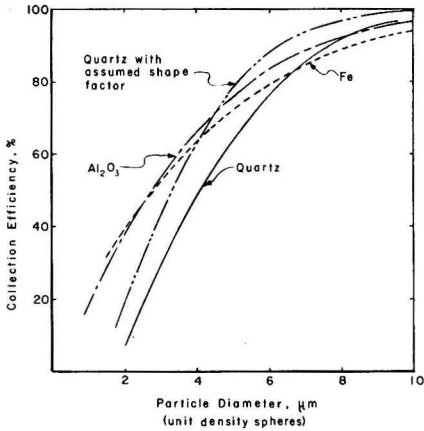


Figure 3. Predicted performance curves for UOP design 2 cyclone. Original calibrations made with Fe, Al₂O₃, and quartz by Dennis et al. (1952)

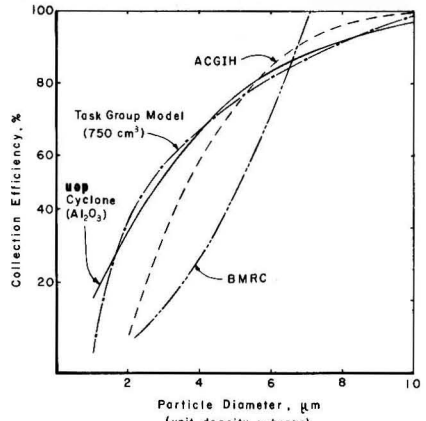


Figure 4. Comparison of various performance curves

and that the quartz particles were similar in shape to sand. When an average ϕ of 0.75 for sand is used, as tabulated by Drew et al. (1950), the quartz data can be scaled using the relationship:

$$\eta \sim d\phi(\rho)^{1/2} \quad (2)$$

The result of this hypothesis is shown in Figure 3. Better agreement with the Al₂O₃ and Fe curves is apparent.

As noted by the American Industrial Hygiene Association (1970), calibration curves for cyclones can be in error if polydispersed particles are used for calibration purposes, as was done by Dennis et al. (1952) for the UOP cyclone. The Association (1970) has compiled a list of cyclones which, according to the most reliable data, conform to the ACGIH or BMRC curves. Unfortunately, none of the recommended cyclones will operate properly at the high flow rates normally used with high-volume samplers (e.g., 40 ft³/min). Rather, they operate at flow rates at least an order of magnitude lower than required.

Since the UOP cyclone has not been recalibrated with monodisperse aerosols, the original calibration curves of Dennis et al. (1952) must suffice at the present time.

Comparison Between Task Group Model, Recommended Performance Curves, and UOP Cyclone

In Figure 4, the combined deposition in the N-P and T-B regions, as predicted by the Task Group Model, is shown for a tidal volume of 750 cm³. Also shown for comparison are the recommended ACGIH and BMRC curves for respirable dust samplers and a predicted performance curve, for unit density spheres, of the UOP cyclone. This curve is identical to the Al₂O₃ curve of Figure 3.

The UOP cyclone curve, based on the Al₂O₃ calibration data, is in good agreement with the Task Group curve while the recommended performance curves fall to the right of the Task Group and cyclone curves.

At this point the relevance of the Task Group Model or the recommended performance curves cannot be judged, although the Task Group model represents the most recent and complete attempt at modeling the behavior of the respiratory system. Because of this uncertainty, the choice of the UOP cyclone for these studies appears to be a reasonable one at the present time.

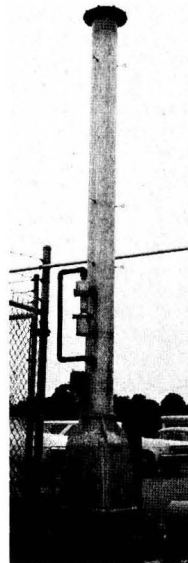


Figure 5. High-volume sampler equipped with cyclone separator

Apparatus

The State of New Jersey has been recently developing alternative configurations for high-volume samplers. One of these, which consists of an aluminum light standard and base, was equipped with a modified UOP, Design 2 cyclone (UOP Air Correction Division, Darien, Conn.) to remove the larger, nonrespirable particulates from the air stream of the high-volume unit. An identical light-standard sampler was used to sample the total suspended particulates. Both samplers were equipped with the General Metal Works, Cleves, Ohio, Model 2000H high-volume unit. The samplers were located in a near-urban location approximately five miles north of Trenton, N.J.

In-house studies have revealed no statistical difference between the data obtained with the box-type high-volume sampler and the light-standard samplers employed in this study.

The light-standard configuration, with the cyclone, is shown in Figure 5. A cone is fitted inside the pole to direct the air sample into the cyclone. The intake height of the light standard is 13 ft above ground.

The original cyclone-collecting chamber, a mason jar, was replaced by a cap and cylinder arrangement, as shown at the base of the cyclone in Figure 5 and schematically in Figure 6. The cylinder is securely interfaced with a quick disconnect clamp and Teflon gasket. In addition, a styrofoam cup was used in the tests in an attempt to weigh the particulates removed from the sample stream. The cup was spring-loaded from below to assure a good seal with the cap shown in Figure 6.

Test Procedure

The samples were collected over a 24-hr interval, which was either continuous or consisted of three, 8-hr daytime intervals. The latter scheme was undertaken to avoid the collection of insects when the material deposited by the cyclone was being collected in a styrofoam cup for weighing. (In normal high-volume sampling, insects appearing on the filter paper can be readily removed by blowing gently on the filter paper. In the cyclone sampler, however, the insects are often dismembered and difficult to remove.)

The high-volume filters (Gelman Type A glass fiber) were weighed in a room having a relative humidity less than 50%, after a suitable equilibration time. The styrofoam cups were allowed to equilibrate in this room for 24 hr before each weighing. The cups were also evaluated for water retention and were unaffected by exposure to high humidity. Direct water contact did increase their weight, but it returned to normal after a reasonable drying period in the weighing room atmosphere.

The sampling flow rate was set approximately at 40 cfm and monitored continuously with a transducer and orifice plate mounted on the outlet of the high-volume sampler. An average flow rate was determined visually from the transducer's stripchart for use in the calculation of total volumetric flow. The stripchart readings never varied more than 2 cfm since the filters never were heavily covered with particulate matter. As noted by Cohen (1973), high-volume samplers are usually operated between 40 and 60 cfm. Cohen demonstrates that high-volume samplers are 3.8% more efficient at 40 than at 60 cfm, presumably because of less particulate penetration at the lower flow rate.

Results and Discussion

The experimental data consist of regular and respirable high-volume measurements and a smaller number of measurements of the coarse fraction removed by the cyclone sampler.

As noted previously, samples were collected either continuously for 24 hr, or for three, 8-hr intervals occurring on consecutive working days and during daylight hours. The latter technique was adopted to avoid the collection of night-flying insects in the cyclone.

A total of 33 sets of the continuous, 24-hr samples were obtained while 17 sets of samples were obtained using the three consecutive 8-hr interval sampling periods. Fourteen measurements of the coarse fraction were also obtained during the consecutive 8-hr interval sampling periods.

Both the regular and respirable high-volume data are distributed normally, or log-normally, to a reasonable approximation. This is evident from the linear correlation coefficients tabulated in Table I, for the normal and log-normal distribution equations

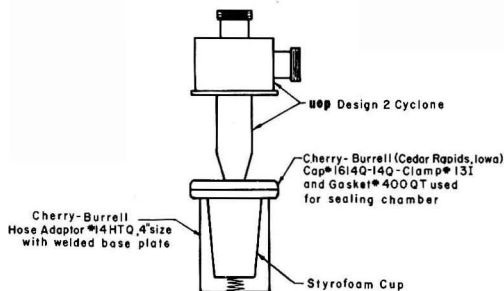


Figure 6. Cyclone with modified collecting chamber

$$c = m + sZ \quad (3)$$

$$\ln c = g + dZ \quad (4)$$

where c is pollution measurement; m , arithmetic mean; s , arithmetic standard deviation; Z , determined from Equation 5; g , logarithmic mean; and d , logarithmic standard deviation. The Z value for each data point, c , is determined by inverting the normal probability integral

$$\int_{-\infty}^Z \frac{e^{-\lambda^2/2} d\lambda}{(2\pi)^{1/2}} = P(Z) \quad (5)$$

where $P(Z)$ is the fractional rank of the data point, c , in the array of all c values.

Similar correlations have been demonstrated so consistently for pollution measurements that Larsen (1971) has proposed extensive modeling techniques for relating air quality measurements to air quality standards using a variety of predictive procedures.

To combine the continuous 24-hr data and the consecutive, 8-hr data, "F" tests were made on the data to demonstrate their similarity. As indicated in Table I, the data have the same sample means at the 95% confidence level.

The normal and log-normal correlation coefficients for the combined data (a total of 50 data sets) are given in Table I. Again, the normal or log-normal correlations are evident for both the regular and respirable data.

It remains to correlate the respirable dust levels with the regular high-volume readings. This was done by using the ratio, respirable $\mu\text{g}/\text{m}^3$ to regular high-volume $\mu\text{g}/\text{m}^3$, for each data set.

The statistical parameters for the ratio data are given in Table I, and alternate data points are shown in Figure 7. The ratio, respirable $\mu\text{g}/\text{m}^3$ to regular $\mu\text{g}/\text{m}^3$, for the combined data is well approximated by a normal distribution, having a linear correlation coefficient of 0.989, and an arithmetic mean of 0.559. The correlation line is included in Figure 7.

Measurements of the particulate weight removed by the cyclone were made for 14 of the daylight-hour type samples. The tests were made by determining the weight increase of a styrofoam cup which had been placed in the collecting cylinder of the cyclone.

In all cases, the measured weight increase of the cups was less than the difference between the regular and the respirable high-volume filter weights. The weight increases were, on the average, 68% less than the expected values. This apparent weight loss most probably occurred because of particle deposition on the walls of the cyclone. Since expected weight increases of the cups were of the order of 50 mg, such losses appear reasonable.

The high-volume sampler, with the cyclone attached, was relatively easy to use and maintain. Occasional cleaning of the cyclone and related piping was felt necessary to

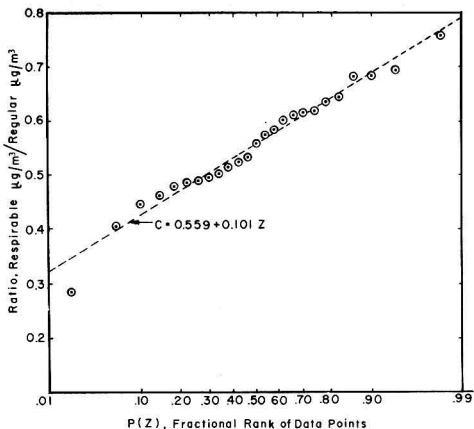


Figure 7. Normal probability representation of relationship between respirable and regular high-volume measurements at near-urban location

prevent re-entrainment of deposited material. On rainy days, the cyclone had a tendency to collect water and the associated high-volume filters appeared to be more water soaked than those mounted in the regular high-volume stack.

Summary

The respirable dust content in the ambient air at a near-urban location has been measured using a high-volume sampler equipped with a cyclone separator which removes the larger particulates. The cyclone has a performance curve for unit density spheres which closely matches a well-known model for the filtering action of the upper respiratory tract (the nasal-pharynx and tracheo-bronchial sections). These curves, however, differ somewhat from those recommended by various occupational health groups as being representative of such filtering action.

Each high-volume sampler was located in a unit which consisted primarily of a light-standard base and pole. The device allowed collection of ambient air at a height of 13 ft.

The respirable dust content, as expressed by the ratio of the respirable dust to the total suspended particulate weight, was normally distributed for this series of tests at a single sampling location. The data had a linear correlation coefficient of 0.989 with the normal distribution function. The average ratio was 0.56. Thus, at the sampling location used in this study, about half of the dust in the sampled ambient air was respirable, according to the model chosen to describe the filtering action of the upper respiratory tract.

These tests demonstrated the utility of the cyclone separator when used with the high-volume apparatus. Field testing at several locations should be made to evaluate the utility of the sampling method and to test the resulting data for correlations such as noted above.

The utilization of such a monitoring technique appears essential to assure that improved technological controls on pollution emissions are effective on smaller respirable particulates, as well as on the larger nonrespirable particles. Further studies should be made to refine the definition of respirable dust and to define sampling techniques which accurately measure the same.

While the results indicate that the "smaller" and "larger" particle components in the air correlate with each other, they are insufficient in themselves to test regularities reported in the particle size distribution of suspended particulates by Junge (1963), Cartwright et al. (1956), Pasceri and Friedlander (1965), and Clark and Whitby (1967).

Acknowledgment

The author is indebted to William Munroe, New Jersey Bureau of Air Pollution Control, for suggesting this study.

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Received for review August 10, 1972. Accepted February 22, 1973.

Benzene and Toluene Distribution in Toronto Atmosphere

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■ This study is novel in that an attempt has been made to obtain instantaneous maps of individual hydrocarbon concentrations (benzene, toluene) by sampling many (up to 12) urban locations simultaneously. Over 1000 air samples were analyzed for nonmethane hydrocarbons during the summer of 1971 in Toronto. Concentrations varied by a factor of 40 or more between sampling locations. Benzene and toluene were identified, and variations of their concentration with time were compared with total hydrocarbon concentration in the same location. Overall average concentrations of benzene and toluene were 13 and 30 ppb, respectively. The overall toluene-benzene ratio was 2.4:1. The study of concentration variations with distance as well as the study of concentration variation with time revealed distinct patterns related to the automobile traffic. Comparison of the time variable patterns for Toronto with those of other North American cities showed many similarities.

Many recent studies of hydrocarbons in air have been performed. Some authors studied specific organic substances—e.g., Stephens and Bursleson (1972), Gordon et al. (1968), Lonneman et al. (1968), Bellar and Sigsby (1970), and Dravnieks and Witfield (1971). Wide ranges of organic pollutants have been described by some other studies—e.g., Cavanagh et al. (1969), Altschuller et al. (1971), Williams (1965), and Grob and Grob (1971). Although some of these (Gordon et al. 1968, Cavanagh et al. 1969, and Altschuller et al. 1971) have reported variation with time very few have attempted to map instantaneous urban hydrocarbon concentrations. None of these studies relate to Toronto.

Experimental

Sampling. One-liter glass sampling bottles were baked in an oven at 120°C prior to every sampling (to desorb any residuals and moisture). At the sampling location, a bottle was unsealed, a bulb aspirator was attached to one of its two outlets, and several volumes of the ambient air were passed through within 3 min. The samples were taken 1 meter above the ground in duplicates. After the bottles were resealed, they were stored in the dark. The samples were analyzed up to 4 hr after the collection.

Trapping and Analysis. In the laboratory, 50 ml of the sample were transferred from the sampling bottle by an oven-baked gas-tight glass syringe. A modified method for trapping described originally by Bellar et al. (1963) was used. The 1/8-in. i.d. freeze-out trap was packed 8 in. with 20% Dow-Corning SF #200 on 60/80 mesh Columpak. A Dry Ice-acetone bath was used for cooling and a 100°C silicone oil for releasing the sample by heating. Liquid gases were not used as coolants because light hydrocarbons were not analyzed. Oxygen and nitrogen condensed in the trap would snuff the detector flame if no purging of the trap were to be used, and condensed oxygen might react with some trapped substances. A Carle six-port sampling valve was used on the dual-column Carle 9000 chromatograph with hydrogen flame ionization detector. A pair of 6-ft 1/8-in. stainless steel columns was packed with 8% SF 96 on

60/80 Chrom. W. Operating conditions were 20 ml/min N₂, 20 ml/min H₂, and 600 ml/min of air at 50°C. The cryogenic trap was flushed with nitrogen after each analysis for 10 min at 100°C.

Trap Efficiency. Trap efficiency was checked in several ways by methods similar to those described by Bellar et al. (1963). Different volumes of standard samples as well as actual air samples were injected and a linear relationship between concentration and volume was found as expected. The linear response of our trapping system which was essential for the quantitative evaluation was not observed for organic materials of C₅ or lower. This behavior was due to the type of the trap packing and also due to the relatively high (-79°C) temperature of the trap. Hydrocarbons of C₆ and higher as well as all aromatic compounds still responded linearly in concentration range well above that found in the atmosphere. The residuum in the cold trap after injection and before flushing with nitrogen was investigated. The injection was complete for all compounds studied at concentration levels investigated. No attempt was made to improve the trap efficiency since its nonlinear response was outside our range of interest.

Peak Identification and Calibration. Some of the 28 peaks obtained were tentatively identified by the combination of a comparison of their retention times on three different columns and by addition of individual standard substances to the original samples. Calibration procedure and its reproducibility were assessed by carrying out periodical tests and measuring the response of the standard concentration mixtures for both compounds. Handling of the standard mixtures was as close as possible to the actual procedure used for the air samples.

All concentrations in this study are in parts per billion (ppb) by volume unless otherwise indicated.

Precision. To establish the precision of the method, atmospheric air was sampled in six sampling bottles and each bottle was analyzed twice. The benzene concentration was 14.3 ± 2.5 ppb; toluene was 25.0 ± 3.6 ppb. These average deviations for 12 analyses are therefore 18.5 and 14.3%, respectively. In practice each analysis was repeated four times. For this situation the two-sided test of hypothesis with coefficient 0.90 yielded the confidence limit ±2.5 ppb from the mean 13.4 ppb which corresponded to 19% error for benzene. Similarly for toluene the confidence limit was ±4.1 ppb from the mean 25.0 ppb which corresponded to 17% error.

Criteria for Compound Selection. Since the number of chemical individuals detected in the atmosphere is high, some criteria had to be used for the selection of the peaks to be quantitatively analyzed. Most of the recent papers dealing with hydrocarbon air pollution are preferentially interested in toxic, odorous, or smog-forming compounds.

The literature dealing with aromatic compounds is scarce (Lonneman et al., 1968; Altschuller et al., 1971) yet the information provided by analyzing these pollutants is pertinent to further studies of hydrocarbon air pollution. The ratio of concentrations of certain contaminants—e.g., toluene to benzene has been suggested as an indicator for hydrocarbon source and the history of the polluting material.

Table I. Concentration of Hydrocarbons; Contaminated-Clean Air Comparison

Peak no.	T_R^a min	Relative concentration		
		York St.	Scarborough College	Concentration ratio
1	0.96	410	6	68
2	1.13	280	6	47
3	1.20	40	U ^b	>40
4	1.63	162	11	15
5	1.76	46	2	23
6	1.97	62	2	31
7	2.37	54	7	8
8	2.75	80	2	40
9	3.10	26	U	>26
10	3.6	16	U	>16
11	3.9	10	U	>10
12	6.0	72	3	24
Total no. of peaks found ^c		28	14	

^a T_R , peak retention time. ^b U, undetected. ^c 3 p.m. August 10, 1971. Not all peaks are tabulated.

Table II. Maximum Measured and Average Concentrations of Benzene and Toluene

Location	Benzene, ppb	Toluene, ppb
Maximum Measured Values		
Toronto, 1971 ^a	98	188
Los Angeles, 1966 ^b	57	129
Average Values		
Toronto, 1971 ^c	13	30
Los Angeles, 1966 ^b	15	37

^a Location no. 16. ^b Lonneman et al., 1968. ^c Location no. 15.

