Environmental
Science & Technology

✓MARCH 1974

earthwatch 214

Environmental
Science & Technology

Volume 8, Number 3, March 1974

ESTHAG 8 (3) 189–286 (1974)
ISSN 0013-936X

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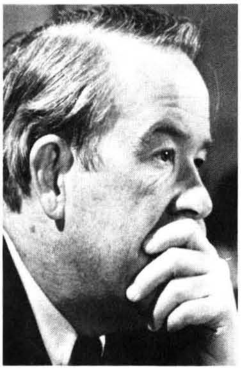

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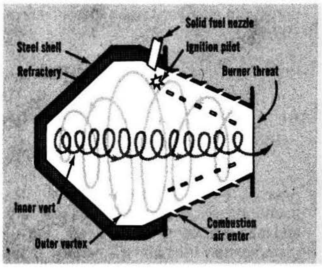

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Published monthly, with additional Pollution Control Directory in November, by the American Chemical Society, from 20th and Northampton Sts., Easton, Pa. 18042. Executive offices: Editorial Headquarters, 1155 16th St., N.W., Washington, D.C. 20036.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

ES&T ON MICROFILM: This publication is available on microfilm. For information, write to: Microfilm, Special Issues Sales, ACS, 1155 16th St., N.W. Washington, D.C. 20036.

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CURRENT RESEARCH

Hydrocarbon composition of urban air pollution 229

W. A. Lonneman, S. L. Kopczynski, P. E. Darley, and F. D. Sutterfield

Air samples from New York and Los Angeles are evaluated for ambient concentrations of hydrocarbons and oxides of nitrogen. Data of this type are essential for planning control strategies to meet the 1975 hydrocarbon air quality standards. Methods are presented for estimating vehicular hydrocarbons in an ambient atmosphere.

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

Credits: 195, *C&EN*'s Fred Zerkel; 196, Dames & Moore; 199, American Air Filter Co., Inc.; 202 (upper), UPI; 203, George Hunter (Toronto, Canada); 210 (4 photos), Combustion Equipment Associates, Inc.; 222 (lower right), Thiokol Chemical Corp.; 223 (2 photos), U.S. Coast Guard

Cover: John V. Sinnett

The Chiyoda THOROUGHBRED 101 Flue Gas Desulfurization Process

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Just two years ago, Chiyoda introduced the Chiyoda THOROUGHBRED 101 Flue Gas Desulfurization Process — a more economical, more effective way to keep the air free of sulfur and other pollutants from power plants, steelworks, refineries, sulfur plants and smelters.

Five installations based on the process are already on stream. Others are scheduled for completion during 1974. And Chiyoda is now working with Hokuriku Electric Power Co., Inc. on a gigantic 652,000 scf/m. capacity plant.

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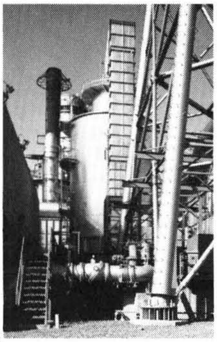

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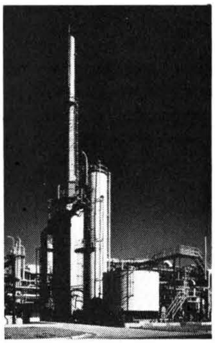
Tohoku Oil Co., Ltd.



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Fuji Kosan	98,000	Oil-Fired Boiler and Claus Sulfur Plant	Kainan
Mitsubishi Rayon	56,000	Oil-Fired Boiler	Otake
Tohoku Oil	8,800	Claus Sulfur Plant	Sendai
Hokuriku Electric Power	467,000	Oil-Fired Boiler	Toyama
Mitsubishi Petrochemical	435,000	Oil-Fired Boiler	Yokkaichi
Daicel	65,200	Oil-Fired Boiler	Aboshi
Amagasaki Cokes	15,500	Industrial Incinerator	Hyogo
Mitsubishi Chemical Industries	250,000	Oil-Fired Boiler	Yokkaichi
Mitsubishi Petrochemical	94,000	Oil-Fired Boiler	Yokkaichi
Hokuriku Electric Power	652,000	Oil-Fired Boiler	Fukui
Gulf Power	53,000	Coal-Fired Boiler	Florida

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EDITORIAL

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

Executive Director: Robert W. Cairns

PUBLIC AFFAIRS AND
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For author's guide and editorial policy, see June 1973 issue, page 517, or write Katherine I. Biggs, Manuscript Reviewing Office, *ES&T*

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

Earthwatching: a new pastime

Good monitoring news comes from Nairobi, Kenya—headquarters for the United Nations Environment Program (UNEP). At last month's intergovernmental meeting on monitoring the consensus was that monitoring is one of the first functions necessary for sound management of the environment. Of course, monitoring is not the only function; the other three, at least according to the consensus, are evaluation of, research into, and exchange of information about the state of the environment as a basis for its management.

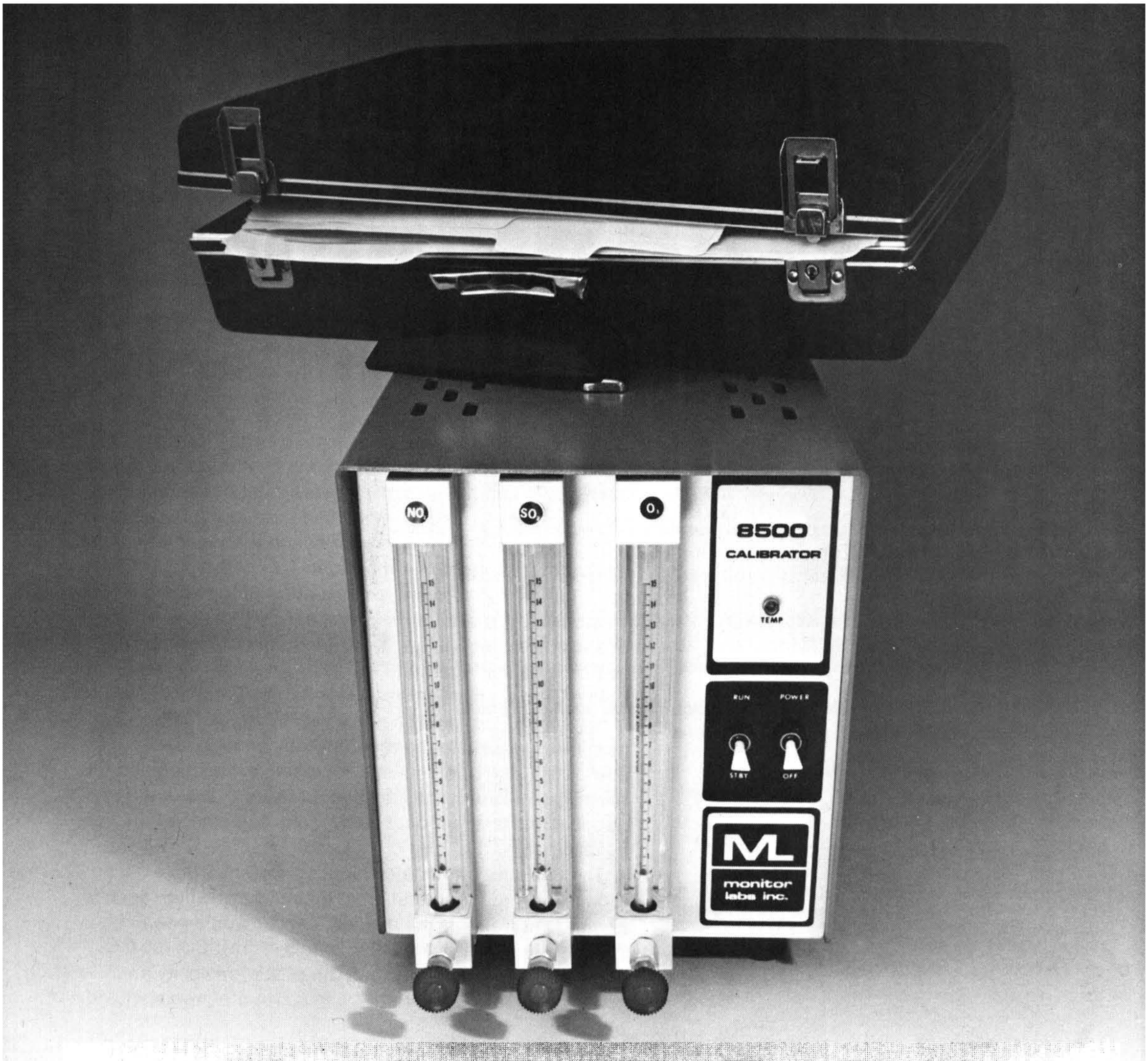
The Global Environmental Monitoring System (GEMS) is big monitoring at its best. And while the collection of data is left mainly to the responsibility of national authorities, the role of GEMS includes formulation and review of internationally agreed programs, coordination of national and international efforts, and assistance to governments.

The first part—the determination of the variables to be monitored and identification of the media in which each is to be monitored—is the easiest, or so it would seem, and this has been done (see p 215 in this issue). But the real challenge lies ahead—evaluation of the feasibility and cost of monitoring a variable with adequate precision and accuracy.

What must not happen is any monitoring slowdown waiting for the "agreed upon" method. Or better in the words of the report of an interagency working group on monitoring for the development of GEMS: "One requirement . . . is common to all; the results of measurements or observations have to be comparable even when obtained by different operators and through different methods. The need, in other words, is to ensure, by the judicious selection and intercalibration of methods and by the determination of reference methods, that even without aiming at unnecessary analytical perfection, the results are not affected by major systematic errors or attributable to the observer or to other factors."

UNEP is "a big order" indeed, Mr. Thacher. Monitoring is a necessary part and a first order of concern. We wish it well.

Stanton S Miller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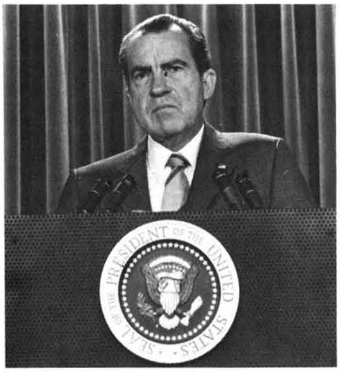
CURRENTS

INTERNATIONAL

Heavy metal pollution in the ground water of Teheran (Iran), originating from Pars Petroleum Refinery liquid waste, has been successfully treated by means of sodium hydroxide coagulation and tertiary treatment with activated carbon. This was important, since Teheran, short of surface water, derives some of its drinking water from underground strata, and essentially lacks sewers at present. The University of Teheran's N. Razeghi and his team designed this water pollution control scheme.

WASHINGTON

In his recent energy message to Congress, President Nixon recommended a 2-year delay on stricter standards for automobiles and tougher taxation of foreign profits by oil companies. In continuing his effort to achieve independence of foreign energy producers, the President suggested financial assistance be given industries producing new sources of energy such as oil from shale and synthetic crude oil from coal. Other considerations that could have environmental consequences include the speeding up of licensing and constructing of nuclear power plants and the expansion of outer continental shelf leasing for oil and gas exploration.



Nixon: energy message

GAO says the current level of federal funding for water pollution research and development will not enable the U.S. to meet 1985 standards. In a 447-page report to Congress, the General Accounting Office said technology is not being developed to achieve the elimination of pollutant discharges as specified in the 1972 law. The report identified seven areas where improvements are needed. These include: determining how pollutants get into the water, what happens to them, and what their effect is; minimizing the cost of treating municipal sewage; and controlling pollution from industrial and nonpoint sources. During 1969–73, the federal government spent about $495 million for water pollution R&D.

On its list of environmental protection spending priorities, the public ranks sewage treatment first, industrial air pollution control second, and solid waste management third. These were the results of an opinion survey, "The American People and Their Environment—1973," conducted for the Environmental Protection Agency. The survey of the J. M. Yiladas Co. (Greenwich, Conn.) also found that persons under 30 and those 55–64 were willing to pay more than other groups to improve the environment. It found that a majority of car owners reacted favorably to an increase of $150 per car to pay for antipollution devices, and that people are willing to pay an average increase of 22% for electricity to control air pollution from generating plants.

EPA Administrator Russell Train has recommended promotion of mass transit from revenue stemming from the windfall profits tax on oil companies. Speaking before the National Resources Conference of the American Farm Bureau Federation, Train explained that the profits tax should be used in a way to cut fuel demand as well as to increase supply. He said as long as the highway trust fund exists there should also be a transit trust fund. In another development, Train announced that the EPA is eliminating parking surcharge regulations from transportation control plans. He noted that the Energy Emergency Bill includes provisions forbidding the imposition of parking surcharges by the EPA.

The widespread concentrations of oil and plastic contaminants in waters found last year by the Commerce Department over 700,000 mi^2 of East Coast oceanic waters have been confirmed in a repeat survey. Analyses recently completed also reveal that most of the tar clumps cluttering the ocean environment from Cape Cod to South America are characteristic of oil wastes dumped from ships and tankers. Conducted by the National Oceanic and Atmospheric Administration's National Marine Fisheries Service, the studies have not yet pinpointed the origin of the plastic particles. They say, however, they do not seem to be harmful to immature fish. Not yet determined is whether larval and juvenile fish populations are harmed by the oil.

Interior Secretary Rogers C. B. Morton is trying to interest industry in cosponsoring a $2-million experimental plant in Oregon to convert lumbering wastes to low-sulfur oil. An appropriation of $1 million has been established for the experimental facility. The rest must come from private funding. The process for extracting oil from wood refuse and other organic wastes was developed by the department's Bureau of Mines as an outgrowth of experiments on better ways of using coal for clean energy. Basically, the wastes are treated with carbon monoxide and steam under high temperature and pressure. Encouraging yields also have been obtained from treating garbage, waste paper, agriculture wastes, and livestock manure.

STATES

A new system for funding wastewater treatment plants in Pennsylvania has been approved by the state's Environmental Quality Board. Funding will be based on water pollution control, stream segment priority, population affected and enforcement status instead of financial need and pollution abatement potential. Projects not funded in a given year can no longer be moved into the next spot on the waiting list. All projects are re-ranked every year, and during the year if additional funds become available. The federal government will provide 75% of construction costs to eligible projects.

The State of Illinois has the sole power to regulate land reclamation affected by surface mining. This ruling by the Peoria County Circuit Court came as a result of a suit filed by Midland Coal Co. against Peoria County. Midland Coal mines approximately 16,000 acres in Peoria County and supplies the coal to public utilities in Illinois and Wisconsin. The county required Midland Coal to segregate prior to mining and replace 6 ft of overburden whereas the Western Illinois Regional Council had recommended that only 1 ft of topsoil on row-crop lands be removed and restored. The coal company has also filed suit against Knox County for similar reasons. The coal from Midland's Knox County mine is shipped to Iowa for utilities' use.

Wisconsin citizens can be environmentally educated at home. Its state EPA has developed a "home training course" consisting of printed matter and tape which aid the understanding of complex new federal–state water quality laws, especially the effects the laws have on Wisconsin municipalities and industries. As an introduction, a 2.5-day training seminar will be held in Chicago. Participants will learn how state laws and codes have been enacted to complement the federal statute. Course material can be borrowed from the district offices of the Wisconsin Department of Natural Resources.

Alaskan school children are drinking RO-pure water. Now water does not have to be hauled by boat or sled. Instead, a reverse osmosis (RO) system is used to reduce the dissolved solids content of well water near the schools. Pilot projects as early as 1971 found that the installation of Du Pont Permasep permeators costs about the same as the schools originally paid for a year's supply of hauled clean water. Based on the success, an RO unit will be added at Barrow this year. The installation will provide 36,000 gal of water per day, 26,000 for students and the rest for hospital and townspeople.

The impact of the new Cave Run Dam in eastern Kentucky on water quality is questioned by EPA. The Army Corps of Engineers is responsible for the construction of the dam which began in 1965 and should be finished by year's end. After reviewing the Corps's draft environmental impact statement, EPA has asked for some answers. The agency is concerned about the extent of the clearing of trees and underbrush around the reservoir (which may affect the color, taste, and odor of drinking water for the residents of Morehead) and the bacteria and phosphorus levels in the reservoir. Frank Christ, a Corps environmental specialist, believes the request will not present any problems.

Monitoring atmospheric visibility

Atmospheric visibility studies in Arizona, New Mexico, and Colorado are being conducted photographically by the consulting firm of Dames & Moore. One study centers on the effect on the air of the Painted Desert and Petrified Forest of adding two 250,000-kW generating units to a power plant at Winslow, Ariz. The other study covers the expected decrease in visual pollution following the installation of new emission control equipment to another power plant in northwest New Mexico on Colorado's San Juan Basin. The power plants are operated by the Arizona Public Service; Dames & Moore takes pictures hourly, seven days a week, for one month in every quarter of one study year, using the photographic photometry technique.

RESEARCH

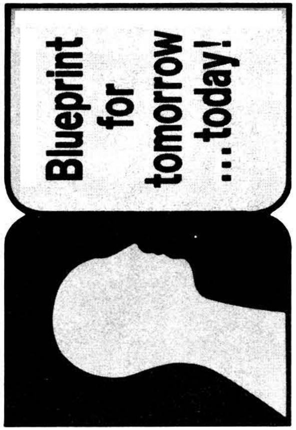
Carbon monoxide (CO) blood levels are influenced greatest by individual smoking habits and urban air quality, according to a Medical College of Wisconsin study commissioned by the Coordinating Research Council. The college surveyed samples of 29,000 blood donors from 18 nationwide metropolitan areas of varying size. Most nonsmokers in suburbs had the lowest CO levels (0.4–1.5%); suburban and urban smokers had the highest (0.6–9.5%); 90% of urban nonsmokers had 1.0–3.2% in Los Angeles and in Manhattan, 0.8–2.3%. Overall, smokers had two to three times more blood CO than nonsmokers. Even the highest CO levels are believed not to impair brain functioning, although that conclusion is not fully confirmed.

TECHNOLOGY

A fumeless in-line degassing process for cleaning and degassing aluminum, which uses harmless nitrogen gas under a salt-flux cover, was announced by the British Aluminum Co., Ltd., of London, The process replaces normal chlorine treatment, and thus obviates chlorine-caused air pollution, as well as the need to install expensive fume-scrubbing equipment.

A petroleum waste digester removes more than 90% of waste oils, greases, and organic matter using a dried bacteria culture. Over 90% of biological and chemical oxygen demand is also removed, according to Wayne H. Coloney, Inc. (Tallahassee, Fla.), designers of the digester. The system is built at less than 25% of the cost of conventional systems; operational costs are reduced by more than 50%. The digester has been in use at the Tamiami Trailways Bus Maintenance Depot, Tallahassee, since 1970. With different bacterial strains, the digester can be used for many different waste programs, says the company.

A closed-loop system for converting wood wastes into steam and activated carbon at lumber, pulp, and paper mills has been patented by Robert E. S. Thompson (Guilford, Conn.). The steam is usable for product processing or electric power production. The activated carbon can filter mill effluents. The new technique brings air and water pollution down to federal standards; cuts water use by 80–90%; allows the 30% of a tree normally wasted to be used as fossil fuel replacement; requires little space; and can return the capital investment in 3–5 years through by-product value.



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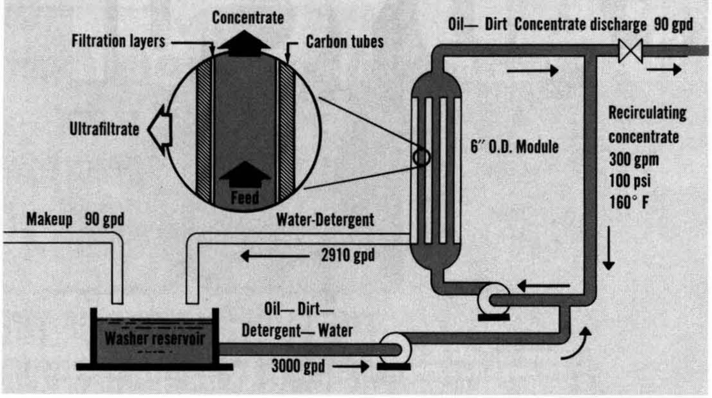
Ultrafiltration in metal washer cleanup



Ultrafiltration may be a key to removing hard-to-separate substances from water, and recovering these materials from the water for reuse. The method, with specially designed porous carbon tubes and propietary inorganic membrane coating, was developed by Union Carbide Corp. The method permits recovery of such materials as paint pigment, textile size, machine coolants, detergents, oils, and other such materials, and afforded at the same time is control of water pollution. The system working in an auto prepaint wash line helped save over 75,000 gpd of water, There is no theoretical limit to system capacity, according to Union Carbide.

Enough oil, gas, and charcoal from abundant garbage, treated with a special microbe strain, to make the U.S. energy self-sufficient now may be possible, says Lyle Atkins of Wallace-Atkins Oil Corp. (Houston, Tex.). Atkins estimates that each ton of garbage, treated by his company's method, will yield 2.2 bbl crude oil ($6/bbl); 430 lb charcoal (4¢/lb); 10,000 ft^3 gas (60¢/mcf, 500 Btu/ft^3); and 80 lb tar ($30/ton).

Graphite might find use as a solar energy collector, says Howard Palmer of the Pennsylvania State University. A thin slab of graphite would be installed in long, well-insulated pipes through which helium would be pumped. The sun's rays, collected by the graphite, would heat the helium to 1100°F; the helium would drive a gas turbine coupled to an electric generator. A 12% efficiency is estimated. According to Palmer, a network of helium pipes on a 4 × 5-mile parcel of desert could provide 1000 MW of power, produce no pollution or waste, and use no water.

INDUSTRY

The Air Correction Div. of Universal Oil Products Co. (UOP) announced the start-up of its first "hot" (600–750°F) electrostatic precipitator (ep) at a 50-MW plant of Iowa Power & Light Co. (Council Bluffs, Iowa). The ep is guaranteed to remove 99.3% of fly ash emissions from the low-sulfur, coal-burning plant. Normally, an ep works at 300–450°F, at which fly ash shows high electrical resistivity, and so degrades ep performance. Higher temperatures seem to reduce this resistivity sharply, so that the ep can achieve high fly ash collection efficiencies with low-sulfur coal. Iowa Power & Light is installing three more UOP ep's at Council Bluffs and Des Moines.

Reynolds Metals Testin

Robert F. Testin, Reynolds Metals Co.'s director of environmental planning, told a California legislative committee that a switch to refillable beverage containers offering energy advantages over nonrefillables "simply doesn't hold water." He said that a conversion to refillables would cost the nation's economy $10 billion. Energy savings would be 0.19% at best, 160,000 jobs would be lost, and secondary packaging and transportation needs and expenses would soar. Also, the amount of deliverable beverage per gallon of gasoline used to transport it would be halved.

Wheelabrator-Frye, Inc. (W-F) recently installed a unique air pollution control system at the Harriman Plant of Tennessee Forging Steel Corp. The uniqueness lies in the steel company's desire for total responsibility for air emission quality; not just interest in engineering or hardware. The W-F system handles 140,000 ft^3 of dust-laden smoke per minute, using 50 hp motor-driven fans that draw the smoke through a 64-in. duct to a 10-module W-F fabric filter. The dust is then collected with Dacron bag-type filters. Total cloth area is 54,200 ft^2. The steel plant's furnace produces over four tons of dust per day.

A hydrogen-powered Chevrolet has been unveiled by Billings Energy Research Corp. (BERC, Provo, Utah). The hydrogen can be provided by liquid hydrogen (LH) or by "hydride," in which hydrogen is stored in iron titanium in a special container. Roger Billings, BERC's president, estimated that LH operating cost would be 2.5¢/mi (gasoline, 50¢/gal would be 3.5¢/mi) at 14 mi/gal. The car can easily be switched to gasoline and back to hydrogen, and with hydrogen, would exhaust "fog" instead of "smog," and would surpass federal emission standards. Possibilities of fire casualties are considered to be remote.

Under its special low-cost antipollution loan program, Chemical Bank (New York, N.Y.) granted a loan to Warrensburg Board & Paper Corp. (Warrensburg, N.Y.) for a water pollution control system. The system will contain a primary classifier, sand filter, trickling filter tower, final classifier, chlorine contact chamber, and drying bed. Usable paper stock will be recycled. Chemical Bank has loaned over $25 million in its program so far; the program started with nonprofit loans to landlords and tenant groups to update incinerators and oil burners and to install garbage compaction units. Interest rates are somewhat below normal commercial rates—i.e., below $9\frac{3}{4}$%.

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INTERVIEW

American Air Filter's Jesse Shaver

What is the sales breakdown for AAF business? Since its formation in 1925, AAF's main thrust has always been toward designing and manufacturing products and systems for control of environmental air. Today, AAF's general activity encompasses air pollution control, air filtration, noise pollution control, and air conditioning, heating, and ventilation. The company keeps no separate figures for these activities because it frequently occurs that orders will include air filtration equipment and air pollution control equipment as well as heating, ventilating, and air conditioning equipment on the same job. Sometimes noise pollution control is also included. Because these activities are intertwined, sales are not broken down into separate categories by function. There is no meaningful method of separating orders by types of products.

What is the fastest growing segment of the business? All categories have had substantial growth and it appears they will continue to expand in the future. My guess is that what is defined as air pollution control probably is growing faster than the others. But it is not a runaway race, other areas are moving ahead as well. With a field like noise pollution control, which started from a small base, the rate of increase is quite good. In air conditioning, recent developments in energy-conserving systems have produced good growth.

As to air filtration, a little background might be helpful here. Air filtration has been on a growth curve of its own since the mid-1920's. At first, AAF predecessor companies had difficulty in establishing the concept of air filtration. Prospects found it difficult to understand the advantages in relation to the cost. In 1929 when the AAF name came into the field with the consolidation of four companies, there were two major classes of customers—automobile finishers and department stores. The former were interested because they had to apply as many as a dozen coats of finish. It was necessary to keep surfaces dust-free during the slow drying of each coat.

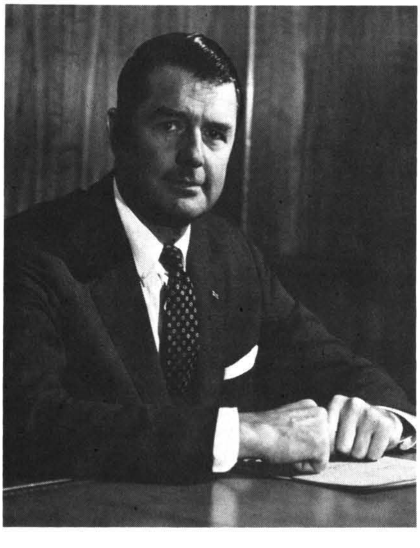
Department store owners were quick to recognize that air filtration reduced merchandise soilage, allowing it to be kept on shelves longer. In such stores air filtration systems could pay for themselves in a matter of months. Gradually others began to recognize the advantage of good air filtration systems.

Now, the basic advantages of air filtration are beginning to be more generally recognized. Today, air filtration systems are being used in food processing, textiles, clean rooms for electronics, and even motor rooms in steel mills. However, there are still large buildings being constructed today with inadequate air filtration systems. As you can see, AAF is involved in many facets of air quality control. However, recognizing the interest of your readers in air pollution control, I would like to channel my remarks toward the air cleaning segment of our business.

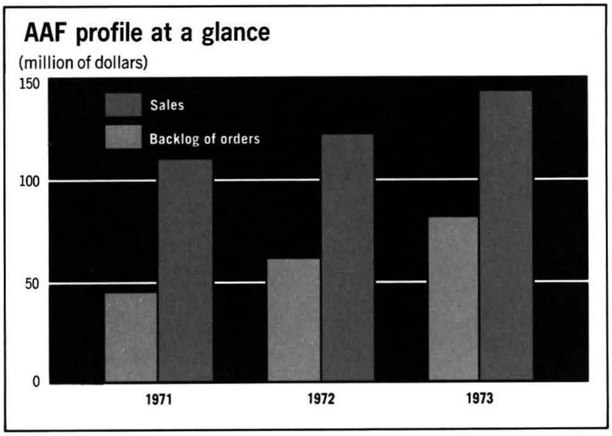
What is the rationale for industry to clean up in light of the current energy crisis and resources considerations? I believe there is a fallacy current with the public in relation to air pollution versus the energy crisis and resources considerations. People appear to believe that air pollution control is going to be relaxed and that standards will be abandoned. This is erroneous. The pressure for and the needs to correct air pollution will not change. Although the pollution controls most familiar to the public, the automotive pollution controls, reduce efficiency in relation to the energy consumed, the same is not true of industrial pollution controls. In this latter area, there is relatively little sacrifice of operational efficiency by the installation of controls. Indeed, in some cases, you can recapture otherwise wasted resources which can then be recycled. As an example, AAF has a system allowing steel mills to collect gases generated by oxygen steel conversion, then recycle the gases as fuel.

I personally do not see much future relaxation in the codes. The possible exceptions are one or two areas where changes would have been required, in any event. One is the previously mentioned automotive area. However, this is not of AAF interest.

Another area where there may be some modification, one which is of definite interest to AAF, is the SO_2 requirement for electric utilities and large industrial fossil-fuel burning plants. From the time the codes were published, many people in the air pollution control industry believed it would be virtually impossible to meet all the requirements under the established timetables. Consequently, it



Jesse M. Shaver is president and chairman of the board of American Air Filter, one of the world's largest suppliers of systems and technology for improving the quality of air. The 54-year-old executive tells ES&T's *Stan Miller that AAF is an international company with 23 foreign subsidiaries, has been in business 49 years, and has doubled in sales since 1968. AAF's corporate motto, "Better Air Is Our Business," very well describes the company's basic and practically exclusive interest in improving air. AAF systems do nearly everything one can do to air—clean it, filter it, heat it, cool it, move it, silence it, and change its moisture content.*



AAF milestones in air quality equipment

1973	Acquired Dynapure mist collectors from General Dynamics
	Licensed for IRSID-CAFL system of gas collection for basic oxygen steelmaking
1972	Mobile bed contactors for SO_2 control
1971	Acquired Pulsco noise attenuation and pressure pulsation systems
1970	Acquired Elex electrostatic precipitators
1968	AMERpulse pulse cleaning cloth collector
1967	Arrestall self-contained dust collector
1962	Electro-Pak electronic air filter
1960	Environmental control systems for Minuteman missiles
1953	Introduced fabric collectors with AMER-jet reverse jet collector
1952	AMER-Clone centrifugal dust collector
1950	Acquired Herman Nelson air conditioning, heating, and ventilation systems
1939	Introduced electronic air cleaning with Electro-Matic self-cleaning electronic filter
1935	Introduced wet collection systems with Type W Roto-Clone
1932	Introduced dust collection in the U.S. with Type D Roto-Clone dust precipitator
1929	American Air Filter Co. formed from predecessor Reed and three other companies
1925	Reed Air Filter Co. established to manufacture air filtration equipment

appears there will be forthcoming modifications in the deadlines, allowing a more practical time schedule for accomplishing the requirements.

What sort of stretch-out do you foresee? I believe an orderly approach needs to be taken to the problem, one that is in keeping with the financial ability of the polluters and capacity of the air pollution control industry to provide the necessary systems. Preferably, we at AAF would like to see the market increase on the order of 15%, 20%, or 25% each year, rather than expanding at an explosive rate. Under the present timetables, the industry would have to expand immediately to something like an impossible 1000% or more each year just to meet the primary requirements. Therefore, AAF looks for a time lapse of at least the next decade or two before the principal air pollution problems are corrected.

CLEANUP PROJECTIONS

What then, is your prognosis for air pollution control cleanup progress over the six years remaining in this decade? In the past half dozen years many estimates have been made by research firms, trade publications, and associations, often based on imprecise figures. Frequently the same forecaster has doubled or tripled his estimate from one year to the next because of the very impreciseness of his previous figures. There still remain several problems when one attempts to estimate this market over the next few years.

One of the problems is that forecasters seldom take into consideration the amount of money required to do the job, as well as the source of those funds. Billions will be required. For example, in the area of SO_2 control alone, estimates of the cost have ranged as high as $30 billion, and I do not recall seeing any less than $5 to $10 billion. In addition, one must also take into consideration potential materials shortages, and a very real long-term shortage of engineers and other competent people needed to handle this type of work. They have to be technically trained first, then gain on-the-job experience. I believe considerable progress will be accomplished over the remaining six years of this decade; however, the biggest part of the iceberg will remain to be done in the 1980's and beyond.

TECHNOLOGY

When will utilities begin to purchase SO_2 stack gas cleaning systems? This is an area in which disagreement has been rife for some time. The federal government is of the opinion that the technology exists, and it is eager to move the utilities rapidly toward installation of this equipment. And, of course, environmentalists are vocal in their support. On the other hand, electric utilities argue that proved, reliable systems do not yet exist. They point out they are being pressed too hard and that the time is not yet right. There is truth in each position because, although there are exceptions, there is hardly any SO_2 system that presently operates on a continuous 24-hr basis, seven days a week. However, it is a fact that the technique for cleaning stack emission has been proved in the laboratory and in test installations.

Utilities are usually managed by prudent businessmen who are cognizant of their shareholders and are careful in their money management. They tend to require substantiated evidence that their expenditures are actually going to meet the needs for which the monies are allocated. All along I have felt that utilities would like to install a test unit and closely observe its progress. After they are confident that the unit can actually achieve its purpose they would proceed with further utilization, adding new units on a regular basis.

How well is the AAF full-scale unit proceeding at the Green River generating plant in western Kentucky? Have other AAF units been purchased by other utilities? The Green River project, a unit of Kentucky Utilities, is an outgrowth of the pilot plant test we operated at Louisville in 1971 and 1972 in cooperation with Louisville Gas & Electric and three other electric utility companies. The Green River project is to go operational in 1975. As for other utilities, there is considerable interest in plants with proved track records. Presently, we are in various stages of negotiation or discussion with more than 20 utilities. As I commented previously, the entire air pollution control industry should receive quite a few orders this year and an increasing number next year. We at AAF anticipate our fair share of these projects. We know what our system can achieve and are willing to contract on a guaranteed performance basis.

SHOWCASE

Can you cite a number of recent air pollution control projects in which the company is involved? AAF has many in our worldwide operations. The Soviet Union recently awarded AAF a $1.9 million contract for air pollution control equipment for what will be the world's largest foundry complex at the immense Kama River truck plant project in central Russia. We won the contract in competition with other international companies based on our experience, expertise and proven equipment.

During the past few months, we also received a $3.5 million project at TVA's Johnsonville steam plant. This involves fitting six large AAF electrostatic precipitators to remove fly ash from the exhaust of six boilers at that TVA plant. In other industries, we recently installed air pollution controls on a major steel mill, a large automotive plant, a major construction equipment fabricating facility, and in woodworking operations and cement mills. Because the need for better air is universal, AAF's systems virtually know no industry boundries.

RESEARCH

Does AAF have any new devices for control of air pollutants? Many of the air cleaning techniques now widely used by others were inventions of American Air Filter. All told, AAF has more than 1000 patents worldwide. Gradually there have been improvements in these techniques. Of course, AAF tries to keep ahead of its many competitors. However, rather than "new" inventions, the process is an on-going series of improvements in the techniques that exist.

Are there likely to be breakthroughs on air pollution control devices in the next few years? In the next six years, there will probably be no pure technological breakthrough. There will, however, be a steady progression of improvements. In our industry, the target is continually to get increased efficiency at lower cost with improved reliability. It is in these areas where the improvements will come. It's a gradual activity which results in general overall improvement. It's unlikely that totally new techniques will be invented. AAF, as well as others, has done a great deal of research and experimental work on many different types of devices. However, one soon arrives at the question of economics. Although we developed some new techniques 25–30 years ago, economic considerations still do not favor their use, even today. Over the years others have done the same.

What makes a control device better today than 10 years ago? For example, what's new with electrostatic precipitators? In almost every instance, if you compare the performance of today's systems with those of 10 years ago you will find they will do better cleaning jobs in terms of efficiency, and they will continue to do their jobs over longer periods with considerably less maintenance. Today's market requires this sort of improvement; however, manufacturers like AAF are continually working to improve the efficiencies of their products in anticipation of market requirements.

> ***"AAF looks to at least the next decade or two before all the air pollution can be corrected."***
>
> AAF's Shaver

As to the electrostatic precipitator, improvement has been along the same lines, increased efficiency and higher reliability. When AAF acquired the Elex precipitator in 1970, Elex already had an outstanding record of technological capability and reliability in the European market. In Europe, reliability has been far more important, and businessmen there are more insistent on performance guarantees than has been the case in the U.S. Consequently, there was more testing and guarantee of reliability there than was the practice in the U.S.

From that base, improvements have continued. There are two recent developments of significance. First is the unbreakable discharge electrode. By using a rigid, tubular assembly in place of the usual wire electrode, one of the major causes of downtime is eliminated—broken wire electrodes. The second major improvement is the change to solid state controls with their inherent reliability and quick response.

What is happening in the area of gaseous emission controls? The principal gas receiving attention is sulfur dioxide. There are various devices, including afterburners and catalytic devices, for removing odors truly offensive to the public. Many noxious gases can be removed with wet systems. Some can be burned with catalytic converters, but converters represent a limited market. Carbon filters are also useful, but again, the market for these controls is in its infancy too. The use of fuel to handle odors is another method, but it is an expensive alternative. Too much fuel is required to heat up a large volume of air to cure a problem that may be caused by only a few parts per million.

How do you silence air? AAF is interested primarily in industrial noise pollution. There are many locations in chemical plants, for example, where the relief of pressures and vacuums causes intense screeching noises that must be eliminated. There are a number of techniques for eliminating them. Basically, these techniques cancel, contain, or absorb noise. Some work on the principle of diverting half the noise to a more circuitous path. That path is designed so that the portion of the noise traveling takes longer to reach the end point, arriving directly 180° out of phase with the other half. When the two rejoin, they cancel one another. Although it sounds somewhat simple, such systems are fairly sophisticated and require extensive knowledge in the field. There is also a market for such devices in the aviation business, where they are installed on the hydraulic landing gear systems to quiet the operation.

PERSONAL ASIDE

What is your background and how did you ascend to the top at AAF? After training as an engineer at Purdue University and as a MBA graduate from the University of Chicago, I worked for many years in the management consulting field with the firm of Booz, Allen & Hamilton in the area of electronics. I joined AAF in 1962. At first, I managed one of the groups and, after working on reorganization of that activity and bringing in another manager, I moved to another group. Over a period of time, I managed each of the major segments of the AAF business before I became president in 1967 and chairman in 1968.

New land use policy in making

A land use policy for the U.S. is slow in coming, and there are disagreements as to its exact form. However, almost everyone agrees we need a more responsible approach to how we use our land

Interest in the U.S. for a positive land use policy is almost overwhelming—everyone seems to be for it. It is slow in coming, and there are disagreements as to its exact form, but government officials, lawyers, and developers all claim that a more responsible approach to how we use our land is mandatory.

One example of this focus is the Fourth Annual Report on the Council on Environmental Quality. This latest in a series of reports to the President on environmental matters is permeated with the theme that proper land use is necessary in solving virtually all our environmental problems. And President Nixon, in his message accompanying the report, firmly supported its contents by saying land use control is perhaps the most pressing environmental issue before the nation. "How we use our land is fundamental to all other environmental concerns," he pointed out, and "there is encouraging evidence that the American people have reached a new perception and appreciation for this challenge."

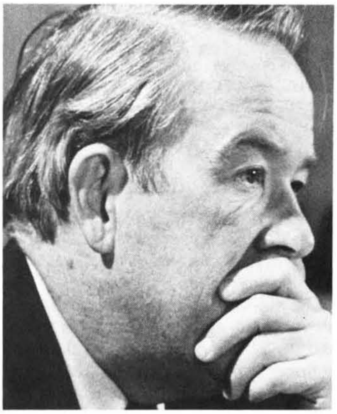
Other support has come from Sen. Henry Jackson (D-Wash.), chairman of the Senate Interior Committee and originator of the already passed Senate bill on land use. Jackson called the measure "the most important bill before Congress."

Sen. Edmund S. Muskie (D-Me.) said recently, in a speech before the Planning and Conservation League, in Anaheim, Calif., that federal legislation is needed to encourage, and, if necessary, to require states to adopt regulatory programs to evaluate and restrain development. He said we need "a national growth policy to guide and effectuate economic development, population control, housing distribution, the use of natural resources, the protection of the environment and the location of government and private development."

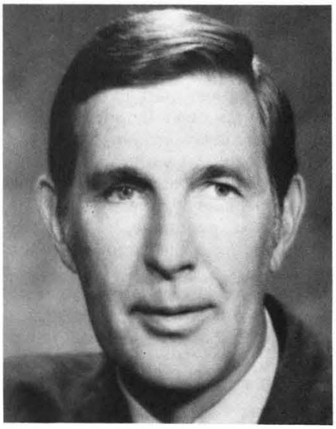
Land use legislation

As to the status of land use legislation, most observers feel there will be a law by early summer. A House bill is out of committee, and is expected to reach the House floor for a vote sometime this month. The Senate bill was passed last June.

The bill in the Senate, however, was weakened before receiving final approval. Strong interest groups made up of developers, the U.S. Chamber of Commerce, the American Farm Bureau Federation, and Liberty Lobby all opposed certain provisions of the bill, and were successful in deleting economic sanctions against states who failed to comply. Specifically, these deleted provisions would have reduced federal funds for highway, airport, and land and water conservation by 7% for the first year of noncompliance, 14% the second, and 21% the third and subsequent years. As it now stands the measure would set up a grant-and-aid system to fund the programs in the various states, but the states rather than the federal government would call most of the shots.



Sen. Henry Jackson
Calls bill most important



Rep. Morris K. Udall
Seeks stronger bill

These groups, which also lobbied against similar sanctions in the House land use bill while it was still in committee, are not, strictly speaking, opposed to federal land use legislation. Daniel Denning, environmental and natural resources staff associate for the U.S. Chamber of Commerce, told *ES&T* that the Chamber's position was not against the concept of federal land use legislation. He said his group felt that the intent, of especially the Jackson bill, did not match its strong provisions. These provisions, he said, contained "line after line" defining what states would have to do in order to get federal grants. "Our position is that the federal government should fund state programs and then get out," he said.

The House bill, as it now stands, also would not impose economic sanctions against states that failed to comply, but it does contain certain provisions for states to meet before receiving the planning funds. These include:

- a central state agency to oversee land use decisions at the local level that could have statewide consequences
- a fully developed statewide land use program whereby areas of critical environmental concern are defined
- an appeal procedure at the state level, which would include open public hearings.

The House bill, when it does come up for a vote, will face a strong attempt to restrengthen it. Rep. Morris K. Udall (D-Ariz.), who chairs the House Interior Committee's environment subcommittee where the House bill originated, has vowed to "put some teeth back into the bill," in-

Under review. *Past U.S. policies in permitting development along some of our coastal areas are being reconsidered in many states*

cluding the economic sanctions. If he is successful, the measure, if passed, would have to be referred to a joint committee. Chances are, however, that the bill, in its final form, will be moderate.

Local level efforts

Federal legislation aside, many state and local governments are at work on laws of their own. The CEQ report notes that Oregon has joined Delaware, Florida, Maine, New York, and Vermont in enacting state land use control legislation. Also, California, New Jersey, and New York have taken recent legislative action to protect their coastal zones.

The report adds that many local communities likewise are showing "a remarkable shift away from historical American boosterism and toward a skepticism about the costs and benefits of unlimited growth." Through such actions as sewer moratoriums and bans on building permits, "communities in all parts of the country are taking steps to place limits on their growth," the report states.

Many laws that affect local land use decisions in indirect ways are already on the books. The federal Clean Air Act is a prime example of this. Since the states are required to provide for the maintenance of ambient air standards, new industry, apartment and office buildings, and shopping centers must be built with consideration as to what additional industry and vehicle exhaust fumes will do to the air. Environmental impact statements must be filed with, and approved by, both state and federal environmental protection agencies.

A good example of water pollution control laws affecting land use decisions took place as a result of the Willamette River project in Oregon. The river, the twelfth largest in the U.S., was grossly polluted 50 years ago. Now, because of strict efforts on the part of the people of Oregon, the waters once again are clean. And as the result of this momentum, attention has now shifted to issues of public access and protection of natural values along the river's banks. Through the Willamette Greenway program, the state is preserving farmlands and other open space through the use of scenic easements. In Portland, a four-lane expressway has been closed and the site redeveloped with housing, shops, and parks so as to refocus the face of the city toward the now-clean river.

Another area of concern that has recently received much legal attention at the state and local levels is that of development of coastal wetlands. These areas provide a natural barrier between the oceans and the shore, and it is estimated that 60 to 70% of the fish caught in U.S. coastal waters would not be there if at one time they had been unable to find shelter, safe spawning or nutrients in a wetland. Yet, as the Earth Satellite program has shown, serious intrusions of high density residential development into wetland areas have already occurred in California, Florida, and New Jersey. In New Jersey alone, 14% of the wetlands were consumed and a substantial additional area affected before state legislation in 1970 halted development.

Situation is widespread

The CEQ report finds that the problem of development on unsuitable land is far more widespread than a look at wetland areas alone would indicate. It documents how residental development in urban flood plains has expanded significantly in recent years. Special problems occur in Baltimore, Denver, Kansas City, and other cities, according to the report. In Denver, for example, it is estimated that the portion of flood plain land in residential use increased from 9.2% in 1960 to 29.9% in 1970.

The report also reviews how development on unsuitable soils in sample counties in California, Florida, and Maryland has caused problems ranging from erosion and flooding to water pollution and landslides. Poor practices were found in all instances. In Montgomery County, Md., adjoining the District of Columbia, it has been discovered that as much development took place on unsuitable land as on suitable land, despite the fact that suitable land was available. Homeowners belatedly discovered that the shallow bedrock and clays underlying their houses shrink and swell to undermine foundations.

The report's chapter on the urban environment describes how private and public groups have joined forces to restore life and vitality to downtown and neighborhood areas alike. By building upon physical resources that already exist in older neighborhoods, many cities are adding new vitality to charm and elegance once in danger of being lost. Cases such as Capitol Hill, in Washington, D.C., Mount Auburn, in Cincinnati, and Butchertown, in Louisville, show that impressive land use gains can be made through the private efforts of those who simply want to live in such neighborhoods.

As one would expect, legal considerations involving land use are becoming more and more complex. The Practicing Law Institute has been holding seminars in various parts of the country to acquaint lawyers with the growing myriad of problems they can expect to face. Donald H. Siskind, PLI program head who conducted one such meeting in New York City recently, pointed out how new and changing laws concerning financing, sewer and water improvements, green areas, zoning and rezoning, labor, and the environmental all must be taken into consideration. Another consideration is the interpretation of the U.S. Constitution's Fifth Amendment, which provides that "private" property shall not "be taken for public use without just compensation." Exactly when can land be taken for public uses, and when is a lawyer's client receiving just compensation? The courts have evolved a number of legal theories for deciding when "taking" occurs, but their decisions across the country have reflected different applications of the theories.

The particulars have not been worked out yet, but some changes in our land use practices are due. For an increasing number of people, land is too important a natural resource to ignore. Federal EPA Administrator Russell E. Train has called it, "the most important environmental issue remaining substantially unaddressed as a matter of national policy." He is not without considerable support from all sectors of the country. WSF

NAS considers energy crisis

The National Academy of Sciences sought answers to problems brought on by the energy crisis at a national two-day forum held in Washington, D.C. The group considered risks and further alternatives

If participants in the National Academy of Sciences' forum on "Energy: Future Alternatives and Risks" are correct, there are alternatives. And the biggest risk, at this point in U.S. history, would be in not doing enough to ensure adequate energy supplies for the future.

The symposium was framed around two days of discussions. The first day's program on the theme of "Alternatives of Supply and Demand," included sessions on reserves and resources, conservation and demand, and environmental health and safety. The second day's program on "Benefits and Risks of Institutional Stability," included sessions on public and private roles, regulation, and choosing the future.

Alvin M. Weinberg, newly appointed director of the Energy Research and Development Office, opened the session by presenting the energy crisis in the theoretical terms of the first and second laws of thermodynamics. He pointed out that our energy output is limited by the first law because our conventional fuel resources, fossil fuels, are limited. The second law limits our energy output "because eventually pollution, resulting from increased energy production, will become unbearable," he said.

As it was set up, the symposium pitted optimist against pessimist. On the one hand, there were those who took the position that technology, in both the short term and the long term, can overcome the crisis. Others argued that these hard thermodynamic limits, of which Weinberg spoke, cannot be circumvented by technology, no matter how ingenuous.

William E. Simon, Federal Energy Office administrator, called for the adoption of a five-point national energy policy, which, he said, would meet both short- and long-term needs. The program would:

- create a central energy organization in the Federal Government that would bring together energy policy and implementation
- establish a permanent energy conservation ethic
- establish a framework of international cooperation with respect to energy
- forge a new relationship between government and industry
- move forward without delay on Project Independence, a significant part of which would include energy research and development

Simon said the U.S. must strive to make conservation, presently forced upon us by the oil embargo, a permanent part of our national life. He also called for cooperation between government and industry in developing our domestic resources—a move that would entail industry's cooperation in providing adequate information about the energy situation. He complained that present information is inadequate and its reliability cannot be checked. "We must develop a permanent energy information system with a built-in auditing program on every aspect of the energy situation—reserves, refining operations, inventories, and production costs," Simon said.

Self-sufficiency

Project Independence, which Simon outlined, would include further development of oil and gas in Alaska and the outer continental shelf, greater utilization of coal, further development of oil shale and nuclear resources, and an increased effort to develop geothermal and solar power. On the question of what could be done immediately to increase daily crude oil production by 200,000 barrels, Simon suggested opening the Elk Hills Naval Petroleum Reserve, renewing drilling in the Santa Barbara Channel, and increasing the maximum efficient rates of lifting oil in several oil fields in Texas.

The environmental considerations that would underlie such measures are staggering, and Simon says the federal government shares the environmentalist's concern. He said the U.S. would take "all reasonable measures to prevent the fouling of our air and water, and the destruction of our land. Any relaxation of environmental standards will be temporary, carefully monitored, and will have a definite terminal date."

S. Fred Singer, professor of environmental sciences at the University of Virginia, took the position that the U.S. does have domestic resources to satisfy its energy needs. "The key in developing these would be in increased exploration and the subsequent drilling for oil." Also, he cited methanol production from coal as an important energy source.

The goal of self-sufficiency might be reached sooner than the year 1980 suggested by the White House, Singer said. This would be due principally to the rapid escalation of energy costs, which would dampen demand, he said. He added that government action may be necessary to facilitate sectoral and geographic allocation problems, to prevent disruptions of the economy, and to alleviate genuine hardships. Such measures will be particularly necessary in the short term, between now and 1977, but less so between then and 1985, Singer concluded.

Charles A. Berg, the Federal Power Commission's chief engineer, countered this argument by saying we need more than just ways to ob-

Alvin M. Weinberg
Gives overall view

tain energy. "We need to develop effective ways to make use of our energy," he said. Berg noted that power plant efficiency has increased over the years, and that we could, in a more general way than we presently are doing, apply up-to-date technology to reduce fuel waste.

Carl Madden, chief economist for the U.S. Chamber of Commerce, called for a new ethic in the development of our energy resources. Scarce resources should be used in ways that their full value is realized, he said. Madden said studies at Oak Ridge National Laboratory conclude that the U.S. can sustain its present standard of living over the long term, but that this would entail the appropriate management of resources. We must very soon adopt wise policies of conservation, resource substitution, recycling, and other options, he warned.

Madden stressed the theme that energy is only one of our resources in danger of being depleted. He was optimistic, however, and said it is technologically feasible, though not presently economical, to extract resources from ordinary rock, or granite. This extraction would require enormous energy supplies. Through nuclear fusion, environmentally clean and effective energy would be available to obtain these needed minerals, Madden said.

Conservation stressed

In approaching the problem more with conservation in mind, Bruce C. Netschert, vice president of National Economic Research Associates, Inc., said the U.S. must cut down gas and fuel consumption at the individual level. The lifting of the present oil embargo at this time would be worse than the embargo itself, he said. He added that the American people would then clamor for the return of former levels of consumption.

Netschert said, in the short run, conservation will reduce consumption to the point that it matches available supply, simply because there is no alternative. In the long run, however, he doubted that conservation alone could do the job. He pointed out that allocation now being applied, and rationing that may follow, can lead to unemployment and loss of jobs that are unacceptable in the long run. Alternatives, such as solar energy and greater efficiency in energy use, must be undertaken to offset these in the future, Netschert said.

In considering environmental health and safety, Chauncey Starr, Electric Power Research Institute president, maintained that the gross impact of environmental controls is to impede the availability of energy. Environmental controls impose constraints on fuels, increase capital costs, and decrease utilization efficiencies, he explained. "In a highly industrialized society such as ours, the continuity of energy supply has a priority that clearly exceeds, on a short-term basis, the priority of the gradual improvement in our total environment or the gradual development of alternative energy resources."


William E. Simon
Pushes Operation Independence

Lee C. White, chairman of the Consumer Federation of America's energy policy task force, said there is no question the need for energy will delay the achievement of environmental objectives, but that it must be defined in advance just how this waivering of controls will be carried out. White outlined a suggested policy that would include: no across-the-board waivers, fixed terms, effective monitoring, and fair and open procedures. He said his feeling was that the American consumer is willing to pay the price for environmental controls. "After all he has to breathe the dirty air, drink questionable water, and come in contact with environmental lead and other substances," White said.

James R. Nelson, professor of economics at Amherst College, called for the establishment of a unified energy agency at the federal level. He characterized an ideal agency as one that:

- does not have regulatory responsibilities
- does have charge of a unified energy research budget of proportions beyond anything yet being discussed
- does have first responsibility for formulating the U.S. position on international energy problems
- is required to report to Congress yearly as to the extent to which regulation has prompted or impeded energy policy objectives

Government role opposed

Philip Sporn, a consulting engineer who directed the development of the American Electric Power Co. into the world's largest investor-owned power system, opposed all plans for a government-implemented energy policy. He acknowledged the need for new institutional devices, but said these should come from private enterprise, with government functioning only as an overseer. On research, Sporn said it is useless when it is undertaken apart from the plant and industry where it is needed. He said he is dead set against a more generalized federal research program.

Petroleum economics authority Richard F. Gonzalez, a consulting economist, joined Sporn in expressing concern over too much federal government intervention. Gonzalez said it would be a mistake to install federal controls in the heat of a temporary crisis. Alfred E. Kahn, economics professor and dean of the College of Arts and Sciences, Cornell University, called for an immediate end to subsidizing oil companies in the form of depletion allowances. Other aspects of Kahn's program include public utility-type status for natural gas, and public utility regulation of gas and electricity.

As to the human values affected by the energy crises, Paul F. Donovan, director of the Office of Energy Research and Development Policy, National Science Foundation, said "The feast is over; we must reduce our energy consumption." Arthur Kantrowitz, chief executive officer of Avco Everett Research Laboratory, said there is a need to institutionalize scientific fact in order to have a data base upon which to form policy in the future.

Historian Robert S. Morison, Cornell University, told the symposium we need a better way of knowing where the U.S. is going. He said there is a need for a kind of common law so that new situations, such as the energy crisis, can be handled using a backlog of common experience.

James Tobin, professor of economics, Yale University, said the changes we must face as a nation because of the reduction in our energy use are not so drastic or revolutionary as some people now believe. "Some teen-agers may no longer have random use of automobiles," he said, "but this change is not on a par with what happened when Americans moved from the farm to the city, and with what is happening today with the new attitudes of women and the accompanying loss of fertility." WSF

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Environmental travels abroad

Graduate-level scientists dreaming of faraway places might look into the Smithsonian–Peace Corps program

Dealing with environmental problems involves a gamut of varied and interdisciplinary efforts in all sorts of surroundings. Different aspects can involve work under conditions ranging between comparative comfort of a large laboratory and extreme rigor in the field; and use of equipment from ultrasophisticated space-age devices to hastily jury-rigged ones.

Those who are imbued with a desire to brave the rigors of the field, as well as an ability to improvise, and a certain amount of idealistic feeling about being a scientific or technical goodwill ambassador, might well look into the Smithsonian Institution–Peace Corps Environmental Program (SI–PCEP). Volunteers with the SI–PCEP enjoy a singular opportunity to travel abroad, add materially to their experience, and perhaps improve their ability to "think on their feet." They may also contribute to some improvement in the lives of people to whom much of America's domestic squalor would seem like opulence beyond the wildest dreams by comparison with the situation of their daily existence.

Far-flung assignments

The SI–PCEP has a great number of possible assignments on which a volunteer may undergo baptism by cultural shock. These assignments could take the volunteer to any of 55 countries in which the Peace Corps has programs, as well as to other countries where the Peace Corps does not operate, but can attach a volunteer to international organizations. Volunteers are often needed for forestry, watershed management, marine biology and fisheries, preservation of endangered species, environmental monitoring, and numerous other endeavors, in many faraway places.

For example, Malawi, southern Africa, called for a volunteer with a degree in botany. Working with the Animal Husbandry Project, he would be responsible for evaluation of productivity of natural grassland and savanna and would investigate their optimal management. He would have to examine effects of cattle grazing on grassland ecology, as well as identify grassland communities and estimate their productivity.

A wood scientist who fancies the surfing and fishing scene might have been interested in possible work in Fiji, where the Department of Forestry wanted a capable person to work with the structure and properties of woods, perform research and surveys, and train local staff.

The United Republic of Cameroon, West Africa, in many ways a vigorous pioneer and leader in African development, was asking for as many as 20 volunteers to assist in building up its inland fisheries program whose goal is to establish a fisheries industry and increase the small farmer's income. The fisheries project involves putting in new fish ponds and improving existing ones; stocking, breeding, and harvesting of fish; and educating local populations in marketing and nutritional aspects of fish farming. Training local technicians and scientists, and demonstrating new techniques are also important phases of the project.

Energy needs play their roles, too. For example, a scientist with a petroleum geology or petrology background was requested to instruct in these fields at either the Catholic University of Quito (Ecuador), or the Polytechnic University in Quito. He would also assist in the operation and maintenance of laboratories.