Results and Discussion

Wide Variation Comparison. To prove the capacity of the method, the air from two locations with significantly different automobile traffic volume was sampled at the same time and then analyzed. The first location (No. 16 on Figure 1) was the intersection of York and Front Streets in downtown Toronto where the traffic is heavy compared to the second location 14 miles northeast at Scarborough College, located just outside the city on an elevated plateau surrounded by vegetation.

The concentration expressed as peak height times attenuation in Table I is only a relative indicator for each individual peak. Twelve selected peaks are illustrated here. Peak No. 8 was identified as benzene (98 ppb, 2.5 ppb) and peak No. 12 as toluene (188 ppb, 8 ppb).

Twenty-fold variations as a function of time in one sampling location have been found by Williams (1965), and we have found similar results for simultaneous samples at different locations. Table I shows that variations by a factor of up to 68 can be expected for hydrocarbon air pollutants. With these large differences in concentration, to consider an error up to 25% was tolerable, permitting the trends of hourly and distance variation to be clearly distinguishable. As may be seen in Table I, the simultaneous concentration ratio of benzene at these two locations in Toronto is 40; the toluene ratio is 24.

Table II compares the maximum and the average measured concentrations of benzene and toluene in Toronto and Los Angeles. The maximum measured concentrations for Toronto are higher. In our case, however, a location with highest concentrations was intentionally sought, and the Los Angeles values were obtained five years earlier.

Even though the average concentration of benzene and toluene in downtown Toronto in 1971 is moderately lower than in Los Angeles in 1966, similarities in the order of concentrations are notable.

Time Variations. Samples were taken continuously at 1-hr intervals for nine days, including one weekend, at the end of August 1971 in downtown Toronto. The sampling site, No. 15, was chosen to coincide with the Atmospheric Environment Service's continuous sampling location 30001 at 67 College Street.

Total hydrocarbon concentrations as monitored by the government station every hour on the hour were averaged over the same time period as our benzene and toluene data. The results were plotted on Figures 2 and 3.

When time variations of benzene and toluene are compared with hourly concentration variations of total hydrocarbons averaged over the same period of nine days, the same maxima can be distinguished, although they are much less pronounced. Benzene and toluene increased

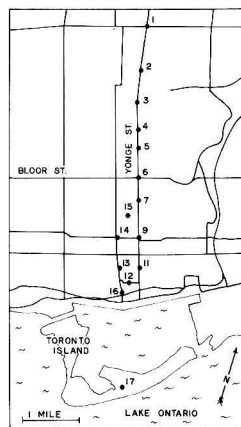


Figure 1. Map of a section of Toronto showing sampling locations and network of highways and important streets

Sampling locations are numbered points on the map

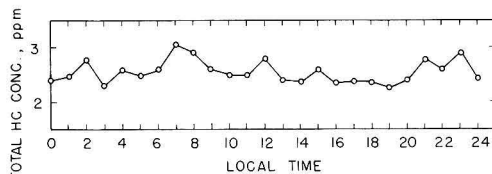


Figure 2. Total hydrocarbon concentration averaged by hour of day for nine days

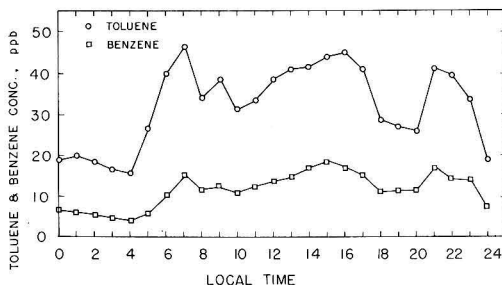


Figure 3. Toluene and benzene concentration averaged by hour of day for nine days

from their daily minimum to maximum by factors of 4.6 and 3.2, respectively, but the total hydrocarbon concentration increased by 26% only.

Our results for both benzene and toluene show three distinct maxima at 0700, 1500, and 2100 hr. These maxima were compared with the maxima of nonmethane hydrocarbons averaged by the hour of the day over several months in various U.S. cities. Maxima in Toronto are closer to those in Chicago—0700, 1600, and 1930 hr, than those in St. Louis—0700 and 1300 hr; Washington, D.C.—0700 hr; Los Angeles—0800, 1700, and 2100 hr; and Pasadena—0730 and 1700 hr. (Compare Figure 2 and Air Quality Criteria for Hydrocarbons, 1970, Figures 3-2, 3-3.)

The 7 a.m. maximum is common for five cities and is shifted to later hours in two other cities. Times of other maxima and also their intensities vary. It is suggested that the sampling location, as well as the daily activities of the urban community, contribute to the difference in traffic patterns, which in turn influence the concentration level of nonmethane hydrocarbons. It should not be forgotten, however, that seasonal changes which may exist, cannot be seen from the above data.

Toronto Island Study. For a more detailed study of concentrations at different locations, Toronto Centre Island (location no. 17) and 67 College Street (location no. 15) were compared for three days. Toronto Centre Island is a summer recreational site. The island is connected to the city by a ferry and no automobiles, except for a few maintenance vehicles, are permitted there. The number of motor boats operating in the vicinity of the island is relatively small. The concentrations on the island show consistently lower readings. The concentration ratio between these two locations varies from 1.4 to 6.3 with an average ratio over all measurements of 3.6 for benzene and 2.6 for toluene. There is little doubt that both aromatics detected at the Island location were supplied by wind transport from the city.

Variation with Location Study. For the study of variations with location at a particular time, the Toronto subway stations were chosen as the sampling locations. The North-South branch of the subway connects the south, downtown business section with the north, predominantly residential area. The downtown section is adjacent to Yonge Street and extends south of Bloor Street. The subway itself probably does not contribute to hydrocarbon pollution. Samples were collected simultaneously at up to 12 different locations.

From the map of sampling locations (Figure 1) and the individual results (Figures 4 and 5), two distinct patterns can be observed: one on weekdays and another on the weekend. The benzene and toluene concentrations increased in the downtown direction five times and six times, respectively, on one particular measurement on a weekday. The pattern of pollution for both weekday results shows that although the absolute levels differ from day to day, the general trend remains unchanged.

This study, as well as the ratio of toluene to benzene discussed later, leaves little doubt that the contamination of the atmosphere is closely linked to automotive transportation in that area. The map (Figure 1) shows an increased concentration of highways in the southernmost part of downtown Toronto. Also the presence of a railway station there with its diesel engine-driven trains should be mentioned.

On Sunday morning, when the traffic levels are very low, all downtown locations remained on or below the lowest weekday level for both aromatics. The only high result was Bloor Street where the early morning traffic was observed to be the highest of all locations sampled.

From Figures 1, 4, and 5, it can also be seen that the

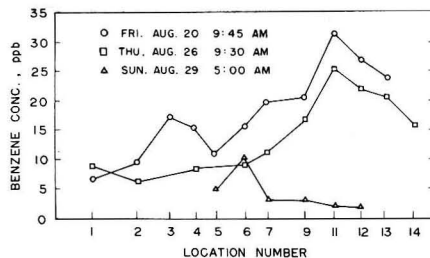


Figure 4. Benzene concentration variation with distance in Toronto at three different times

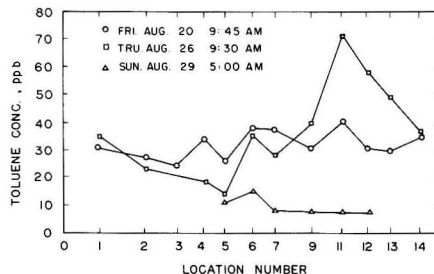


Figure 5. Toluene concentration variations with distance in Toronto at three different times

location no. 16, arbitrarily used for the detection of the high hydrocarbon concentration during weekdays, was a good choice.

Toluene-to-Benzene-Ratio

The concentration of various automobile exhaust components has been measured many times by numerous investigators. Since the ratio of exhaust components can be readily calculated, Lonneman et al. (1968) suggested a comparison of this toluene-benzene ratio with the one in atmospheric samples. The resulting agreement or difference between these ratios would indicate degree of contribution to the air pollution by the automobile as the pollution source.

Toluene-benzene ratios obtained from analyses of automobile exhaust emissions from groups of various model automobiles (Bonamassa and Wong-Woo, 1966) and atmospheric samples in Los Angeles (Lonneman et al., 1968) were compared with those from our study. In the automotive study toluene-benzene ratios ranged from 1:1 to 2.8:1 and the overall average was 1.8:1. In the Los Angeles study, the ratios ranged from 1.4:1 to 4:1; 90% of all values ranged from 1.5:1 to 3.5:1 and the overall average was 2.5:1. From our study in Toronto the overall average ratio was 2.4:1 with all values between 1.5:1 and 4:1. These results are close to those from Los Angeles.

The ratio calculated from the results of Grob and Grob (1971) in the atmosphere of Zurich gives the value 0.72:1 which is significantly different from those on the North American continent. This difference may be caused by different climate, composition of gasoline, or pollution source.

To explain the difference between the average ratio from the automobile exhaust (1.8:1) and that in Los Angeles (2.5:1), Lonneman et al. (1968) suggested that the atmosphere has a significant additional source of toluene such as solvent losses.

Figure 2 shows that both the benzene and toluene concentrations vary daily with the same pattern, linked to the traffic rush hours, which suggests a source common to both compounds. Figures 4 and 5 show that at different points in the city, the changes in concentrations of both aromatics have similar trends. Thus for these Toronto data there seems to be no support for the concept of any stationary source of toluene. The results given in this paper seem to indicate only the automobile as a major source of benzene and toluene in the Toronto atmosphere.

The reason for higher toluene-benzene ratio in the air than in the exhaust remains in doubt. Consideration of this question must include possible inapplicability of Bonomassa and Wong-Woo's results to Toronto. Physical and chemical changes may occur between emission and air sampling and therefore only direct analysis of the air can provide actual values of atmospheric concentrations of hydrocarbons because the aromatic content of gasolines and of exhaust emissions varies considerably. In fact, the relatively high toluene-benzene ratio in gasoline vapor points to the possibility of direct evaporation of gasoline as a source.

More extensive investigation of the ratio changes with time and distance are needed to clarify the discrepancy.

Although sampling by means of discrete samples taken on a time and distance grid is subject to errors of the order of 25%, these analyses for aromatic hydrocarbons are useful. They give a much more detailed trace of the concentration patterns than steady state sampling procedures at a fixed location. The data obtained show that a precision, sufficient to identify the space-time variation, can be expected. Wide variations with time or distance were found which correspond to the variations in traffic density. This is in contradiction with total hydrocarbon con-

centration results which show only slight variations with time or distance.

Acknowledgment

The authors thank Allison McGeer, Park Gee, Dennis Gousheff, Ramesh Kumar, Christopher Liu, Justin Chow, Robert Patterson, and John Musil who carried out the sampling and analysis. We are also grateful to the Department of the Environment of the Province of Ontario for their cooperation and assistance.

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Received for review August 22, 1972. Accepted February 9, 1973. The Federal Government of Canada provided the financial assistance under the Opportunities for Youth Project No. 300-793.

Metal Contamination of Urban Woody Plants

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■ During the fall, 1970, leaf and twig tissue representing the growth of the previous growing season was collected from six woody plant species throughout the city of New Haven. Sugar maple was also sampled from remote northern New Hampshire and Vermont. These tissues were analyzed for Al, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Na, Sn, Zn, and V by atomic absorption spectrophotometry. Co and Sn were not detected. V was present in only a few samples from two city species. All other metals were found in all New Haven woody plants and in the sugar maples from remote areas. Cd, Cu, and Mn were present in "normal" amounts. Al, Cr, and Ni were present in "slightly above" normal amounts. Fe, Pb, Na, and Zn were present in "above normal" amounts. The mean Pb concentrations exceeded most Pb concentrations determined for trees in areas with geologic Pb deposits or adjacent to primary highways. Washing and analysis with an electron microprobe failed to provide conclusive evidence with regard to the specific location of the Pb on or in the tissue sampled.

Metals, especially heavy metals, are phytotoxic at high concentrations. Relative to vegetation, Heggstad (1971) has listed heavy metals as one of the ten most important groups of air pollutants. Most information regarding metal toxicity and plants stems from studies involving metal ore deposits, mining, smelting, and other industrial operations or pesticide use (Antonovics et al., 1971). Roadside and urban areas are also potentially stressful environments for plants because of metal contamination (Lagerwerff and Specht, 1970; Purves and Mackenzie, 1969, 1970).

Urban air, relative to nonurban locations, may have elevated concentrations of several metals (Larsen, 1964; Morrow and Brief, 1971; Schroeder 1970). A trend of increasing metal pollution in city air has been evident in recent years (Ludwig et al., 1970; U.S. EPA, 1971), especially in the Northeast (Lazrus et al., 1970).

The initial step in evaluating the potential significance to plant health of metals introduced into the air and soil of a city is to establish the plant burden and the location of various metals on or in the plants. This study represents such an effort for six woody plant species growing in New Haven, Conn.

Materials and Methods

Plant samples were collected during September and November 1970 within the city of New Haven. This 48-km² city, with a population of approximately 150,000, had had the following geometric means for suspended particulates in $\mu\text{g}/\text{m}^3$: 1966–101, 1967–83, 1968–68, 1969–86, and 1970–93 (unbound National Air Surveillance Network data). The mean of quarterly measurements (from one sampling station) of atmospheric lead content of New Haven air was 2.60 $\mu\text{g}/\text{m}^3$ in 1970 (Connecticut State Department of Health, Hartford).

Duplicate intact branch (leaf plus twig) samples (encompassing the growth of the previous growing season) were collected from ornamental specimens located throughout the city in industrial, commercial, and residential sections. All tree samples were collected from the outer portion of the lower crown approximately 2 m above the ground. At each collection site, the horizontal distance from the tree (or shrub) base to the nearest street was determined along with the vertical height of the sample above ground. Samples were carefully collected with polyethylene gloves and placed in individual polyethylene bags. In the laboratory the samples were air dried and stored in a cold room until preparation for analysis. Species sampled in greatest numbers and included in this report are Norway maple (*Acer platanoides* L.)—64 trees, pin oak (*Quercus palustris* Muenchh.)—24 trees, sugar maple (*Acer saccharum* Marsh.)—14 trees, yew (*Taxus* spp.)—20 shrubs, eastern hemlock (*Tsuga canadensis* [L.] Carr.)—16 trees, and Norway spruce (*Picea abies* [L.] Karst.)—8 trees. To obtain "normal" values for metal content of trees growing in relatively unpolluted environments, 25 sugar maple trees growing in remote sections of northern New Hampshire and Vermont were sampled during the summer of 1971.

To distinguish external from internal tissue contamination, one sample from each duplicate collection from each plant was washed. The washing procedures were selected in accordance with criteria that have been established for washing plant tissues for trace contaminant analysis (Taylor, 1956; Weinstein, 1969). The washing techniques were varied and included the following: for pin oak and sugar maple, 30 sec of vigorous agitation in metal-free water; for Norway maple, 60 sec of vigorous agitation in 1.0% hexadecyltrimethylammonium bromide (detergent) followed by metal-free water rinse; for eastern hemlock, 60 sec of vigorous agitation in 0.1% hexadecyltrimethylammonium bromide followed by metal-free water rinse; for yew, 30 sec of vigorous agitation in 0.05% hexadecyltrimethylammonium bromide and 0.05% *N*-(hydroxyethyl)-ethylenediaminetriacetic acid (chelate) followed by metal-free water rinse; for Norway spruce, 30 sec of vigorous agitation in 0.05% hexadecyltrimethylammonium bromide and 0.05% diethylenetriaminepentaacetic acid (chelate) followed by metal-free water rinse.

Following division of some samples into leaf (needle) and twig portions, all samples were dried at 80°C and ground in a Wiley mill through a 20-mesh screen, redried at 80°C and ashed at 450°C. The ash was then dissolved in 6*N* nitric acid, and the selected metals were determined by atomic absorption spectrophotometry. Analyses were conducted for Al, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Na, Sn, Zn, and V. With the exception of Al and Sn, all of these have densities >5 and hence are classified as heavy metals (Passow et al., 1961). An air-acetylene flame was used for all metals except Al and V which required nitrous oxide-acetylene.

To determine the specific location of Pb on or in our samples, selected specimens were examined with an elec-

tron probe X-ray microanalyzer. The microprobe technique potentially permits the accurate determination of a concentration of an element in a 1–2- μ -diameter location. Leaf tissue to be examined was collected, excised, and sectioned in a cryostat (Satter et al., 1970). Specimens and standards were prepared for microprobe examination using standard procedures (Humble and Raschke, 1971; Sawhney and Zelitch, 1969; Tousimis, 1966). Unwashed leaf cross sections, 48 μ thick, of all six species were examined by this technique. Standard conditions of the microprobe were accelerating potential 15 kV, specimen current 50 na, spot diameter 2 μ , and X-ray line *M α* .

Results

Atomic Absorption. All results are expressed on a dry weight basis. Expression of the data on an ash weight basis and on an intact shoot (leaf plus twig) basis is available in the microfilm edition of this journal (Tables 2, 3, 4). Errors due to preparation and analytical procedure were minimal. Our readings were confirmed by independent analysis by outside laboratories and our equipment calibrated on known standards. There was no significant difference ($P = 0.95$) between any of the metal levels of samples subjected to the various washing procedures and unwashed samples. All data presented, unless otherwise indicated, are of washed specimens.

Co and Sn were not detected by the analytical procedure employed. If present, these metals probably exist at levels below 0.1 $\mu\text{g}/\text{g}$. V was detected in only a few sugar maple and eastern hemlock samples. In both instances the highest V concentration was 150 $\mu\text{g}/\text{g}$ and was found in the twigs.

All other metals were detected in all species sampled from New Haven and in all sugar maples examined from remote areas. Table I contains a list of the range of metal contents for all tissues sampled from trees growing in remote areas of northern New Hampshire and Vermont. Comparison with the values of Table I and values contained in the literature permitted ranking of the 10 metals detected. Cd, Cu, and Mn were considered to be present in "normal" amounts (Table II). Al, Cr, and Ni were considered to be present in "slightly above normal" amounts (Table III). Fe, Pb, Na, and Zn were considered to be present in "above normal" amounts (Table IV).

Considerable differences were noted with respect to metal contents and tree species. Species with metals present in elevated amounts relative to other species in this

Table I. Range of Metal Contents of Growth (Twigs and Leaves) of Current Growing Season of 25 Sugar Maple Growing in Remote Sections of Northern New Hampshire and Vermont^a

Metal	Dry wt basis, $\mu\text{g}/\text{g}$
Aluminum	360–702
Cadmium	0–5
Chromium	0.3–11
Cobalt	Not detected
Copper	5–17
Iron	7–144
Lead	0–20
Manganese	136–347
Nickel	0.3–21
Sodium	12–51
Tin	Not detected
Vanadium	Not detected
Zinc	19–73

^a Samples were collected during the summer of 1971 approximately 2 m above the ground from trees more than 1.5 km from the nearest road.