Ghana, in West Africa, has called for volunteers to assist in studies concerning effects of insects on plant growth and selection of pest control methods. Moreover, Ghana has recently established an Environmental Protection Agency (EPA), and could conceivably request volunteers to work with the Ghanaian EPA.

The foregoing were some examples where SI–PCEP volunteers may assist on the international environmental scene and have an opportunity to see some rather exotic parts of the world. Requests for such volunteers significantly increased, as of November 1973, for service beginning during the winter and spring of 1974. Much of the increase was in the fields of natural resource conservation and ecological research.

Joining the tour

Skilled volunteers are recruited mainly from universities; however, potential candidates elsewhere, holding applicable degrees or equivalent credentials, and interested in this service, should probably come forward. Since its inception toward the close of 1970, about 480 volunteers, recruited directly by the SI–PCEP, have been posted to various countries. Many of the volunteers come from postgraduate schools, and are majoring in biological sciences or natural resource management.

A volunteer's length of tour normally will be 24–27 months, including his language training time. During his tour, he will receive living allowances to cover modest in-country living costs. In addition, $75/month will be held in the U.S. for each volunteer, and paid him on the completion of his tour. In some cases, a volunteer might get academic credit for his tour, provided he can make the proper arrangements with his university.

Likely assignment countries, winter/spring 1974

Africa	Central & South America
Botswana	Belize
Cameroon	Brazil
Ghana	Chile
Ivory Coast	Colombia
Kenya	Ecuador
Lesotho	El Salvador
Liberia	Honduras
Malawi	Peru
Niger	Uruguay
Swaziland	Venezuela
Asia	**Indian & Pacific Oceans**
India	Fiji
Korea	Seychelles
Malaysia	Tonga
Philippines	
Thailand	

Source: Smithsonian Institution, Office of Ecology

In other cases, couples can volunteer for overseas assignments, in which case, both husband and wife would receive living allowances. However, assignments in which families can serve are very few, and no more than three children, or two school-age children, may accompany their parents.

All volunteers must be U.S. citizens; this requirement covers both husband and wife in the case of couples. Those who feel that they qualify as volunteers, are interested in environmental matters, and also in "roughing it" a bit with the SI–PCEP, should contact Robert K. Poole, Office of Ecology, Smithsonian Institution, Washington, D.C. 20560. Bon voyage! JJ

The great coal rush of the 1970's

The need for power plants using oil to switch back to coal, and comply with clean air rules simultaneously, has the electric utilities all steamed up

The generation of electric power at many, if not most power plants, is a matter of well-understood technology. Steam is produced, brought up to high temperatures and pressures, and used as the motive power for the generating machinery. There was plenty of cheap fuel available to make this steam. Also, air and thermal water pollutions originating from a steam power plant were not matters of great general concern.

Now, however, environmental quality is a matter of at least some public concern; what is more, the sins of the energy wastrels, a subject of stern warning since 1954, according to the American Petroleum Institute, have come home to roost. Still, electric power must continue to be produced, and in ever-increasing quantities, to satisfy accelerating demand. Fueling many of the boilers which will make the steam needed to generate this power is somewhat problematical these days.

Unfortunately, fossil fuels will feed the larger part of these boilers for the foreseeable future, and these fuels may not always be immediately available. Listed in increasing order of pollution potential, such fuels comprise gas, oil, and coal. Although gas is the cleanest burning fuel, gas will become less and less available to power plants. The same will hold true for clean and even dirty oil. Coal, therefore, which often has a high sulfur content, and is therefore considered the dirtiest of fuels, will feed hungry boilers increasingly.

Shoveling coal

In view of the current petroleum shortages, the federal government, in late 1973, asked that, where possible, power plant boilers now fired by oil switch to coal. In some cases, proposed fossil-fueled power plants, planning to employ oil-fired boilers, will have to revise their plans and go to coal-fired boilers. Thus, low-sulfur coal would be the desired fuel, but it may be almost as scarce as low-sulfur residual oil, at least at present. Many plants that cannot convert to coal would be granted variances from clean air standards so that they may fire their boilers with high-sulfur oil. Clean air variances will also cover coal firing for a limited time.

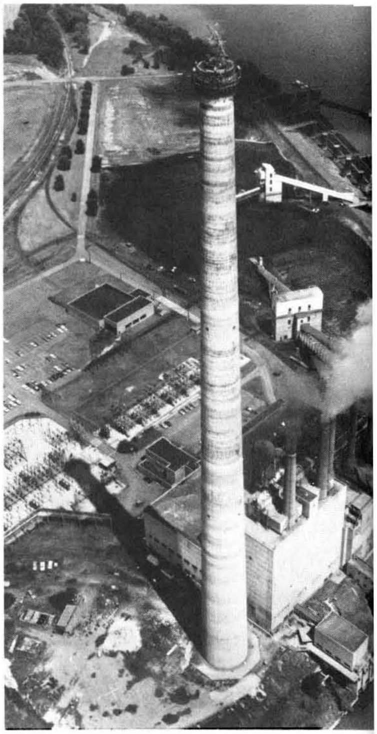
Now it is easy to talk glibly of conversion from oil to coal (or vice versa), solid waste, or whatever else comes to mind. The engineering, economic, and environmental headaches involved, however, might act as sobering rebuttals to blithely offered prescriptions for instant alternative fossil-fuel energy.

For example, some 26 electric utilities in New England and on the Eastern Seaboard have recently received telegrams from the federal government, in which they were strongly urged to switch from oil to coal. The basis for selection of the 26 utilities contacted was a trade-off of factors of petroleum shortage and environmental risk.

In 1971, Potomac Electric Power Co. (PEPCO, Washington, D.C.) spent between $2 and $3 million to convert its Buzzard Point plant in Washington from coal to oil, largely to comply with clean air rules. Now, PEPCO has been directed to reconvert the plant to coal, a task requiring about 3 months. Costs will be considerably less than those of the original coal-to-oil conversion; nonetheless, they will be heavy. Moreover, the reliability of a coal supply for the immediate future might not be guaranteed. In addition, storage space for coal has been diminished because of oil tank installation in what used to be a coalyard. Long-neglected coal conveyor belts, pulverizers, and other associated equipment would have to be refurbished.

PEPCO has also decided on two pulverized coal-fired boilers, 900 MW each, which can also be fired by oil (full-load). Solid waste may be considered as a future nonfossil fuel additive for the boilers. These boilers will supplement three existing pulverized coal boilers of 185 MW each at PEPCO's Dickerson plant near Point of Rocks, Md. Combustion Engineering, Inc. (C-E) is to build and install PEPCO's boilers. PEPCO has provided for electrostatic precipitation for particulate removal, and is to have SO_x treatment. One boiler should go on stream in December 1977, and the next in 1978.

At Chalk Point, Md., C-E is to provide PEPCO with two 660-MW oil-fired boilers (start-up summer 1974 and 1976, respectively) to supplement two pulverized coal-fired boilers of 360 MW each, built by Babcock and Wilcox, Inc. (B&W). The 660-MW boiler to go on stream in summer 1974 is designed for partial convertibility to coal. The other 660-MW boiler can also be modified by installation of enough equipment to pulverize and handle coal and ash, and perform associated functions, so that the boiler can use up to 33% coal in an emergency. As this goes to press, however, such modification is not planned. The original B&W boilers have been converted to dual fuel—



Power station. *A tall, cleaner nonsmoker replaces five stacks*

Boiler air pollution control operating costs and investment
(Millions of dollars)

Fuel[a] Equipment[b]	Coal, 0.7S EP	Coal, 1.5S FF	Coal, 1.5S EP	Coal, 3.0S Scrub	Oil No. 2	Oil No. 6
Operating costs/year						
Fuel	4.87	4.87	6.96	3.69	8.47	6.91
All other operating costs	0.39	0.43	0.22	0.78	0.03	0.08
Total direct cost	5.26	5.30	7.18	4.47	8.50	6.99
Depreciation at 6%	0.28	0.19	0.19	0.60	...	0.06
Total	5.54	5.49	7.37	5.07	8.50	7.05
Investment						
Permanent investment	4.70	3.10	3.20	10.00	...	1.00
Working capital required	1.00	1.00	1.28	0.82	1.65	1.35
Total	5.70	4.10	4.48	10.82	1.65	2.35

[a] 0.7S = 0.7% sulfur coal
1.5S = 1.5% sulfur coal + No. 2 oil
3.0S = 3.0% sulfur coal
No. 2 = No. 2 fuel oil
No. 6 = 0.7% sulfur, No. 6 fuel oil

[b] EP = electrostatic precipitators
FF = fabric filters
Scrub = limestone tail-end scrubbers

Source: American Society of Mechanical Engineers Paper No. 73-IPWR-5

that is, to full option of coal or oil firing.

The new 660-MW boilers for Chalk Point will be able to burn high-sulfur oil. They are fitted with Peabody-Galion scrubbers for particulate removal; SO_x cleaning systems can also be retrofitted. However, if these boilers had to be converted to coal, they could operate on partial load at best, and two years would be necessary to effect such a conversion.

In some cases, dual-fuel boilers with complete fuel interchangeability are specified. Baltimore Gas and Electric Co. has ordered two such boilers from B&W. These boilers are to be 600 MW each.

Another example of a coal-fired power plant is a 650-MW plant that Allegheny Power System, Inc., plans to build near St. Marys, W.Va. The plant will cost $265 million, and is expected to start up in 1978. This represents about $407 per kW, and includes pollution control by a method as yet unannounced, as well as materials and construction. By contrast, a 650-MW coal unit, brought on stream in December 1973 at the same site, cost $196 per kW of capacity.

Coal headaches

The principal headache resulting from coal firing is that burning most types of coal produces particulate matter, and sulfur and nitrogen oxides. Federal EPA new source performance standards (NSPS) permit 0.1 lb of particulate per million Btu, and 0.2 lb of NO_2 per million Btu. For SO_x, 1.2 lb/million Btu are permissible with coal, and 0.8 lb/million Btu with oil.

In view of the current petroleum squeeze, and resulting paucity of low-sulfur oil and natural gas, which some power plants have been burning increasingly of late in order to comply with clean air rules, certain variances to compliance with these rules are being granted. These variances are allowed so that use of dirty oil, or better, coal which the U.S. has in relatively large potential supply, may be encouraged for the time being. Such variances, however, will almost certainly not remain in force for very long; yet, no miraculous surfeit of clean oil or gas appears on the horizon. One answer to this dilemma will have to be found in improved stack gas cleaning technology. Indeed, EPA will push strongly to see that power plant SO_x cleaning facilities are installed as expeditiously as possible; Deputy Administrator John R. Quarles, Jr., was most specific about this point in a press conference last month.

The question of cleaning stack emissions, and especially of SO_x removal, seems to have elicited a dichotomy of views. One belief, expressed in many quarters of the utilities industry, is that SO_x cleaning technology is at worst, essentially nonexistent, and at best, "almost there," but not yet ready for large-scale use. An opposing tack was taken late in 1973 by the Industrial Gas Cleaning Institute (IGCI), which said that the U.S. pollution control industry has the technology, people, and financial muscle to bring about effective SO_x cleaning. However, IGCI warned, these capacities may be disbanded if no adequate market exists to support them.

Probable supply is another headache, at least over the near term. When the Government orders electric utilities to switch from oil to coal, it assumes that sufficient coal is readily available to effect this conversion. In the U.S., for the time being, the availability of coal, like that of oil, may be a "sometime thing."

To be sure, coal production has increased of late, but it is still not enough to meet the demand that would result from a sudden, wholesale conversion to coal on the part of the electric utilities now on oil or gas. Moreover, this demand could soon materialize as a result of present national energy policy.

In December 1973, Carl E. Bagge, president of the National Coal Association (NCA), estimated that the coal industry produced 590 million tons of coal during 1973. He said that the industry could increase this production by 110 million tons—equivalent to about 484 million bbl of oil—if optimum conditions prevailed. Among these conditions are labor stability, adequate transportation, relaxation of price controls, delay in timetables for environmental cleanup, and an end to federal harassment and unnecessary mine closings.

According to Bagge, the obstacles to bringing about these conditions are formidable. For example, transportation of mined coal is an acute problem. Bagge estimated that at least $6 billion will have to be spent on adequate railroad rolling stock for coal shipments. Moreover, the coal industry will not expend much effort or investment unless it can be sure that its revenues will not be a "flash in the pan."

For the future

First of all, scarce or not, oil will continue to be used as a boiler fuel to some extent over the years to come. Some plants simply cannot convert to coal. However, in such cases, more efficient oil burning and gas cleaning facilities, so that high-sulfur oil can be used, will be rigorously required.

Nevertheless, as far as fossil fuels are concerned, the electric power industry will probably rely increasingly on coal and its derivatives. After all, coal is basically still plentiful in the U.S.; new methods are being developed to make cleaner burning fuels and useful chemical by-products from coal; and use of coal would promote the self-sufficiency of the U.S. for its energy needs.

Certainly, costs will be high if, simultaneously, energy requirements are to be met and improvement of environmental quality is to be achieved. The U.S., however, is blessed with the economic resilience and technological ingenuity to realize both aims. The long-run cost will be very low in comparison with the price of being in the thrall of nations which do not always wish the U.S. well. JJ

Liabilities into assets

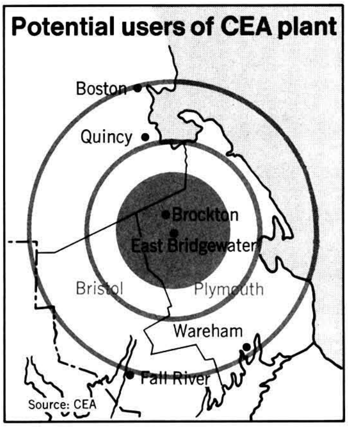
Garbage-to-power: conversion can satisfy as much as 10% of U.S. needs

The name of the game is Fuel. If we had as much fuel as we have rubbish, we would win each and every time. Since we are obviously losing, the consolation is to convert the garbage into some form of usable energy. Such resource recovery can also solve other critical problems:

- the banning of open burning
- the unavailability of sanitary landfill
- the lack of fuel required to operate municipal incinerators

Europe has been making wise use of its solid refuse long before the current oil crisis. Amsterdam, for instance, has burned trash for the last 60 years to release heat for the production of steam. This steam is forced under pressure through high-temperature turbines to generate 6% of that city's electricity, the equivalent of a town the size of Santa Barbara, Calif. (population 72,000).

By 1975, Germany expects to serve 25% of its total population by burning their garbage in installations equipped with steam heat recovery systems. The list goes on.


Potential users of CEA plant

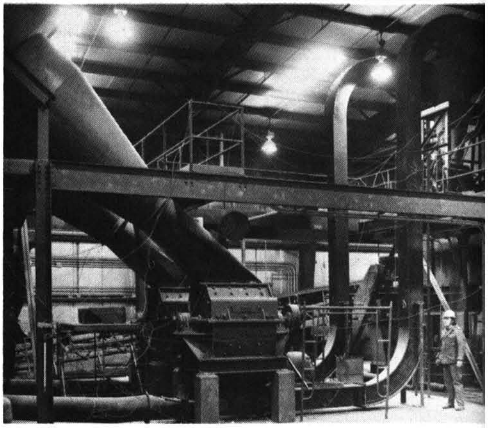
Source: CEA

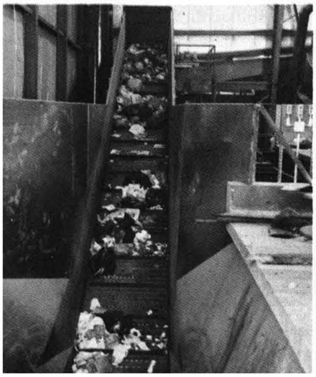
In the U.S., the urban population generates over 136 million tons of refuse per year. The heat content of the combustible portion is roughly 1433 trillion Btu. If this heat energy is used entirely for the production of electricity, it could produce 136 billion kWh or 10.9% of the electric energy from conventional steam generating equipment in 1970. This same energy also corresponds to the heat content released by burning 5417 million tons of low-sulfur coal or 228 million barrels of low-sulfur residual fuel oil.

Trash-to-power

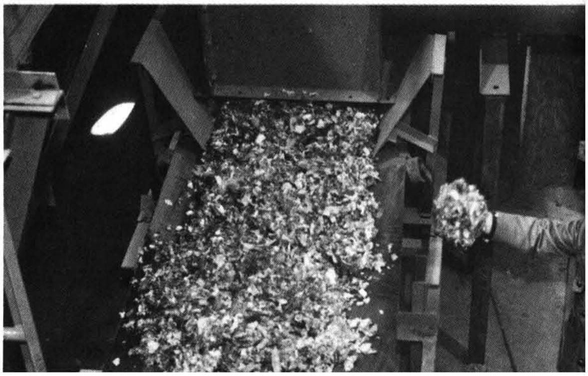
Many projects in the U.S. are indicating that refuse is a good fuel source. Some of them are patterned after the European experience of direct burning for the release of heat and then steam. Essentially, refuse is used as a supplementary fuel source in a conventional fossil fuel boiler. Two cases in point are the earlier St. Louis, Mo. (EPA-funded) and more recent Lynn, Mass. plants.

The Lynn venture, due to go on-line at a General Electric facility in 1975, plans to collect 1200 tons of household garbage daily from 16 surrounding communities. The resulting 350,000 lb of steam generated per hour should produce as much as 35,000 kWh of electricity.





Trash-to-fuel cycle. Municipal truck dumps garbage at receiving hopper; garbage is conveyed into primary shredder/classifier; primary shredded garbage is dried and cycloned into secondary mills and air-conveyed into Eco-Fuel storage bin; Eco-Fuel emerges from bin conveyer, ready for delivery to utility or other energy user for power generation



Trash-to-fuel

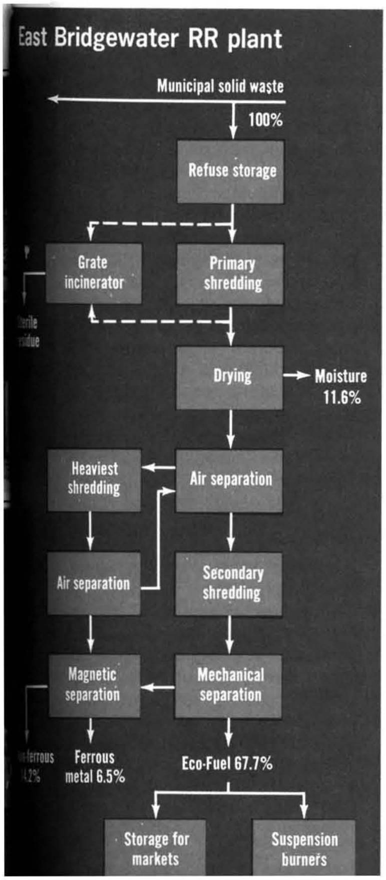
The new idea is to first convert the solid waste into a self-sufficient fuel before being used by an electric utility. This process surpasses the trash-to-power method, which, in the case of St. Louis, provided only 10% of the total heat input needed.

Certain demonstration projects have proved the feasibility of going directly from trash to fuel. Examples that come to mind are Union Carbide's 5-tpd pilot plant in Tarrytown (N.Y.), and joint lab studies by York Research and Combustion Equipment Associates in Stamford (Conn.). As a result, the process has gone commercialized.

Some companies are building facilities which will convert refuse to a fuel gas by pyrolysis—a method of chemical decomposition by heat. These include Monsanto Environ-Chem Systems, Inc. (Baltimore, Md.), Garrett Research and Development Co. (San Diego, Calif.), and Union Carbide (Charleston, S.C.).

CEA concept

A step ahead of the fuel game, Combustion Equipment Associates has developed a process for deriving a solid fuel from solid wastes. Their $10 million, 1200-tpd East Bridgewater, Mass. plant was opened for business last October.



Communities within a 10–25 mi radius from East Bridgewater send their garbage to the privately owned center. Wastes are picked up by specially equipped front-end loaders, passed through a conveyor system, and fed to primary shredders. They are dried and classified in an air separator in which a light combustible fraction is separated from the heavier noncombustible fraction containing ferrous and nonferrous materials.

The heavy fraction is further shredded and classified to segregate any remaining combustibles which are then recycled to the first air separator. The separated heavies are combined with the noncombustibles; ferrous metals (6.5% of total wastes) are recovered by magnetic separation and sold; nonferrous materials (14.2% of total) such as glass, dirt, aluminum, zinc, lead, and copper are sterilized for clean fill or further processed for recovery.

The light fraction is reduced further in size and fed to a mechanical separator to remove the rest. The final product (67.7% of total) is a solid "fuel."

Eco-Fuel

This refined combustible fraction recovered from municipal solid waste is:

- a grayish substance with popcorn consistency
- ½-in particle size
- 7–10 lb/ft^3 in density
- low in sulfur content
- 78.5% combustibles (paper, wood, leather, rubber, plastics, textiles, food and yard wastes), 11.5% ash, and 10% moisture
- high in heating value—6900 Btu/lb
- odor free
- stable over an indefinite storage period

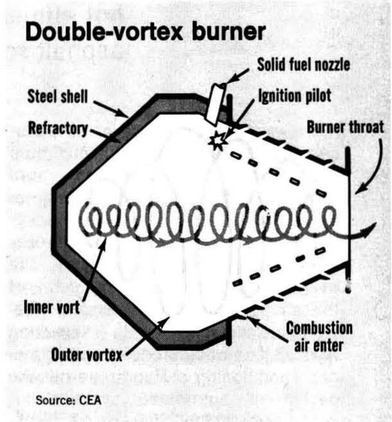
Fired in a specially designed CEA double-vortex burner coupled to an existing boiler, Eco-Fuel will generate as much steam as pulverized coal, on an equivalent weight basis. The nature and amount of fly ash from coal or Eco-Fuel are comparable. Particulate removal in both instances is easily affected by electrostatic precipitators or fabric filters.

Eco-Fuel mixes well with combustion air because of its physical characteristics, achieving a less than 8-ppm carbon monoxide equilibrium concentration at furnace exit temperatures of 2100–2300°F. It also burns at a lower adiabatic flame temperature, so that NO$_x$ emissions are lower than those from coal-fired boilers.

DV burners

This double-vortex system combines turbine technology with suspension fuel burning and is recommended for optimal performance of Eco-Fuel. The CEA design allows complete fuel combustion with minimal emissions, thereby releasing more heat.

The burner, a double cone-shaped combustion chamber with one end closed and the other opened to exhaust the combustion gases, is housed within a windbox into which fuel and combustion air enter tangentially. The mixture spirals toward the closed end in an outer vortex before reversing travel toward the open end in an inner vortex. Larger fuel particles are recirculated back into the outer vortex for complete burning.



Source: CEA

In a nutshell, the solid fuel is converted to a gas, mixed with air, heated to ignition temperature, and oxidized. Exit gases are clean. Ash and slag are removed by an ejection system within the burner, eliminating the need for a secondary collection unit.

Everybody benefits

Conservative estimates point out that as much as 10% of the U.S. power requirements can be met with garbage. Towns can be rid of their unsightly garbage at costs comparable to what they are now paying for dumping. Any enterprise can build these refuse processing plants with private financing. Take the case of CEA, their East Bridgewater facility charges $9.25/ton refuse. This sum is sufficient to amortize the 20-yr investment of $10 million. CEA can also profit by selling the end product marketed as Eco-Fuel; ideally, to a utility in close proximity to the refuse plant, thus minimizing transportation costs. It has recently signed a 10-year contract with Weyerhaeuser Corp. (Mass.). The latter has agreed to purchase over 770,000 tons of Eco-Fuel, roughly equivalent to 2 mbbl of oil for use in one of its boiler plants. The not so tasteful subject of garbage has become a good conversation piece. LCG

Sonic gas cooling systems cut..

Sonic Development Corp.'s units cool hot effluent gases from smelters in Arizona and asphalt roofing plants in Los Angeles

Optimum performance of air pollution control equipment with minimum maintenance cost requires more careful attention to preconditioning of the effluent gases. The use of ultrafine water sprays is helpful in pretreating gas stream to enhance the collection efficiency and reliability of the air pollution control system. Recently developed sonic atomizing nozzles and computerized analysis of gas conditioning problems permit the design of automated systems for cooling hot effluent gases. Such systems can be used to upgrade existing installations or to reduce the size and cost of new installations.

Sonic evaporative cooling equipment from Sonic Development Corp. (Upper Saddle River, N.J.) is now operating in numerous foundries, smelters, liquid waste incinerators, and various industrial furnaces with excellent results. In a typical application, sonic atomizing nozzles were installed in a cooling chamber at the Hayden, Ariz., facility of Kennecott Copper Corp. with the basic work handled by the plant engineering staff and operating personnel.

James Stocker, smelter operations superintendent at the Hayden operation, says that off-gases from the fluidized bed reactor are cooled from 1100–800°F before cleanup by an electrostatic precipitator. As originally designed, the cooling chamber used 30 conventional spray nozzles operating at hydraulic pressures up to 350 psig. Two sonic nozzles replaced the 30. The finer atomization delivered by these nozzles provided total water evaporation and eliminated the earlier experiences of wet chamber bottoms, sludge buildup, and unscheduled shutdowns. Stocker says the nozzles at the Hayden facility were installed in 1970, and in the past three years have saved many thousands of dollars by reducing plant downtime.

What is useful to smelter operators has been found useful by other manufacturing operations including asphalt roofing plants. For example, the Celotex Corp. recently installed a sonic gas cooling system in their Los Angeles asphalt roofing plant to cool hot gas fumes before cleaning by a Johns-Manville high-energy air filter (HEAF).

According to Lloyd Pfaff, senior project engineer for the Celotex Corp., the sonic system cooled 22,000 acfm from 150–130°F—the optimum temperature for efficient filtration by the glass fiber media. "Without the fine atomization of the sonic nozzles," Pfaff reports, "evaporative cooling could not have been accomplished in the existing ductwork within the available residence time of 1.6 sec. The sonic atomizing system enabled us to avoid costly shutdowns and satisfy EPA regulations."

Why spraying?

In evaporative cooling, water injected into a hot gas stream evaporates and absorbs heat from the gas. Virtually every problem associated with evaporative cooling systems is traceable in some way to the nozzles used to inject water into the gas stream. The low-cost pressure nozzle commonly used in such systems is inherently incapable of producing the ultrafine droplets required for evaporation and cooling. Large water droplets produced by such nozzles agglomerate with dust particles to form sludge or pass through the cooling chambers to foul collection equipment.

Kennecott's Stocker
"Nozzles . . . have saved many thousands of dollars . . ."

The large droplets also cause localized cooling resulting in refractory spalling and severe distortion of sheet metal ducts. The small orifices required for pressure nozzles clog frequently and wear rapidly causing high maintenance costs and frequent shutdowns. Lacking turndown capability, pressure nozzles cannot be modulated to suit varying inlet temperatures but must be actuated separately or in banks to achieve even crude flow modulation.

To compensate for the poor atomization, designers must often increase the required water volume by 50% to allow a "safety" factor, thus further compounding nozzle problems and creating a secondary water pollution problem. The combination of poor atomization, erratic cooling, and slow system response is often the cause of baghouse fires and precipitator malfunctions. These severe field problems clearly indicate the need for more sophisticated and reliable gas cooling equipment.

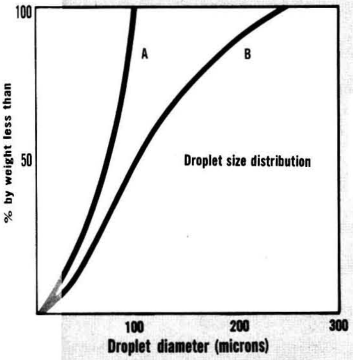
Preconditioning

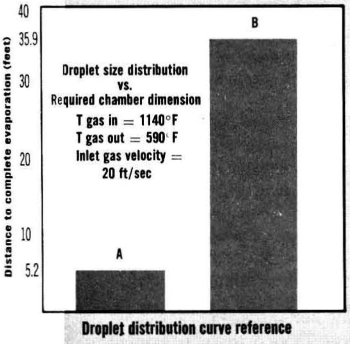
In addition to cooling hot gases, fine water sprays also play a critical role in the preconditioning of the gas stream and significantly affect the performance and efficiency of the pollution control equipment. With electrostatic precipitators, efficiency of collection is a function of the electrical resistivity of dust particles.

Many dusts, such as glass and cement, have inherently high resistivi-

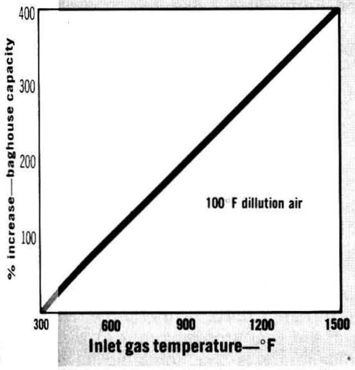
Why sonic cooling?

The smaller the droplet size the smaller the cooling chamber

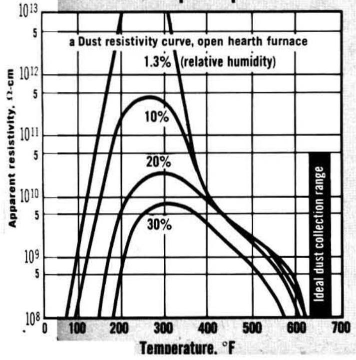




Use of dilution air for cooling increases baghouse requirement



Humidity improves efficiency of electrostatic precipitator



air pollution control costs

ties and, at normal collection temperatures of approximately 300°F, cannot be properly collected unless humidity levels approaching 30% are achieved. Hence, fine water sprays not only cool the hot gases but also condition the gas stream by raising the humidity level to enhance the collection efficiency of the precipitator.

With bag collectors, temperature and humidity controls are also critical. Precise control of cooling water is required to ensure temperature control below the limit of the materials and the prevention of condensation by maintaining the gas stream above the dew point.

Once it is recognized that water sprays play a critical role, not only in the cooling of hot gases, but also in the preconditioning of the gas stream to enhance collection efficiency, the need for improved design of gas conditioning systems becomes obvious.

Savings

Substantial cost savings can be realized by the use of improved gas cooling equipment in place of dilution cooling techniques. Dilution cooling involves the use of ambient outside air to dilute the gas stream and reduce its temperature. This technique increases the total cfm of gas to be treated with a corresponding increase in the size of collection equipment.

In a typical case, 100,000 cfm of dry air at 1500°F is increased to 185,000 cfm when cooled to 500°F by dilution with 100°F outside air. At $1.50/cfm cost of baghouse capacity using glass bags, the cost in excess baghouse capacity is $127,500. By contrast, the cost of a complete evaporative cooling system (including the cooling chamber) is $0.50/cfm or $50,000. The resulting savings in using evaporative cooling in place of dilution cooling is $77,500.

Smaller chamber size

The importance of small droplets to cooling chamber dimensions is shown. A conventional pressure nozzle (*B*) producing maximum droplets to 250 μ requires a chamber of 35.9 ft in length. By contrast, Sonic Development's atomizing nozzles require only 5.12 ft for complete evaporation at the same water flow rate. Hence, to achieve dry bottom operation with smaller, lower cost cooling chambers, atomizing systems capable of producing extremely fine droplets are required.

Automating the cooling system

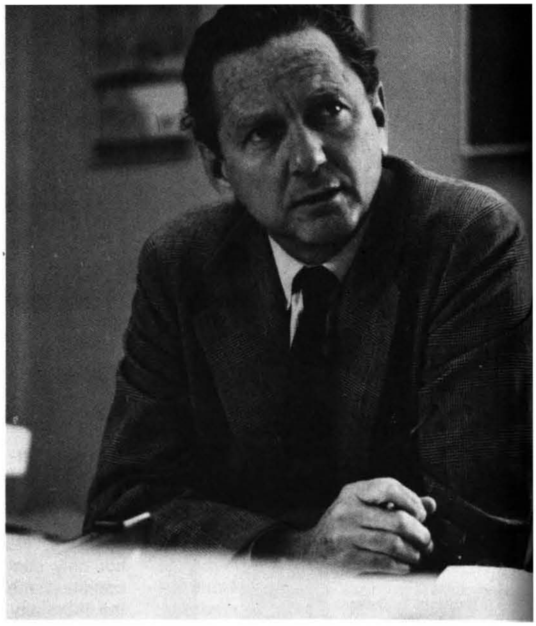
Equipped with accurate engineering data from computer studies together with nozzles capable of producing ultrafine atomization, we now are able to design a control system to modulate water flow to suit varying inlet gas conditions. For new installations, a complete system includes a cooling chamber, sonic atomizing nozzles, temperature sensors, automated flow controls, and an air compressor. In existing installations, the nozzle/control package can be retrofitted to the existing cooling chamber.

An automated control system takes full advantage of the modulation capabilities of the sonic nozzles and provides rapid system response. The temperature sensor at the inlet dictates the liquid flow rate to the nozzles and downstream sensor provides trimming feedback to correct for any system errors while providing fail-safe protection against excessive temperatures at the collector. The system is designed to use only the volume of water required to accomplish cooling thereby eliminating wetted walls, refractory spalling, sludge buildups and water wastage, carryover, and recycling problems.

Until recently, gas cooling has been the weakest link in most pollution control systems. The development of new evaporative cooling techniques using sonic atomizing nozzles and automated controls overcome the problems normally associated with wet systems while providing substantial cost savings.

What's happened since Stockholm?

The United Nations Environment Program has a Stockholm Action Plan, a Governing Council, an Environment Fund, and soon will start up its Earthwatch Program and Referral System



UNEP's Thacher
"A big order indeed"

Peter Thacher, director of UNEP's Geneva office, reminds *ES&T* that the June 1972 conference concluded with approval of 109 recommendations, the so-called Stockholm Action Plan accompanied by an agreed Declaration of Principles. He says, "These principles do not have the force of law, but they represent a political consensus by the intergovernmental community of the world which has a political significance and, in some cases will, in years ahead, become codified international law in much the same way as the law with regard to outer space was codified a decade ago."

At the end of the conference (*ES&T*, Aug. 1972, p. 682), "All of these recommendations were pious expressions of goodwill and intention," Thacher says. "They were paper resolutions."

But in December 1972, the UN General Assembly endorsed the Stockholm Action Plan and created an intergovernmental body of 58 States to serve as a policy-making and priority-setting mechanism. The body is known as the Governing Council of UNEP. Last September, Maurice Strong, executive director of UNEP and secretary-general of the Stockholm conference, and others moved to new headquarters in Nairobi, Kenya. Key personnel accompanying Strong included Mustapha Tolba, deputy executive director of UNEP, Robert A. Frosch, assistant executive director of UNEP, and Paul Berthoud, director of the Environment Fund.

The work of UNEP touches on such diverse questions as how to stop the spread of the deserts and how to protect the vitality of the oceans. By now, however, governments have created the institutional machinery to make the plans a reality; they have established a $100 million fund for the next five years for getting these plans under way. Signed on December 15, 1973, Public Law 93-188 provides for U.S. participation in UNEP.

"It is clear that $100 million will be completely inadequate to cover all the work that needs to be done," Thacher explains. "In effect, the Fund is leverage money. The money will help the operating entities, including the specialized agencies of the UN system—the World Health Organization (WHO), the World Meteorological Organization (WMO), as examples—to conduct particular activities within the overall program.

"The goal of the UNEP in the broadest sense is to protect and enhance the quality of the human environment for present and future generations," Thacher says. "A big order indeed."

The oceans

In the case of the oceans, the British government convened a conference of governments in late 1972, which agreed on a convention specifying a prohibited list of substances that may not be deliberately dumped in the ocean under any circumstances, as well as a "gray" list for which a special licensing procedure has been agreed by a large number of coastal states that are becoming parties to the convention.

Another specialized agency of the UN, the Intergovernmental Maritime Consultive Organization (IMCO) (*ES&T*, July 1968, p. 510), has sponsored a conference at which a Convention for the Prevention of Pollution from Ships was agreed to by a large number of states. In recent months, the French government and a large number of European states have agreed on a convention to block marine pollutants from land into rivers and to block direct discharges.

Earthwatch program

"One of the areas in which UNEP has devoted the greatest attention after the Stockholm conference is the broad assessment program labeled Earthwatch," Thacher says. In the monitoring area, the task is to provide early warning of trends that are of significance to man's health or well-being.

"Today we have a list of categories of pollutants that will be treated with considerable attention in the next years," he continues. "In the broadest terms, the categories include heavy metals, chlorinated hydrocarbons, and other specific materials such as asbestos." Monitoring is expected to yield differing results from different parts of the globe; but one of the real problems in the areas of monitoring is the compatibility of one set of data with any other. Hence, a main objective will be not only the intercalibration of measurements within a particular medium but also across media. What is essential is that the data be intercomparable.

Perhaps an example is in order to illustrate the necessity of early warning. "In the case of some of the food which is exported from Africa to Europe, already some crops are being turned away because of the pesticide residue levels which are higher than those allowed by the standards set by the consuming State," Thacher says. Needless to say, these crops, such as coffee and cocoa, are of very great economic importance to the exporting African state and of considerable importance to the consumer in Europe.

Another example: Years ago, suddenly one day the Philippine tuna fish industry was put out of business because the U.S. adopted a protection standard that set a limit on methyl mercury lower than levels already carried by Philippine tuna with the result that a major market suddenly disappeared.

"At that point an early warning, if there had been one, would have been too late," Thacher adds. "We need to know what the levels are today, if possible yesterday, certainly tomorrow, in order to see the trend. If we cannot produce harder data for decision makers, at the national level, they will continue to make choices which are based on hard economic data that are valid for at least the short term. But if we can selectively produce stronger data, data that stand up against hard analysis, then we can hope to have an impact on these decisions."

Rising levels of harmful chemicals in food in international trade risk endangering the exports of many countries, especially developing countries, which may be denied admission for the sake of protecting the consumer. Conversely, there is the danger that some developing countries unwittingly admit imported food that is harmful to their citizens.

Plans for the global environment monitoring system (GEMS) were formulated at the first session of the Governing Council, at Geneva last June 12–22. The first step would be to plan for the monitoring of levels of pollutants considered to be important in air, water, food, soil, and biota, with particular reference to those found in several media.

An interagency working group on monitoring has been established; members are organizations of the UN system, including WHO, WMO, UNESCO, IOC, IAEA, FAO, together with UNEP. This group met during 1973; they have prepared a report for the establishment of a global environment monitoring system within the Earthwatch program.

In effect, then, many of the activities proposed for the monitoring portion of Earthwatch are already being undertaken to some degree by governments and intergovernmental and nongovernmental bodies.

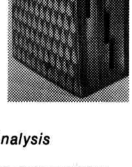
The ultimate objective of the Earthwatch program is to provide early warning of impending changes or trends, whether man-made or natural, in any part of the environment that threatens directly or indirectly to cause significant harm to man s health or well-being. At present, there is no systematic means for determining which pollutants are significant, within the meaning of recommendation 85 of the Stockholm conference. Even though there may be general agreement as to the hazards caused by certain broad classes of pollutants, in many cases only a few countries have the capability to measure the levels of these pollutants in the media involved. In almost no case has there been sufficient inter-

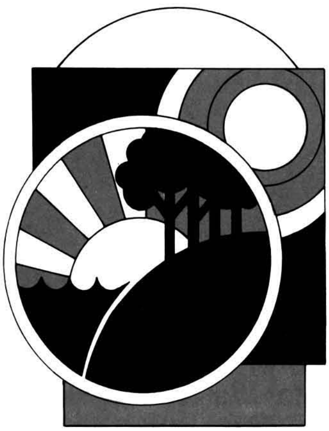
Global Environment Monitoring System (GEMS)

List of priority pollutants	Media
Sulfur dioxide and sulfate	**Air**
Suspended particulate matter	**Air and water**
Carbon monoxide	**Air**
Carbon dioxide	**Air and oceans**
Oxides of nitrogen	**Air**
Ozone, photochemical oxidants and reactive hydrocarbons	**Air**
Mercury	**Man, soil, food, biota, water**
Lead	**Same**
Cadmium	**Same**
Halogenated organic compounds (DDT, PCBs, Dieldrin, and the like)	**Same**
Petroleum hydrocarbons	**Water**
Nitrates, nitrites, nitrosamines	**Food**
Mycotoxins (alfatoxins)	**Food**
Asbestos	**Air**
Selected microbial contaminants, esp. *Salmonella*	**Food and water**
Selected indicators of water quality—biological oxygen demand, dissolved oxygen, pH, and coliform bacteria	**Water**
Selected indicators of soil salinity and acidity/alkalinity	**Soil**

Note: It is considered that radionuclides and ionizing radiation from peaceful uses of nuclear energy do not give rise to priority pollution problem at the present time. The term "water" includes the oceans.

Source: UNEP.





calibration to give any assurance that useful comparisons of acquired data can be made.

In any case, this year special attention will be given to the development of an international capability to measure, on a repetitive basis, levels of pollutants of greatest international concern.

Referral system

Another initiative considered at the first session of the Governing Council last June is the activation of the IRS, the International Referral System. A basic function of the IRS would be to give a specific user a selective listing of the names, addresses, and attributes of those information sources most likely to satisfy his information needs and help him solve his environmental problems. The sources of information to which a user would be referred include formal information services, information analysis centers, data files, and small groups of individuals with expert knowledge.

An IRS demonstration project is under way today. This exercise involves:

- creation of a demonstration IRS file of information sources
- examination of how best to design the IRS so that it may respond to the real needs of its users
- study of the possible relationship between IRS and major existing or planned environmental information systems.

Other contacts

"One of our principal contacts with the scientific community has been the International Council of Scientific Unions," Thacher explains. "Some years ago, its Scientific Committee on Problems of the Environment (SCOPE) assisted considerably in shaping the monitoring and other recommendations for the Stockholm conference. SCOPE recently established a Working Group on Environmental Assessment and Monitoring and will be involved in future monitoring programs."

UNEP also deals with many other organizations outside the UN system including:

- European Community in Brussels
- Organization of American States (OAS)
- Council for Mutual Economic Assistance (CMEA) (Moscow)
- Nordic Council
- OECD (Paris)
- Rhine Commissions
- Danube Commission
- Regional development banks
- a whole variety of international organizations
- a whole variety of nongovernmental organizations. SSM

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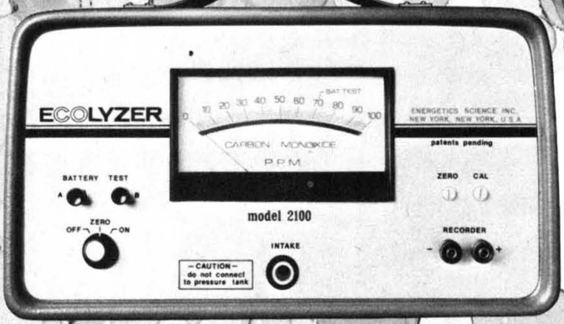

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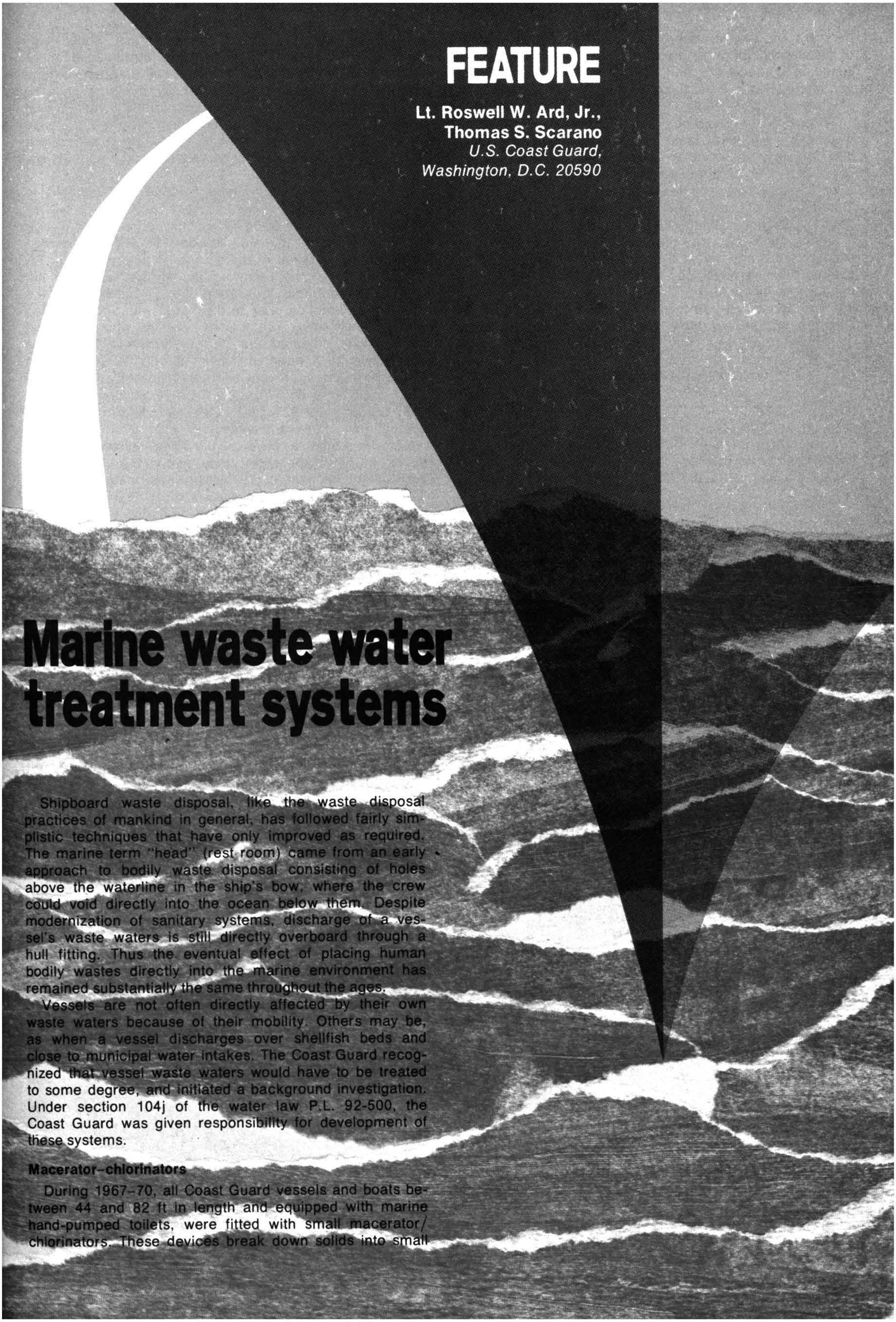

FEATURE

Lt. Roswell W. Ard, Jr.,
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U.S. Coast Guard,
Washington, D.C. 20590

Marine waste water treatment systems

Shipboard waste disposal, like the waste disposal practices of mankind in general, has followed fairly simplistic techniques that have only improved as required. The marine term "head" (rest room) came from an early approach to bodily waste disposal consisting of holes above the waterline in the ship's bow, where the crew could void directly into the ocean below them. Despite modernization of sanitary systems, discharge of a vessel's waste waters is still directly overboard through a hull fitting. Thus the eventual effect of placing human bodily wastes directly into the marine environment has remained substantially the same throughout the ages.

Vessels are not often directly affected by their own waste waters because of their mobility. Others may be, as when a vessel discharges over shellfish beds and close to municipal water intakes. The Coast Guard recognized that vessel waste waters would have to be treated to some degree, and initiated a background investigation. Under section 104j of the water law P.L. 92-500, the Coast Guard was given responsibility for development of these systems.

Macerator–chlorinators

During 1967–70, all Coast Guard vessels and boats between 44 and 82 ft in length and equipped with marine hand-pumped toilets, were fitted with small macerator/chlorinators. These devices break down solids into small particles and then expose them to a concentrated charge of disinfectant prior to discharge. The actual units consisted of a macerator and holding tank in one unit and accommodated a 3-gal flush treated with 60 ml of 5.25% chlorine solution.

Several in-service problems were noted—motors with insufficient capacity, leaks, treated liquid flowing back into the toilets, excessive salt deposits in the holding tank, and loss of effectiveness of the chlorine solution after aging. Effluent analysis showed that the amount of chlorine solution used was insufficient for disinfection at 1965 Public Health Standards (PHS).

During 1965–70, large macerator/chlorinators were installed on several Coast Guard vessels with pressurized sanitary flushing systems. The 28 vessels equipped with this system included the 75-ft tow boats constructed during this period, all 110-ft harbor tugs in the 3rd and 9th Districts, and several buoy tenders. The treatment device consisted of a 15-gal macerator/holding tank, a 20-gal storage-injection tank that treated each batch with 250 ml of 12.5% chlorine solution, and a control panel. After an in-service evaluation, the following problems were noted: backflow of liquid from the macerator tank to the chlorine storage tank, need for a careful adjustment of the amount of injected chlorine solution, and loss of effectiveness of the disinfectant after aging. Of the effluent samples tested, 38% showed coliform densities in excess of PHS.

Early systems

The earliest prototype shipboard waste water treatment systems evaluated by the Coast Guard in the mid 1960's were of the biological type, consisting of an aerobic system installed on a 210-ft medium endurance cutter, and a trickling filter unit installed on a 180-ft buoy tender. Their design was based on land-developed technology with minor modifications for shipboard use. These systems used activated sludge, trickling filtration, sedimentation, and disinfection. No means of on-board sludge disposal were provided. After extensive modifications, the results were unsatisfactory because of poor mechanical reliability, adverse effects produced by ship motion, wide variation of waste water loading rates, and the deleterious effects of such toxic substances as pine oil disinfectants.

A carbon adsorption system was next evaluated in 1969. Wastes were macerated against a screen in the receiving/maceration tank and fed through a series of columns filled with activated carbon filtration/adsorption beds for the removal of solids and soluble organics. Air was supplied to the receiving/maceration tank and the final carbon column to support the bio-oxidation of the wastes. Disinfection prior to discharge was accomplished with an ultraviolet light source. Results after extensive modification indicated that the system provided inadequate treatment when operating at one third its design hydraulic capacity. Initial shore testing showed average BOD reductions of 37% and average suspended solids (SS) reduction of 27%. An excessive coliform count was present in all of the samples tested.

Also in 1969, a physical/biological system was installed on board the 180-ft buoy tender, the USCGC *Sassafras*. Another improved version was installed on the 210-ft medium endurance cutter, the USCGC *Alert*. The major components of the system included a preaeration disintegrator (hydraulic comminutor), vacuum aeration tower, settling tank, chlorine storage tank, and chlorine contact/ejection tank. The hydraulic and organic design loadings for the *Alert* system were based on that of the *Sassafras*, both having approximately the same crew size. During testing, the hydraulic load for the *Alert* was two-and-one-half times greater than the *Sassafras*'s.

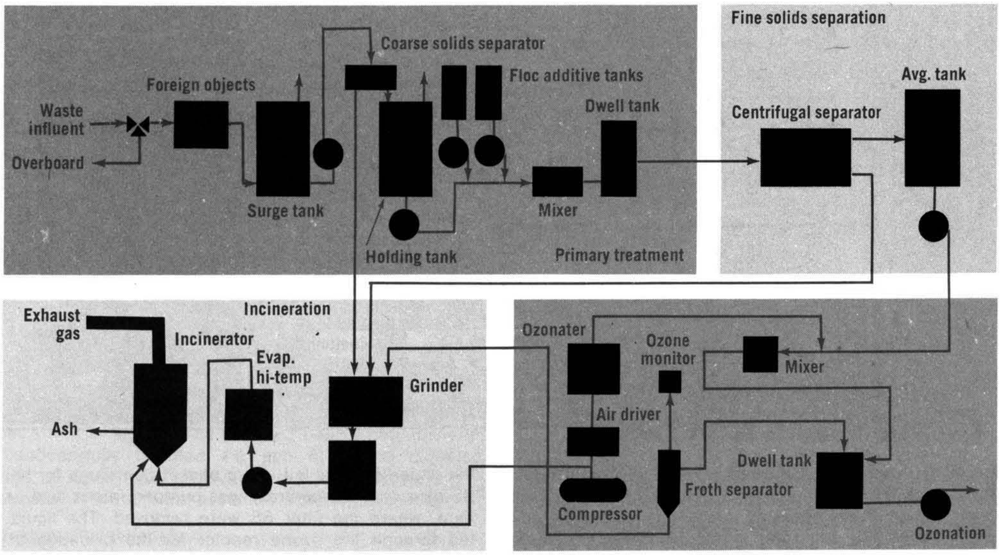
TABLE 1

Vessel constraints and waste water characteristics

Parameter	50-Man system	20-Man system
WASTE WATER CHARACTERISTICS		
Waste water sources	Combined sanitary, galley, scullery, laundry, deck drains	Combined sanitary, galley, scullery, laundry, deck drains
Diluent water	Salt, brackish, or fresh	Salt, brackish or fresh
Influent characteristics		
BOD	1000 mg/l. (av)	500 mg/l. (av)
Suspended solids	1000 mg/l. (av)	500 mg/l. (av)
pH	6–9	6–9
Temperature	28–95°F	28–95°F
Influent hydraulic loading		
Total	5000 gal/day	700 gal/day
Average per capita	100 gal/man/day	35 gal/man/day
Peak flow	300% of av	200% of av.
Effluent requirements		
BOD	50 mg/l. or less	50 mg/l. or less
Suspended solids	50 mg/l. or less	50 mg/l. or less
Total coliform (mpn)	240/100 ml or less	240/100 ml or less
PHYSICAL CONSTRAINTS		
Weight	5000 lb (dry)	1000 lb (wet)
Volume	300 ft^3	50 ft^3
Dimensions	8.5′ long × 5′ wide × 7′ high	3′ long × 4′ wide × 4′ high
ENVIRONMENTAL CONSTRAINTS		
Ambient air temp	40–140°F	40–140°F
Permanent trim	3° from horizontal	3° from horizontal
Permanent list	15° from vertical	15° from vertical
Pitch	10° up or down	10° up or down
Roll	30° from vertical, 10-sec period	40° from vertical, 10-sec period
ELECTRICAL POWER		
Type	440-V, ac, 3-phase	120/208-V, ac, 3-phase
Maximum available	10 kW	4 kW

FIGURE 1

50-man screening-centrifugation system



From this experience it was determined that the volume of waste water generated is a function of both the crew size and the number of water-using facilities.

Average influent BOD for the *Alert* system was 954 mg/l. while average effluent BOD was 270 mg/l. for a BOD reduction of approximately 72%. The average influent and effluent SS concentrations were 793 mg/l. and 474 mg/l., respectively, achieving an average SS reduction of approximately 40%. It should be noted that this system was heavily overloaded hydraulically and suffered a correspondingly severe reduction of retention time in the treatment system. Bacteriological analyses for total coliform were inconclusive. Corrosive deterioration and metal fatigue affected several parts of the system and there was no means for on-board sludge disposal.

Recently, some of the small vessel classes have been fitted with unitized toilets that recirculate the flush water and utilize a chemical in the flush water as a dye, biocide, and odor suppressant. These toilets are periodically dumped into an on-board holding tank and recharged for further use. The dramatic reduction in hydraulic loading has greatly increased the time between main holding tank pumpouts for these vessels.

Unfortunately, initial reports have indicated an odor, minor clogging when the toilets are dumped into the main holding tank, and crew complaints of discomforts caused by high units.

Limitations and characteristics

Although no operational systems resulted from the testing of available marine waste water equipment, valuable experience and insight were gained. Additional information was obtained on shipboard limitations—space, weight, power constraints; dynamic effects of ship motion on waste water treatment processes; and the character of vessel waste waters.

Vessels have several constraints. Power constraints of on-board waste water treatment are the limitations of available electrical energy and/or fuel oil. Space constraints are severe on military vessels which are compartmentalized to allow for the isolation of battle damage. The weight and location of the treatment system are also critical on small recreational boats and some military classes. Comparatively, commercial vessels are less affected by the above limitations.

Vessel waste systems require special aesthetic and safety considerations because of the restrictive environment on the ship. Formation of noxious, potentially explosive, or toxic gases should be prevented. Operational and maintenance requirements should not require extensive time or special skills beyond those normally available to the host vessel. Recycled flush water should not be visually objectionable, emit malodors, or carry pathogens. Other considerations include a corrosion-resistant system, a service interval compatible with the mission profile of the host vessel; and the utilization of expendable materials that do not have excessive weight, space, or handling requirements.

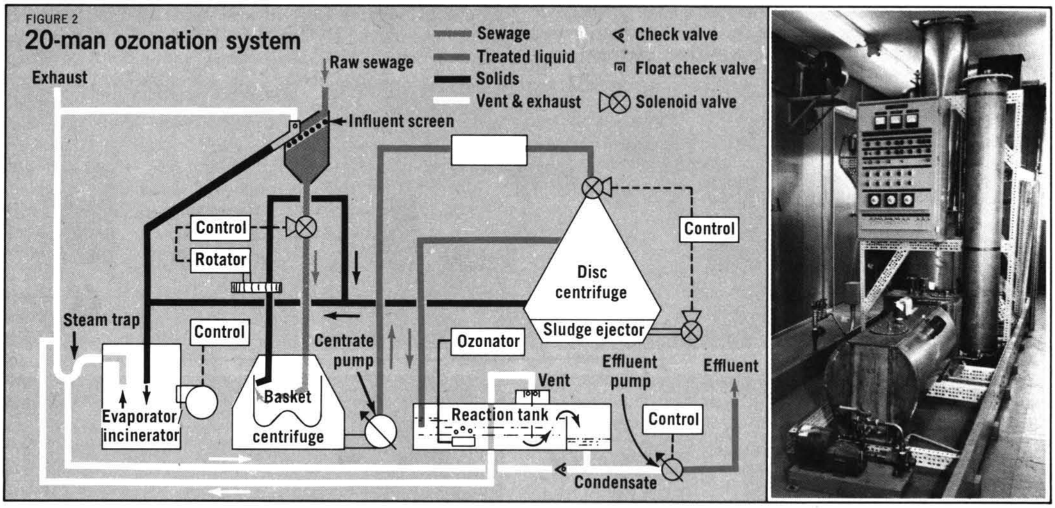
Vessel waste waters are dependent on the types of flushing system (hand-pumped or pressurized), waste water (sanitary only or combined), and vessel; crew size; number of water-using fixtures; geographic location of the vessel; weather; vessel mission profile; and cargo carried. For example, hydraulic flow can vary from 2 gal per capita per day (gpcd) for sanitary wastes in a reduced flush system to 100 gpcd for combined waste water and a standard flush system. Similarly, average BOD can vary from 1122 mg/l. for the sanitary waste waters of an 82-ft patrol boat to 712 mg/l. for the combined waste waters of a 180-ft buoy tender.