Table II. Woody Plants Growing in City of New Haven with "Normal" Amounts of Cadmium, Copper, and Manganese^a

Species	Total trees sampled	Average distance from nearest street, m	Tissue analyzed ^b		Dry wt basis, $\mu\text{g/g}^c$		
			Organ	Number of trees	Cadmium	Copper	Manganese
Pin oak (<i>Quercus palustris</i> Muenchh.)	24	1.4	Leaves	12	2.3 ± 0.2 ^d 1.5-3.0 ^e	11 ± 0.6 9-15	393 ± 69 163-860
			Twigs	12	2.3 ± 0.2 1.0-3.0	9 ± 0.5 6-11	145 ± 10 96-195
Sugar maple (<i>Acer saccharum</i> Marsh.)	14	1.8	Leaves	7	1.0 ± 0.1 0.5-1.5	6 ± 0.4 6-8	599 ± 176 163-1,275
			Twigs	7	0.8 ± 0.1 0.5-1.5	10 ± 0.9 7-14	191 ± 29 129-338
Norway maple (<i>Acer platanoides</i> L.)	64	2.0	Leaves	32	1.1 ± 0.1 0.5-2.0	9 ± 0.9 0.5-31	414 ± 64 69-1,799
			Twigs	32	0.7 ± 0.1 0.5-2.0	10 ± 0.6 7-22	126 ± 7 44-181
Eastern hemlock (<i>Tsuga canadensis</i> [L.] Carr.)	16	3.7	Leaves	8	0.9 ± 0.1 0.5-1.0	8 ± 0.7 6-11	219 ± 32 35-326
			Twigs	8	1.2 ± 0.2 0.5-1.8	16 ± 1.0 13-19	152 ± 30 36-331
Yew (<i>Taxus</i> spp.)	20	3.8	Leaves	10	1.2 ± 0.2 0.5-2.5	9 ± 0.6 7-12	427 ± 106 218-1325
			Twigs	10	2.0 ± 0.4 0.5-4.1	12 ± 1.2 8-21	303 ± 81 97-957
Norway spruce (<i>Picea abies</i> [L.] Karst.)	8	4.8	Leaves	4	0.7 ± 0.2 0.5-1.0	6 ± 0.9 5-8	270 ± 59 153-338
			Twigs	4	0.8 ± 0.2 0.5-1.0	15 ± 0.9 13-16	113 ± 22 69-139

Note: Complete table has been placed with the American Chemical Society Microfilm Depository Service.

^a Branch samples were collected during the fall of 1970, approximately 2 m above the ground from trees located within 8 m of streets.

^b Washed growth of the previous growing season only.

^c Expression of the data on an ash weight basis is available in the microfilm edition of this journal.

^d Mean and standard error.

^e Range.

Table III. Woody Plants Growing in City of New Haven with "Slightly Above Normal" Amounts of Aluminum, Chromium, and Nickel^a

Species	Total trees sampled	Average distance from nearest street, m	Tissue analyzed ^b		Dry wt basis, $\mu\text{g/g}^c$		
			Organ	Number of trees	Aluminum	Chromium	Nickel
Pin oak (<i>Quercus palustris</i> Muenchh.)	24	1.4	Leaves	12	702 ± 29 ^d 450-800 ^e	3.8 ± 0.8 2.3-12.5	10 ± 0.6 6-13
			Twigs	12	626 ± 34 500-900	2.8 ± 0.4 1.2-5.7	8 ± 1 5-16
Sugar maple (<i>Acer saccharum</i> Marsh.)	14	1.8	Leaves	7	179 ± 40 100-400	1.9 ± 0.3 1.2-3.4	14 ± 2 9-28
			Twigs	7	122 ± 16 75-200	2.3 ± 0.2 1.8-3.4	11 ± 1 8-17
Norway maple (<i>Acer platanoides</i> L.)	64	2.0	Leaves	32	629 ± 30 200-1,149	2.8 ± 0.2 1.2-6.2	6 ± 0.6 .05-15
			Twigs	32	471 ± 22 100-734	1.6 ± 0.1 1.1-2.3	2 ± 0.3 .05-6
Eastern hemlock (<i>Tsuga canadensis</i> [L.] Carr.)	16	3.7	Leaves	8	509 ± 60 225-675	2.8 ± 0.4 1.2-4.6	8 ± 1 5-13
			Twigs	8	411 ± 43 227-600	3.5 ± 0.4 1.2-4.6	11 ± 2 6-22
Yew (<i>Taxus</i> spp.)	20	3.8	Leaves	10	205 ± 27 25-300	3.9 ± 0.3 2.3-5.7	10 ± 1 5-19
			Twigs	10	190 ± 35 14-371	6.0 ± 1.4 2.3-16.3	9 ± 1 4-13
Norway spruce (<i>Picea abies</i> [L.] Karst.)	8	4.8	Leaves	4	300 ± 76 150-400	2.6 ± 0.4 2.3-3.4	7 ± 1 5-8
			Twigs	4	342 ± 36 275-400	4.9 ± 0.4 4.6-5.7	7 ± 1 5-9

Note: Complete table has been placed with the American Chemical Society Microfilm Depository Service.

^a Branch samples were collected, during the fall of 1970, approximately 2 m above the ground from trees located within 8 m of streets.

^b Washed growth of the previous growing season only.

^c Expression of the data on an ash weight basis is available in the microfilm edition of this journal.

^d Mean and standard error.

^e Range.

Table IV. Woody Plants Growing in City of New Haven with "Above Normal" Amounts of Iron, Lead, Sodium, and Zinc^a

Species	Total trees sampled	Average distance from nearest street, m	Tissue analyzed ^b		Dry wt basis, $\mu\text{g/g}^c$			
			Organ	Number of trees	Iron	Lead ^d	Sodium	Zinc
Pin oak (<i>Quercus palustris</i> Muenchh.)	24	1.4	Leaves	12	386 ± 32 ^e 193-515 ^f	121 ± 14 55-220	475 ± 96 25-1,350	137 ± 11 65-209
			Twigs	12	124 ± 13 70-214	67 ± 10 25-125	377 ± 47 190-645	49 ± 5 19-68
Sugar maple (<i>Acer saccharum</i> Marsh.)	14	1.8	Leaves	7	315 ± 36 214-510	64 ± 12 35-120	174 ± 25 100-280	111 ± 13 47-158
			Twigs	7	119 ± 8 82-148	113 ± 20 38-195	408 ± 78 185-815	72 ± 12 36-134
Norway maple (<i>Acer platanoides</i> L.)	64	2.0	Leaves	32	512 ± 47 186-1,349	146 ± 18 45-485	470 ± 50 100-1,300	142 ± 16 28-429
			Twigs	32	123 ± 8 50-254	101 ± 10 10-300	434 ± 38 150-950	66 ± 5 21-134
Eastern hemlock (<i>Tsuga canadensis</i> [L.] Carr.)	16	3.7	Leaves	8	331 ± 62 114-665	91 ± 18 25-180	130 ± 16 65-205	54 ± 7 30-98
			Twigs	8	345 ± 36 193-500	315 ± 75 155-760	184 ± 24 95-282	117 ± 13 70-177
Yew (<i>Taxus</i> spp.)	20	3.8	Leaves	10	421 ± 32 201-530	139 ± 20 40-240	383 ± 94 75-1,115	351 ± 55 109-650
			Twigs	10	326 ± 33 170-481	177 ± 29 70-371	379 ± 84 51-1,020	293 ± 35 116-510
Norway spruce (<i>Picea abies</i> [L.] Karst.)	8	4.8	Leaves	4	325 ± 54 232-421	75 ± 16 45-100	200 ± 63 75-275	102 ± 12 80-122
			Twigs	4	459 ± 58 360-560	163 ± 41 100-240	278 ± 49 190-360	119 ± 20 94-157

Note: Complete table has been placed with the American Chemical Society Microfilm Depository Service.

^a Branch samples were collected, during the fall of 1970, approximately 2 m above the ground from trees located within 8 m of streets.

^b Washed growth of the previous growing season only.

^c Expression of the data on an ash weight basis is available in the microfilm edition of this journal.

^d Portion of lead data previously reported (Smith 1972).

^e Mean and standard error.

^f Range.

study included Al, Cd, and Na for pin oak; Mn and Na plus a few V readings, for sugar maple; Al and Na for Norway maple; Al, Cr, Fe, Pb, Ni, plus a few V readings, for eastern hemlock; Fe, Mn, Ni, and Zn for yew; and Fe for Norway spruce.

Association of metals with leaves (needles) and twigs also showed considerable variation. Al was highest with the leaves of all species except Norway spruce where it was highest with the twigs. Cd was highest with the leaves of the maples, equally distributed with pin oak, and highest with the twigs of all the conifers. Cr was highest with the leaves of pin oak and Norway maple and highest with the twigs of sugar maple and all conifers. Cu was highest with the twigs of all species except pin oak where it was highest with the leaves. Fe was highest with the leaves of all species except hemlock where it was highest with the twigs. Pb was highest with the leaves of pin oak and Norway maple and highest with the twigs of sugar maple and all conifers. Mn was highest with the leaves of all species. Ni was highest with the leaves of pin oak, sugar maple, Norway maple, and yew; equal with Norway spruce; and highest with the twigs of hemlock. Na was highest with the leaves of pin oak, Norway maple, and yew and highest with the twigs of sugar maple, hemlock, and Norway spruce. Zn was highest with the leaves of pin oak, sugar maple, Norway maple, and yew and highest with the twigs of hemlock and Norway spruce. Some of these differences were not significantly different statistically.

Microprobe A number of problems were encountered in adopting the electron probe X-ray microanalyzer to our needs. A minimally acceptable peak-to-background ratio

of 3:1 was obtained with a 50 $\mu\text{g/ml}$ standard. The limit of instrument resolution, under the conditions employed, was probably between 50-100 $\mu\text{g/g}$. Most leaf cross sections scanned by the probe proved negative for this concentration of Pb. The cross sections of one Norway maple leaf and one hemlock needle taken from trees with high Pb burdens, however, had counts suggestive of a slight degree of internal Pb contamination. The Norway maple leaf had higher Pb counts associated with the palisade cells relative to the mesophyll or epidermal cells.

Discussion

Collecting tree and shrub branches in an urban environment is difficult to accomplish in a statistically random fashion because of the varied constraints imposed by unequal species distribution and access opportunities. Individual trees of each of the six species were sampled from industrial, commercial, and residential sections. A conscious effort was made to avoid concentrated sampling in specific areas. The results, therefore, approximate "city-wide" averages and probably would have differed significantly if all of the sampling had been accomplished in specific sections of New Haven. Collection of samples only from the lower crown biases the results but permits a relatively large number of trees to be conveniently sampled. Trees acquire the metals of interest in this study via uptake from the soil solution or particulate impaction from the atmosphere on aerial organs. Considering these routes of acquisition there is no strong evidence to suggest that the lower crown region would give an extremely atypical representation of the entire crown.

The fact that none of the washing procedures provided statistically significant differences in metal content for any tree and metal examined, suggests that either the washing procedures were inadequate to remove superficial deposits or a large portion of the metals was located inside the tissues. Analysis of wash solutions revealed that low concentrations of metals were present. Washing employed in an experiment of this type must be designed to remove surface materials but not leach internal compounds. Procedures employed in this study met these criteria, but failed to provide conclusive evidence in regard to localization of the metals.

The greatest initial difficulty in evaluating the pathological significance of the metals examined in this investigation was to establish a "normal" or "baseline" content. Our standard of comparison was developed by sampling trees growing in relatively unpolluted environments and by reviewing published concentrations obtained from trees and shrubs growing in nonurban locations (Bowen, 1966; Cannon, 1960; Goldschmidt, 1954; Heggen and Strock, 1953; Likens and Bormann, 1970; Lounamaa, 1956; Price, 1970; Robinson and Edgington, 1945; Scott, 1955; Shacklette, 1970). Both of these standards of comparison have numerous disadvantages. Norway maple and yew are difficult to find in areas of low pollution load. Sugar maple was selected for sampling in remote areas because of its convenient abundance. Usefulness of published metal concentrations in plants is diminished by variation in sample acquisition, analysis, and time and place of collection among several other variables. The most disturbing aspect of literature values, however, is their frequent gross disparity. Likens and Bormann (1970), for example, list the range of Na content for the foliage of several New Hampshire trees as 10-22 $\mu\text{g/g}$ while Scott's (1955) review lists the range of Na content for the foliage of numerous North American trees as 360-2900 $\mu\text{g/g}$. Clearly, a judgment regarding the normalcy or abnormalcy of metal content is somewhat arbitrary. Greatest accuracy is achieved by developing a summary range integrating data personally acquired from remote locations with data obtained from several literature sources.

Application of this technique to the New Haven tree data provided "normal, slightly above normal, and above normal" designations. Inclusion of Cd, Cu, and Mn in the normal category suggests that these metals probably do not have phytopathological potential at the present level of introduction into the New Haven ecosystem. Previous analysis of mercury in New Haven woody plants (Smith, 1972) would also place this metal in the normal category. Inclusion of Al, Cr, and Ni in the slightly above normal category suggests that these metals may be present in somewhat greater amounts than might be expected in rural, nonindustrial locations. Since Cr and Ni are considered very toxic elements and Al moderately toxic (Bowen, 1966), additional effort should be made to consider their phytotoxic potential in urban areas. Sullivan (1969a) reported that no evidence of plant damage due to airborne Cr could be found in the literature. Although little information is available on the air pollution effects of Ni on vegetation (Sullivan, 1969b), this metal is capable of causing abnormal plant physiology (Hewitt, 1948; Lagerwerff, 1967; Schroeder et al., 1962; Tso, 1966). Al is probably present in amounts considerably below the threshold of toxicity for the plants examined.

Of the metals designated present in above normal concentrations; Pb is very toxic, Zn is moderately toxic, Fe is slightly toxic, and Na relatively harmless (Bowen, 1966). Zn and Fe like Al, are probably present in amounts considerably below the threshold of toxicity for the plants examined. The Na threshold of toxicity is approximately 5000

$\mu\text{g/g}$ for several plant species (Smith, 1970). The highest Na levels found are only approximately $\frac{1}{5}$ of this threshold concentration. A major source of Na introduction into the roadside environment, however, is the use of NaCl during the winter for deicing purposes. During the winter (1969-70) preceding the plant collections for this study, 11 storms occasioned the use of 13.6×10^5 kg of NaCl on city streets in New Haven. Since the tree sampling was conducted in the fall, much of the Na introduced the previous winter may have been removed via leaching. In order to assess the phytotoxic potential of Na, plant sampling should be done in the winter or spring.

Since Pb is biologically nonessential and is associated with New Haven trees in definitely elevated and abnormal amounts, it is of greatest concern. The Pb content of plants growing in natural relatively unpolluted environments is approximately 1 $\mu\text{g/g}$ (Warren and Delavault, 1960; Webb and Millman, 1951; Worthington, 1955). The average Pb contents revealed in this study are generally more than 100 times this value. An extensive literature review has revealed that our maximum Pb values exceed almost all reports for woody plants, even those from areas with Pb deposits (for example, Cannon, 1955; Harbaugh, 1950; Lounamaa, 1956; Smith, 1971; Warren and Delavault, 1960; Warren et al., 1966; Webb and Millman, 1951; Worthington, 1955). While acute tree injury has been ascribed to Pb contamination (Låg et al., 1969; Primault, 1958), a recent review concluded that naturally occurring Pb is not toxic to vegetation (NAS, 1971). This latter conclusion is based on incomplete evidence in regard to the localization of Pb within plant tissues, the chemical form of the Pb, and the ability of Pb to cause subtle (perhaps without acute symptoms) stress such as enzyme impairment. Pb is capable of interfering with the activity of several enzymes (NAS, 1971).

The use of the electron probe X-ray microanalyzer failed to provide definitive information on the localization of Pb on or in leaf tissue. This failure was due in part to the difficulty of preparing adequate standards. Evaporation of Pb salts of known concentration directly on the carbon rods (used to support specimens being examined) proved most suitable. Failure also may have been due in part to a lack of Pb on or in the leaves examined, a lack of localization of the Pb on or in the tissues, or a failure to examine a large enough (hence representative) number of samples. Since the limit of resolution of the microprobe appeared to be approximately 50-100 $\mu\text{g/g}$, more sensitive histochemical techniques may yield more information in regard to Pb localization. Several of these procedures are presently being employed in this laboratory.

The aggregation of men and machines in urban areas creates stresses that influence vegetation growing in these environments. Of the numerous metals introduced into the atmosphere of cities, Pb appears to have the greatest potential to cause abnormal plant physiology. The hypothesis that Pb is capable of causing subtle, nonacute plant damage will be supported or rejected only after it is found where lead occurs and in what chemical form it exists in the plant.

Due to the variation revealed with respect to metal concentration and species and metal location and leaves (needles) and twigs, it is important to examine several species and to analyze both leaves and twigs in a study of this type. It is hoped that these data will provide useful comparisons with past and future investigations.

Acknowledgment

The author thanks Edward Weber, Geology Department, Yale University, for assistance with the microprobe.

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Received for review November 8, 1972. Accepted March 19, 1973. Work supported by the Connecticut Research Commission, Grant RSA-71-20. **Supplementary Material Available.** Tables 2, 3, and 4, in complete form, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit checks or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number ES&T-73-631.

NOTES

Extraction of Dispersed Oils from Water for Quantitative Analysis by Infrared Spectrophotometry

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■ Some parameters that optimize the extraction of dispersed oils from water for quantitative analysis by infrared spectrophotometry (ir) are examined, and an improved extraction procedure is recommended. Trichlorotrifluoroethane, an essentially nonpoisonous solvent (1000 ppm TLV), is compared with carbon tetrachloride, which is highly poisonous to operating laboratory personnel (10 ppm TLV). Both solvents are usable for extracting dispersed oils from water, and for their quantitative analysis by ir, but trichlorotrifluoroethane is preferred. Changes in extraction efficiency following small additions of sulfuric acid and sodium chloride are examined. Great improvement results in extraction efficiency, but no further improvement derives from addition of more salt. Absorbance measurements are at 2930 cm^{-1} in 10-mm path length cells.

Many biological processes necessary for the survival of aquatic organisms may be adversely affected by the presence of extremely low levels—0.1 mg/l.—of petroleum oils in water. Jacobson (1972), for example, has shown that kerosine extracts in water, in the part-per-billion range, upset the chemotactic response of *Nassarius obsoletus* to oyster and scallop tissue. Identification of the particular oil and its quantitative determination in the water column are essential properly to monitor and assess potential biological damage resulting from oil spill incidents.

The development of a method that can be used to rapidly and completely extract dispersed oils from water for quantitative analysis by infrared spectrophotometry, and one that can be safely used in a mobile laboratory operating at the scene of a spill incident is described in this paper. Methods currently available for the quantitative analysis of petroleum dispersed in water are broadly identified as gravimetric and spectroscopic procedures.

Table I. Fraction of Oil Removed by Individual Extracts from Synthetic Dispersions Containing 5 MI of 50% H₂SO₄ and 5 Grams of NaCl

No. of 25-ml extractions	Percent recovered ^a							
	South Louisiana Crude Oil		No. 2 Fuel Oil		Bachaquero Crude Oil		No. 6 Fuel Oil	
	Freon 113	CCl ₄	Freon 113	CCl ₄	Freon 113	CCl ₄	Freon 113	CCl ₄
1	92.6	94.4	97.2	97.8	90.0	95.4	91.1	92.2
2	99.3	99.7	99.5	100	98.7	99.5	98.7	98.6
3	99.8	100	100		99.7	99.9	100	100
4	100				100	100		

^a Determined as $A/A_T \times 100 + B$; A, infrared absorbance at 2930 cm⁻¹ due to the extract of interest; A_T, sum of absorbances at 2930 cm⁻¹ of all the extracts (ΣA); B, total percent oil recovered by the previous extracts.

The gravimetric methods produce losses of the more volatile petroleum fractions making their use questionable for measuring light oils and distillates. Spectroscopic methods are inherently more sensitive and accurate, as indicated by Harva and Somersalo (1958). Infrared and ultraviolet procedures therefore seem to hold greater promise for yielding sensitive and accurate techniques.

The extraction of petroleum pollutants from water is a necessary part of quantitative analysis by either gravimetric or spectroscopic methods. Parameters that influence these extractions are evaluated in this study, and an optimum extraction scheme is presented. These parameters include the degree to which additions of acid and salt influence extraction efficiency and the utility of trichlorotrifluoroethane (Freon 113) and carbon tetrachloride (CCl₄) for such extractions; the latter solvent is highly toxic when inhaled (10 ppm TLV) or when absorbed through the skin (Sax, 1968).

The literature contains reports on the extraction of oils from water with carbon tetrachloride and trichlorotrifluoroethane, and acid and salt have previously been used to increase extraction efficiency. The American Petroleum Institute's spectroscopic procedure (1958) utilizes carbon tetrachloride as the extracting solvent, after addition of sulfuric acid and salt. Carbon tetrachloride is also used in a spectroscopic procedure developed by the Beckman Instrument Co. (1968) without, however, the addition of acid or salt. Freon 113 is used as the extracting solvent in a gravimetric procedure reported by the American Public Health Association (1971), following addition of sulfuric acid, but not salt. These methods suggest that there is a lack of uniformity and general agreement about the advantages of using acid and salt. They also do not examine the extent to which additions of these materials influence extraction efficiency, or the possibility of using Freon 113 for spectroscopic analyses. Freon is safer than carbon tetrachloride from the analyst's viewpoint.

In the present study four oils were used to compare the efficiencies of the two solvents and the influence of acid and salt: No. 2 Fuel Oil, which is a low-viscosity distillate oil (2.4 cSt at 100°F); No. 6 Fuel Oil, which is a high-viscosity residual oil (2300 cSt at 100°F); South Louisiana Crude Oil which has a low viscosity (4.8 cSt at 100°F); and Bachaquero Crude Oil which has a moderately high viscosity (1070 cSt at 100°F). Consecutive extractions of each oil from synthetic dispersions in water were carried out with each solvent; the quantity of oil in the individual extracts was monitored by measuring the oil absorbance band intensity at 2930 cm⁻¹ in the ir spectral region (Figure 1). This band is not unique to oils, but derives from the CH₂ group that is common to many organics. Freon 113 and carbon tetrachloride yield minimal absorbance in the 2930 cm⁻¹ region and are amenable for such analyses.

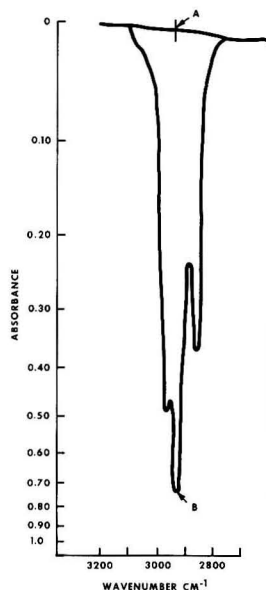


Figure 1. Infrared absorbance band of No. 2 Fuel Oil dissolved in Freon 113 (0.034% W/V), using 10-mm path length silica cells; Freon is in the reference beam

Absorbance at 2930 cm⁻¹ is determined as the difference between points A and B

The changes in extraction efficiency that accompanied additions of sulfuric acid and sodium chloride were established by monitoring resulting changes in the quantity of oil separated by the individual extracts. The degree to which the dispersed oils were separated by each extract, following addition of acid and salt, is also estimated (Table 1). Since the tabulated results are derived solely from our synthetic oil-water dispersions however, they should not be extrapolated to other types of dispersions without further study.

Experimental

Apparatus. Perkin Elmer Model 457A and Beckman IR-33 infrared grating spectrophotometers were used for the determinations. Absorbance of the solutions was measured in 10-mm path length glass-stoppered rectangular silica cells (Beckman Instruments, Inc., Catalog No. 580015).

Reagents. Extractions were performed with Freon TF (Freon 113) solvent (E. I. Du Pont De Nemours and Com-

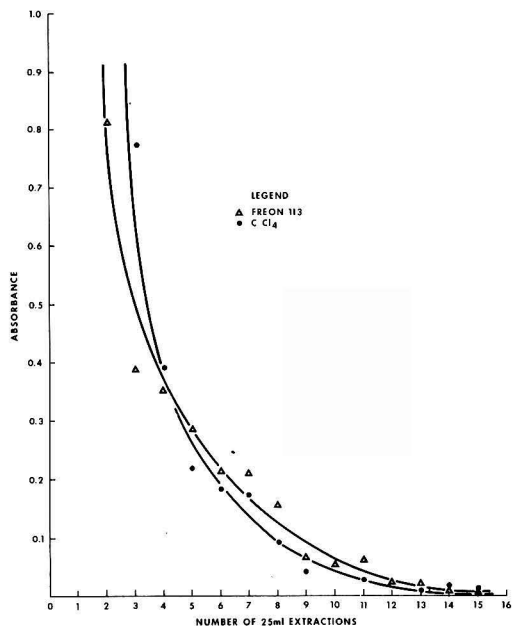


Figure 2. Number 2 Fuel Oil extracted from 1-liter duplicate synthetic oil-water samples containing no added acid or salt

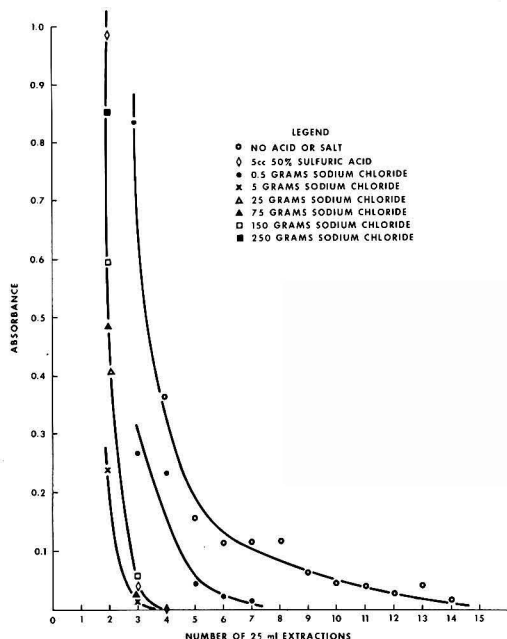


Figure 3. Number 2 Fuel Oil extracted from similar 1-liter synthetic oil-water samples containing acid or salt

Acidified sample is extracted with Freon 113; untreated sample and samples containing the indicated amounts of salt are extracted in CCl_4

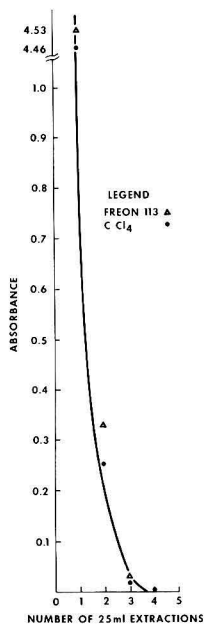


Figure 4. South Louisiana Crude Oil extracted from 1-liter duplicate synthetic oil-water samples containing 5 grams of sodium chloride and 5 ml 50% sulfuric acid

Absorbance intensities greater than 1.0 are calculated values

pany, Inc.), and carbon tetrachloride, spectroanalyzed (Fisher Scientific Co., Catalog no. C-199).

Procedure. Synthetic 1-liter oil-water samples containing identical concentrations of emulsified oil were prepared by shaking 5-ml portions of each test oil with 1½ liters of tap water for 1 min in 2-liter separatory funnels. The mixtures with No. 2 Fuel Oil, No. 6 Fuel Oil, and South Louisiana Crude Oil were allowed to separate undisturbed for 15 min, while the mixture with Bachaquero Crude Oil was allowed to separate for 1 hr. The homogeneous oil-water emulsions obtained as bottom layers were used to prepare the duplicate synthetic 1-liter samples. This was accomplished by mixing two 500-ml portions of each emulsion with an equal amount of tap water, in 2-liter separatory funnels. Subsequent extraction of the oils from the synthetic samples was also carried out in these funnels.

The relative extraction efficiencies of Freon 113 and carbon tetrachloride and the influence of acid and salt were examined by extracting the 1-liter synthetic samples with successive 25-ml portions of each solvent; acid and salt were added to some of the samples (Figures 2-4). The quantity of oil in each extract was monitored by measuring the oil absorbance band intensity at 2930 cm^{-1} in 10-mm path length silica cells (Figure 1). Extraction efficiencies and the effects of sulfuric acid and sodium chloride were determined by plotting the absorbance of each extract as a function of the number of 25-ml extractions (Figures 2-4). Removal of oil from water was considered complete only after attaining zero absorbance. That the absence of an infrared absorption band indicates "complete" extraction of oil was also shown by submitting residual water, emulsified with No. 2 Fuel Oil and extracted with Freon 113, to analysis by the gravimetric procedure of the American Public Health Association (1971). No oil was found in this water. The fraction of total emulsified oil separated by each extract was estimated by determin-

ing the ratio of its absorbance to the sum of the absorbances of all the extracts (Table I).

Results and Discussion

Freon 113 and carbon tetrachloride were found to be about equally effective for extracting the dispersed oils from water. Virtually the same number of extractions with each solvent effected removal of the oils (Figures 2 and 4). Additions of sulfuric acid and sodium chloride dramatically improved extraction efficiency. In the absence of these materials, the complete separation of No. 2 Fuel Oil was not possible even after 15 separate 25-ml extractions with carbon tetrachloride and Freon 113. However, complete separation of oil was achieved with only four extractions when 5 grams of sodium chloride and 5 ml of 50% sulfuric acid were added to the 1-liter synthetic samples. The addition of more than 5 grams of salt yielded no further improvement (Figures 2 and 3). Four 25-ml extractions with either solvent achieved complete separation of all the test oils when these quantities of acid and salt were added to the synthetic 1-liter samples (Figure 4). In these latter determinations, more than 90% of each emulsified oil was removed by the first extract (Table I).

Freon 113 is recommended as the solvent of choice for extracting dispersed oils from water, because it is virtually as efficient for these extractions and as usable for the infrared determination of oil as carbon tetrachloride, but is much less poisonous to laboratory personnel. It is especially preferable to carbon tetrachloride in situations where adequate ventilation may be lacking, such as in some mobile laboratory and field use.

The recommended procedure for extracting dispersed

oils from water is the addition of 5 ml of 50% sulfuric acid and 5 grams of sodium chloride to 1-liter samples. Extraction should be carried out with four 25-ml portions of Freon 113 in 2-liter separatory funnels. Checks for acidity (below pH 3) and completeness of extraction should be performed. Initial dilution is to 100 ml. Seawater samples are an exception because they already contain adequate salt and can therefore probably be analyzed without addition of sodium chloride. Such samples were not examined in the present study, however. A "blank" determination of the reagents and water should be performed to prevent interference with the oil measurement at 2930 cm^{-1} by extraneous solvent extractable organics.

Acknowledgment

Special thanks are given to Joseph Lafornera for providing valuable background information, and to Henry Jeleniewski, Michael Killeen, Susan Rattner, and Peter Furth for their assistance.

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Received for review August 10, 1972. Accepted March 26, 1973.

Baseline Concentrations of Light Hydrocarbons in Gulf of Mexico

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■ A 2500-mile survey of light hydrocarbon concentrations in surface water of the Gulf of Mexico was conducted to determine baseline concentrations for a program to identify problems related to oceanic environmental quality. High concentrations seem to be associated solely with man's activities in the vicinity of ports and offshore petroleum drilling and production operations and in one case on the high seas, near a tanker reportedly discharging "clean ballast water."

Oceanic oil pollution has been a popular subject in governmental circles, in the news media, and in some technical journals. Dialog has been concerned mostly with the obvious deleterious effects of spills on near-shore ecosystems and beach properties. These dramatic short-term effects have masked interest in the disposition of some of the more soluble components of petroleum such as the

light hydrocarbons which may be transported downward via turbulent mixing of water masses and laterally with currents. These processes lead to unnaturally high light hydrocarbon concentrations over areas and volumes much larger than the visible extent of the spills. In this paper we give a light hydrocarbon baseline for one of the most important areas of the world in so far as oil pollution is concerned, the Gulf of Mexico. Also we show examples of large increases in concentrations due to several different man-made sources.

Experimental

Analyses of light hydrocarbons are performed with a modified Beckman process gas chromatograph (Model 320 Programmer and Series D analyzer). Figure 1 shows the modification of the Series D analyzer. For surface profiling, gases are continuously stripped from the seawater by a 12-stage booster pump which has a restricted inflow (1.6 l./min). The vacuum produced by the restriction of the booster pump inflow, strips about 50% of the total gases from solution. Analysis of water before and after stripping

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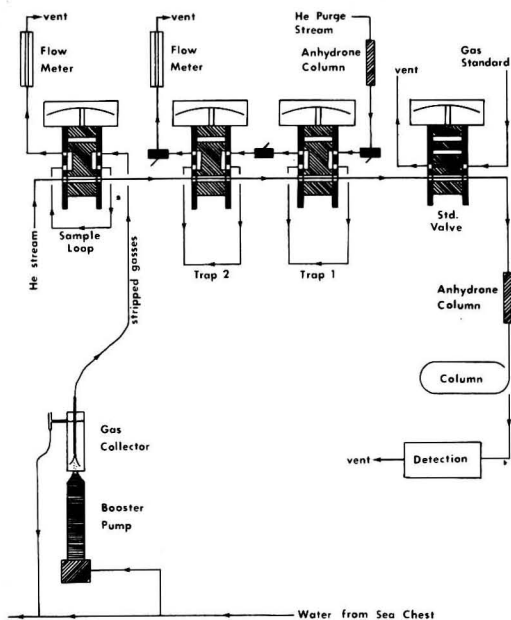


Figure 1. Schematic of hydrocarbon "sniffer"

indicates that approximately 50% of the light hydrocarbons are also stripped. The stripped gases are collected and are pushed by hydrostatic pressure through a 1.76-ml sample loop. The gases in the sample loop are injected approximately every 5 min into the chromatographic stream for analysis. Water for surface profiling is obtained from the sea chest of the *R/V Alaminos*. The sea chest intake is about 3 meters below the sea surface. About 75% of the stream flow from the sea chest (6 l./min) bypasses the booster pump to keep lag time in the system short. There is a 10-min lag between the time the water enters the sea chest and when the stripped gases reach the detector for analysis.

The gas chromatographic system consists of a flame ionization detector with a 10% Nujol on alumina column. The 5-ft $\frac{1}{4}$ -in. o.d. column is thermostated at 75°C to give a retention time of 3.8 min through isobutane at a flow rate of 60 ml/min. Light hydrocarbons are analyzed by three different methods. First, relative hydrocarbon values are obtained in surface profiling by stripping gases as described above. Absolute values can be obtained by McAuliffe's method (McAuliffe, 1971) of multiple-phase equilibrium. This method involves equilibrating 25 ml of purified helium with 25 ml of sample water in a 50-ml syringe. A portion of the equilibrated helium is injected into the chromatographic stream by the sample loop. For open ocean concentrations of light hydrocarbons this method is sensitive enough only for methane, but in waters with higher concentrations (e.g., the Upper Gulf Coast and harbors) this technique offers a quick and easy method for determining both methane and higher hydrocarbons. For

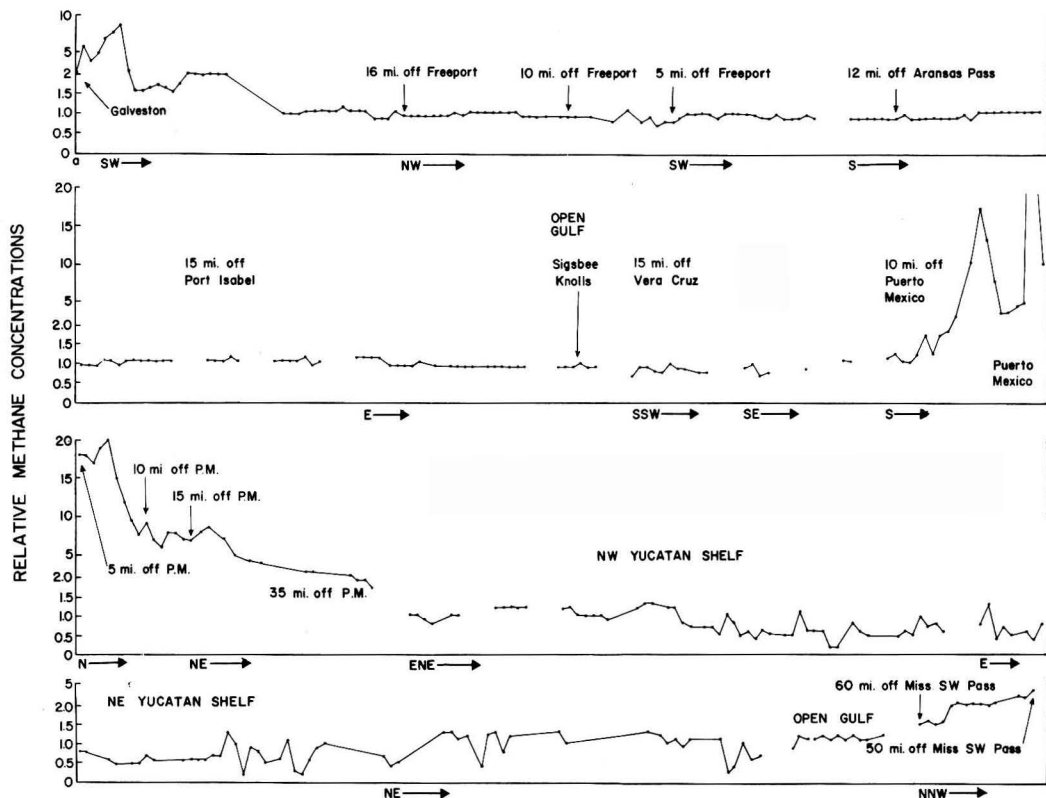


Figure 2. Relative methane concentrations in surface water for the Gulf of Mexico. Relative concentrations are multiples of surface open ocean concentrations where $\text{CH}_4 \sim 5 \times 10^{-5}$ ml/L

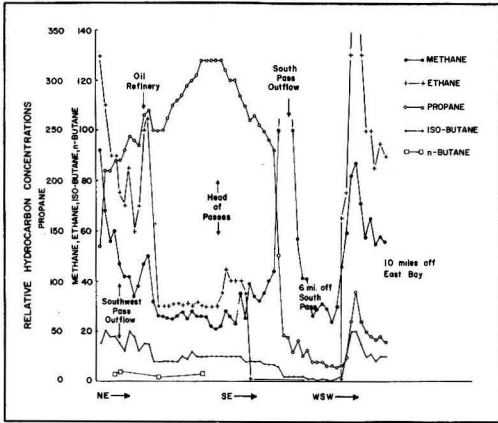


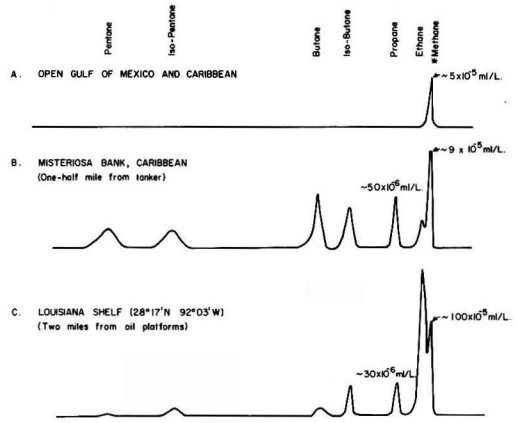
Figure 3. Relative hydrocarbon concentrations in surface water in the vicinity of the Mississippi River Delta. Relative concentrations are multiples of surface open ocean concentrations where $CH_4 \sim 5 \times 10^{-5}$ ml/L, $(C_2H_4 + C_2H_6) \sim 3 \times 10^{-6}$ ml/L, $C_3H_8 \sim 0.8 \times 10^{-6}$ ml/L, $i-C_4H_{10} \sim 0.1 \times 10^{-6}$ ml/L, $n-C_4H_{10} \sim 0.6 \times 10^{-6}$ ml/L

lower concentrations of light hydrocarbons the technique of Swinnerton and Linnenbom (1967) is used. This involves purging 1 liter of seawater with purified helium and collecting the light hydrocarbons in two cold traps for subsequent injection into the helium stream when the traps are heated. Standardization of the system is accomplished by injecting 1.26 μ l. of a gas standard into the chromatographic stream.