CG development contracts

Following these observations, performance goals and design specifications were developed for treating the Coast Guard's 50-man and 20-man shipboard waste water systems (Table 1). A 50-man, 210-ft medium endurance cutter was fitted with a surge tank which dampened the effects of hydraulic flow variations (Figure 1). Combined waste waters entered the tank before going into a vibrating screen for coarse solids removal and subsequent disposal of solids in an incinerator. A coagulant was added to the waste water en route to the centrifugal

FIGURE 2

20-man ozonation system



separator where the coagulated fine SS and light liquid fractions of the waste were separated from the main stream. Hydraulically operated internal collectors periodically removed the separated solids from the centrifuge bowl to be fed to the incinerator. The centrate was pumped to the ozone reactor for oxidation of the dissolved organics, removal of residual solids, and disinfection before being pumped overboard. Initial feasibility testing gave a BOD and SS reduction of 89% and 95%, respectively, with an influent of 50% galley and 50% human wastes. Despite the encouraging early results, this system was too complex to warrant further testing.

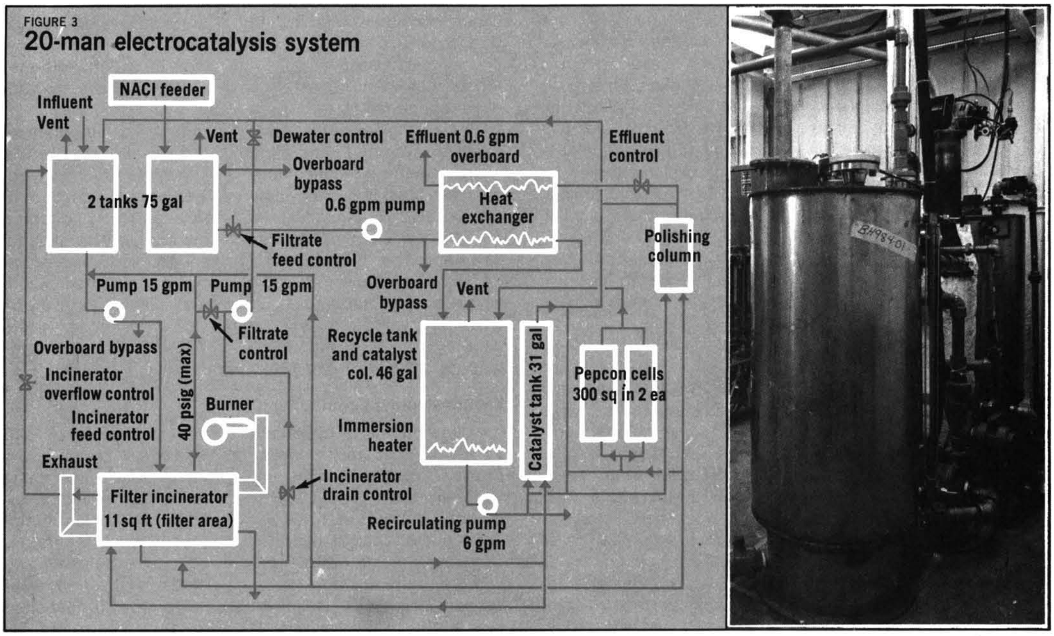
In May 1972, a successful laboratory feasibility study was completed for a 20-man ozonation system. Average BOD removal was 85% and SS removal 89%. In this system (Figure 2), the coarse solids were removed by a screening device and dropped into an incinerator while the underflow was led into a basket centrifuge for heavier SS removal. The centrate was pumped into a disc centrifuge, where the finer SS were removed. The liquid was fed through the ozone reactor for the oxidation of dissolved solids and disinfection of the effluent before discharge.

A full-scale prototype was then built for shore testing and shipboard testing on a harbor tug (Figure 2). Initial shore results were very encouraging.

In July 1972, a successful laboratory phase was completed for another 20-man system, based on electrocatalysis (Figure 3). BOD and SS reductions of 88% and 91% were obtained. The influent was received by a surge tank and pumped through a filter/incinerator that filtered out the coarse solids with sintered metal filter elements. Periodically, the trapped coarse solids were incinerated directly on the filter elements. The filtrate was pumped into

FIGURE 3

20-man electrocatalysis system



the secondary treatment cycle and passed through electrolysis cells that electrolytically generate sodium hypochlorite from the saline waste waters (salt must be added to the system during freshwater operation). The chlorinated wastes were recirculated through a catalyst column that accelerated the oxidation of the organics and the disinfection. A small immersion heater and heat exchanger were used in the secondary treatment component to increase the efficiency of the catalyst by raising the temperature of the waste water. In June 1973, full-scale prototype (Figure 3) was built. Initial shore results have been promising.

The feasibility of using membrane separation and sludge incineration has been studied. In a proposed system application, all the wastes were macerated and the coarse solids removed with a centrifuge and led to the incinerator. The waste water was pressurized and pumped through a succession of membrane filters. The ensuing filtrate was discharged overboard and the resultant sludge incinerated. A concentration ratio greater than 130 was obtained during the concept feasibility testing, using raw untreated sewage with a total solids of 1000 mg/l. Thus, 260 liters of sewage would have given about 2 to 1 of sludge. The compact pebble-bed incinerator successfully handled $4\frac{1}{2}$ gph of a 6% digested sludge. BOD and SS removals were 76% and 90%, respectively. Presently, wet oxidation is undergoing study.

Developmental rationale

One of the two main approaches after the background investigation will be to develop effective systems for Coast Guard vessels. New system development efforts and process feasibility testing will be initiated. Promising results will lead to building a full-scale prototype, shore testing, vessel installation, and field testing.

The continuing attention placed on developments outside of the Coast Guard will undoubtedly mean that worthy processes and systems will come to Coast Guard attention. These systems will be procured and tested to determine their merits.

The second major approach will be to evaluate existing systems and develop promising processes for all other vessels, especially the recreational types. Again, those processes that prove themselves in their feasibility evaluation will be subjected to additional testing, prototype component development, and demonstration testing as appropriate.

The opinions or assertions contained herein are the private ones of the writers and are not to be construed as official or reflecting the views of the Commandant or the Coast Guard at large.

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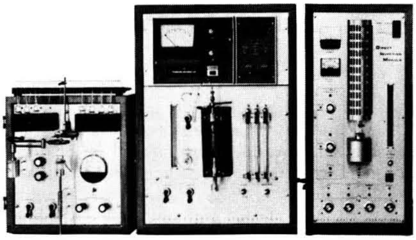

Detecting pollutants with chemical-sensing electrodes

Almost all analytical chemists find it necessary, at one time or another, to make measurements at very low levels. Most often nowadays, the analyst is looking for traces of toxic materials in sewage or in waste waters. Chemical-sensing electrodes have many advantages in such applications. They are relatively inexpensive devices, are fast to respond, and are unaffected by turbidity or color in the sample. Because the response is logarithmic in nature, the precision (up to the limit of detection) remains constant over the entire measuring range: A fluoride measurement at 0.1 ppm will have the same precision as a measurement at 1000 ppm. Electrodes are unique in another sense; they are probably the only analytical devices completely independent of the volume or weight of the sample.

Until the mid 1960's, the only specific ion electrodes available were the classical pH and the glass sodium electrodes. Starting with the commercial availability of Ross's calcium electrode and the solid state electrodes for sulfide and fluoride, the use and acceptance of electrodes have been growing year by year. Orion's bibliography now includes more than 600 papers describing electrodes in analytical application.

Since electrodes now include those for ammonia and sulfur dioxide, both of which are neutral species, the original term "specific ion electrodes" or "ion selective electrodes" must now be broadened to "chemical-sensing electrodes."

Analytical methods

The development of new electrodes has been paralleled by development of analytical methods using electrodes. Since many of these methods are applicable to low-level measurements, it is important first to view them briefly.

The direct calibration methods are the simplest and most commonly used procedures. Standards are prepared by serial dilution or by adding a series of small increments to an initially large volume (the "liter beaker method").

For many ions, the calibrating standards can be prepared in a distilled water background, but some caution must be exercised if the ionic strength of the samples varies from sample to sample or if the samples will have a different background from the standards. For trace determinations in relatively pure water, small variations in sample ionic strength have almost no effect, since the activity of an ion changes little at low ionic strength. For trace determinations in waste waters where samples have high and variable backgrounds, these variations can have a marked effect on the estimated concentration.

One way of handling this variation problem is to add a sufficiently high level of a background ion to both standards and samples so that the normal variations would not have any effect. This procedure has been recommended in standard procedures (ASTM Standards, Part 23, D 1179-72). However, in trace work this technique introduces, in turn, a new problem—the possibility of introducing trace contaminants from the material used to provide the background. Techniques for recognizing this problem will be discussed later.

Aside from the problem of possible contaminant introduction, the use of "ionic strength adjustors" presents serious difficulties for those electrodes that are not highly selective, such as some of the liquid membrane types. Nevertheless, where the samples are of relatively fixed ionic strength and composition (for example, analyses after combustion or ashing) and when there are many repetitive samples to be run, the direct measurement technique is the easiest and simplest.

The known increment methods consist of taking an initial reading in the sample, adding a known amount of the species to be measured, and then taking a second reading. This procedure, now called "known addition," has been widely adopted and is especially valuable for work at low levels, since the second reading is always at a higher level. The concentration may be determined from direct-reading known addition scales now available on meters, from computer printout tables supplied by electrode manufacturers, or found in instruction manuals for the newer electrodes.

The converse of known addition is known subtraction, where the loss of a sensed species after addition of a reagent is measured. This technique is of less general use in trace analysis because it moves the concentration in the wrong direction. It is useful in dealing with species that are unstable at low levels, such as sulfide: The difference in reading for a pure cadmium acetate solution before and after the addition of a sample containing sulfide is much easier than the direct measurement of low levels of sulfide, where air oxidation during the time of measurement may be a problem. Known subtraction is also useful in situations where there is no electrode for the species to be measured—chlorine by subtraction of a known iodide solution.

Known addition and known subtraction are usually done under conditions where the ionic strength of the sample does not change much between the two measurements. If this is the case, it is not necessary to know the ionic strength or make any corrections for it. If complexing agents are present for the species being measured, they must be present in excess so that the fraction of ions which are bound remains constant during the measurement.

Titrations are slower but more precise than direct measurements. Electrodes can be used to follow titrations. However, in order to have a good end-point break using conventional plotting techniques, the initial level should be at least two orders of magnitude greater than the level at the end of titration. Almost by definition, there are very

Not affected by turbidity, color, volume, or weight of sample, these devices respond to many species in waste waters at low levels

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few situations in trace analysis when this can occur. With special plotting techniques, however, many microchemical titrations become possible.

Detection limits

Determining the lower limit of detection of an electrode is usually not a simple experimental procedure. A series of successively more dilute standards is prepared, until a value is ultimately reached which does not change appreciably with further dilution. For almost all electrodes, this lower limit is caused by the solubility of the membrane material itself. The only exception to this rule is for the glass pH and sodium electrodes, where the ultimate limit is set either by the presence of interferences, or the absence of a sufficient number of ions in the sample fails to provide a thermodynamic equilibrium within a reasonable time.

For solid state electrodes, the apparent concentration of the measured species can be calculated from the solubility product of the membrane material. For instance, the solid state chloride electrode membrane contains silver chloride, which has a solubility product of about 1.2×10^{-10}. This means that in an unstirred solution, the portion of the solution next to the membrane will have a chloride level of approximately $10^{-5}M$ from the dissolution of the membrane material. If the solution is stirred,

Commercially available chemical-sensing electrodes

	Type of electrode	Lowest detection limit	Interference	Removal technique
Ammonia	GS	10^{-6}	—	—
Bromide	SS	—	—	—
Cadmium	SS	10^{-7}	Cyanide	Add hypochlorite
Calcium	LM	10^{-5}	—	—
Carbon dioxide	GS	—	—	—
Chloride	LM	10^{-5}	—	—
Chloride	SS	5×10^{-5}	—	—
Cupric	SS	10^{-7}	Ferric	Add sodium fluoride
Cyanide	SS	10^{-6}	Sulfide	Add lead carbonate
Fluoride	SS	10^{-7}	Aluminum	Complexing with CDTA
Hydrogen	G	—	—	—
Iodide	SS	—	—	—
Lead	SS	10^{-7}	—	—
Monovalent cation	G	—	—	—
Nitrate	LM	10^{-5}	Chloride	Add silver sulfate
Nitrogen oxides	GS	—	—	—
Perchlorate	LM	—	—	—
Potassium	LM	10^{-5}	—	—
Silver/sulfide	SS	—	—	—
Sodium	G	10^{-7}	—	—
Sulfur dioxide	GS	—	Nitrogen oxides	Add sulfamic acid
Thiocyanate	SS	—	—	—
Water hardness	LM	10^{-8}	—	—

GS = gas-sensing, LM = liquid-membrane, G = glass, and SS = solid-state.

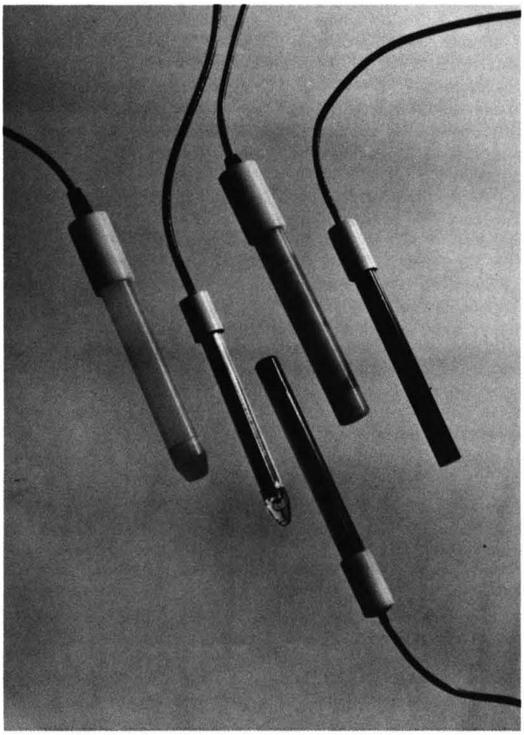
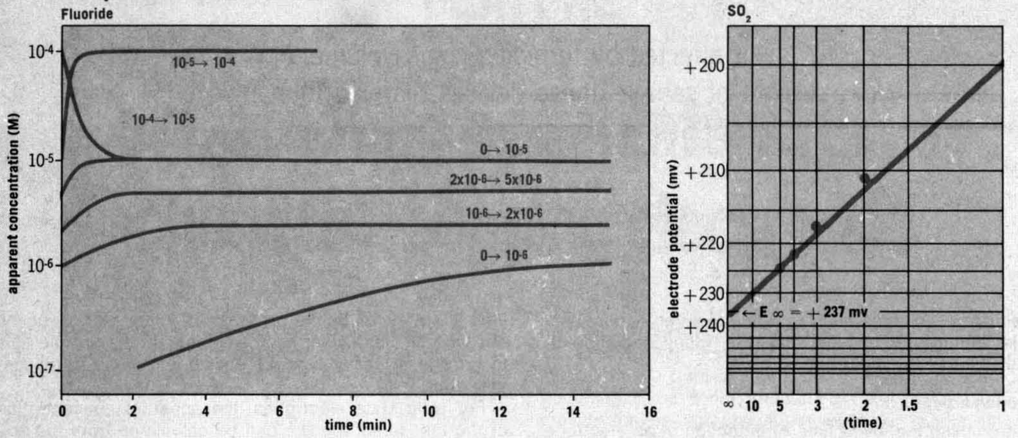


FIGURE 1

Time response curves



the chloride level adjacent to the membrane will fluctuate as the stirring removes more or less of the dissolved material.

If a standard is prepared which contains $10^{-5}M$ chloride, there will be an equal contribution of chloride from the dissolution of the membrane material. As a matter of defining a relatively fixed point, the lower limit of detection of an electrode is usually taken as the point at which the contribution from the membrane solubility is equal to the apparent concentration. This point can be found by extrapolating from higher concentrations to the reading in distilled water.

Most electrodes have lower limits of detection than the chloride electrode, since the membrane materials are less soluble. Silver bromide, for example, has a solubility product of 5×10^{-13}, and the lower limit of detection is approximately $7 \times 10^{-7}M$. For lanthanum fluoride, the membrane material in the fluoride electrode, the solubility product for the single crystal material used in making the electrode is apparently many orders of magnitude less soluble than the freshly precipitated material. The fact that the limit of detection is much lower than anticipated from the solubility product has been discussed by Lingane (*Anal. Chem.*, **39,** 881, 1967) and others.

The same considerations hold for liquid membrane electrodes. In this instance, the electrode inventor tries to reduce water solubility by making the organic molecules as large as possible, but he is limited by other factors such as the need to keep the molecule soluble in suitable solvents and the need to maintain adequate ionic mobility within the organic phase.

Low-level problems

The problem of adsorption, common to all low-level analytical procedures, is by no means a simple one. Certain generalizations are possible, however. Glass containers and beakers are generally unsatisfactory, because of the ion exchange properties of glass. Plastics are generally preferred, with Teflon apparently showing the least amount of adsorption (*Anal. Chem.*, **42,** 1002, 1970). Prerinsing or prestorage of solutions having a similar low level of the desired ion has been recommended as a technique for reducing the effects of adsorption.

Manahan (*Anal. Chem.*, **45,** 836, 1973), working with the copper electrode at very low levels, suggested the use of an acetate buffer to prevent adsorption of copper. In the presence of excess acetate, the fraction of free copper is fixed, so that there is no interference with electrode procedures.

The problem of contamination can come from the reagents used in the analysis, the water used to prepare samples, or even from the air. For example, distilled water prepared in tin-lined copper-distilling equipment may contain significant quantities of copper. And lab tissues used for wiping electrodes may well contain fluoride. Heavy metals which interfere with sulfide determinations have been found in sodium hydroxide solutions. Reagent contamination can be minimized by the use of ultrapure reagents, available from some suppliers, and by preliminary treatment with ion exchange resins, particularly resins having chelating properties.

Time response is another problem. All electrodes become slower as the solutions become more dilute. In the case of gas-sensing electrodes, such as ammonia or SO_2, the lower limit of detection for the electrodes is set by the maximum acceptable time in which a reading can be obtained (typically 5–10 min). The SO_2 electrode responses (Figure 1), for example, are faster in the direction of increasing concentration, as can be seen by comparing the two uppermost curves (going from 10^{-5} to $10^{-4}M$, and the reverse). Full response going from zero to $10^{-6}M$ cannot be reached in less than 15 min. On the other hand, full response, going from 10^{-6} to 2×10^{-6} is reached within 5 min.

Working at very low levels means long waiting periods for equilibrium. This wait can be remedied by using the recently developed Time Response Paper. With this paper, initial readings taken within the first few minutes are extrapolated to give the reading at "infinity" time.

The problem of interferences is more serious in low-level work because in most cases it is the measured ion to the interfering ion ratio which determines whether interferences will occur. In the case of glass and liquid membrane electrodes, the effect of an interference is gradual; for any given level of the ion to be measured, increasing amounts of the interference cause a gradually increasing error.

For example, hydrogen ions are an interference for the glass sodium electrode. Most of the commercially available glass sodium electrodes actually have about a 100:1 preference for hydrogen ion over sodium. This means that at low levels of sodium ion in neutral solution, there will be an interference from hydrogen ion. At pH 5 ($10^{-5}M$ activity of hydrogen ion) the electrode begins to respond to hydrogen ion at a level of around $10^{-3}M$ sodium ion. At pH 7, interference begins at about $10^{-5}M$ sodium. For low-level sodium measurements, the solution must be made alkaline with gaseous ammonia or organic amines. Similar curves can be prepared for sodium interference with the glass pH electrode, and chloride interference on the liquid membrane nitrate electrode.

For these electrodes, the equation describing the effect of the interference on the observed potential has been given in various forms, typically:

$$E = E_0 + S \log (A + K_i A_i^{z_i/z}) \qquad (1)$$

where E equals the observed electrode potential; E_0 equals a constant whose value depends on the choice of reference electrode; S equals the electrode slope (59.16 mV at 25°C); A equals the activity of the ion being measured; A_i equals the activity of the interfering species; z equals the charge on the ion being measured; z_i equals the charge on the interfering ion; K_i equals a selectivity constant.

The equation can be used to estimate whether an interference is likely to occur, and selectivity constants are given in the manufacturer's literature. Such "constants" are not truly constant, and vary with the ratio of the species, temperature, and other factors. As a result, it is not practical to attempt to correct for the presence of interferences by the use of selectivity constants.

One interesting case which can be derived from the equations is that of sodium interference for the calcium electrode. Since the charge on the calcium ion is 2 and on the sodium is 1, the term for the activity of the sodium ion must be squared. As a result, there will be less sodium interference for the calcium electrode (given the same ratio of calcium to sodium) in a dilute solution.

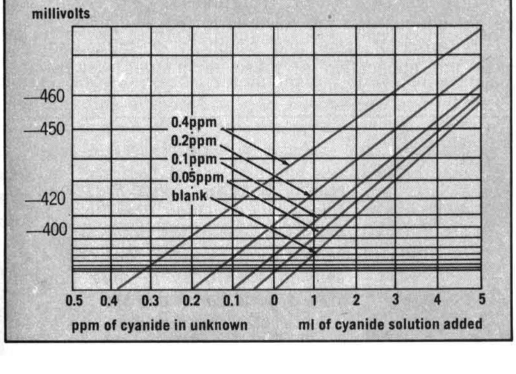
For some of the solid state electrodes, the manufacturer's literature indicates that the interference "must be absent." This would be true, say, for silver or mercury with the copper electrode, since cupric sulfide in the membrane surface would be converted to silver or mercury sulfide. In actual practice, there is no observed interference below $10^{-7}M$ of the interfering ion. Interferences in low-level work are best handled by chemical pretreatment of the sample.

How to lower the detection limit

All of the simple concentration techniques which are used by the microchemist are applicable to electrode work. Thus, extraction of species such as fluoride has been used to bring the fluoride level up to a point where it can be measured (*Anal. Chim. Acta,* **53,** 23, 1971). The use of chelating of complexing ion exchange resins (*Soil Sci.*, **108,** 266, 1969), the use of distillation to concentrate volatile species such as cyanide (ASTM D-19 Water Committee, March 1973), and similar techniques are well-known. Techniques from other fields might also be applied, but thus far have not been reported. For example, in a variation on paper chromatography, a dilute solution could be evaporated from the end of a paper strip the end of which could be re-equilibrated with a much smaller volume of water.

FIGURE 2

Gran's Plot technique



Reducing membrane solubility can also lower the limit of detection set by the solubility of the membrane material. There are two ways in which this solubility can be reduced.

First, the measurements can be made at temperature below that of room temperature. For example, the expected chloride ion activity in solutions of saturated silver chloride are shown as a function of temperature from 5–45°C. It can be seen that decreasing the temperature from 25° to 5° would lower the limit of detection by a factor of about 2.7 to a limit of 5×10^{-6} chloride.

An alternative procedure is to reduce the solubility of the membrane material by using an organic solvent background. There is a balance between the advantage gained from depressing the lower limit of detection and dilution of the sample, typically at about 90–95% organic solvent.

Changing the chemistry can in some instances lower the limit of detection. The titration of calcium with EDTA, using the calcium electrode, is good down to only about $10^{-3}M$ calcium. This is because of the relatively high lower limit of this electrode ($10^{-5}M$) and sodium interference from the sodium EDTA used for the titration.

To remedy this (*Anal. Chem.,* **41,** 1900, 1969), a small amount of copper is added to serve as an indicator, and the copper or cadmium electrode is used. As long as there is free calcium in the solution, the dissociation of the added metal-EDTA complex is relatively unaffected by the additions of EDTA to the solution. When all the calcium has reacted, further small increments of EDTA cause a large change in the level of free cadmium or copper in the solution.

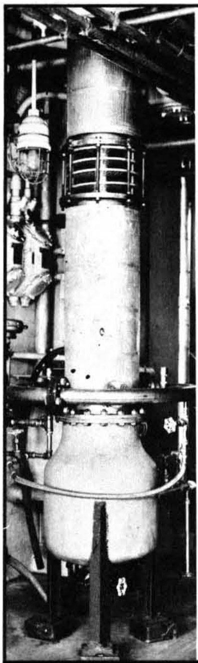
Recently, the measurement of low levels of cyanide in industrial waste discharges has become of considerable interest. Legal requirements of maximum cyanide discharges in the range 0.01–0.1 ppm are not uncommon. The lower limit of detection for the cyanide electrode is about 0.1 ppm.

The silver-sensing electrode has, on the other hand, an extremely low limit of detection, particularly for silver activity. A novel scheme has recently been proposed (*Anal. Chem.*, **44,** 2227, 1972) in which an indicator, consisting of a dilute solution of potassium silver cyanide, is used. Potassium silver cyanide dissociates to a small extent in dilute solutions, giving a small level of free silver and free cyanide. It has been estimated that a $10^{-5}M$ potassium silver cyanide solution has a free silver ion activity of approximately $10^{-9}M$. Any addition of free cyanide, such as mixing with an outside sample, causes a large change in the free silver activity in the solution. Species which might be expected to interfere, like chloride, do not because the silver is entirely present as the cyanide complex. The lower limit of the indicator procedure, when combined with the Gran's Plot technique discussed below, is probably about 0.01 ppm.

The use of special plotting techniques, such as Gran's Plot, is a useful technique for work at low levels. As suggested by Equation 1, all potentiometric ion-sensing electrodes obey the Nernst equation:

$$E = E_0 - (RT/nF) \log A \qquad (2)$$

where E equals observed potential; E_0 equals a constant which depends on the particular electrode and on the choice of reference electrode; R equals the gas constant; T equals the temperature in degrees Kelvin; n equals the



charge on the ion; *F* equals the faraday, also a constant; *A* equals the activity of the species, in many analytical procedures directly proportional to the concentration.

A calibration curve can be prepared by plotting *E* vs. log *A*, or by plotting antilog of both sides, using the equation antilog $E/S = K + A$. A paper (by assuming a slope of 58 mV per decade) has been developed for plotting electrode readings directly against the concentration. Since the original procedure, using linear paper, was suggested by Gran in 1952, the paper was named "Gran's Plot" paper. To further simplify the plotting, papers are available which correct for the volume change on making a series of additions, by skewing the millivolt lines. Thus, for a series of 1-ppm additions, made by adding 1-ml portions of 100 ppm each, to a 100-ml solution, the 1-ppm additions may be plotted as 1, 2, 3, 4, and so on, even though by the fifth addition there is a 5% change in the volume.

The special usefulness of the Gran's plotting technique is that, unlike conventional logarithmic plots, these antilogarithmic plots may be extrapolated back to zero concentration. This is especially useful for low-level work, as in the case of the calibration curve prepared in a solution which already contains some cyanide. Each point on the calibration curve (Figure 2) is displaced by the amount of cyanide initially present, and a "best fit" line can be drawn which extrapolates back, not to zero, but to the original concentration present. This is known addition in which several additions are made, and the best fit line is taken. Since the additions are at higher levels than the amount originally present in the sample, electrode responses are fast and stable, and problems such as adsorption are of less consequence.

Gran's Plot techniques are particularly useful for low-level titrations because the lower limit is usually set not by the electrode, but by the solubility of the precipitate formed during the titration. If, instead of using the actual solubility, one extrapolates to zero concentration, then the lower limit of a titration may be increased by as much as a factor of ten. For example, during the titration of chloride with silver nitrate, at a chloride level of $5 \times 10^{-5} M$, it is not possible to determine the end point from a conventional titration curve, inasmuch as the inherent solubility of silver chloride in water is about $10^{-5} M$. If the same data are replotted on Gran's Plot paper, the points taken when there is excess silver present (and hence when the solubility of silver chloride is repressed) can be extrapolated back to find the correct end point because, in an ideal titration, there would be zero concentration of silver chloride at exactly the stoichiometric end point.

Valuable tools

Chemical-sensing electrodes can be used in a wide variety of analytical techniques for detecting many chemical species at low levels. More care and thought are naturally required in this work than in routine measurements at higher concentrations. Nevertheless, the techniques are not difficult and the rewards to the analytical chemist, in terms of ease and simplicity of measurement, make the application of these techniques well worthwhile.

Martin S. Frant, *Vice-President of Research at Orion Research Inc., has been part of the group which invented and brought the chemical-sensing electrodes to their present state of acceptance and use.*

CURRENT RESEARCH

Hydrocarbon Composition of Urban Air Pollution

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■ Air samples were collected at sites in Los Angeles and New York to evaluate compositional detail of the hydrocarbons and oxides of nitrogen. The compositional details provide a wealth of information allowing for the estimation of source contribution and photochemical potential of an ambient atmosphere. The need to inventory an ambient atmosphere for source contribution is important for evaluating control strategy required to meet the 1975 air quality standards. The manuscript describes two methods for estimating vehicular hydrocarbons in an ambient atmosphere.