The light hydrocarbon data obtained from the "sniffer" during surface profiling are relative values since total extraction of the gases from the seawater is not obtained. The open ocean values are assigned a relative value of one, making the relative hydrocarbon concentrations reported in this paper multiples of open ocean concentrations. Thus, a relative methane level of 10 will be approximately equal to 50×10^{-5} ml/l. or ten times the open ocean level for methane of 5×10^{-5} ml/l. Comparison of relative methane values obtained by the sniffer with absolute concentrations determined by McAuliffe's method shows that the proportion of methane extracted with the total gases is fairly linear with increasing concentrations above open ocean levels. Thus, the relative light hydrocarbon data obtained from the sniffer can be converted into absolute concentrations. The open ocean levels assumed for methane, ethane, ethylene (not separated), and propane are reasonably accurate. The open ocean levels assumed for the butanes, however, are rather arbitrary, since butanes at open ocean levels are below the detection limits of the sniffer. The relative variations for the butane concentrations are accurate, but the use of the relative values to convert to absolute concentrations may involve considerable error.

Results and Discussion

Figure 2 shows the baseline concentrations of methane for much of the Gulf of Mexico. The letters along the abscissa indicate directions and are located at the approximate points where course changes were made. The points indicate single determinations and are a minimum of 1 mile apart. Discontinuities in the lines represent much larger distances. High concentrations are found in the vicinity of three major ports; Galveston, Tex., the southwest pass of the Mississippi River, and Puerto Mexico. Figure



*Methane attenuated relative to other peaks. $\times 10$ in Figures A and B, and $\times 100$ in Figure C
Figure 4. Gas chromatograms for three typical situations. Retention times in minutes are as follows: $C_1 - 0.4$, $C_2 - 0.6$, $C_3 - 1.0$, $i-C_4 - 2.0$, $n-C_4 - 2.6$, $i-C_5 - 5.8$, and $n-C_5 - 7.2$

3 indicates that ethane, propane, and the butanes, as well as methane, are extremely high in and around the Mississippi River passes. For the open ocean these higher molecular weight hydrocarbons are barely detectable with our system. A typical chromatogram is shown in Figure 4A. Figure 4B is a chromatogram for water about one-half mile from a tanker which had been discharging "clean ballast water." Figure 4C is a chromatogram for water about 2 miles from several oil platforms. Absolute concentrations for two profiles collected on the baseline cruises are shown in Figure 5. These samples were collected in Niskin bottles and stored in 1-liter glass-stoppered bottles

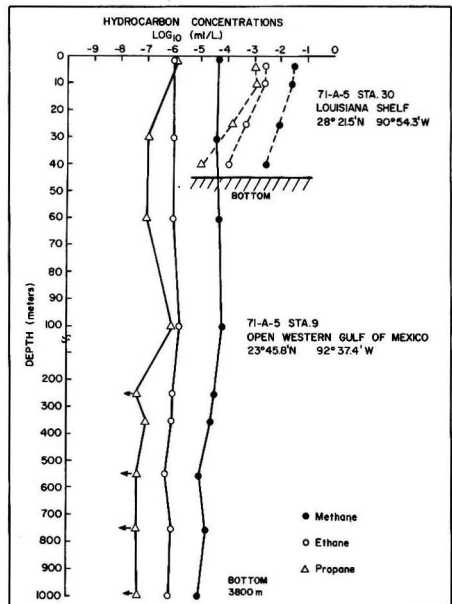


Figure 5. Absolute hydrocarbon concentrations for typical shelf and open Gulf of Mexico stations

using HgCl_2 as a preservative. They were analyzed by J. W. Swinnerton at the Naval Research Laboratory by the method of Swinnerton and Linnenbom (1967). The Louisiana shelf station has three orders of magnitude higher hydrocarbon concentrations than the deep open Gulf station. On the north Gulf shelf between the Mississippi Delta and Galveston several areas of similar high hydrocarbon concentrations were encountered. Usually they seemed to be associated with oil platforms but natural seeps cannot be ruled out as a contributing factor.

These four figures point out the major sources, magnitudes, and extent of man-made hydrocarbon pollution associated with ports, offshore petroleum drilling, and pro-

duction platforms and tankers which contaminate the open ocean because of naive operating procedures.

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Received for review September 18, 1972. Accepted April 4, 1973. This project was supported in part by NSF Grant No. GX-30196. Parts of this paper were presented at a symposium on "Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in the Earth's Environment" sponsored jointly by the American Geophysical Union and the American Meteorological Society and held in St. Petersburg, Fla., August 15-17, 1972.

Identification of Aliphatic Amines Volatilized from Cattle Feedyard

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■ Basic organic N-compounds volatilized from a cattle feedlot and collected in dilute acid were characterized. Direct gas chromatographic (gc) analysis of the acid solutions and gc separation of the pentafluorobenzoyl derivatives of the malodorous volatiles were used in their identification. Methyl, dimethyl, ethyl, *n*-propyl, iso-propyl, *n*-butyl, and *n*-amylamines were among the basic N-compounds emanating from a high density cattle feedyard.

Recent concern over the effects of animal feeding operations on the environment has prompted studies to determine if there is nitrogen pollution from runoff, nitrate percolation, or ammonia volatilization from high density cattle feedlots. The magnitude of a cattle feedlot's potential for atmospheric contamination with nitrogen compounds is seen in the estimate that 360 cattle on a 1-acre lot annually deposit 12 tons of urea-N in urine. This is about half of the total N that the cattle excrete (Viets, 1970). The urea in urine is rapidly hydrolyzed to ammonia, 85-90% of which can be volatilized (Stewart, 1970). Ammonia and volatile organic bases containing N are probably also released from decomposing manure, but no data are available on forms or amounts (McCalla and Viets, 1969). Before the environmental impact of feedlot volatiles can be assessed, their chemical identity must be established.

Hutchinson and Viets (1969) and Elliott et al. (1971) demonstrated that ammonia volatilized from cattle feedlots is absorbed by nearby surface waters, thereby enriching them with nitrogen. Both authors reported all basic nitrogen collected in dilute acid traps as ammonia because the analytical method used—steam distillation with magnesium oxide (Bremner and Keeney, 1965)—was not specific for individual nitrogen compounds. Other investigators have suggested that amines may be volatilized from hog (Miner and Hazen, 1969; Merkel et al., 1969) and chicken (Burnett, 1969) wastes. Our investigation was conducted to identify some of the basic organic N-containing compounds volatilized from a cattle feedlot and collected in dilute acid traps.

Experimental

Dilute acid (0.01N H_2SO_4) traps described by Hutchinson and Viets (1969) collected basic compounds volatilized from a 4000-6000-head beef cattle feedlot located about 4 km southeast of Fort Collins, Colo. A trap located farther than 3 km from small feedlots or irrigated fields, and 15 km from large feedlots or cities, was used as a reference blank. Each collection was returned to the laboratory, filtered, and evaporated to near dryness at 50°C under vacuum. The resultant residue was taken up in a few milliliters of the dilute acid and analyzed for ammonia and amines by gas chromatography (gc). The mixture was then heated to 130°C to remove interfering organic compounds such as alcohols. The charred material was taken up in a few milliliters of water, and filtered. The procedure was repeated with known quantities of standard amines which were recovered quantitatively.

Two gc methods were used—direct analysis of dilute acid solution, and inspection of pentafluorobenzoyl derivatives (pentafluorobenzoyl chloride obtained from Pierce Chemical Co.) of the unknown compounds. A Tracor MT-220 gc equipped with hydrogen flame ionization detector was used for direct amine analysis. With this technique (Andre and Mosier, 1973a), the aqueous amine salts are converted to the volatile amine in the injection port of the gc. The columns used for direct analysis were 2-meter \times 4-mm i.d. (1/4-in. o.d.) U-tubes packed with (a) 28% Pennwalt 223 and 4% KOH on 80-100-mesh Gaschrom R (Applied Science Laboratories), and (b) 50-60-mesh Chromosorb 103 (Johns-Manville). The injection port contained an 8-cm \times 4.23-mm i.d. FEP Teflon tube packed with 20-30-mesh Ascarite. The following chromatographic conditions were empirically determined: carrier gas (He), 80 ml/min for (a) and 120 ml/min for (b); column oven temperature, 100°C for (a) and 130°C for (b); detector temperature, 315°C for both; inlet temperature, 200°C for both; sensitivity, 8×10^{-11} to 128×10^{-11} a.f.s. with 1-mv recorder for both columns. The amine standards, obtained from Eastman Kodak Co. and Polyscience Corp., were prepared for direct gc analysis by dilution with 0.01N sulfuric acid. The concentration range of 1-100 $\mu\text{g}/\text{ml}$ was examined routinely by using 5- μl . injections.

The derivatized amines were analyzed on a Tracor MT-150 gc equipped with an electron capture detector. The column systems used were (a) 6% DEGS on 80-100-

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mesh Chromosorb WHP, and (b) 10% Igepal CO 880 on 100-110-mesh Anakrom SD in 6-ft \times $\frac{1}{8}$ -in. stainless steel columns. The chromatographic conditions were as follows: carrier gas (He), 20 ml/min for system (a) and 40 ml/min for system (b); column oven temperature, 145°C for (a) and 175°C for (b); detector temperature, 300°C; inlet temperature, 200°C, sensitivity, 50 ng/ml range. Pentafluorobenzoyl chloride derivatives of the feedlot volatiles and known amine compounds were formed directly in aqueous solution by a method described by Andre and Mosier (1973b), and then extracted into benzene.

Results and Discussion

Direct gc analyses of the acid trap concentrates showed that 10 compounds can be observed (Figure 1). To identify these compounds, the first of three procedures was to compare the retention times of the unknown materials with those of standard aliphatic amines. Table I shows that ammonia and methyl, dimethyl, trimethyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and *n*-amylamines have retention times that correspond with peaks observed in the sample chromatograms. These comparisons, even though conducted on two completely different column systems, imply that the basic feedlot volatiles are the specific amines but are not indisputable proof. Basicity of the individual peaks was confirmed by diverting the column effluent at the appropriate retention times into an aqueous solution where an increase in pH was observed for each.

To further substantiate the tentative identification made by direct gc analysis, a portion of the sample whose chromatogram appears in Figure 1 was mixed with the standard amines methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and *n*-amylamines in concentrations approximately equal to those observed in the sample. Analysis of this mixture showed that addition of the six known compounds neither increased the number of peaks in the sample chromatogram nor distorted the peak shape of any of the six peaks. This comparison more firmly substantiates the first suggestion that methyl dimethyl (and/or ethyl), *n*-propyl, isopropyl, *n*-butyl, and *n*-amylamines are volatilized from the feedlot.

The identities of the sample amines were confirmed from the gc analysis of their pentafluorobenzoyl deriva-

tives (Figure 2). This technique facilitates the separation of ethyl- and dimethylamines as well as the resolution of the other tentatively identified compounds. Retention times of the derivatives of both sample amines and known standard amines are listed in Table II. Peaks in the sample chromatograms correspond to all seven amines previously suggested to be present, including both ethyl and dimethylamines.

Table I. Gas Chromatographic Retention Times for Known Amine and Feedlot Volatiles on Two Column Systems

Sample	Retention times	
	Column 1, ^a min	Column 2, ^b min
Ammonia	0.16	0.24
Methylamine	0.32	0.43
Dimethylamine	0.51	0.71
Trimethylamine	0.47	0.79
Ethylamine	0.55	0.79
Diethylamine	1.50	2.84
Triethylamine	...	7.64
<i>n</i> -Propylamine	1.34	2.05
Isopropylamine	0.83	1.34
<i>n</i> -Butylamine	2.76	5.20
<i>sec</i> -Butylamine	1.81	3.63
<i>t</i> -Butylamine	1.02	2.05
Isobutylamine	...	3.94
<i>N</i> -methylethylamine	0.95	1.38
<i>N</i> -methylbutylamine	3.78	7.96
<i>N</i> -methyldiethylamine	1.81	4.10
<i>n</i> -Amylamine	4.65	12.61
Isoamylamine	...	10.72
Field collections		
1 ^d	0.16, 0.32, 0.47, 0.71, 0.87, 1.18, 1.34, 1.50, 2.76, 4.73	0.24, 0.47, 0.71, 0.79, 1.10, 1.34, 1.73, 2.05, 5.28, 12.61
2 ^e	0.16, 0.32, 0.55, 0.87, 1.18, 1.34, 2.92, 4.81	0.24, 0.47, 0.79, 1.18, 1.42, 1.74, 2.05, 5.28, 12.61
3 ^f	0.16, 0.32, 0.55, 0.63, 0.87, 1.34, 2.76, 4.73	0.24, 0.47, 0.87, 1.34, 1.74, 1.97, 2.52, 4.89, 12.69
4 ^g	...	0.24, 0.47, 0.87, 1.34, 1.65, 1.97, 2.44, 4.96, 12.69
2 and 3	0.16, 0.32, 0.55, 0.63, 0.87, 1.34, 2.76, 4.73	0.24, 0.39, 0.79, 1.34, 1.42, 1.74, 2.52, 5.12, 7.17, 12.61
3 before ashing	...	0.24, 0.47, 0.79, 1.34, 1.74, 2.05, 2.68, 5.12, 12.61
Blank ^h	0 ⁱ	0

^a Penwalt 223 column; conditions described in experimental section.
^b Chromosorb 103 column; conditions described in experimental section.

^c Determination not made.

^d Material collected during the period 9-20 to 10-27-71.

^e Material collected during the period 10-27-71 to 1-29-72.

^f Material collected during the period 1-29 to 3-6-72.

^g Material collected during the period 3-6 to 3-22-72.

^h Blank located as described in experimental section.

ⁱ Zero reading indicates no compounds detectable within instrumental detection limits.

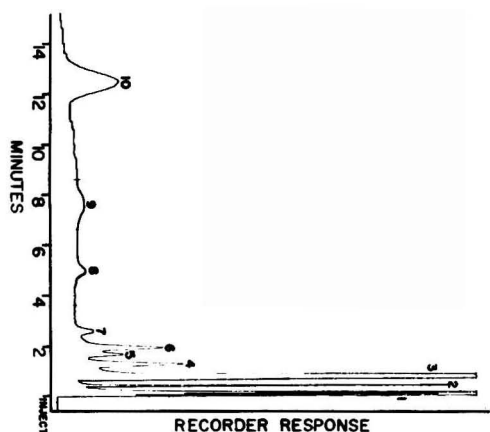


Figure 1. Chromatogram of direct gc analysis of feedlot volatiles collected in dilute acid

Traps 2 and 3 combined. Chromosorb 103 column. Each peak has been characterized as follows: (1) ammonia, (2) methyl, (3) ethyl, (4) isopropyl, (5) unknown, (6) *n*-propyl, (7) unknown, (8) *n*-butyl, (9) unknown, and (10) *n*-amylamine

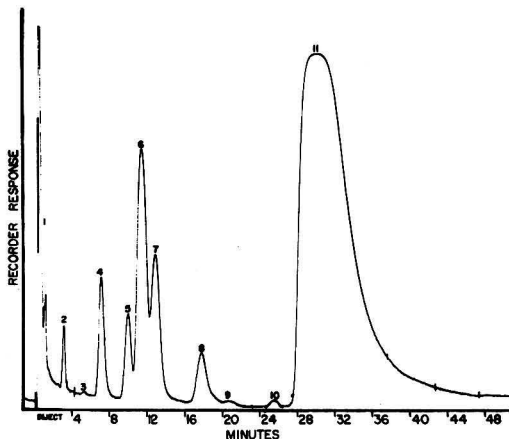


Figure 2. Chromatogram of gc analysis of pentafluorobenzoyl chloride derivatives of feedlot volatiles collected in dilute acid

Traps 2 and 3 combined. Column used was 10% Igepal CO 880 on Anakrom SD. The identity of the peaks, pentafluorobenzoyl derivatives, is as follows: (1) injection, (2) dimethyl, (3) unknown, (4) isopropyl, (5) methyl, (6) ethyl, (7) *n*-propyl, (8) *n*-butyl (9) unknown, (10) *n*-amylamines, and (11) ammonia

To have samples of manure volatiles more readily available than from the field traps, fresh cattle manure was brought into the laboratory in covered plastic buckets. Air was pulled over the manure surface and bubbled through 0.01*N* sulfuric acid. Direct gc analysis of the acid solutions indicated that the materials trapped were not representative of the volatiles trapped in the field. Even though air was continuously drawn over the manure, the alcohol levels collected were much higher than those trapped in the field. The alcohols identified tentatively by gc retention time comparisons overshadowed the amine concentrations. They also had gc characteristics so similar to isopropyl, *n*-propyl, and *sec*-butylamines that no differences could be observed. Ethanol (produced in largest quantity), isopropanol, and *n*-butanol were trapped. These observations are presented so that the reader will be aware that the "typical" head gas analysis of waste products is not necessarily characteristic of what is observed naturally.

Although our studies have been qualitative, we did estimate the amount of each of the identified compounds relative to the amount of ammonia. This was accomplished by making a series of dilutions and comparing the peak area of the amine with that of ammonia or the peak area of the amine's pentafluorobenzoyl derivative with that of the ammonia derivative. The ratios of these areas, which agreed closely in the two comparisons, were methyl (100:0.5-1.0), dimethyl (100:0.1-0.5), ethyl (100:1-2),

Table II. Gas Chromatographic Retention Times for Pentafluorobenzoyl Chloride Derivatives of Amine Standards and Feedlot Volatiles

Sample	Retention times	
	Column 1, ^a min	Column 2, ^b min
Dimethylamine	3.15	2.84
Isopropylamine	8.51	6.86
Methylamine	12.37	9.69
Ethylamine	14.66	11.11
<i>n</i> -Propylamine	15.76	12.53
<i>n</i> -Butylamine	21.35	17.57
<i>n</i> -Amylamine	29.79	25.45
Ammonia	42.71	29.79
Feedlot volatiles ^c	0.63, 2.29, 3.23, 4.96, 5.52, 6.86, 7.49, 8.51, 12.45, 14.74, 15.84, 21.51, 23.64, 29.94, 42.55	0.87, 2.29, 2.84, 5.04, 6.78, 9.69, 11.03, 12.53, 17.57, 20.49, 25.37, 29.79

^a Column 1: 6% DEGS on 80-100 mesh Chromosorb W-HP. Conditions as indicated in experimental section.

^b Column 2: 10% Igepal CO 880 on 100-110 mesh Anakrom SD. Conditions as indicated in experimental section.

^c Combination of field traps =2 and =3 which represent collection of feedlot volatiles over the period 10-27-71 to 3-6-72.

n-propyl (100:0.1-0.5), isopropyl (100:0.5-1.0), *n*-butyl (100:0.05-0.1), and *n*-amylamine (100:0.05-0.1). These comparisons indicate that the amines identified may constitute about 2-6% of the basic material volatilized from a cattle feedlot relative to ammonia.

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Received for review Nov. 6, 1972. Accepted February 26, 1973. This research was supported in part by the Environmental Protection Agency. Contribution from the Agricultural Research Service, USDA, in cooperation with Colorado State University Experiment Station, Scientific Journal Series No. 1784. Trade names and company names are included as a matter of convenience to the reader, and such inclusion does not constitute any preferential endorsement by the U.S. Department of Agriculture of products named over similar products available on the market.

Ammonium Nitrate in Airborne Particles in Los Angeles

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■ After extraction of benzene solubles from airborne particulate matter collected at four Los Angeles sites, a still larger fraction can be extracted with methanol. This contains mostly inorganic materials. Qualitative tests, Kjeldahl titration, 2,4-xyleneol nitrate determination, and infrared spectra show it to be principally ammonium nitrate. This salt comprises approximately 10–15% of the total airborne particles in composite samples collected over the year 1971–72.

In treatment of airborne particulate matter sampled from Los Angeles air, conventional benzene extracts averaged 6–9% of the total suspended particulate matter. After their removal an even larger fraction (up to 30% of the total) could then be extracted by methanol. This methanol-soluble, benzene-insoluble material is mostly inorganics, predominantly ammonium nitrate. Nitrate levels in Los Angeles had been reported previously to be unusually high (U.S. Environmental Protection Administration, 1970).

Lundgren (1970) showed qualitatively the presence of crystalline ammonium nitrate in aerosols by x-ray diffraction. Stephens and Price (1972) collected a synthetic aerosol by impaction and found its infrared spectrum resembled that of atmospheric aerosol in Riverside, California. The work reported here shows that ammonium and nitrate are approximately equivalent in particulate samples collected over long time periods and comprise over 10% of the particle weight in some locations in Los Angeles.

Experimental Section

Large samples of airborne particulate matter were collected at four Los Angeles locations shown in Figure 1. Trailer-mounted collectors based on the design of Begegan and Colucci (1962) were operated continuously on alternate weeks. The samplers at all four sites were turned on or off each week within a few hours of one another. Sampling at site 1 began August 1969. All four samplers were run for one year from June 1971 to June 1972. In each trailer a large centrifugal blower drew 150 m³/min through a pleated fiber glass filter (Flanders Filter Co.) of 25 m² area. Each filter was used for a total of two weeks' actual operation, making 12 filters in all at each site for the year. (The total air volume sampled per unit area of filter corresponds roughly to operation of a standard Hivol or Staplex-type sampler for a little over two days.) After exposure the filters were sawed apart.

For the data reported here, composites were made up for each location consisting of a one-half pleat from each of the 12 monthly filters, thereby representing a combined yearly average. Each composite was extracted successively with benzene, methanol, and water, each for 24 hr in a

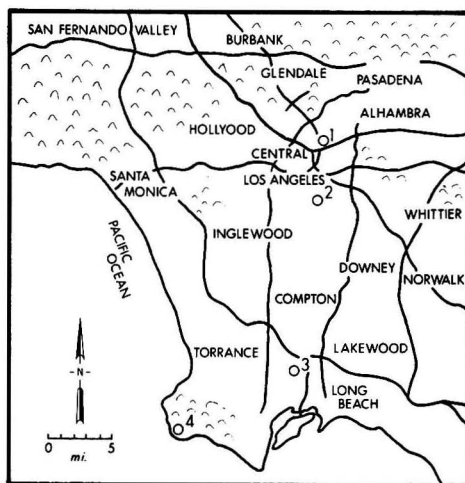


Figure 1. Particle sampling locations in Los Angeles, with major freeways

glass Soxhlet extractor. The organic solvents were removed and residues evaporated to constant weight in vacuum rotary evaporators at not over 40°C. Composite methanol extract residues amounted to 2.5–8.1 grams at the various sampling locations. Blank (unexposed) filter was also carried through the extraction sequences, and all yields and analytical values were corrected for blank contribution. Approximate total particulate sample yields were estimated by subtracting the weight of six blank unused filter pleats from the weights of the sample filter composites. All solvents were reagent grade or better.

A chromatogram on silica gel of a methanol extract from site 1 was run, using acetone-alcohol mixtures for elution. A large center cut was obtained which deposited white crystals on solvent evaporation. The crystals did not char in a flame and released ammonia odor in aqueous base. They gave an intense green color with carbazole in concentrated H₂SO₄, indicative of nitrate (Treadwell and Hall, 1942).

The following analyses were run on the methanol extract. Ammonium contents were determined by a standard Kjeldahl distillation and titration (without a digestion step). Nonaqueous titrations were also run in pyridine with tetrabutylammonium hydroxide (Buell, 1967b; Cundiff and Markunas, 1956); in acetonitrile with HClO₄ (Fritz, 1953); in acetic anhydride, after standing overnight, with HClO₄ (Wimer, 1958; Streuli, 1958); and in methanol with KOH. The ammonium is apparently titratable as an acid in pyridine or methanol and as a base resembling certain acetyltable nitrogen bases in acetonitrile or acetic anhydride, as classified by Buell (1967a). Nitrate was determined by the 2,4-xyleneol method (Saltzman, 1970). Infrared spectra of ammonium nitrate and of

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**Table I. Properties of Methanol Extracts of Airborne Particles
Los Angeles, June 1971–June 1972**

Air concentration	$\mu\text{G}/\text{m}^3$				Neut equiv/ m^3				
	1	2	3	4	1	2	3	4	
Location no.									
			Acids						
KOH/Methanol					327	427	214	95	
Bu ₄ NOH/C ₅ H ₅ N ^a									
Strong					40	—	7	7	
Medium	3.6 ^b	5.1 ^b	2.2 ^b	0.8 ^b	200	287	121	47	
Weak					101	88	66	22	
					Total	341	375	194	76
			Bases ^c						
Type 2 and 3A					109	43	72	59	
Type 3B	3.6 ^b	5.2 ^b	2.4 ^b	0.9 ^b	202	292	136	48	
Type 4					24	0	15	11	
					Total	335	335	223	118
NH ₄ ⁺ (Kjeldahl)	3.2	4.7	2.2	0.9	180	260	120	50	
NO ₃ ^{-d}	15.4	18.9	8.6	4.8	248	305	139	78	
Methanol extract	35.7	40.4	24.0	11.7					
Benzene extract	19.5	11.5	6.5	1.8					
Total particulate, approx.	215	131	102	32					

^a Buell, 1967b. ^b Calculated as NH₄. ^c Buell, 1967a. ^d Saltzman, 1970.

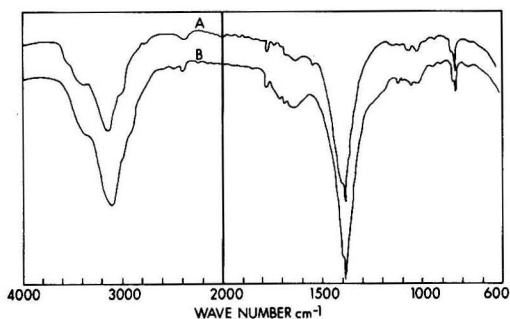


Figure 2. Infrared spectra (curves offset vertically), KBr pellets

- a. NH₄NO₃
- b. Methanol extract of composite of filters from site 2

the methanol extracts in KBr pellets were obtained on a Beckman IR-18 spectrometer.

Results and Discussion

In Table I analytical data for the methanol extracts are reported as air concentrations in terms of weight and equivalents. Total acids by titration in methanol and in pyridine are consistent. The type differentiation in pyridine allows comparison of "medium" strength acid with ammonium by Kjeldahl determination. (The "strong" acids in pyridine may include nitric acid since there is an excess of nitrate over ammonium at all locations.) The ammonium titrates as a base in acetonitrile or acetic anhydride and by Buell's classification scheme (Buell, 1967a) acts like type 3B bases. These values also may be compared with Kjeldahl results. In some cases, of course, there may be other acids or bases not measured in the Kjeldahl procedure. The infrared spectra in Figure 2 match in detail. The only strong infrared-absorbing species in the sample from site 2 appear to be ammonium and nitrate. The combined weights of ammonium and nitrate vary from 9–18% of the total particulate sample at the four locations.

**Table II. Ammonium and Nitrate Yields from Site 1
During Three Years
Yearly Composites of Filtered Particulate Samples**

Time interval for composite	NH ₄ , $\mu\text{g}/\text{m}^3$ air	NO ₃ , $\mu\text{g}/\text{m}^3$ air	Molar ratio, NO ₃ /NH ₄
8/69–8/70	2.8	8.8	0.91
8/70–8/71	3.4	10.0	0.86
6/71–6/72	3.2	15.4	1.40

The data shown in Table II for site 1 over three years indicate an increase in nitrate, but some variation in year-to-year weather conditions may have occurred. The nitrate-ammonium ratio at site 1 became greater than unity the last year, and was above unity at all four locations. Ammonium nitrate is presumably the product of reaction between ammonia and nitric acid, either in the gas phase or in or on aerosol particles. Urban ammonia concentrations have been estimated to be up to 0.2 ppm (140 $\mu\text{g}/\text{m}^3$) with averages of one tenth that value (Jacobs, 1960), somewhat above the ammonium levels found here in particles. Nitric acid is a product of the photochemical smog process. The nitrate precursor oxides of nitrogen, NO and NO₂, averaged over long periods in Los Angeles air (from data collected by the Los Angeles County Air Pollution Control District) correspond to a level of about 400 $\mu\text{g}/\text{m}^3$ if calculated as nitrate, which is much above any nitrate level found in particles. It is not certain whether ammonia or nitric acid is originally in excess, since neither the local concentrations of ammonia in Los Angeles nor the extent of conversion of oxides of nitrogen to nitric acid is known.

The presence of nitrate in foods and water has been of concern because of possible biological effects (Archer et al, 1971). Although the probable exposure to airborne nitrate would usually be less than to nitrate in foods, the fact that it may be deposited directly in the respiratory system as the readily soluble ammonium salt might make its entry into biochemical processes occur more easily.

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Received for review November 30, 1972. Accepted March 27, 1973. This study was conducted under contract PH 43-NCI-68-1030 within the Special Virus Cancer Program of the National Cancer Institute, National Institutes of Health, Public Health Service.

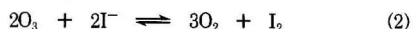
CORRESPONDENCE

Stoichiometry of Ozone-Iodide Reaction: Significance of Iodate Formation

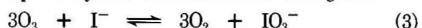
SIR: Recently Parry and Hern [*Environ. Sci. Technol.*, 7, 65 (1973)] found that iodate is formed in the reaction of ozone and iodide. This is considered important because the standard method for ozone determination is based on the liberation of iodine from a neutral potassium iodide solution according to Equation 1:



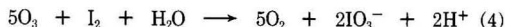
The 1:1 ratio of ozone to iodine given in Equation 1 has been questioned by Boyd et al. [*Anal. Chem.*, 42, 670 (1970)], who found a ratio of 1.5:1. However, the 1:1 ratio was confirmed by two groups: Kopczyński and Bafalini [*Anal. Chem.*, 43, 1126 (1971)] and Hodgeson et al. [*Anal. Chem.*, 43, 1123 (1971)]. In their paper Parry and Hern incorrectly state this reaction as:



When using either borosilicate glass or quartz frits to introduce the ozone into the iodide solution, Parry and Hern found that not only was iodine formed but also iodate. Two possible pathways for iodate formation were given:



and



In acidic solution, iodate will oxidize iodide to iodine:



Consideration of the stoichiometry of Equations 1, 3, 4, and 5 shows that if the iodide solution is acidified just before the determination of iodine, no stoichiometric error will be involved. The iodine formed via Equation 5 will be

equal to that which would have been formed according to Equation 1 from the ozone used in Equation 3 or 4. Therefore, if the determination of iodine is carried out under the proper conditions, no error will result from the formation of iodate.

This knowledge will be most useful to people working with ozone concentrations higher than those found in polluted atmospheres (~0.5 ppm). Parry and Hern found that at very low ozone concentrations iodate formation does not appear to be significant. At "higher" ozone concentrations, the iodine formed is usually titrated with sodium thiosulfate. Acidification just before titration is a simple matter and will ensure the decomposition of iodates.

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University of Montana
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SIR: The gist of Mr. Schmitz's comments makes a point which, though not specifically stated in the paper, is evident from the data. The total amount of iodine formed after acidification of the collection solution was taken in our paper as a measure of the ozone, as a little study of Figure 1 would indicate. [See abscissa of Figure 1 where the O_3 concentration was measured by the total ($\text{IO}_3^- + \text{I}_2$).] We, therefore, agree with Schmitz's comments but feel the point he raises was implicit in the original paper.

Edward P. Parry

North American Rockwell Science Center
Thousand Oaks, Calif. 91360

INDUSTRY TRENDS

International Paper Co. (Springhill, La.) is beginning construction on a \$14-million environmental improvement program at the Springhill mill. The new project will be in addition to a \$4-million pollution control project which began at the mill in August 1972. New facilities deal almost completely with air pollution control.

Envirex Inc., a Rexnord Co., has agreed with the De Laval Separator Co. (Poughkeepsie, N.Y.) to supply De Laval's full line of sludge dewatering centrifuges to the municipal market. The move will enhance De Laval's marketing opportunities since the company does not have the organization or related equipment to enter the complete municipal systems market. Envirex will market the De Laval separators under the Rex brand name.

Diversified Earth Sciences, Inc. (Los Angeles, Calif.) is filing a registration statement with the Securities and Exchange Commission covering a pro-

posed offering of 500,000 shares of common stock as follows: 350,625 shares are to be sold by the company, 105,547 by certain selling stockholders, and 43,828 through the exercise of a warrant to be purchased by the underwriters from the holder.

Peabody Engineering has been awarded a \$1.3-million turn-key project to convert boilers at the City of Detroit Mistersky Generating Station from pulverized coal to fuel oil. Objective of the conversion is to reduce total pollutants emitted by the utility operated by Public Lighting Commission of the City of Detroit. Peabody will design, engineer, fabricate, and install all components required for the conversion.

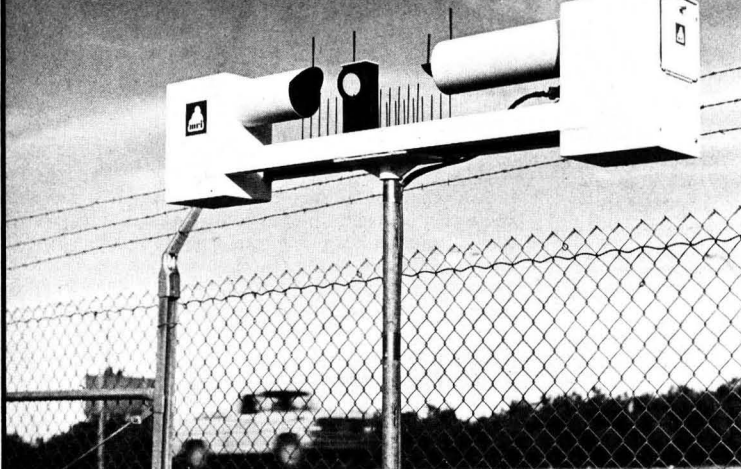
Poly Con Corp. (Ramsey, N.J.) has been awarded a \$416,800 contract for a prototype sulfur dioxide control facility at the TVA Widows Creek Plant in northeast Alabama. Poly Con's scrubber was designed as the result of findings from tests made on

various wet limestone scrubbing processes conducted on a smaller scale at TVA's Colbert and Shawnee Steam Plants in cooperation with the EPA. TVA's Widow Creek Plant, which will provide 550,000 kW of power, will be a major research facility for air pollution control. TVA's tentative cost estimate of the entire project is \$42 million.

Grumman Ecosystems Corp. (Bethpage, N.Y.) has acquired Scientific Ecology, Inc., and Power-Pac Enterprises, Inc., both of New Jersey. Scientific Ecology, Inc., designs and constructs solid and air waste facilities, including recycling plants; incinerating, thermal oxidizing, and scrubbing facilities; and shredder and compactor installations. Power-Pac manufactures a proprietary line of precast refractory and concrete chimney and refuse systems.

L&M Environmental Sales, Inc. (Greenville, S.C.) has been awarded a turn-key contract in excess of a quarter million dollars for the construction of a modern sanitary landfill operation in Williamsburg County, S.C. The new landfill operation is to be completely designed, engineered, and constructed by L&M and turned over to the county ready to run. All mechanical and structural components are to be furnished by L&M.

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The new landfill will utilize the HEIL pulverization process which shreds waste into odor-free, cohesive material and destroys its food value to rodents, insects, and other vermin.

Rust Engineering Co. (Birmingham, Ala.) has signed a contract with Mead Corp. (Dayton, Ohio) for engineering and construction of an expansion in excess of \$15 million at Mead's Chillicothe, Ohio, plant. The expansion will apply to Mead's specialty paper production, and work is already in progress. Rust is also performing the engineering and resident engineering services for the 650-ton-per-day N.S.S.C. corrugating medium mill for Mead Corp. at Stevenson, Ala., on the Tennessee River. The mill, costing approximately \$50 million, will be located on a 962-acre site, and about 10% of the mill's cost will be in pollution control facilities.

Systems Control, Inc. (Palo Alto, Calif.) has received a contract from the State of Washington, Department of Ecology, to analyze mathematical models and develop guidelines for their use by local planning agencies in preparing water quality management plans. The use of mathematical models to develop water quality plans is a prerequisite for communities to be eligible for state and federal cost-sharing on the construction of waste water treatment facilities.

Dart Industries, Inc. (Los Angeles, Calif.) has been appointed distributor in the U.S. and Canada for fully automatic pressure filters manufactured by Eberhard Hoesch and Sohne of Duren, West Germany. The Hoesch automatic filters have application in a variety of industries including water and waste treatment, chemicals, pigments, dyestuffs, intermediates, paper, plastics, metallurgical, and food processing.

General Electric Ordnance Systems (Pittsfield, Mass.) received a contract from the federal EPA for further work with a GE-developed infrared laser atmospheric monitoring system (ILAMS). Under the contract, a GE breadboard model will be modified to allow ILAMS to monitor and measure ozone concentrations in urban environments. Mounted in a trailer, ILAMS will be used in field measurement tests to compare the system's unique long-path monitoring capability to those of conventional instruments.