Since the development of gas chromatography, several attempts have been made to sample the atmosphere for hydrocarbon pollutants. The earliest report of atmospheric hydrocarbons was made by Eggertsen and Nelsen (1958). The paper outlined a procedure for trapping large volumes of air and included some data of atmospheric analyses. Neligan (1962) presented a detailed description of the C_2–C_7 aliphatic hydrocarbon species in the Los Angeles atmosphere. The comparison of hydrocarbon composition of these air samples to auto exhaust resulted in the identification of other sources of the paraffinic hydrocarbons. These other sources were attributed to natural gas leaks, gasoline evaporation, and industrial sources.

Similar observations were made by Altshuller and Bellar (1963) for the paraffinic hydrocarbons, especially ethane, propane, and isobutane in the Los Angeles area. They reported ambient concentrations for these species five to ten times larger than those observed from auto emissions. For the most part, the other hydrocarbon species measured compared well to compositional measurements of auto exhaust from dynamometer studies.

Stephens and Burleson (1967) compared the composition of individual C_2–C_6 aliphatic hydrocarbons analyzed in air samples collected in Riverside, Calif., to auto exhaust, gasoline (both vapor and liquid), and natural gas to evaluate pollutant sources. The olefin pollutant ratios to acetylene were compared in morning and afternoon samples, and the decrease of these ratios in afternoon samples was attributed to photochemical losses. The high concentration of ethane observed was attributed to natural gas sources. They suggested a combination of vehicular emissions, gasoline evaporation, and natural gas and oil field losses as sources of the propane species. They suggested the lower pollutant ratios of ethylene and propylene to acetylene observed in the morning samples compared to auto exhaust emissions were due to the mixing of fresh exhaust with reacted pollutants from the previous days.

Stephens and Burleson (1969) used irradiated air samples to evaluate air samples in terms of hydrocarbons present, hydrocarbons reacted, and original hydrocarbon levels. Estimates were made for morning concentration levels from those observed in afternoon samples using first-order kinetics and rate constants determined from flask reactions of ambient air samples. The method left many questions unanswered, such as the extent of nitric oxide loss compared to hydrocarbon reacted.

Altshuller et al. (1971) presented diurnal patterns of a variety of individual aliphatic and aromatic hydrocarbon species. From these patterns, they were able to show auto exhaust as a common source for many of these species.

They presented patterns from two locations in the Los Angeles basin; namely, DOLA (downtown Los Angeles) and Azusa. Compositional variations were observed at these two locations primarily of the aliphatic hydrocarbons. The transportation of heavily polluted air masses from DOLA was observed in the diurnal pattern of hydrocarbons at the Azusa site. Even though the hydrocarbons at the Azusa site were generally one half of those reported at DOLA, mid-afternoon oxidant concentrations were of comparable magnitude on many occasions.

Many of these reports were limited by the lack of detail of hydrocarbon composition. In most of these papers, comparisons were made of ambient air pollutants to auto exhaust obtained from dynamometer studies. Hydrocarbon composition of auto exhaust obtained in this manner varies with vehicle, gasoline and test cycle used, and is not necessarily representative of the vehicular emission observed in the actual atmosphere.

This paper deals with alternate methods for evaluating vehicular emissions in an ambient atmosphere. The paper also presents atmospheric hydrocarbon data from the eastern coast, in particular the New York–New Jersey area.

Experimental

Atmospheric air samples were collected in 70-liter, 2-mil Tedlar bags (Du Pont Co.) by means of an automatic sequential air sampler. The trapping system used for concentrating large air samples was similar to those outlined in previous work (Lonneman et al. 1968; Bellar et al. 1963).

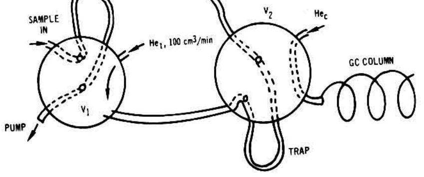

Figure 1. Trapping system for gas chromatographic analyses

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[1] To whom correspondence should be addressed.

The trapping device is shown in Figure 1. Three gas chromatographic systems were used to analyze the hydrocarbon species. The technique for each gc system is described below:

C_2–C_5 Aliphatic Hydrocarbons (Excluding C_4 Olefins)

- The technique of injection
  - The concentration setup is described in Figure 1.
  - The trap was a 1-ft × ⅛-in. stainless steel column packed with 60–80 mesh dilute nitric acid washed silica gel grade 58 (Grace Labs).
  - The analytical column was an 8-ft × ⅛-in. stainless steel column packed with the same silica gel substrate at 30°C.
  - The loop volume was 72 cc.
  - The helium trap flow rate He_t was 90 cc/min.
  - The helium column flow rate He_c was 40 cc/min.
- Sampling procedure
  - Air was pulled from a sample bag through the sample loop at ambient pressure by means of a pump. In the meantime the trap was immersed in liquid nitrogen.
  - Sample valve V_1 was turned to the inject position routing the He_t flow through the loop, pushing the sample through the trap. This period was usually 6 min or enough time to flush the loop several times.
  - At the end of this time period, the liquid nitrogen was removed and the trapped oxygen was vented to the atmosphere for a period of 5–8 sec.
  - At the end of this period, valve V_1 was turned to the fill position, and simultaneously valve V_2 was turned to the inject position.
  - The column helium, He_c front flushes the trapped C_2–C_5 aliphatic hydrocarbons through the trap and onto the analytical column.
  - After a period of 1½ min, valve V_2 was turned back to the fill position. This period was sufficient for the quantitative injection of the C_2–C_5 aliphatics onto the analytical column. If this time period was extended, the higher molecular weight hydrocarbons and water would break through the trap and onto the analytical column resulting in the deactivation of the silica gel substrate.
- During the sample analysis, helium flow He_t back flushes the higher molecular weight hydrocarbons and water off the trap preparing it for the next sample.

C_4–C_8 Aliphatic Hydrocarbons

- The technique for injection of the C_4–C_8 aliphatic hydrocarbons was similar to that for the C_2–C_5 systems with the following differences.
  - The trap was a 1-ft × ⅛-in. stainless steel column packed with 10% Carbowax 1540 on 60–80 mesh Gas Chrom Z.
  - The analytical column was a 300-ft by 0.06-in. i.d. open tubular column coated with dibutylmaleate at ice water temperature. A 1-ft × ⅛-in. trap containing 10% 1,2,3-tris(2-cyano)ethoxy propane (TCEP) was used after the column to prevent bleeding of the dibutylmaleate substrate to the detector.
  - The loop volume was 90 cc.
  - The helium trap flow rate, He_t, was 100 cc/min.
  - The helium column flow rate, He_c, was 70 cc/min.
- Sampling procedure was similar to the C_2–C_5 system with the following differences.
  - The period for venting trapped oxygen to the atmosphere was 1–2 sec. When the liquid nitrogen was removed, the trap was immersed in a beaker of water at room temperature.
  - After a period of 30 sec, valve V_2 is turned back to the fill position. This period was sufficient for the quantitative injection of the C_4–C_8 aliphatics onto the analytical column and prevents the injection of the heavier molecular weight aromatics hydrocarbons onto the column.

C_6–C_{10} Aromatic Hydrocarbons

- The technique for injection of the C_6–C_{10} aromatic hydrocarbons was similar to that described for the C_2–C_5 aliphatics with the following differences:
  - The trap was a 1-ft × ⅛-in. stainless steel column packed with 60–80 mesh glass beads.
  - The analytical column was a 300-ft. × 0.06-in. i.d. open tubular column coated with *m*-bis-*m*-phenoxyphenoxy benzene at 70°C.
  - The loop volume was 150 cc.
  - The helium trap flow rate, He_t, was 100 cc/min.
  - The helium column flow rate, He_c, was 70 cc/min.
- Sampling procedure was similar to the C_2–C_5 system with the following differences:
  - The time period for venting trapped oxygen was 1–2 sec. When the liquid nitrogen was removed, the trap was immersed in a beaker of water at room temperature.
  - Valve V_2 was not returned to the fill position until the completion of the analysis. This period was usually 30 min.

The carbon monoxide and methane species were separated on an 8-ft × ⅛-in. stainless steel column packed with 60–80 mesh 13× molecular sieve (Wilken Instrument Co.) at 70°C. Nitrogen was used as the carrier gas. Hydrogen was added to the carrier gas effluent at the exit of the column via a Swagelok tee. The mixture was routed through a 1-ft × ¼-in. copper column packed with reduced nickel on firebrick catalyst (40–60 mesh) to the flame-ionization detector. The catalyst temperature was maintained at 450°C. The catalyst was prepared by wetting untreated firebrick with a saturated solution of nickel nitrate. The substrate was dried and exposed to a hydrogen atmosphere at 450°C for a period of 12 hr. The catalyst served to reduce carbon monoxide to methane.

Results and Discussion

Air samples were collected in 70-liter Tedlar bags for detailed compositional analysis. The study included the following three items:

Samples (400) collected in Downtown Los Angeles during the fall months of September, October, and November 1968. The air samples represented a 1-hr integrated sample.

Samples (310) collected at various sites located throughout the New York–New Jersey area during the summer months of June, July, and August 1969. Each air sample was collected over a 2-hr time period.

Samples (10) collected in the Lincoln Tunnel over a ½-hr period.

The three gas chromatographic procedures produced 52 measurable hydrocarbon peaks representing the C_1–C_{10} hydrocarbons. The higher molecular weight hydrocarbons (C_{11}–C_{12}) were observed on occasion but at very low concentration levels. Some of these peaks represented more than one hydrocarbon component that were not completely resolved. The overlap of paraffinic and olefinic species was not a significant problem, especially with more abundant components. There were overlaps between benzene and some of the C_7 and C_8 paraffins, especially methyl cyclohexane.

The summation of concentrations of these peaks in parts-per-billion carbon was considered to represent the total hydrocarbon concentration. This assumption was confirmed by the comparison of this value with that obtained with a Beckman Model 109A Total Hydrocarbon Analyzer. The problems encountered, however, with the total hydrocarbon analyzer are numerous including response variation with sample air flow rate; variation in response factors of the individual hydrocarbon species in air; response due to water vapor (relative humidity) (Lucero, 1972); and temperature variation effect on the electronics of the system.

On many occasions, however, the concentration comparisons were in good agreement. In addition to this comparison, no other measurable peaks corresponding to other hydrocarbon species were observed on the chromatogram.

Detailed hydrocarbon composition of an ambient atmosphere serves as a fingerprint for estimating source contribution to the overall hydrocarbon burden, permits evaluation of the photochemical smog potential of an ambient atmosphere due to hydrocarbon reactivity, and provides input for estimating emission control requirements necessary to attain the 1975 hydrocarbon air quality standards.

Dynamometer results have been used to compare ambient samples to automotive tail pipe emissions (Stephens, 1967; Stephens, 1969; Altshuller, 1971). However, there are large uncertainties involved in extrapolating the results of dynamometer studies to the real atmosphere. Since dynamometer studies cannot practically cover all combinations of parameters affecting automotive emissions, estimates of emission into the atmosphere are based on measurements from "typical" vehicles, using "typical" fuels and operating under "typical" driving conditions. Emission measurements made under real driving conditions can minimize many uncertainties inherent in dynamometer measurements.

Table I. Average Hydrocarbon Ratios[a] to Acetylene in Lincoln Tunnel

Component	Ratio of component to C_2H_2 and std dev
Ethylene	1.33 ± 0.14
Isobutane	0.34 ± 0.05
n-Butane	0.97 ± 0.12
Propylene	0.61 ± 0.07
Isopentane	1.25 ± 0.14
Isobutylene } Butene-1 }	0.34 ± 0.04
Sum of C_4 olefins	0.60 ± 0.07
n-Pentane	0.62 ± 0.07
Sum of C_5 olefins	0.53 ± 0.08
Cyclopentane } 2-Methylpentane }	0.76 ± 0.08
3-Methylpentane	0.34 ± 0.04
n-Hexane	0.36 ± 0.05
2,4-Dimethyl pentane	0.34 ± 0.04
2,2,4-Trimethyl pentane	0.27 ± 0.23
Toluene	1.27 ± 0.23
Ethyl benzene	0.22 ± 0.03
p-Xylene	0.25 ± 0.03
m-Xylene	0.70 ± 0.15
o-Xylene	0.28 ± 0.04
Sum of C_8 aromatics	1.44 ± 0.25
3 & 4-Ethyl toluene	0.38 ± 0.05
sec-Butyl benzene } 1,2,4-Trimethyl benzene }	0.40 ± 0.06
Sum of paraffins	6.81 ± 0.92
Sum of olefins	3.24 ± 0.32
Sum of aromatics	3.87 ± 0.58
Total nonmethane hydrocarbons	13.9 ± 1.5
Carbon monoxide	63.4 ± 6.1

[a] Ratios were calculated from component concentrations in parts-per-billion carbon.

Air samples collected along roadways represent a larger number of vehicles and gasolines in actual use. However, these sampling locations are subjected to air ventilation and circulation characteristics resulting often in hydrocarbon concentrations only two or three times higher than that of surrounding atmosphere. Under such conditions, strong and variable emissions from nonvehicular sources may prevent the accurate determination of a vehicular emission factor. The operation of the automobile on any given roadway may not be representative of the composite urban traffic, and accurate vehicular emission factors may require information on traffic density and sampling at roadways under different traffic conditions.

The Lincoln Tunnel constructed under the Hudson River connecting New Jersey with Manhattan is heavily traveled. The controlled ventilation of the tunnel provides hydrocarbon concentrations four to five times larger than those observed in roadway samples, and 10 to 15 times higher than those observed in the ambient atmosphere. Contribution of hydrocarbons from other sources are expected to be insignificant at these concentrations. A wide range of vehicles using a variety of gasolines produces a representative automotive atmosphere. As with roadway samples, however, one must incorporate assumptions regarding the comparability of tunnel traffic and the composite urban traffic.

The comparison between the tunnel atmosphere and that observed at ambient atmospheres throughout the city can be made between hydrocarbon composition or ratios of individual hydrocarbons. Acetylene was used as a normalizing species since it serves as a convenient means of comparing individual hydrocarbons or sums of hydrocarbons.

Two assumptions were made about the acetylene species; namely,

The only source of acetylene in the urban areas was from automotive sources. This is a valid assumption, except in vicinities of acetylene plants or areas where acetylene is used for an industrial application.

The acetylene species for practical purposes is photochemically unreactive. This postulate has been confirmed in other studies (Stephens, 1967; Kopczynski, 1972).

Because of its excellent correlation with acetylene, carbon monoxide could also be used as a normalizing species. However, acetylene was selected since the magnitude of its concentration was comparable to other hydrocarbon species; and it was analyzed by gas chromatography using cryogenic concentration techniques.

The normalization factors for some of the major individual components, total hydrocarbon, sums of paraffins, olefins, and aromatics are listed in Table I. The concentrations of the components used to calculate these ratios are parts-per-billion carbon. The total hydrocarbon factor does not include methane, ethane, and propane since these components are largely representative of natural sources in the ambient atmosphere. Benzene was also excluded from the total hydrocarbon factor since interference in its gas chromatographic analysis by paraffinic components was identified. In the table, ethylene is observed to be the most abundant pollutant in the automotive atmosphere followed closely by toluene and isopentane. Fifty percent of the identified components have ratios valued below 0.20 with 62% of these below 0.10. Seventy percent of the identified species with ratios above 0.10 have a standard deviation range better than ±15%.

The superior precision in the standard deviation range

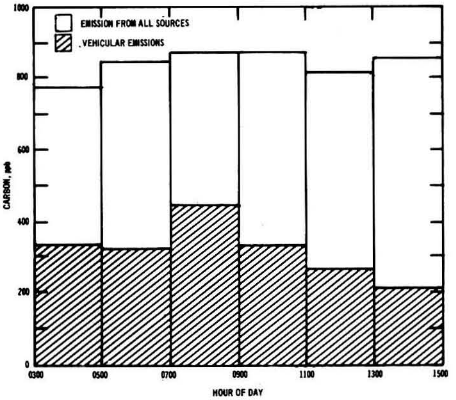

Figure 2. Linden. Average total hydrocarbon (less methane, ethane, propane, and benzene) vs. time

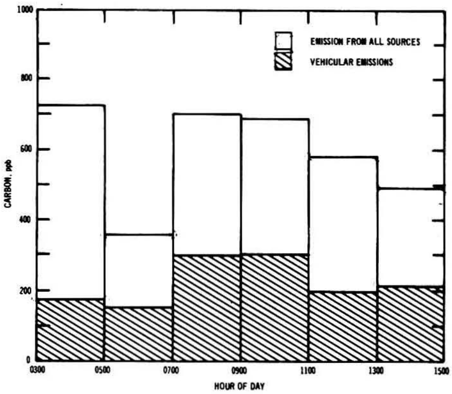

Figure 3. Bayonne. Average total hydrocarbon (less methane, ethane, propane, and benzene) vs. time

for the ratio of the sum of the olefins to acetylene may result from the fact that the major olefins, in particular ethylene and propylene, represent pollutants produced by the combustion process and are not significant constituents of gasoline. Since acetylene is also produced exclusively by the combustion process, it seems reasonable that these components compare that well.

However, the paraffins and aromatics are components of gasoline. Their presence in tail pipe emissions is due to both the combustion process and survival. These effects combined with the compositional differences of the various gasolines used by automotive traffic may explain the higher standards deviation ranges observed for the ratios to acetylene for both the sum of paraffins and aromatics. More severe deviation in ratios are observed for the heavier hydrocarbons such as toluene, *m*-xylene, and 2,2,4-trimethyl pentane than the lighter paraffins such as isobutane through C_6 species.

The standard deviation range about the mean ratio for many of these components and the summation of components are low enough to be used as factors to evaluate the hydrocarbon composition at several locations throughout the area in terms of vehicular and nonvehicular sources.

Samples were collected at four sampling sites throughout the New York–New Jersey area. Two sites were located at industrial areas of New Jersey southwest of Manhattan; namely, Linden and Bayonne. The other two sites were located in the nonindustrial areas of Brooklyn and Manhattan. At each site 8–13 air samples were collected and analyzed for each 2-hr time periods during the time interval of 3:00 a.m.-5:00 p.m. The average total hydrocarbon (excluding methane, ethane, propane, and benzene) for each sample period is given in Figures 2 through 5. The estimated vehicular total hydrocarbon for each time period was calculated by multiplication of the 13.9 factor from Table I by the average acetylene concentration. From the figures, it is obvious that the observed total hydrocarbon concentration exceeds the estimated vehicular total hydrocarbons at all sample sites at all sample times, indicating other sources of hydrocarbon. This is especially true for the Linden and Bayonne sites where industrial sources are more predominant.

The 7:00–9:00 a.m. sample interval represents a time period of peak vehicular traffic, generally associated with a mild morning inversion. The highest total hydrocarbon concentration is expected during this period. It is also expected that most of the total hydrocarbon would be attributed to vehicular sources. The Brooklyn site is the only location where both of these expectations are observed. The vehicular total hydrocarbon peak does not occur at the Manhattan site until the 9:00–11:00 a.m. period. This is possibly explained by the transport of heavily polluted air from midtown Manhattan to the sampling site located 7–8 km north.

The highest percentage of total hydrocarbons accountable as vehicular emission occur during the 7:00–9:00 a.m. time period at the Brooklyn and Linden stations and 9:00–11:00 a.m. at the Bayonne and Manhattan sites. At all other time periods the contribution of hydrocarbons from other sources increases at all sampling locations. This fact is observed by the greater difference between the observed total hydrocarbon and that estimated from vehicular emissions. These other sources include industrial and gasoline evaporative losses from parked vehicular fuel tanks. The contribution of hydrocarbon from evaporated fuel tank losses are expected to increase significantly during the afternoon hours owing to the increase in ambient temperatures. The decrease in the estimated vehicular hydrocarbon concentration during the afternoon hours is probably due to the breakup of the morning inversion ac-

Table II. Ratio[a] of Sum of Paraffins, Olefins, and Aromatics to Acetylene at New York–New Jersey Stations at 7:00–9:00 a.m.

	Bayonne	Linden	Manhattan	Brooklyn	Tunnel
Σ Paraffins	17.79	14.65	8.33	9.22	6.81
Σ C_4 paraffins	4.51	4.06	1.73	1.83	1.41
Σ C_5 paraffins	6.10	4.37	2.80	2.79	1.90
Σ Olefins	5.11	4.86	2.64	2.79	3.24
Σ C_4 olefins	1.12	0.93	0.47	0.49	0.59
Σ C_6 olefins	0.07	0.10	0.03	0.07	0.08
Σ Aromatics	10.85	8.57	5.97	7.81	3.87
Toluene	4.18	3.31	2.11	2.96	1.27
Σ C_8 aromatics	4.55	3.51	2.95	3.34	1.44
Σ $C_9 + C_{10}$ aromatics	2.12	1.75	0.91	1.51	1.16
Ethylene	1.97	1.69	1.10	1.20	1.33
Propylene	0.73	1.04	0.34	0.38	0.61
Av acetylene concn, ppb carbon	21.3	30.4	48.2	51.1	

[a] Ratios were calculated from component concentrations in ppb carbon.

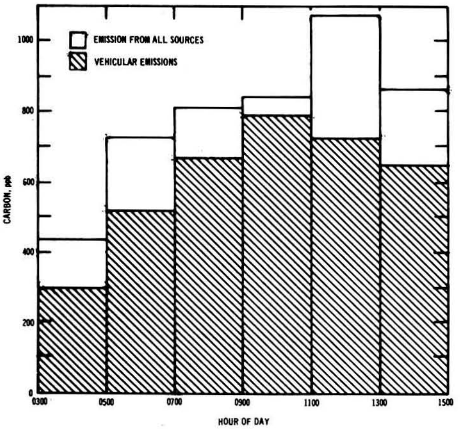

Figure 4. Manhattan. Average total hydrocarbon (less methane, ethane, propane, and benzene) vs. time

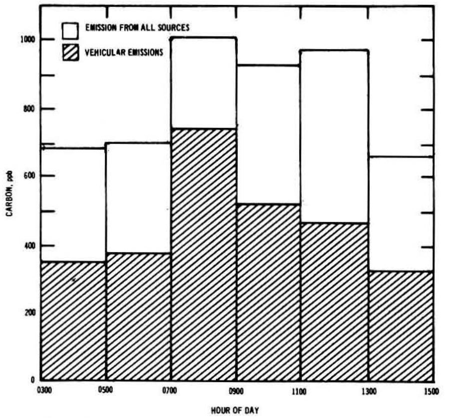

Figure 5. Brooklyn. Average total hydrocarbon (less methane, ethane, propane, and benzene) vs. time

companied by better air ventilation characteristics. These meteorological changes indicate little beneficial effect at any station, in particular Linden, where the observed total hydrocarbon concentration is generally unchanged. This would indicate that industrial sources of hydrocarbons are increasing during the afternoon hours.

With the exception of two time periods, at the Linden, Brooklyn, and Bayonne stations (Brooklyn 7:00–9:00 a.m. and Bayonne 5:00–7:00 a.m.), the hydrocarbon concentration from nonvehicular source exceeds 240 ppb carbon. This would indicate the need for further reduction of industrial emissions to meet the 1975 air quality standards.

More detailed information of hydrocarbon composition was obtained by the comparison of tunnel ratios in Table I to those calculated at the sampling stations. Because of the enormous amount of data, these calculations were limited to the 7:00–9:00 a.m. time period, and the average ratio determined for all sampling periods. The results are recorded in Tables II and III. Presentation of data in this form permits a more detailed evaluation of hydrocarbon composition at each sampling site, allows for convenient comparison of composition at each station, and in general permits the evaluation of the nonvehicular hydrocarbon composition. Since the automobile is considered as the major source of the overall hydrocarbon burden at the urban locations, the 7:00–9:00 a.m. sampling period with the associated automotive traffic density should be representative of the highest percent of vehicular emissions. In Table II this is generally true for the nonindustrial sampling sites and obviously not true for the industrial sites.

Table III. Ratio[a] of Sum of Paraffins, Olefins, and Aromatics to Acetylene at New York–New Jersey Station at All Times

	Bayonne	Linden	Manhattan	Brooklyn	Tunnel
Σ Paraffins	19.50	19.08	8.51	11.29	6.81
Σ C_4 paraffins	5.34	5.24	1.97	2.47	1.41
Σ C_5 paraffins	6.48	5.65	2.89	3.21	1.90
Σ Olefins	4.83	5.75	2.21	2.97	3.24
Σ C_4 olefins	0.99	1.35	0.39	0.50	0.59
Σ C_6 olefins	0.11	0.14	0.05	0.05	0.08
Σ Aromatics	12.77	11.70	6.74	11.3	3.87
Toluene	5.20	4.84	2.16	4.77	1.27
Σ C_8 aromatics	5.89	4.87	2.67	4.67	1.44
Σ $C_9 + C_{10}$ aromatics	1.68	1.99	1.91	1.86	1.16
Ethylene	1.83	1.91	1.08	1.28	1.33
Propylene	0.54	0.87	0.31	0.38	0.61
Av acetylene concn, ppb carbon	15.9	21.7	43.7	32.1	

[a] Ratios were calculated from component concentrations in ppb carbon.

The Manhattan sampling site during this time period demonstrates the nearest comparison to the tunnel composition. The paraffin–acetylene and aromatic–acetylene ratios at the Manhattan site are greater than in the tunnel composition. The obvious explanation for these observations is other sources of paraffins and aromatics contributing to the air quality at the Manhattan site. The lower olefin–acetylene ratio at the Manhattan site can be accounted for by photochemical reaction losses, since the sunlight intensity during the midsummer months in New York at the 7:00–9:00 a.m. time period is comparable to that observed at midafternoon in Los Angeles during the fall smog season.

If the hydrocarbon composition of the 7:00–9:00 a.m. time period at the Manhattan site is selected as being more representative of average vehicular emissions than the tunnel samples, other sources of paraffins and aromatics are still observed at the Brooklyn site. Irrespective of which composition is selected, other significant sources of all hydrocarbon classifications are observed at both the Linden and Bayonne sites.

Table III represents the average ratio of component to acetylene for all sample times. As expected, the hydrocarbon composition at each sampling station demonstrates greater divergence from the tunnel composition. The extent of photochemical reaction loss of the olefin components is even more significant. Likewise the contribution of paraffinic and aromatic species from other sources are more pronounced. At the industrial sites, sources of all types of hydrocarbons are indicated.

Sunlight irradiation of air samples in plastic bags and glass containers, as well as a variety of simulated chamber studies (Stephens, 1967; Kopczynski, 1972), indicate the rather high reactivity of many paraffinic and aromatic species. The reactivity of di- and trimethyl-substituted aromatics exceeds that of ethylene. Yet, in these ambient atmospheres no significant loss of these species was observed. This is shown in Table III where the hydrocarbon to acetylene ratio at all sample times is higher for the C_8 and C_{9-10} aromatics than similar ratios found in Table II for the 7:00–9:00 a.m. period. Lower ratios should be observed if these species had reacted. Since there is no evidence to conclude a different photochemical mechanism, it must be assumed that the continuous contribution of fresh pollutants of this type masks their consumption in the photochemical process. However, when evaluating data as average concentration over a period of three months, the possibility of one or two unusual days biasing the average concentration must be considered. The hydrocarbon composition will vary at each site with atmospheric conditions and sources strength. On days of high oxidant, the atmosphere is stable and stagnated. Wind velocities are low, and more significant photochemical losses of all reactive hydrocarbons should be observed.

It would perhaps be more fitting to lump gasoline evaporative emissions from parked automobiles with the vehicular emission factor since this fuel reserve is associated with the automobile. The inability, however, to estimate a factor representative of all gasolines, vehicle density, and ambient temperature requires that these sources be combined with other nonvehicular sources.

Our laboratory studies have shown that a temperature range of 21–32°C has very little effect upon compositional changes of the vapor over gasoline. However, increases of approximately 20% in total hydrocarbon concentration in the vapor were observed. Even though it may be difficult to estimate hydrocarbon burden due to evaporative losses, it is safe to assume that the burden may increase as much as 20% during the afternoon hours.

Ratios of compounds or sums of compounds to acetylene can be used to observe transport of hydrocarbons from an industrial complex to a nonindustrial location. This approach was used to compare compositional variations in Manhattan when the wind direction was from the industrial complex located west to southwest, and when the wind was from other directions. The results of this approach are given in Figure 6. Sources of paraffins and aromatics from the industrial complex located west to southwest significantly affect the hydrocarbon composition at Manhattan. The olefins are only slightly affected.

The results in Figure 6 are only intended to show the effect of wind direction on compositional changes. The results should not be interpreted to indicate increase in hydrocarbon concentration. In fact, the total hydrocarbon concentrations in Manhattan at times were higher when the winds were from north and east.

Air samples were collected in Los Angeles on both weekdays and Sundays. The total hydrocarbon concentration (less methane, ethane, propane, and benzene) for each 1-hr integrated sampling period is plotted in Figure 7. Each point on the curve represents an average concentration for 25 weekdays or 10 Sundays.