Biospherics, Inc. (Rockville, Md.) announced that Seneca Falls, N.Y., will be the first municipality to conduct a full-scale demonstration of the PhoStrip process to remove phosphate from sewage. The state of New York has ordered Seneca Falls to remove phosphate from its sewage effluent by mid-1974. Because it

will be the first municipality to put the process into full-scale operation, Seneca Falls will be accorded a royalty-free license by Biospherics.

Microseal Corp. (West Lafayette, Ind.) wholly owned subsidiary of Great Lakes Chemical Corp., has announced the commercialization of its No-Swab process for use in glass bottle and holloware manufacture. Customary swabbing every few minutes is eliminated, and air pollution is greatly reduced since no smoke is generated when the No-Swab process is used.

Monsanto Enviro-Chem Systems, Inc., has announced appointment of NGK Insulators Ltd., Nagoya, Japan, as Japanese distributor for Brink fiber bed equipment. According to Monsanto's spokesman, NGK has long been involved in the pollution control field, particularly in the development, engineering, and construction of water treatment and sewage treatment plants.

Chem Pure, Inc. (Bridgeton, Mo.) has been awarded a contract to build the first zero-flow sewage treatment plant for use in the State of Oregon. In the 50,000-gal-per-day tertiary plant, the process sewage water will be recycled back to the toilets and fresh make-up water will be supplied

from the drains of the drinking water fountains. Surplus water in the plant's reservoir tank can be automatically pumped off to a sprinkling system which waters the grass and shrubs. The plant will convert raw sewage into a clear, odorless effluent and meets all air and water pollution standards.

B. F. Goodrich (Akron, Ohio) is supplying the largest known installation of polyvinyl chloride trickling filters for purifying waste water at Stockton, Calif. The filters priced at nearly \$2 million are being installed for the City of Stockton as a part of a program to protect the environment through the purification of the area's waste water. The 1.5 million ft³ of the PVC trickling filters will replace three rock filters in the Stockton municipal water quality control plant.

Pollution Control—Walther, Inc. (Birmingham, Ala.) announced a contract with Weyerhaeuser Co. for the supply and erection of two electrostatic precipitators to be used in Weyerhaeuser's new low-odor recovery boiler system—reported to be one of the largest of its kind in the U.S. The contract calls for completion of the pollution control system by early 1975 at Weyerhaeuser's Plymouth, N.C., facility.

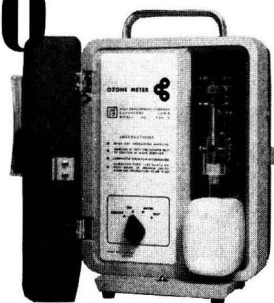
Theirs: \$5,000, \$4,900, \$4,200, \$3,000, \$2,760, \$1,795 . . .

Ours: \$950

Model 724-2M Ozone Meter

Continuous sampling; 0-1 ppm; .005 sensitivity; less than 1 minute rise time; completely self contained system; tiny maintenance and operating cost; portable; strip chart recorder optional.

There are many other reasons why our 724-2 Series Ozone Meters have been the most widely used O₃ (Oxidant) measuring instruments in the world for more than ten years. In industrial hygiene, laboratory studies, ambient monitoring, and many other applications. We'd like to show you exactly why our monitor is Number One. Contact us for complete information. Monitors also available for NO₂, Cl₂, F₂, Br₂, I₂.

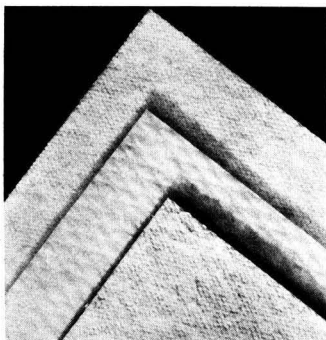


AIR MONITORING DIVISION
2212 East 12th St.,
Davenport, Iowa 52803

NEW PRODUCTS

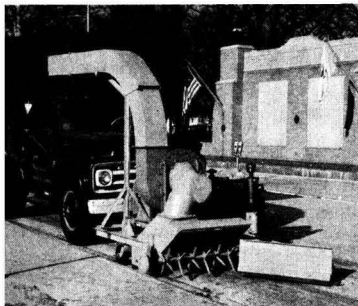
Gas-monitoring system

A gas-monitoring system can measure NO, SO₂, CO, CO₂, and opacity in stack gas on a simultaneous and continuous basis. Separate sampling is not required, and reliability and low maintenance are enhanced. The system monitors single or multigas emissions in power plants, refineries, foundries, and other similar facilities. Environmental Data Corp. **61**



Air filter media

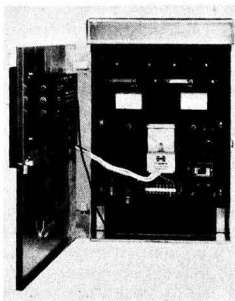
Glass fiber air filter media will enable equipment manufacturers to provide filters covering a wide range of efficiencies. When installed in air-cleaning filters, these media help keep building interiors clean and help combat air pollution by trapping dust particles. The media are composed of borosilicate glass fibers laid down in a thin felt and bonded with phenolic resin. Johns-Manville **62**



Leaf-loading machine

A leaf-loading machine, which can quick-attach to any truck with a snow-plow hitch, shreds, loads, and air-packs piled leaves and reduces them to one seventh their original bulk. The

hitch allows immediate truck replacement. Thus, several trucks can serve one loading unit, and the loader is kept in operation continually. The Flink Co. **63**



Corrosion protector

An automatic cathodic protection system prevents corrosion in water tanks and treatment units. Confused balancing and I-R drop error are eliminated in the 100% solid state system. Other featured advantages are direct protective level readouts and controls from 0-100% of rated capacity. Harco Corp. **64**

Atmosphere monitor

A detection instrument protects employee health by continuously monitoring the atmosphere for the presence of toluene diisocyanate. The device continuously draws a measured amount of ambient air through a slowly moving band of chemically treated filter paper. TDI in the atmosphere reacts with the sensitized paper tape to form a stain proportionate to its concentration in the sample. MDA Scientific, Inc. **65**

Bottle coating

Ionomer resins as a coating for glass bottles provides manufacturers with a transparent and tough material that decreases breakage. The applied "film" also allows greater opportunity for a thinner glass bottle construction. Bottles coated with the material are visibly more transparent than those coated with polyethylene and plastics. Du Pont Co. **66**

Odor-testing device

An odor level testing device developed by the Public Health Service is being manufactured. The scentometer measures the odor level in thresholds by drawing air through a pair of

activated charcoal filters to make it odor free. The air mixes with a measured amount of air admitted through one of a series of calibrated holes, and the operator determines which hole corresponds with the threshold response. Barnebey-Cheney. **67**

Sulfur analyzer

An analyzer provides accurate and instantaneous measurement of the sulfur content in residual fuel oils and petroleum distillates. The instrument provides the user with a digital readout of the sulfur percentage by weight in sample specimens. It employs nondispersive X-ray fluorescence generated by a radio isotope. Princeton Gamma-Tech, Inc. **68**



Oxygen monitor

An oxygen monitoring technique can measure dissolved oxygen content of industrial effluents, as well as check the aerobic and microbic waste reduction processes in water and sewage treatment. Both a portable oxygen analyzer and a continuous oxygen monitor are available, and both are easy to use. The sensor is calibrated at the temperature of the liquid to be checked. The reading of the dissolved oxygen content percentage on the meter can then be taken. Edmont-Wilson **69**

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

Converter unit

An external attachment unit converts a chemiluminescent nitrogen oxides analyzer into a heated system, making it ideal for the measurement of diesel and aircraft engine emissions. The module, working in conjunction with a Thermo Electron analyzer, eliminates the need for condensate traps in the sample line. The sample is heated within the module up to the point where pressure is reduced, and further heating is unnecessary. An external self-draining water trap prevents condensate from entering the analyzer's bypass system. Thermo Electron Corp. 70

pH and conductivity analyzers

A new line of portable pH and conductivity analyzers enhances a mechanism for the monitoring of bodies of water, plant effluents, in-plant processes, municipal water, and treated sewage. Designed primarily for field use, the analyzers feature environmental temperature compensation. They analyze and record to an accuracy of $\pm 2\%$ full scale for 30 days on self-contained batteries. A battery check button allows for easy battery strength monitoring. All units contain an internal electronic calibration check for rapid standardization. Wheaton Scientific 71

Incinerator

A new compact, inexpensive incinerator is capable of handling zero through Class VI burnables. These include copper wire insulation, transformers, industrial solid waste, scrap products, trash, and miscellaneous material. Equipped with 350,000 Btu burners, a multiple chamber base, and two afterburners of 350,000 Btu each, the unit is operative on either natural or propane gas. It will handle 500 lb of solid waste per hour and is guaranteed to operate with no visible emissions and at emission rates below acceptable levels. The United Corp. 72

Microcoulometer

A completely new microcoulometer features direct digital readout for rapid and accurate trace determinations of total amounts of nitrogen, sulfur, and halogens contained in solids, liquids, and gases. The device's digital display, speeds data interpretation, resulting in a 30% saving in operator time. Another major advantage is the elimination of a recorder/integrator combination, which results in a 50% reduction in system size. The unit incorporates integrated circuits, solid state switching, and BCD output for printers and computers. Envirotech Corp. 73

Filter material

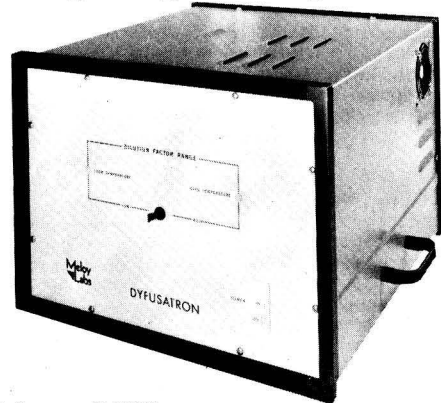
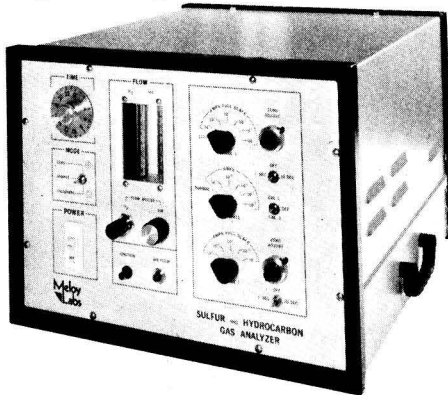
A new type of catalytic filter material acts chemically and physically to remove noxious gases, smoke, and odors. Called Sanilan, the material is available in slab and loose fill form. It is designed for original equipment applications in residential, commercial, and industrial air conditioning, ventilating, and humidifying systems and portable units, as well as in a variety of other consumer appliances. The product consists of open-cell urethane foam with a catalytically active oxidation-reduction system. It operates at normal ambient temperatures to absorb odors and fumes, and then chemically decompose them. Avmetco Corp. 74

ODS pump

A new ODS pump line featuring suction lift has been developed for the pumping of sewage in sewage treatment plants. The pumps are low in maintenance costs, cannot be overloaded, and allow for the thickest possible consistency of sludge. They were designed to pump extremely abrasive material. The manufacturer claims they also eliminate packing and seal maintenance, feature corrosion resistant linings, have small space requirements, are entirely air operated, and require no electrical connection. Dorr-Oliver Inc. 75

For On-Stream Analysis

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The right way to go because these sulfur analyzers meet the rigid Federal Regulations specified for Air Monitoring Instruments. Each has been adapted for specific on-stream analyses in process procedures.

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When coupled to the D-1000, a diffusion instrument, continuous, accurate and precise sample dilution adapts these analyzers to on-stream analysis for process control and source monitoring. The D-1000 overcomes the usual pneumatic dilution operating problems and limitations. It can handle dilution factors larger than 10^7 for most process gas stream samples where sulfur is a pollutant or impurity.

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NEW LITERATURE

Flocculants. Eight-page booklet describes company's synthetic cationic, polyelectrolyte flocculant. Literature gives details of physical properties and performance as a saveall additive, retention aid, drainage aid, and methods of application for the flocculant. Also included are mill results, laboratory studies, and studies of effectiveness in the field. National Starch and Chemical Corp. **91**

Flash photolysis catalog. Twenty-page catalog describes applications of flash photolysis technique and components and subsystems available for pollution control. Xenon Corp. **92**

Oil skimmer. Fifteen-page report shows equipment being used to clean up oil spills in harbors and open ocean. Report also presents a method for calculating the performance of oil skimmer when operating in an oil spill. JBF Scientific Corp. **93**

Air pollution control. New 30-page illustrated brochure covers entire line of systems and equipment for solving air pollution problems. Bulletin includes product and application data on electrostatic precipitators, fabric filters, mechanical dust collectors, scrubbers, and sulfur dioxide control systems. Research-Cottrell Inc. **94**

Activated charcoal. New technical bulletin package covers company's line of filters for removing odors with activated charcoal. Unit consists of a fiber structure coated with activated charcoal which has low resistance to air flow and possesses high absorption capacity for odor removal. Barnebey-Cheney, Inc. **95**

Mercury removal. Bulletin describes mercury removal process based on sodium borohydride reduction. Publication covers overall features, application, operation, and performance of the system and details a typical waste water system and typical gas stream system with schematic diagrams. Koertrol Corp. **96**

Vibration mountings. Designers' guide to vibration isolation mountings, shock control mountings, and elastomeric flexible couplings includes product listing of hundreds of standard mountings and couplings available off-the-shelf. Lord Corp. **97**

Tubular filters. Company's series of tubular filters for liquid filtration is described in six-page bulletin. Filters are available as single tubes with flow

rates from 1-300 gpm or manifolded into multiple filter arrangements with rates from 100 to 3100 gpm. Wide variety of reusable filtering elements is described. Durco **98**

Management service. New booklet describes company's air quality management service which offers accurate, inexpensive way of determining present and future effects of manufacturing emissions on ambient air quality. Service includes in-stack measurement, prediction of concentration profiles, and validation of the profiles by monitoring with mobile vans. Du Pont **99**

Solid waste management. New publication describes company's services in solid waste management. Roy F. Weston, Inc. **100**

Air pollution. Illustrated brochure describes solutions to industrial air pollution problems. Equipment mentioned includes chemical absorption towers, venturi scrubbers, and two-stage systems utilizing venturi and tower devices in combination. Also covers equipment performance, characteristics, dimensions, and specifications. Pollution Control Systems **101**

New products. Bulletin NP-73 describes Psychro-Dyne Portable RH Meters, Physio-Dyne Heat Stress Meter, Sling Psychrometer, Volt-A-Trol Voltage Regulators and Speed Controls, Moisture Monitors, Liquid Level Detectors, and Pollutrol Room Air-Purifiers, ETC, Commercial Products Division **102**

Thermal incineration. Leaflet describes indoor units, outdoor units at ground level, and rooftop units. Lists fume incinerator features and discusses heat exchangers. AER Corp. **103**

Catalog. Features selected instrumentation and apparatus for environmental investigation and pollution control. Detailed information and photographs covering instruments for all areas of environmental studies including sampling devices, water pollution test kits, gas analyzers, safety equipment, plasticware, liquid dispensers, and many other general laboratory time-saving items. Horizon Ecology Co. **104**

Synthetic polymers. Reprint describes synthetic polymers used for coagulation and flocculation of suspended solids in potable water treatment.

Includes diagram showing the electrostatic effect of coagulation and the mechanism of bridging by flocculants. Also covers the use of synthetic polymers as filter aids and sludge dewatering aids. Nalco Chemical Co. **105**

Membrane filters. Manual contains "how-to" information covering nearly every use of Millipore membrane filters in microchemical analysis. Over 50 procedures for sampling, sample preparation, and analysis described in detail and illustrated. Intended as handbook for the analytical laboratory worker and reference for classroom use. Millipore Corp. **106**

Flotation system. Bulletin describes recovery or removal of carbon black, latex, oil, plastics, and certain fibers from water by the flotation process. Removal of oil and emulsified oil from process water streams to meet exacting standards readily accomplished. Flotation systems applicable to refinery waste water, tank car washing, hydrocarbon processing plants, steel mill waste, rolling mill insoluble oils, and similar waste water streams. Joy Manufacturing Co., Denver Equipment Div. **107**

Submersible pump. Illustrated catalog describes electric submersible pumps for waste water and raw water use. Provides detailed flow vs. head performance curves. Also includes photos and information about the company's extensive engineering, testing, and certification facilities where capacities up to 10,000 gpm and heads to 462 ft can be measured with extreme accuracy. Flygt Corp. **108**

Cationic polymer. Bulletin No. 12-64 describes WT-2635, a liquid cationic polymer for solid/liquid separation in municipal and industrial waste water treatment system. Polymer may be used as a primary coagulant or coagulant aid in all types of solids/liquid separation processes including filtration, sedimentation, flotation, and centrifugation. Calgon Corp. **109**

Odor glossary. Listing of terms used in odors and their control, and published by manufacturer of activated charcoal and adsorption equipment. Glossary was developed for training personnel, and the company is now making this available to others interested in odors, what causes them, and odor control. Barnebey-Cheney **110**

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BOOKS

Transfer of Radioactive Materials from the Terrestrial Environment to Animals and Man. R. John Garner. 57 pages. Chemical Rubber Co Press, 18901 Cranwood Parkway, Cleveland, Ohio 44128. 1972. \$12.50, hard cover.

Examination of the sources, species, and quantities of radionuclides which may enter the biosphere. Also explains how they may be distributed and indicates by what mechanisms they may enter animals and man. Pathways identified as having major importance are treated generally, and individual nuclides are used to illustrate the importance of individual pathways under specific circumstances.

Growing Against Ourselves: The Energy-Environment Tangle. S. L. Kwee, J. S. R. Mullender, Eds. xix + 252 pages. D.C. Heath & Co., 125 Spring St., Lexington, Mass. 02173. 1972. \$15, hard cover.

The present volume contains most of the papers prepared for the colloquium, "Electrical Energy Needs and Environmental Problems," sponsored by the John F. Kennedy Institute and the Future Shape of Technology Foundation in The Hague. A descriptive and comparative analysis of problems, policies, and future strategies.

Fight for Wildlife, Ecology Kit-1. Follet Publishing Co., 1010 W. Washington Blvd., Chicago, Ill. 60607. 1972. \$4.95.

Educational kit designed to alert children aged 10-16 to the dangers threatening the environment and its creatures. Each kit contains a wall poster detailing the problem, guides on how to publicize environmental threats in the child's home town, membership cards for an "eco-patrol," stationary, and various charts and display material. Fight Pollution, Ecology Kit-2 also available.

Disaster by Oil. Jeffrey Potter. xii + 301 pages. Macmillan Co., 866 Third Ave., New York, N.Y. 10022. 1973. \$7.95, hard cover.

Book explores the effects of massive supertanker spillages and offshore drilling blowouts upon nature. Author tells how important natural balances are upset when delicate marine plants are destroyed, and how fish, birds, seals, and even humans die as a result of these disasters. He charges that the Government is ineffective in such matters, and that industry is too greedy.

Methods of Air Sampling and Analysis. Intersociety Committee. xvii + 480 pages. American Public Health Association, Inc., 1015 18th St., N.W., Washington, D.C. 20036. 1972. \$12.50, hard cover.

Book is the first published effort by the Intersociety Committee to provide a "tentative" methodology for analyzing the pollution content of air samples. The study specifically discusses analytical procedures for determining sulfur, halogen, nitrogen, carbon, hydrocarbon, metal, and radioactive and particulate matter content. It also sets up suggested abbreviations and symbols for use by scientific personnel.