The effect of weekday morning traffic on the hydrocarbon burden in the stable Los Angeles atmosphere is observed by the sharp twofold increase in total hydrocarbon concentration. As expected, no traffic peak is observed on Sundays. In fact, the Sunday total hydrocarbon decreases continually throughout the day. A similar observation can be made from the weekday curve between the 5:00–6:00 a.m. and 1:00–2:00 p.m. sampling periods. This drop should not be interpreted as a decrease in hydrocarbon sources, but rather a decrease in the atmosphere stability from the nighttime inversion.

An interesting observation is made when the average total oxidant curves for the same weekday and Sunday sampling periods are compared. These curves are included in Figure 7. The average oxidant concentration from the Sunday curve is higher at all sampling periods than the weekday curve. This is not expected in view of the higher

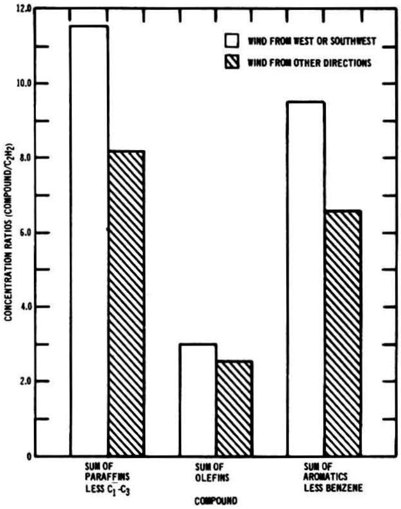

Figure 6. Effect of wind direction on pollutant ratios in Manhattan

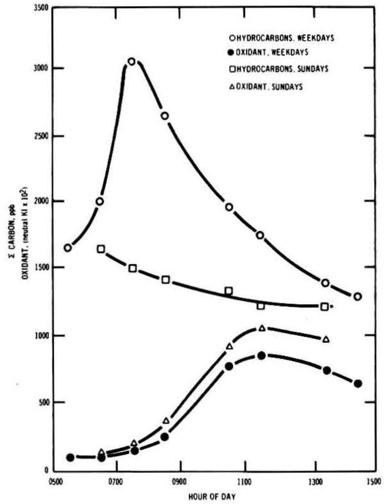

Figure 7. Diurnal pattern of hydrocarbons (less methane, ethane, propane, and benzene) and oxidant in downtown Los Angeles, September–November 1968

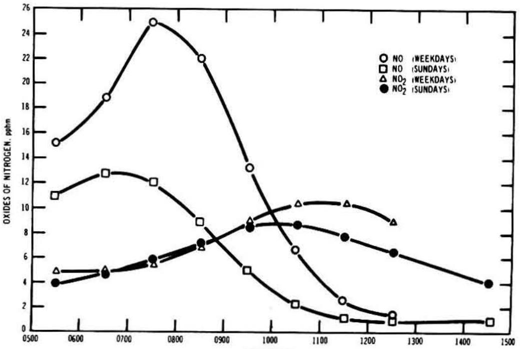

Figure 8. Diurnal pattern of oxides of nitrogen in downtown Los Angeles, September–November, 1968

concentrations of hydrocarbons and nitrogen oxides observed during the weekdays. However, these observations are possibly explainable by the oxides of nitrogen composition. Plots of NO and NO_2 for the 25 weekdays and 10 Sundays under consideration are given in Figure 8. (Both oxidant and oxides of nitrogen data were obtained from Los Angeles A.P.C.D.) Even though the total NO_x concentration for the weekday average is higher than the Sunday samples, NO_2 becomes the dominant NO_x species more than an hour earlier on Sundays. Consequently, the conditions for oxidant formation occur earlier on Sunday than weekdays. Also, since more nitric oxide is available to react with ozone during the weekdays, the conditions for oxidant formation are more favorable on Sundays.

Since tunnels were not available in Los Angeles, a different approach was used to calculate vehicular emission factors. If the weekday total hydrocarbon build-up during the 6:00–9:00 a.m. time period is assumed to be entirely from automotive sources, then a typical average vehicular hydrocarbon composition can be determined by subtracting the 6:00–7:00 a.m. average total hydrocarbon concentration from the 7:00–8:00 a.m. averages. A vehicular total hydrocarbon factor was calculated by a ratio of this difference to that determined for acetylene. Vehicular factors for a variety of hydrocarbon components and combined hydrocarbon components were calculated using this method. The calculated vehicular concentration for each of these selected components was ratioed to the observed concentration at the time periods of 7:00–8:00 a.m. and 1:00–2:00 p.m. The results in terms of percent vehicular emissions are listed in Table IV.

In Table IV the 7:00–8:00 a.m. sample is observed to contain the highest percent of vehicular composition for most of the selected hydrocarbon components and sum of hydrocarbon components. The percentage of adjusted total hydrocarbon attributed to auto emissions during this time period was determined to be 70%. Similar to the New York and New Jersey sites, the olefins can be mostly attributed to vehicular sources. However, other sources of olefins are indicated, especially on Sundays at 7:00–8:00 a.m. where as much as 18% of the olefins is attributed to nonvehicular sources. Unlike the N.Y.-N.J. nonindustrial sites, the percentage of olefins estimated as vehicular sources never exceeds 100% during the late morning and afternoon hours.

Table IV. Emission Factors and Percent Contribution of Vehicular Emissions to Pollutants in Downtown Los Angeles

	Weekdays		Sundays	
Pollutant	7:00–8:00 a.m.	1:00–2:00 p.m.	7:00–8:00 a.m.	1:00–2:00 p.m.
CO	93	84	87	80
Ethylene	92	93	84	98
n-Butane	62	38	38	30
Isopentane	72	52	54	50
Toluene	79	54	65	60
Σ HC (less methane, ethane, propane, benzene)	70	46	48	42
Σ Paraffins	72	47	48	43
Σ Olefins	92	90	82	97
Σ Aromatics	59	34	34	30
Emission Factors				
Σ Paraffins/C_2H_2	5.88			
Σ Olefins/C_2H_2	1.95			
Σ Aromatic/C_2H_2	3.42			
Total nonmethane HC/C_2H_2	11.3			

Inasmuch as substantial oxidant concentrations are observed in Los Angeles during the afternoon hours, extensive photooxidation of the olefins is expected. The fact that the olefin concentration on weekdays does not significantly change from 7:00–8:00 a.m. to 1:00–2:00 p.m. would indicate other important sources of olefins. The 15% increase in vehicular olefins observed at 12:00–2:00 p.m. from 7:00–8:00 a.m. on Sundays can be interpreted as reaction of the atmospheric olefins by photochemical processes. The vehicular factor of 1.95 for the sum of olefins is substantially lower in the Los Angeles area compared to the 3.24 factor determined in the Lincoln Tunnel of New York and is possibly explained by different gasoline compositions in the two areas.

The method used to calculate the olefin factor does not account for photochemical losses occurring during the 6:00–8:00 a.m. time period. The ultraviolet intensity during the 6:00–8:00 a.m. period in Los Angeles for several selected days of clear skies ranged from 0.15–0.21 mW/cm.^{2} This range is approximately one third the range of 0.50–0.60 mW/cm^2 observed in New York during the similar time period. Because of the lower ultraviolet intensity and generally lower temperature observed during the fall months in Los Angeles the photochemical loss of olefins is expected to be significantly less than those observed in New York during this earlier morning period.

The paraffin components attributed to vehicular sources amounts to 72% during the morning 7:00–8:00 a.m. time period. This percentage is only slightly lower than that observed in the nonindustrial areas of New York during a similar time period. The vehicular source percentages of both *n*-butane and isopentane are in good agreement to the total paraffins. The lower percentage of *n*-butane compared to isopentane may be explained by either stronger industrial sources or the higher volatility of *n*-butane from gasoline evaporative losses.

The vehicular estimate of the aromatic components during both time periods suggests strong industrial and solvent loss sources. The rather low 59% vehicular percent during the 7:00–8:00 a.m. time period is not unreasonable in view of the very low 34% observed at the 1:00–2:00 p.m. sample period. During the 7:00–8:00 a.m. sampling period, 79% of toluene, the most abundant aromatic component, is attributed to vehicular emissions. This indicates stronger nonvehicular sources of C_8–C_{10} aromatics, contradicting to some extent the observations reported by Lonneman et al. (1968). Integrated 1- and 2-hr air samples were collected in an effort to eliminate problems of inhomogeneity and incomplete mixing within the air masses. Losses of aromatics to the surfaces of the bag containers used to collect the air samples are expected to be insignificant from laboratory investigations.

Not included in this report is the discussion of the methane, ethane, and propane concentrations observed in these ambient atmospheres. These components are generally considered to come from natural sources and probably are uncontrollable. High concentration of propane from refineries and leakage from liquid propane storage tanks have been observed in many of our air samples during both New York and Los Angeles studies. The concentrations of both ethane and propane are generally higher in the Los Angeles area. A combined concentration ranging from 500 to 600 ppb carbon for the two species has been observed on several occasions in the downtown Los Angeles site.

Conclusion

Methods for estimating ambient hydrocarbon composition as vehicular and nonvehicular sources were presented for Los Angeles and the New York–New Jersey metropolitan areas. Assumptions were made in the calculation of these vehicular factors. However, these factors do provide a means for evaluation of the hydrocarbon air quality affecting a metropolitan area. Information of this type is essential for planning control strategies required to meet 1975 hydrocarbon air quality standards.

Similar calculations were made to demonstrate the effect of wind direction on the hydrocarbon composition in Manhattan.

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Received for review July 16, 1973. Accepted October 29, 1973.

Adsorption of 2,4-D from Aqueous Solution by Fulvic Acid–Clay Complex

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■ The adsorption of 2,4-D (2,4-dichlorophenoxy acetic acid) from aqueous solution by a fulvic acid–clay complex has been investigated. The equilibrium data followed the Freundlich-type isotherm. The relatively low values of the "isosteric" heat of adsorption indicated a physical type of adsorption.

In recent years several reports have been published on the adsorption of 2,4-D by clay minerals (Weber et al., 1965; Weber and Gould, 1966; Weber et al., 1968; Bailey et al., 1968; Haque et al., 1968). However, the clay fraction in soils and sediments is closely associated with organic matter and exists in the form of an organoclay complex (Greenland, 1965). The intimate association of clay and organic matter would likely cause a considerable modification of the clay adsorptive properties. Therefore, it appears more appropriate and realistic to study the adsorption of 2,4-D by the organoclay complex rather than by pure clay mineral.

Recently, Miller and Faust (1972) investigated the sorption of 2,4-D by several organoclay complexes. The latter were prepared by treating dimethylbenzyl octadecylammonium chloride and various benzyl and aliphatic amines with Wyoming bentonite. However, the nature of the organic matter in soils differs profoundly from the organic compounds used by Miller and Faust (1972). Thus, the adsorption behavior of their organoclay complexes may differ significantly from those found in soils and sediments.

This communication reports on the adsorption of 2,4-D by a fulvic acid–clay complex prepared by treating fulvic acid (FA) with Na-montmorillonite. The FA-montmorillonite complex appears to be very similar to the fine clay fraction of some soils (Kodama and Schnitzer, 1971).

Materials and Methods

The FA originated from the Bh horizon of a Podzol soil from eastern Canada and accounted for about 75% of the organic matter in the original soil sample. Methods of extraction and purification as well as a number of analytical characteristics of the FA have been described (Schnitzer and Khan, 1972). The montmorillonite used was the <0.2-μ fraction of a Wyoming bentonite obtained by sedimentation and centrifugation techniques from the original sample. The clay was saturated with sodium by repeated washing with 1*N* NaCl solution. Excess salt was removed by washing and by dialysis against distilled water until free of chloride, and finally was freeze dried.

The FA–montmorillonite complex was prepared as described by Kodama and Schnitzer (1969). FA (500 mg) was taken in a glass-stoppered Erlenmeyer flask and dissolved in 50 ml of distilled water. A 10-ml aliquot of clay suspension, containing 200 mg of montmorillonite, was added to the solution and the total volume was made up to 75 ml with distilled water. The contents of the flask were shaken for 18 hr and then centrifuged. The residue was dried at about 60°C under vacuum and stored in a desiccator over P_2O_5. The FA–clay complex thus prepared contains 62 and 38% of clay and FA, respectively. Slightly more than one half of the FA is adsorbed in the interlamellar spaces of the clay, with the remainder on external surfaces (Kodama and Schnitzer, 1969). On the basis of infrared and differential thermogravimetric analyses it has been shown that the main FA forms adsorbed in and on the clay were undissociated or slightly dissociated FA, and to some extent, Na–FA (Schnitzer and Kodama, 1967).

Analytically pure 2,4-D (2,4-dichlorophenoxy acetic acid) was used in this study.

A known amount of FA–clay complex (15 mg) was weighed in several Corex centrifuge tubes, and shaken for about 1 hr with 7.5 ml of distilled water to allow adsorption of water on the adsorbent. After this, a known volume of 2,4-D solution (7.5 ml) of varied concentration (0–40 ppm) was added and the tubes were shaken for 24 hr at 5° and 25°C. The suspensions (pH $\simeq$ 3.5) were cen-

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trifuged off to obtain clear supernatant solutions. If we assume that the pK of 2,4-D is 2.7, then in the suspensions about more than one half of the herbicide was present in the ionic form.

An aliquot of the supernatant solution was acidified to about pH 1 with 6N H_2SO_4 and extracted with ether. The ether extract was first dried over anhydrous Na_2SO_4, then its volume was reduced to about 0.5 ml using a rotary evaporator. The residue was taken up in a small volume of methanol and methylated with an ether solution of diazomethane, generated from Diazald. A few drops of hexane were added in the flask and the excess of diazomethane was removed by allowing it to evaporate in the fumehood. The resulting material was taken up in hexane, and an appropriate aliquot of the solution was injected into a gas chromatograph for quantitative analysis of 2,4-D. The amount of 2,4-D ester present in the sample was calculated by comparing the sample's peak height (in the linear response region) with that of the appropriate standards. Blanks, consisting of the same amount of the herbicide used in the presence of FA-clay complex, were run concurrently. Recoveries of 2,4-D in the blanks ranged between 97 and 101%.

A Hewlett-Packard model 7610A gas chromatograph equipped with a Ni^{63} electron capture detector was used in this study. The glass column (1200 × 4 mm) was packed with 5% ethyl acetate fractionated Dow Corning high-vacuum grease on Chromosorb W DCMS, 80–100 mesh. The carrier gas was 95% argon and 5% methane mixture, which was also used for purging the detector.

Results and Discussion

An analysis of the data revealed that they can be best represented in terms of the empirical Freundlich adsorption isotherm as:

$$X = KC^n \tag{1}$$

where X is the amount of adsorbate taken up by unit mass of the adsorbent, C is the equilibrium concentration in solution, and n and K are constants representing the slope and the intercept of the isotherm, respectively. By plotting log X against log C (Figure 1), reasonably good straight lines were obtained indicating the general conformity of the adsorption data to the linear form of the Freundlich equation.

Table I. Freundlich Isotherm Constants for Adsorption of 2,4-D on Organoclay Complex

Temperature, °C	Slope, n	Intercept, log K
5	0.76	0.815
25	0.83	0.716

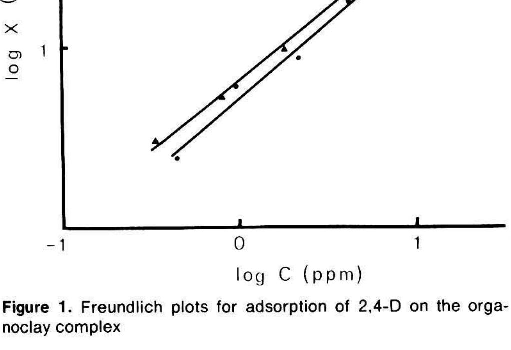

Figure 1. Freundlich plots for adsorption of 2,4-D on the organoclay complex

The value of n decreased with decrease in temperature (Table I) which is in accordance with the Freundlich-type isotherm (Hayward and Trapnell, 1964). At both temperatures the value of n was less than unity, indicating a convex, or L-type, isotherm. This type isotherm may arise due to a minimum competition of solvent for sites on the adsorbing surface (Hayward and Trapnell, 1964). Values of n that are less than unity have also been reported for the adsorption of 2,4-D, isocil, and bromacil on the humic acid (Haque and Sexton, 1968; Haque and Coshow, 1971). However, montmorillonite surface gave a value of n that was greater than unity, indicating a concave, or S-type, isotherm (Haque and Coshow, 1971).

According to Lambert (1967), the equilibrium between the solute adsorbed (X) and concentration of solute in solution (C) can be expressed as:

$$X = \alpha C + \beta C^2 + \gamma C^3 + \ldots . \tag{2}$$

α, β, and γ are the adjustable coefficients used to fit the data. For the adsorption of many pesticides on soil colloids, γ and higher coefficients are negligible, and β is small. Hence, the constant, α, may be taken as a measure of equilibrium constant, K_e. Under certain conditions, K in Equation 1 is a sufficiently good approximation of K_e. Thus, the intercept (log K) of the Freundlich plots (Figure 1) can be taken as an indirect measure of the relative free energy changes ΔG ($= -RT \ln K_e$) of 2,4-D on the FA-clay complex surface. The constant, K, gives an indication of extent of adsorption.

Examination of log K values in Table I shows that the adsorption capacity of the FA-montmorillonite complex for 2,4-D was smaller than that of humic acid (Haque and Sexton, 1968). However, the values were much greater (Table I) than those reported for montmorillonite (Haque and Sexton, 1968). An increase in temperature resulted in a decrease of K value, thereby indicating the exothermic nature of adsorption (Kipling, 1965). Yamane and Green (1972) obtained similar results in a study of *s*-triazine herbicides adsorption on soil material. However, they attributed the apparent exothermic nature of adsorption of triazines to the temperature dependence of the herbicide-water interaction.

It is likely that the FA molecules adsorbed on the clay are preferentially oriented in accordance with the sheet structure of montmorillonite (Schnitzer and Kodama, 1967). The resulting organic surface then adsorbs the 2,4-D molecules. The extent of the adsorption will be partly determined by the physical and chemical nature of the initial organoclay surface. The results of Miller and Faust (1972) for the adsorption of 2,4-D onto an organoclay complex, show that the latter adsorbed about 58 μmol of 2,4-D per gram of the complex covering about 60% of the available surface. Furthermore, the adsorption increased considerably at a lower pH approaching to almost a coverage of 100%. Our studies indicated that the organoclay complex, prepared by treating FA with montmorillonite, adsorbed about 6.5 and 5.2 μmol of 2,4-D per gram of complex at 5° and 25°C, respectively (Table I).

In view of the foregoing it appears that 2,4-D sorption covered only a small proportion of the FA–clay complex surface. The large adsorption values observed by Miller and Faust (1972) appear primarily due to dimethylbenzyl octadecylammonium chloride and various other benzyl and aliphatic amines sorbed on clays. Although the occurrence of these organic compounds in waters is possible, as they are used in detergents, their presence in soils and waters in measurable amounts have not been reported. Therefore, caution should be exercised when predicting the pesticide adsorption by organoclay complexes in soil and aquatic environments. While our work dealt exclusively with a soil FA, there is considerable evidence that FA in waters is, in many respects, similar to that in soils (Fotiyev, 1967; Schnitzer and Khan, 1972). Thus, the naturally occurring organoclay complexes appear to be very similar to the FA-montmorillonite complex used in this study.

From the adsorption data at 5° and 25°C (Figure 1, Table I) we may approximate the "isosteric" heat of adsorption ΔH (Koral et al., 1958). Assuming the chemical potential of 2,4-D in the liquid phase (μ_l) is equal to the chemical potential of 2,4-D at the organoclay surface (μ_s), we may write:

$$\mu_l{}^o + RT \ln a_l = \mu_s{}^o + RT \ln a_s \tag{3}$$

where a_l and a_s are the activities of 2,4-D in the liquid and on the surface, respectively. For a very dilute solution, a_l is proportional to the equilibrium concentration, C. Assuming that the activity of 2,4-D at the organoclay surface does not change when the amount adsorbed (X) is kept constant, Equation 3 after differentiation can be expressed as:

$$\frac{\Delta H}{R} = \frac{H_o{}^s - H_o{}^l}{R} = \left[\frac{\partial \ln C}{\partial (1/T)}\right]_X \tag{4}$$

where $H_o{}^s$ and $H_o{}^l$ are the partial molal enthalpies of 2,4-D on the surface of the organoclay complex and equilibrium solution, respectively.

The "isosteric" heats of adsorption ΔH, expressed as a function of the amount of 2,4-D adsorbed, were estimated from Equation 4. The values were all negative and vary from about −1.2 to −0.3 K cal/mol with increasing surface coverage. The ΔH values are approximately of the same order of magnitude as those reported for 2,4-D adsorption on other surfaces (Haque and Sexton, 1968). For humic acid, the values varied from about −2.0 to +2.0 K cal/mol with increasing surface coverage (Haque and Sexton, 1968). The relatively low heat of adsorption values are of the order which suggest that the probable mechanism of 2,4-D adsorption on the organoclay complex was a physical or van der Waals-type adsorption (Glasstone and Lewis, 1962).

From this study it is obvious that the mobility and persistence of 2,4-D in soils or waters will partly be a function of adsorption of the herbicide onto surfaces such as FA–clay complex. A knowledge of the adsorption processes will aid in predicting the distribution of the herbicide in the soil and aquatic environments.

Acknowledgment

The technical assistance of R. Mazurkewich is much appreciated. We thank The Dow Chemical Co., Midland, Mich., for supplying the analytically pure 2,4-D sample. We are grateful to M. Schnitzer and H. Kodama for donating FA and pure montmorillonite samples.

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Received for review March 27, 1973. Accepted October 29, 1973.

Hydrogen Sulfide Adsorption by Manganese Dioxide and Activated Carbon

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Annual hydrogen sulfide emissions to the atmosphere are made up of approximately 100 million tons from natural processes and 3 million tons from man's activities (Robinson and Moser, 1970). Hydrogen sulfide, therefore, does not rank as a major atmospheric pollutant in terms of bulk emissions. It does, however, constitute a very significant localized air pollutant in the vicinity of petroleum refineries, kraft mills, viscose plants, gas works, sewage pumping stations, canneries, and animal processing plants (Harding and Landry, 1966; Ellis, 1958; Nonhebel, 1964; Roberts and Farrar, 1956; Air Pollution Engineering Manual, 1967; Natusch, 1970).

In many cases H_2S can be effectively removed from air by adsorption. The most commonly used solid filter material for high efficiency adsorption of small amounts of H_2S is granulated activated carbon (Barnebey, 1958). A number of either pure or mixed metal oxides have also been

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■ Hydrogen sulfide was adsorbed in a fixed bed with an active form of manganese dioxide impregnated on sawdust and with several activated carbons. The efficiencies for H_2S removal were measured as functions of H_2S concentration, flow rate, particle size, relative humidity, and bed depth. The outlet concentration of H_2S from a bed of MnO_2–sawdust is considerably below that from a bed of activated carbon of the same volume and at the same conditions, often by more than an order of magnitude. The useful capacity of the MnO_2–sawdust bed (the amount of H_2S which can be adsorbed before the efficiency drops below a predetermined value) can be greater than four times that of activated carbon. The efficiency of the MnO_2–sawdust has a maximum at a relative humidity of 80%. Both MnO_2–sawdust and activated carbon are inefficient below 20% RH.

employed (as pellets or granules) to adsorb H_2S (Banerjee et al., 1959; Dodonov, 1959; Singh, 1965; Topsoe, 1969). In general, their efficiencies are less than those of the better activated carbons, but their capacities are superior.

In this paper we discuss the adsorption of H_2S on a solid filter which is a manganese oxide deposited on the surface of wood sawdust; the filter is prepared by reaction of $KMnO_4$ with the sawdust. For convenience, the oxide is denoted by MnO_2 although its exact form has not yet been determined. Its performance is also compared to several commercially available activated carbons. Both the efficiency and capacity of the MnO_2–sawdust are superior to those of all activated carbons tested. The influence of a number of operating parameters on H_2S removal efficiency and capacity was determined. Some data correlation has been made with a view toward possible use in preliminary system design and/or scale-up. A standard preparation of MnO_2–sawdust was employed and its performance assessed as a function of H_2S concentration (0.4–80 ppm), relative humidity (8–90%), flow rate (20–600 ft/min), bed depth (1–3 in.), and particle size (4–6, 6–8, 8–10, and 10–14 mesh, Tyler). Hemlock and fir sawdusts were employed and limited studies were carried out with the hard inner ring of ground corn cobs.

Experimental

Apparatus. The MnO_2–sawdust or activated carbon to be tested was held in a bed through which an air–H_2S mixture was drawn by a vacuum pump. The desired concentration of H_2S in the inlet to the bed was obtained by mixing the main air stream with a second stream of high H_2S concentration; the latter was contained in a laminated Milar balloon (approximately 2000 ppm H_2S) or a gas cylinder (approximately 1% H_2S, Linde Division of Union Carbide). The desired relative humidity was obtained by humidifying or dehumidifying the main air stream. The adsorbent filter material was held in position by a stainless steel wire mesh and was compacted gently until a reproducible standard pressure drop across the bed was achieved for a given height of the filter bed. The diameter was usually 3 in., although some runs were made with a diameter of 1 in. H_2S conentrations in the inlet and outlet streams were determined with a Gelman Model 23000 paper tape sampler utilizing a silver nitrate impregnated tape (Natusch et al., 1972). The optical density of the resulting silver sulfide spot was measured with a Gelman Model 14101 paper tape densitometer.

Preparation of MnO_2–Sawdust. MnO_2-sawdust was prepared as follows: After it was graded for size and dried to ambient moisture content, a 200-gram sample of sawdust was placed in a 1500-ml beaker and soaked in 1000 ml of 1% reagent grade sodium hydroxide solution for 2 hr. The sodium hydroxide solution was then drained off and the sawdust washed with 1000 ml of water to remove any extracted material.

The sawdust mixture was transferred to a 20-liter Pyrex container, covered with water, and heated to 80°C. Crushed technical grade granular $KMnO_4$ (Carus Chemical Co.) (200 grams) was then added. The mixture was stirred rapidly and the highly exothermic reaction between sawdust and permanganate was considered complete when it ceased to produce heat. After removal of the liquid, the MnO_2–sawdust was placed on a 20-mesh screen to dry under an exhaust hood. (Note: If this material is taken to complete dryness at a temperature greater than 100°C over a period of days, it can ignite.) The final material has a bulk density of about 0.38 g/cm^3.

No effect of storage life on either the activity or capacity of MnO_2–sawdust for H_2S has been observed over a period of at least two years. The majority of the MnO_2 prepared in this way adheres firmly to the surface of the sawdust (or ground corn cobs) and is not dislodged by passage of air through the sawdust particles.

Operating Conditions. Unless otherwise stated, all the filter materials were presented in a 1-in. deep and 3-in. diameter bed. The particle size was 8–10 mesh and air containing 5 ppm of H_2S at 60% RH and 75°F was passed through this bed at 200 ft/min. These values were varied individually from the standard conditions given to determine the effect of individual parameters on the efficiency and capacity of each filter material for adsorbing H_2S.

Results

Performance of MnO_2–Sawdust and Activated Carbons. The performance of various adsorbents in removing H_2S from air, under the standard conditions given above.

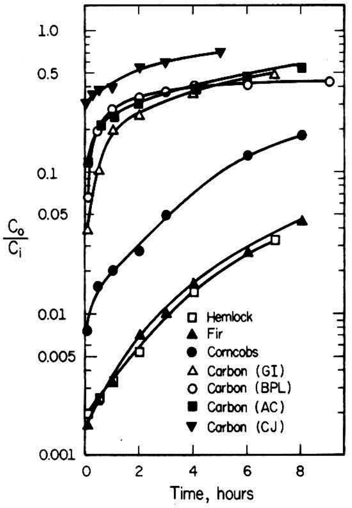

Figure 1. H_2S outlet/inlet concentration ratio vs. time for various materials

200 ft/min, 5 ppm H_2S, 8–10 mesh, 60% relative humidity, 1-in. bed depth, 75°F

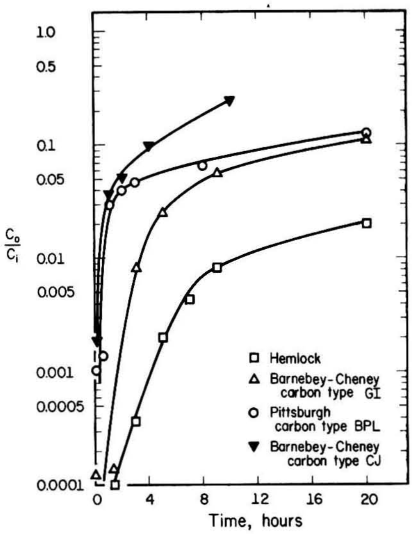

Figure 2. H_2S outlet/inlet concentration ratio vs. time for various materials
20 ft/min, 8-10 mesh, 80 ppm H_2S, 1-in. bed depth, 60% relative humidity, 75°F

is presented in Figure 1. The ratio of the H_2S concentration in the air leaving the bed (C_o) to the concentration in the inlet stream (C_i) is shown as a function of time.