Organic Chemicals in the Soil Environment, Vol. 2. Cleve A. I. Goring, John W. Hamaker, Eds. xii + 443-968 pages. Marcel Dekker, Inc., 95 Madison Ave., New York, N.Y. 10016. 1972. \$26.50, hard cover.

Presents a unified picture of the principles that govern the behavior of all types of organic substances in soil, and illustrates the applicability of these principles to a wide variety of synthetic organic chemicals. Intended for agronomists, soil scientists, chemists, entomologists, plant pathologists, plant physiologists, horticulturists as well as graduate students involved in research and development of pesticides and other organic derivatives.

Energy Research Needs. Sam H. Schurr. xii + various pages. National Technical Information Service, Dept. of Commerce, Springfield, Va. 22151. 1972. \$13.50, paper.

Identifies the many subjects on which research is essential to understanding of the long-term energy situation in the U.S. The findings are presented against a comprehensive analysis of the problems to which research should be addressed.

Guide to National Petroleum Council Report on United States Energy Outlook. John B. McLean, Warren B. Davis. 40 pages. National Petroleum Council, 1625 K St., N.W., Washington, D.C. 20006. 1972. \$1.50, paper.

Projects the energy picture between now and 1985, reviews options open to man, and recommends specific changes in government policies and programs to increase supplies of domestic energy. Covers oil and gas, nuclear energy, oil shale, and other energy forms.

Action for Wilderness. Elizabeth R. Gillette, Editor. 222 pages. Sierra Club Books, 597 Fifth Ave., New York, N.Y. 10017. 1973. \$2.25, paper.

Book begins with the premise that not enough progress is being made to preserve our wilderness resources. Intended to be a manual for pro-wilderness activists, and activists-to-be, it seeks to show that the survival of wilderness areas is too important a problem to be left to the whims of congressmen and government agencies. It maintains "private" steps need to be taken.

The Do-It-Yourself Environmental Handbook. E. J. Koestner, J. J. McHugh, R. Kircher, Eds. 76 pages. Dayton Museum of Natural History, 2629 Ridge Ave., Dayton, Ohio 45414. 1972. \$1.95, paper.

Book has two basic parts. The master checklist presents an overall view on how man pollutes and can reduce each person's contribution to pollution. The Action Guide explains how to undertake tasks to make the world a better place now and in the future.

Water Pollution Chart. Roy G. Scarfo Inc., P.O. Box 217, Thorndale, Pa. 19372. 1972. \$2.50.

Chart lists major pollutants, the aquatic food chain, mercury cycle, nitrogen cycle, hydrologic cycle, physical and chemical data, and estimated prevalence of water pollution in the U.S. Roy G. Scarfo Inc. also has charts depicting air and noise pollution.

Oil Pollution and Marine Ecology. A. Nelson Smith. ix + 260 pages. Plenum Publishing Corp., 227 West 17th St., New York, N.Y. 10011. 1973. \$14.50, hard cover.

Brings together data on the technical and biological aspects of oil spill contamination in the oceans. Book is an attempt to inform industrial and administrative officials of the complexity of life in the sea and the less direct effects pollution may have on marine ecosystems.

Man, Machines and Tomorrow. M. W. Thring. xiii + 127 pages. Routledge & Kegan Paul, 9 Park St., Boston, Mass. 02108. 1973. \$7, hard cover.

Investigates the ways in which technologists can solve the problems our technological society has brought upon itself. Professor Thring is hopeful for the future of mankind and seeks to establish the possibility of a real machine-served Utopia in which all men and women are free to seek self-fulfillment.

MEETING GUIDE

July 18-20 Ann Arbor, Mich.
Symposium on Wastewater Effluent Limits. University of Michigan and others

Designed to consider material of interest to water pollution scientists and administrators connected with both government and industry, water economists, and attorneys. *Contact:* John J. Gannon, School of Public Health, University of Michigan, Ann Arbor, Mich. 48104

July 18-21 Columbia, Md.
NLC Training Seminar/Land Use Planning. Council of State Governments

Contact: Council of State Governments, Iron Works Pike, Lexington, Ky. 40505

July 24-26 Denver, Colo.
Water Conditioning Association International. 28th Annual Convention and Exposition.

Contact: WCAI, 330 S. Naperville St., Wheaton, Ill. 60187.

July 30-August 3 University Park, Pa.
Modern Developments in Combustion Technology Seminar. Pennsylvania State University

Will emphasize kinetics, pollutants, radiation, noise, and related topics. *Contact:* H. B. Palmer, 320 M.I. Bldg., University Park, Pa. 16802

August 1-3 Fort Collins, Colo.
Development and Population Alternative Futures for the West. Colorado State University

Will study the impacts and consequences of growth in the West as it affects the overall quality of life. *Contact:* Office of Conferences and Institutes, Center for Continuing Education, Colorado State Univ., Fort Collins, Colo. 80521

August 8-10 Atlanta, Ga.
1973 Cryogenic Engineering Conference. U.S. Department of Commerce

Overall theme of Energy and Environment. *Write:* Jack E. Jensen, Program Chairman, Brookhaven National Laboratory, 1 E. 4th, Upton, N.Y. 11973

August 13-15 Philadelphia, Pa.
National Conference on Environmental Engineering Education. Drexel University and others

Will formulate academic guidelines for training the next generation of environmental engineers, administrators, and technologists. *Contact:* Office of Continuing Professional Education, Drexel University, Philadelphia, Pa. 19104

August 13-17 Philadelphia, Pa.
8th Intersociety Energy Conversion Engineering Conference. ACS and others

Write: Arvin H. Smith, Thermo Electron Corp., 85 First Ave., Waltham, Mass. 02154

August 14-16 Boulder, Colo.
Symposium on Instrumentation for Monitoring Air Quality. American Society for Testing and Materials and others

Critical overview of monitoring instrument performance. *Contact:* ASTM, 1916 Race St., Philadelphia, Pa. 19103

August 20 Chicago, Ill.
Fine Particle Society. Annual Meeting

Contact: G. A. Turner, Department of Chemical Engineering, University of Waterloo, Waterloo, Ont., Canada

August 21-24 Chicago, Ill.
International Conference on Particle Technology. IIT Research Institute and Illinois Institute of Technology

Contact: R. Davies, Conference Director, IIT Research Institute, 10 W. 35th St., Chicago, Ill. 60616

August 22-24 Saskatoon, Sask., Canada

International Specialty Symposium on Waste Water Treatment in Cold Climates. University of Saskatchewan and others

Write: E. Davis, Civil Engineering Department, University of Saskatchewan, Saskatoon, Sas., Canada S7N 0W0

August 26-31 Chicago, Ill.
American Chemical Society. 166th National Meeting

Contact: A. T. Winstead, ACS, 1155 16th St., N.W., Washington, D.C. 20036

August 29-September 1 Pacific Grove, Calif.

First International Conference on Environmental Mutagens. Environmental Mutagen Society

Contact: International Conference on Environmental Mutagens, c/o Bruce N. Ames, Department of Biochemistry, University of California, Berkeley, Calif. 94720

September 6 Washington, D.C.
Third Eco-Technic Recycling Conference. National Association of Secondary Material Industries, Inc.

Contact: NASMI, Inc., 330 Madison Ave., New York, N.Y. 10017

September 10-12 Washington, D.C.
Marine Technology Society. 9th Annual Conference

Covers pollution problems, coastal zones, development, and other environmental topics. *Write:* Marine Technology Society, 1730 M St., N.W., Washington, D.C. 20036

September 11-13 Chicago, Ill.
National Noise and Vibration Control Conference. American Industrial Hygiene Association and others

Will cover environmental noise, product noise, and industrial noise. *Contact:* Sound and Vibration, 27101 E. Oviatt Rd., Bay Village, Ohio 44140

September 11-13 Philadelphia, Pa.
11th Annual Liberty Bell Corrosion Course. Engineers' Club of Philadelphia and National Assoc. of Corrosion Engineers

Will cover corrosion, coatings, water, and waste material. *Write:* John M. Donohue, Publicity Director, Liberty Bell Corrosion Course, Betz Laboratories, Inc., Somerton Rd., Trevese, Pa. 19047

September 15-20 Denver, Colo.
1973 International Public Works Congress and Equipment Show. American Public Works Association

Technical sessions on solid wastes, transportation, water resources, and other topics. *Write:* Alfred J. Kuhn, Director, American Public Works Assoc., 1313 E. 60 St., Chicago, Ill. 60637

September 16-18 Oregon City, Ore.
Environmental Technology Show. Clackamas Community College

Second annual symposium. *Contact:* Clackamas Community College, 19600 S. Molalla Ave., Oregon City, Ore. 97045

September 19-20 New York, N.Y.
Conference on Environmental Engineering Problems in Industrialized and Developing Countries. World Federation of Engineering

Papers on energy, iron and steel industry and extraction of nonferrous metals, the chemical industry and oil refining, and agriculture. *Write:* Ann Cook, WFEO Conference Manager, Savoy Place, London WC2R 0BL, England

September 19-21 Winnipeg, Man., Canada

Western Canada Water and Sewage Conference and others. American Water Works Association and others.

To be held in conjunction with Annual Convention Western Canada Section AWWA, Western Canada Pollution Control Association, and Federation of Associations on the Canadian Environment. *Contact:* D. A. Shillabeer, Secretary-Treasurer, P.O. Box 3212, Postal Station D, Edmonton, Alta., Canada

September 23-26 Tulsa, Okla.
National Forum on Growth with Environmental Quality. Metropolitan Tulsa Chamber of Commerce and others

Will question America's ability to strike a balance between ecological and conservation interests and continued economic growth. *Contact:* Bruce Carnett, Manager, Public Relations, Metropolitan Tulsa Chamber of Commerce, 616 S. Boston Ave., Tulsa, Okla. 74119

September 24-28 Las Vegas, Nev.
Symposium on Noble Gases. EPA and the University of Nevada

Contact: A. Alan Moghissi, Chairman, Program Committee, Noble Gases Symposium, U.S. EPA, P.O. Box 15027, Las Vegas, Nev. 89114

September 25-28 San Francisco, Calif.

Geothermal Resources Council. 1973 General Meeting

Contact: GRC, P.O. Box 1033, Davis, Calif. 95616

September 26-28 Waitsfield, Vt.

Rural Environmental Engineering: A Conference on Water Pollution Control Technology in Low-Density Areas. University of Vermont and University of Maine

Write: William J. Jewell, Department of Civil Engineering, University of Vermont, Burlington, Vt. 05401

September 26-30 New Orleans, La.
International Symposium on Underground Waste Management and Artificial Recharge. American Association of Petroleum Geologists and others

Includes technical papers and field trips. *Contact:* Leslie Bowling, General Chairman, 1417 NBC Bldg., New Orleans, La. 70112 or the American Association of Petroleum Geologists, Box 979, Tulsa, Okla. 74101

September 28-October 5 Cleveland, Ohio

Water Pollution Control Federation. 46th Annual Conference

For details: R. A. Canham, WPCF, 3900 Wisconsin Ave., N.W., Washington, D.C. 20016

September 30-October 3 Hot Springs, Ark.

Soil Conservation Society. 28th Annual Meeting

Theme is "Plants, Animals, and Man." *Write:* Soil Conservation Society of America, 7515 Northeast Ankeny Rd., Ankeny, Iowa 50021

September 30-October 5 Vail, Colo.
Earth Sciences and Environmental Policy Making. Geological Society of America

Attendance limited by invitation. *Write:* Bruce B. Hanshaw, Water Resources Div., U.S. Geological Survey, Federal Center, Denver, Colo. 80225

October 1-2 Cincinnati, Ohio

Secondary Fiber Pulping Conference. Technical Association of the Pulp and Paper Industry

Contact: H. O. Teeple, TAPPI, One Dunwoody Park, Suite 130, Atlanta, Ga. 30341

October 1-3 Ottawa, Canada
International Conference on Land for Waste Management. Canadian Society of Soil Science

Will cover waste disposal and utilization in soils, evaluating such systems, and identifying problem areas. *Write:* M. K. Ward, Executive Secretary, International Conference on Land for Waste Management, National Research Council, Ottawa, Ont., Canada K1A 0R6

October 2-5 Orlando, Fla.

Symposium on Remote Sensing in Oceanography. International Society for Photogrammetry

Will cover offshore, coastal, and estuarine areas. *Contact:* Paul G. Teleki, Coastal Engineering Research Center, 5201 Little Falls Rd., N.W., Washington, D.C. 20016

October 6-10 Clearwater, Fla.

Annual International Environmental Sanitation & Maintenance Management Educational Conference/Exposition. Environmental Management Association

Related to environmental sanitation maintenance industry. *Write:* Environmental Management Assoc., 1710 Drew St., Clearwater, Fla. 33515

October 7-12 Boston, Mass.

International Symposium on Fine Particles. Electrochemical Society

Write: W. E. Kuhn, 498 Rhodes Hall, Univ. of Cincinnati, Cincinnati, Ohio 45221

October 9-10 Pittsburgh, Pa.

Industrial Health Foundation. 38th Annual Meeting

Write: Daniel C. Braun, IHF, 5231 Centre Ave., Pittsburgh, Pa. 15232

October 9-12 Washington, D.C.

Association of Official Analytical Chemists. 87th Annual Meeting

Papers on analysis of pesticides, food additives, and related subjects. *Contact:* L. G. Ensminger, Executive Secretary, AOAC, Box 540, Benjamin Franklin Station, Washington, D.C. 20044

Courses

July 9-13 Madison, Wis.

Urban Transportation Planning. University of Wisconsin

Fee: \$275. *Write:* William R. Baker, Program Director, University of Wisconsin-Extension, Dept. of Engineering, 432 N. Lake St., Madison, Wis. 53706

July 29-August 3 Henniker, N.H.

Preparation of Environmental Impact Statements. Engineering Foundation

Fee: \$160. *Write:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

July 30-August 10 Cambridge, Mass.

Energy: A Unified View. Massachusetts Institute of Technology

Contact: Director of the Summer Session, MIT, Room E19-356, Cambridge, Mass. 02139

August 6-8 University Park, Pa.

Technology of Powders and Fine Particles. Pennsylvania State University

Covers the role of particulate matter in air and water pollution. *Contact:* Richard Hogg, 24 Mineral Sciences Bldg., Pennsylvania State University, University Park, Pa. 16802

August 12-17 Denver, Colo.

Process' and Environmental Analytical Instrumentation. Instrument Society of America

A concurrent course, "Sampling and Sampling Systems for Process and Environmental Instrumentation," is also offered. Fee: \$300. *Write:* ISA, Education Department, 400 Stanwix St., Pittsburgh, Pa. 15222

August 19-24 Henniker, N.H.

Energy Conservation at the Point of Use. Engineering Foundation

Fee: \$160. *Write:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

August 20-24 Dearborn, Mich.

Institute on Noise Control Engineering. Seventh Presentation.

Training in the solution of factory, environmental, and product noise problems. *Write:* James H. Botsford, Director, Institute on Noise Control Engineering, P.O. Box 3164, Bethlehem, Pa. 18017

August 20-24 Ann Arbor, Mich.

Summer Institute on Industrial and Municipal Water Pollution Control—Physicochemical Processes. University of Michigan

Tuition: \$275. *Contact:* Walter J. Weber, Jr., Dept. of Civil Engineering, The University of Michigan, Ann Arbor, Mich. 48104

August 27-31 Berkeley, Calif.

Combustion Sources of Air Pollution and their Control. University of California

Fee: \$275. *Contact:* Continuing Education in Engineering, University of California Extension, 2223 Fulton St., Berkeley, Calif. 94720

September 5-7 Chicago, Ill.

Noise Control of Mechanical Equipment in Buildings Seminars. Bolt Beranek and Newman Inc.

Also given in other locations throughout the fall. *Write:* Gloria A. Cianci or Carol Q. Sudol, Bolt Beranek and Newman Inc., 50 Moulton St., Dept. B, Cambridge, Mass. 02138

September 10-14 Berkeley, Calif.

Environmental Impact Assessment of Nuclear Power Generation. University of California and Teknekron, Inc.

For details: Continuing Education in Engineering, University of California Extension, Berkeley, Calif. 94720

September 24-26 Washington, D.C.

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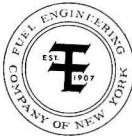
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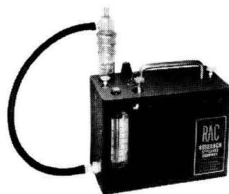


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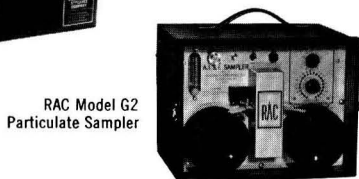
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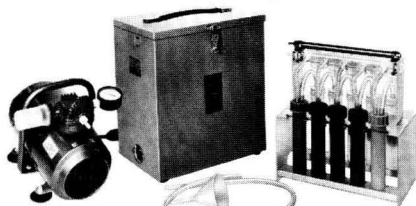
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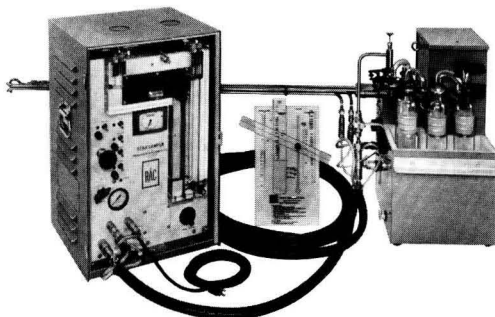
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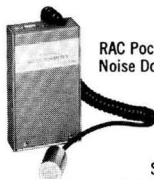
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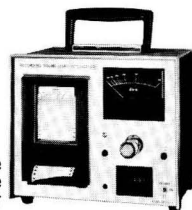
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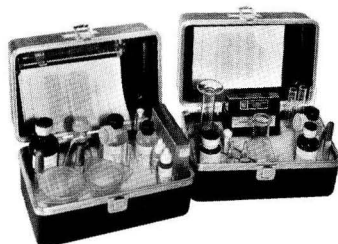
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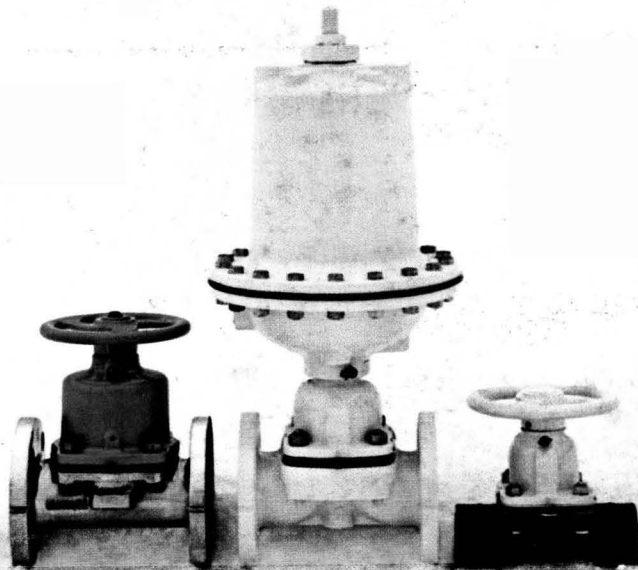
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