The MnO_2 impregnated fir and hemlock are considerably more efficient in removing H_2S from air than any of the activated carbons tested. (Activated carbons were obtained from Barnebey-Cheney Inc., types CJ, GI, and AC and Pittsburgh Activated Carbon, type BPL; type CJ is impregnated with a metal oxide. The bulk density range is 0.41–0.63 g/cm^3.) The MnO_2-sawdust filter is at least an order of magnitude better than the carbons over the course of the 8-hr run.

We also investigated the efficiency of ground corn cobs impregnated with MnO_2. As can be seen in Figure 1, this material is less efficient than the MnO_2-sawdust but more efficient than the activated carbon. The part of the corn cob used in this work is very hard, and the lower efficiency compared to the sawdust substrate may be due to a lower surface area.

To run at conditions closer to those which might be obtained in practice, MnO_2-sawdust was tested against three activated carbons at a flow rate of 20 ft/min and an H_2S concentration of 80 ppm. The results are shown in Figure 2. These results show the performance of the activated carbons relative to MnO_2-sawdust to be somewhat improved with respect to the previous testing conditions. However, none of the activated carbons is comparable to MnO_2-sawdust in activity.

The foregoing experiments were stopped before the efficiency of H_2S removal had dropped to zero; however, we did carry out a few runs to complete, or nearly complete, bed exhaustion. Some results are shown in Figure 3 (200 ft/min, 5 ppm H_2S) for both MnO_2-hemlock and carbon type GI. At higher concentrations, similar results are obtained although both the MnO_2-sawdust and the carbon are exhausted in a shorter time. For example, at 80 ppm and 200 ft/min, the two curves cross at 4½ hr at which time the efficiency of each has dropped to 15%; the hemlock and carbon are exhausted in 8 and 10 hr, respectively.

The capacities of these filters can be found by integrating data such as those shown in Figure 3. In this way, one obtains the total mass of H_2S adsorbed before the filter efficiency drops below some specified value. Capacities in grams of H_2S removed/gram filter are shown in Figure 4 for MnO_2-hemlock and carbon type GI for H_2S inlet concentrations of 5 and 80 ppm as functions of efficiency. The capacities of the MnO_2-sawdust filter are significantly higher than those of the activated carbon. For example, consider an inlet H_2S concentration of 80 ppm. The total H_2S adsorbed by the MnO_2-sawdust before the efficiency drops below 60% is 0.075 g/g whereas for the carbon, it is 0.00425 g/g. For an inlet H_2S concentration of 5 ppm, the sawdust and carbon adsorb 0.084 g/g and 0.0171 g/g, respectively, before the efficiency drops below 60%. The capacity of the hemlock at exhaustion is roughly 0.12 g/g (either H_2S level) while that of the carbon is 0.1 g/g (either H_2S level).

H_2S Concentrations. The behavior of the MnO_2-sawdust and activated carbon type GI at various H_2S concen-

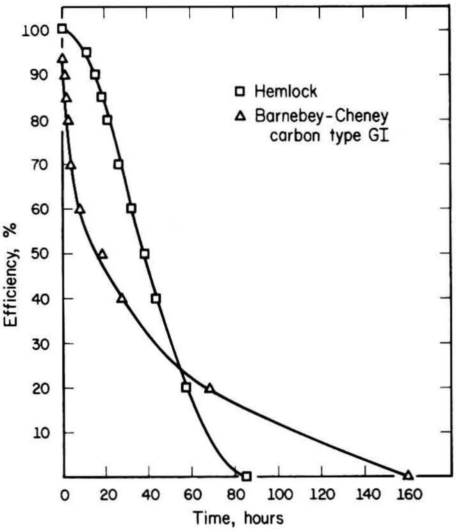

Figure 3. Efficiency vs. time
5 ppm H_2S, 200 ft/min, 8-10 mesh, 1-in. bed depth, 60% relative humidity, 75°F

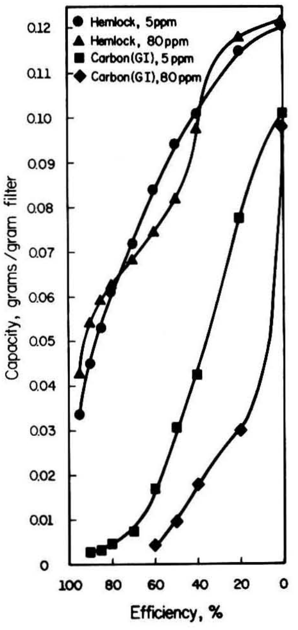

Figure 4. Capacity as a function of desired adsorption efficiency
Bed diameter, 3-in.; bed depth, 1-in.

trations may be compared as in Figure 5, where the ratio of the H_2S concentrations in the effluent and inlet streams is shown as a function of the total mass of H_2S fed to the filter on a per gram of filter basis. In the case of MnO_2-sawdust, the filter efficiency increases somewhat with the concentration of H_2S passing through the bed. This behavior is consistent with reaction kinetics in which the rate of reaction between MnO_2 and H_2S is a positive function of the H_2S concentration. The activated carbon efficiency, however, varies inversely with H_2S concentration. This is consistent with predictions based on the activated carbon adsorption isotherm (Kipling, 1956).

Relative Humidity. The variation of filter activity with relative humidity is shown in Figure 6 for MnO_2-sawdust and carbon type BPL. On the left-hand side of Figure 6 the ratio of C_o/C_i at 80% RH to that at any humidity level is shown for both filters $[(C_o/C_i)_{80\%\mathrm{RH}}/(C_o/C_i)]$. This ratio is essentially independent of time except at the onset of a run where efficiency is nearly 100% at all humidity levels. The efficiency of MnO_2-sawdust peaks at about 80% RH. A similar maximum is often observed for the rate of corrosion of metals by H_2S with varying RH (Backlund, 1966). This maximum is attributed to a reduction in the rate of H_2S reaction at high humidity owing to the formation of a film of water on the reactive surface. Thus, the rate of mass transfer of H_2S to the surface becomes partially liquid-film controlled. The same effect would also be expected to occur for activated carbon; however, it should be much less apparent owing to the lower activity of the carbon. In practice, no convincing activity peak is observed for activated carbon.

On the right-hand side of Figure 6 is shown the variation of C_o/C_i with time at RH equals 80%. MnO_2-sawdust is superior in performance to the activated carbon at all RH levels; however, neither performs well at low humidities (<20% RH). Figure 6 provides a concise design basis for efficiency variation with time at all RH levels. For hemlock;

$$\log\,[(C_o/C_i)_{80\%\,\mathrm{RH}}/(C_o/C_i)]$$

$$= 3.19 \log(\mathrm{RH}) - 6.06 \qquad 20\% \leq \mathrm{RH} \leq 80\%$$

$$= -13.6 \log(\mathrm{RH}) + 25.9 \qquad 80\% \leq \mathrm{RH} \leq 90\%$$

Temperature. Preliminary studies were conducted to determine whether the activity and capacity of MnO_2-sawdust depend on temperature at constant relative humidity (40% RH). No substantial effect was observed over the temperature range 75-113°F. In this narrow temperature range any increase in the rate of chemical reaction may be offset by a decrease in the rate of adsorption of reactant. Control by diffusion or mass transfer would also explain the experimental temperature behavior. The latter is suggested by results presented in this paper.

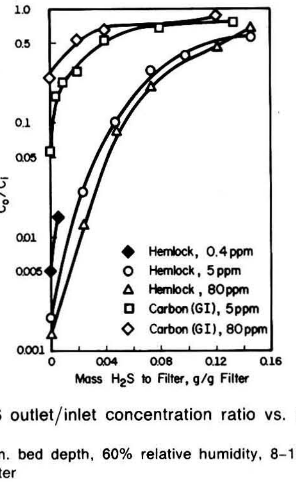

Figure 5. H_2S outlet/inlet concentration ratio vs. mass of H_2S feed

200 ft/min, 1-in. bed depth, 60% relative humidity, 8–10 mesh, 75°F, 3-in. bed diameter

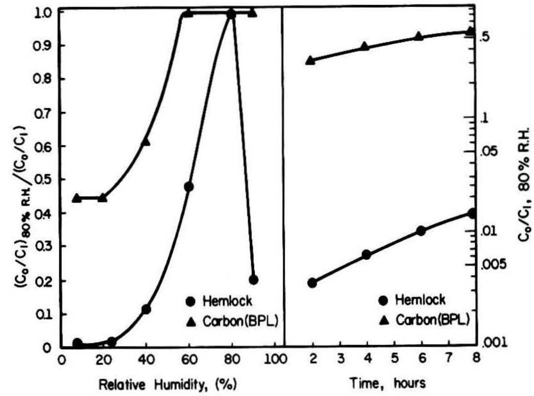

Figure 6. Dependence of H_2S outlet/inlet concentration on relative humidity (left) and on time for RH = 80% (right)

Hemlock and Pittsburgh carbon type BPL, 200 ft/min, 5 ppm H_2S, 1-in. bed depth, 75°F, 8–10 mesh

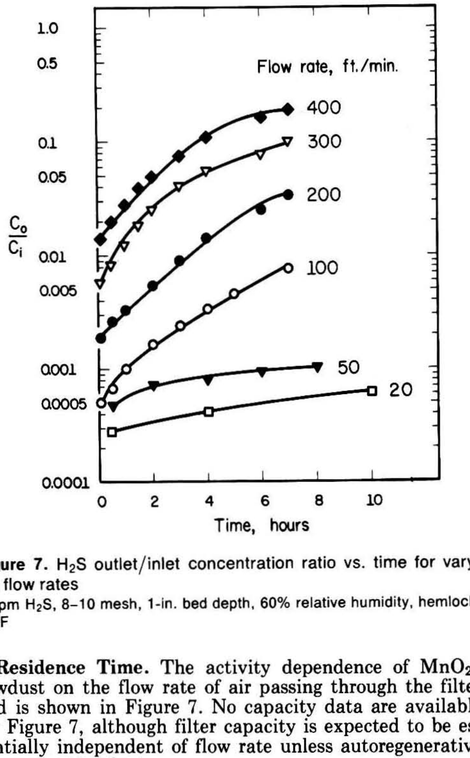

Figure 7. H_2S outlet/inlet concentration ratio vs. time for varying flow rates

5 ppm H_2S, 8–10 mesh, 1-in. bed depth, 60% relative humidity, hemlock, 75°F

Residence Time. The activity dependence of MnO_2-sawdust on the flow rate of air passing through the filter bed is shown in Figure 7. No capacity data are available for Figure 7, although filter capacity is expected to be essentially independent of flow rate unless autoregenerative processes take place.

The dependence of the activity of MnO_2-sawdust on the depth of the filter bed was also investigated. The ratio of the concentration of H_2S in the outlet stream to that of the inlet, of course, decreases as the depth of the bed is increased. If there were no mass transfer or channeling effects and if the activity were independent of H_2S concentration, the ratio should initially decrease exponentially with increasing bed height; if the ratio decreases by some multiplicative factor when the bed depth is increased from 1-2 in., it should decrease by the same factors when the bed depth is further increased to 3 in. In practice, the change from 2-3 in. is somewhat less. For example, at the conditions of Figure 1, the ratio C_o/C_i at the beginning of a run is 0.002, 0.0006, and 0.0004 for bed depths of 1, 2, and 3 in., respectively.

Mass Transfer Effects. An H_2S molecule in the gas stream must be transported to the surface of the solid MnO_2-sawdust before it can react. A high free gas stream velocity reduces the external mass transfer resistance. Thus, by varying the gas flow rate and the filter bed depth simultaneously to maintain a constant residence time, the importance of mass transfer limitations in the filter bed can be assessed. The results of such an experiment are shown for MnO_2-sawdust in Figure 8.

Clearly under these experimental conditions there is a significant mass transfer reduction in the efficiency of adsorption of H_2S by MnO_2-sawdust.

Particle Size. The dependence of H_2S removal on particle size for MnO_2-hemlock and carbon type BPL is given by:

$$R = 5.48 \times 10^{-7} d_p^{-2.87} \qquad \text{MnO}_2\text{-hemlock}$$

$$= 2.48 \times 10^{-3} d_p^{-1.19} \qquad \text{Carbon(BPL)}$$

R is the ratio of the quantity (C_o/C_i) for mesh size 8–10 Tyler to that at any given mesh size $[R = (C_o/C_i)_{8\text{-}10\ \text{mesh}}/(C_o/C_i)]$. This value is independent of time, except initially, where conversion is approximately 100% for all mesh sizes. The characteristic material dimension, d_p in feet, was taken as the average aperture opening for a given mesh size range. The above correlation was determined at a superficial gas velocity of 200 ft/min, H_2S concentration of 5 ppm, 60% RH, 75°F, and 1-in. bed depth for a mesh size range 4–14 Tyler. These correlations may be used in conjunction with Figure 1 for rough design purposes. As expected, the rate of H_2S removal increases monotonically as the particle size is decreased from 4–6 to 10–14 mesh. It should be noted that even the largest sawdust tested (4–6 mesh) is a more efficient adsorbent than the smallest carbon (10–14 mesh). For both MnO_2-sawdust and the carbon, the H_2S removal efficiency increases with decreasing particle size because of the reduction of mass transfer resistance within the particles. For the MnO_2-sawdust adsorbents, there is also the additional factor that the smaller particles probably contain a larger mass of MnO_2 per unit bed volume since the MnO_2 is found only in a layer near the outside of the sawdust particles.

Pressure Drop. We have measured the pressure drop across the bed of MnO_2-sawdust at velocities up to 300 ft/min for various mesh sizes. The pressure drop $\Delta p/L$ (in. H_2O/ft bed) is given by

$$\frac{\Delta p}{L} = a v^{1.26}$$

a	Tyler mesh
0.017	4–6
0.044	8–10
0.054	10–14

where v is the superficial gas velocity in ft/min. The pressure drops are similar to those across a bed of carbon (Adsorption Handbook, 1973).

Optimization. No attempt was made in this work to optimize the performance of MnO_2-sawdust by varying preparative parameters. Preliminary investigations have, however, indicated that considerable improvement in the performance of MnO_2-sawdust can be achieved by varying a number of preparational parameters. These studies will be reported later.

Discussion

The foregoing performance tests have clearly established the superiority of MnO_2-sawdust over some of the better activated carbons for the adsorption of H_2S. However, while MnO_2-sawdust can be readily prepared, it is not commercially available at present and must be discarded after use. In practice, activated carbon used in odor control applications is rarely regenerated. The possibility of regeneration is attractive and is being investigated for MnO_2-sawdust.

MnO_2-sawdust has the disadvantage that it will ignite if allowed to dry out completely over a period of days at a temperature above 100°C. The material has remained stable when operated for a period of weeks at temperatures over 100°C in the presence of steam and even when ambient air (70°F, 55% RH) is heated to 120°C and passed through the bed. However, high-temperature (>100°C) operation should be approached with caution. The problem can be overcome by presenting the active MnO_2 on nonflammable substrates such as pumice, vermiculite, perlite, or coke although there is a marked decrease in performance (Natusch and Sewell, 1970).

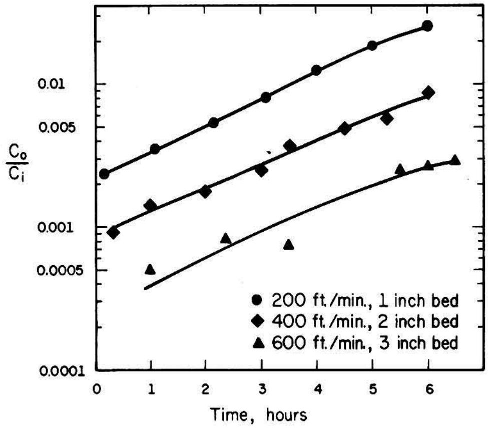

Figure 8. H_2S outlet/inlet concentration ratio for constant residence times and varying flow rates

8–10 mesh, 5 ppm H_2S, 60% relative humidity, 75°F

In attempting to make a general correlation for the behavior of the MnO_2-sawdust in fixed bed applications for H_2S removal, one realizes that the system is transient, that there are substantial mass transfer effects both within and outside the particles and that the reaction kinetics are unknown. The task is thus quite difficult and only part of the picture is available. It is already clear that many physical and chemical properties of the MnO_2 present on MnO_2-sawdust are quite different from those of any other MnO_2 yet reported (Bienstock and Field, 1960; Korshunov and Vereshchagin, 1966). The material appears to be most similar to δ MnO_2.

The overall reaction of MnO_2-sawdust with H_2S can be written

$$MnO_2 + 2H_2S \rightarrow MnS + S + 2H_2O$$

indicating that 1 mole of MnO_2 is capable of adsorbing 2 moles of H_2S. For the MnO_2-sawdust used here, a standard 1-in. deep bed (diameter = 3 in.) contains 40 grams of MnO_2-sawdust which, in turn, contains approximately 11.8 grams of MnO_2. For this bed configuration, calculations based on the results given in Figure 3 show that only about half the total MnO_2 reacts with H_2S before the bed is exhausted. Additional capacity can, however, be obtained by agitating the exhausted MnO_2-sawdust to expose fresh MnO_2.

Work is presently in progress on the basic nature of the MnO_2-sawdust to produce a more active filter material and to obtain and correlate further the data necessary for the design of filter beds under a variety of conditions.

Acknowledgment

The corn cobs were donated by the Coeval Co. of St. Joseph, Ill., and samples of activated carbons were donated by the Barnebey-Cheney Co., and the Pittsburgh Activated Carbon Division, Calgon Corp.

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Received for review March 22, 1973. Accepted October 29, 1973. This work was partially supported by the United States Environmental Protection Agency under grants US EPA R801603 and US EPA CSD 4048.

Lead, Cd, Zn, Cu, and Co in Streams and Lake Waters of Cayuga Lake Basin, New York

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■ Waters of 12 tributary streams of Cayuga Lake were studied to determine the levels and seasonal and geographic patterns of trace elements in the Cayuga Lake basin, a primarily rural area. Trace elements in soluble form (filtered water) and in suspended particulates were studied. The trace element concentrations were generally low, but a seasonal pattern reflecting higher concentrations with high stream flow was noted in the case of Pb. Values for streams of rural areas reflect levels associated with normal geochemical processes and soil weathering. An impact of urbanization was reflected in higher levels of the trace elements in suspended particulates carried by these streams that flow through Ithaca, N.Y. A basis has been established to evaluate changes in trace element load with future changes in land use and urbanization.

Trace metals in surface waters of major rivers in the U.S. (Kopp and Kroner, 1968), as well as their permissible limits in drinking water (Federal Water Pollution Control Administration, 1968), have been determined with the growing recognition of their importance to plants, animals, and man. Remaining largely undetermined are the levels of trace metals in surface waters of rural areas that provide an insight into natural levels due to soil weathering and geochemical processes. The present report focuses on trace elements in water and suspended particulates of the Cayuga Lake basin, a primarily rural area with a local population center in Ithaca, N.Y.

Cayuga Lake Basin

Cayuga Lake basin is part of the Finger Lakes region in central New York. Cayuga Lake, a deep, mesotrophic body of water 61.4 km in length serves as a catchment basin of water from numerous (approximately 125) tributary streams. In the northern part, the streams drain an area underlain primarily by well-drained soils formed in calcareous drift (Cline, 1961). In the southern part, extensive areas of poorly drained soils occur on shaly drift over Devonian shales. Because of poor soil drainage, more land in the southern part is devoted to pastures and forage crops, that provide good ground cover, than in the northern part of the study area. Woodlands also occupy more land (Child et al., 1971) in the southern part (40%) than in the northern part (20%).

The lake's outlet is to the Erie canal system at the northern end of the lake. Three streams that flow through Ithaca at the southern end of the lake provide points of observation of waters that flow through a local population center.

Methods and Materials

Twelve streams were selected for study within the drainage basin (Figure 1). Soils, geologic characteristics of the uplands, and modified stream flow characteristics and gradient were important considerations in the selection of the streams. Canoga Creek was selected because it is primarily fed from groundwater. Trumansburg Creek was selected to provide a point of observation below a sewage treatment plant. Fall Creek, Six-mile Creek, and Cascadilla Creek were selected to provide observation of stream water flowing through an urbanized center without discharge from sewage treatment plants. Sampling stations on these streams were located upstream from bridges of major roadways in this area. Four stations previously located for limnological study (Mills and Oglesby, 1971) were used as sample collection sites of lake water samples.

A sampling procedure focusing on periods of high- and low-stream flow was followed over a five-month period from March through August of 1970. The larger streams were sampled nine times during this period but several of

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the smaller ones had dried up and could not be sampled in late summer. All of the samples were collected on a given sampling date. The time lapse between the collection of the first and last sample on any sampling day varied from 4–8 hr.

Samples of lake water were collected in June, July, and August from four stations. The sampling dates for the collection of these samples were not the same as those for stream water sampling.

A plastic bucket was used to collect the samples of stream water. The samples were transferred to acid-washed polyethylene bottles. A nonmetallic VanDorn sampler was used to obtain samples of the lake water. Samples were obtained at the surface and at depths of 5 and 10 meters and were transferred to acid-rinsed polyethylene bottles. The temperature of the water was recorded at time of sampling.

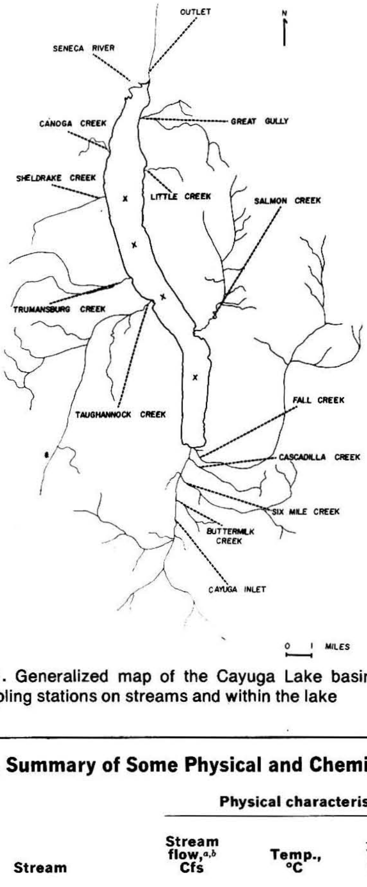

Figure 1. Generalized map of the Cayuga Lake basin showing the sampling stations on streams and within the lake

Most of the samples were filtered within 2–3 hr after collection but some were stored in a refrigerated room until they could be filtered during the latter part of the day. Two-liter portions of stream water and 6-liter portions of lake water were filtered under suction through a 2.5-cm glass fiber filter (Reeve Angel) placed in a filter crucible. The filtration system was free of metal and rubber. The filtered water was then transferred to a 4-liter separatory funnel, ammonium citrate buffer was added, and the pH adjusted to 8.5 with NH_4OH. The trace elements were then complexed with dithizone in CCl_4 and removed by drawing off the CCl_4 phase (Beeson et al., 1965). The aqueous phase was washed with CCl_4 and the washings were combined with the original organic phase. The CCl_4 phase was then digested in the presence of 2 ml of 70% $HClO_4$ and evaporated to dryness. The residue was dissolved in exactly 10 ml of 0.01*N* HCl and transferred to ½-oz. bottles with plastic-lined caps.

The glass fiber filter with the particulate matter was carefully removed from the crucible and transferred to a platinum crucible, dried, weighed, and then fused with Na_2CO_3. Silica was dehydrated with HCl and removed by filtration and the filtrate transferred to a 125-ml separatory funnel. The dithizone procedure described earlier was used to concentrate the trace elements. The residue after removal of CCl_4 and dithizone was evaporated to dryness, dissolved in 0.01*N* HCl, and stored in ½-oz. bottles for analysis.

The concentration of Pb, Cd, Zn, and Cu was determined on the HCl solutions by atomic absorption analysis. Standards were prepared by adding increments of Pb, Cd, Zn, and Cu to 0.01*N* HCl solutions. Cobalt was determined by the nitrosocresol method on aliquots (5 ml) of the unknown solution (Beeson et al., 1965). Blank corrections of the filtered water were made using double-deionized water carried through the entire procedure from filtration to analysis, and those for particulate analysis, by the use of Na_2CO_3 fusion blanks.

Preliminary recovery studies were made using double-deionized water and a sample of stream water to which increments of Pb, Cd, Zn, Cu, and Co were added. Recoveries of 96–100% of the amounts added were obtained. These recoveries were consistent with results of earlier studies of Pb, Cd, Cu, and Zn in blood (Kubota et al.

Table I. Summary of Some Physical and Chemical Characteristics of Stream Water Samples

	Physical characteristics (means)				Chemical characteristics (means)				
			Suspended solids						
Stream	Stream flow,[a,b] Cfs	Temp., °C	Total, mg/l.	Volatile, mg/l.	pH	Total alkalinity as $CaCO_3$, mg/l.	Conductivity at 25°C, µmho/cm	Soluble reactive phosphorus, µg/l.	NO_3–N, mg/l.
Primarily rural									
Canoga	4.6	10.6	52	17.2	8.2	190	799	53	0.25
Great Gully	11.0	10.7	38	4.9	8.2	178	429	14	0.88
Little Creek	...	8.3	18	2.5	8.1	159	444	27	0.73
Sheldrake	...	9.6	22	5.1	8.2	127	352	177	0.79
Taughannock	71.0	12.7	42	13.0	8.3	97	306	16	0.46
Salmon	110.0[a]	10.1	72	11.9	8.2	159	392	26	0.88
Inlet	35.4[a]	11.8	57	8.7	8.3	113	276	18	0.24
Buttermilk	8.8	13.6	34	9.6	8.3	91	236	24	0.17
Urbanized									
Trumansburg	...	10.0	22	4.6	8.2	123	324	174	0.46
Six Mile	55.0	12.2	63	17.0	8.2	70	229	34	0.18
Cascadilla	16.0	13.8	107	18.0	8.3	76	272	514	0.39
Fall Creek	179.0[a]	13.4	72	13.9	8.3	85	230	91	0.37

[a] Mean annual as measured by U.S. Geological Survey, Ithaca, N.Y. [b] All other stream flows are mean annual as estimated from limited data.

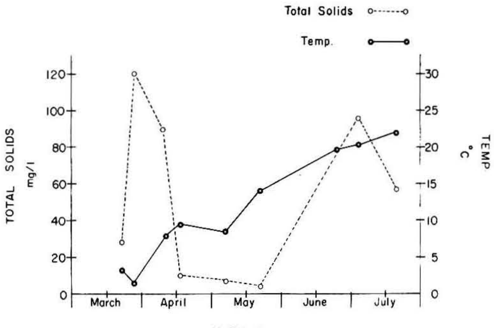

Figure 2. Seasonal transport pattern of total suspended particulates and temperature changes of streams

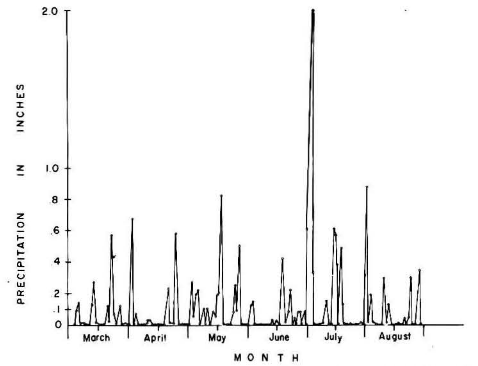

Figure 3. Precipitation recorded in Ithaca during period of study

1968) made using the same procedure and in recovery studies of Co added to soil and plants (Beeson et al. 1965).

The preconcentration procedure, combined with atomic absorption analysis, gave detection limits of about 0.01 μg/ml of the Pb, Cd, Cu, and Zn in the HCl solution. This level is equivalent to about 0.05 μg of the element per liter of filtered water. Use was made of a 10-cm cuvette to detect amounts of Co in the range of 0.01 μg.

Portions of the unfiltered samples were used to define some of the physical and chemical properties of the water samples. Procedures described in "Standard Methods for the Examination of Water and Waste Waster;" (Amer. Public Health Assoc., 1965) were used except of the determination of soluble reactive P determined by the method of Strickland and Parsons (1968).

Discussion of Results

Characteristics of Stream Waters and Sediments. A summary of chemical and physical characteristics of the stream waters is presented in Table I. The pH of the waters was uniformly high, but streams draining areas of calcareous soils had higher alkalinity than did those of the noncalcareous soil area. Conductance was also higher for the more northern streams and especially for Canoga Creek. Nitrate–N concentrations were high relative to most natural waters, especially for the northern streams. Soluble reactive P was quite variable and extremely high in a few tributaries. The general level of suspended solids transported by streams was low.

The stream sediment load in relation to sampling dates is presented in Figure 2, together with rises in mean temperatures of stream waters. Sediment load was highest in samples collected on March 27, when stream flow was high following a period of heavy rains and rapid thaw. The precipitation recorded in Ithaca for the period of study is presented in Figure 3. Canoga Creek, a stream fed primarily by groundwater sources, was the only stream that did not reflect marked increases in sediment load with high stream flow during this period. The temperature rise of Canoga Creek water was also low relative to other streams, reaching a high of 17°C on July 20. The water temperature of Six Mile Creek, Cascadilla Creek, and Fall Creek, by contrast, was slightly higher (1–2°) than the means of all streams during each sampling period.

Trace Elements with Sampling Date. Changes in mean concentration of soluble Pb and Pb in suspended particulates of 12 streams are presented in Figure 4. The concentration of soluble Pb was highest in samples of early spring, after which it tended to level off. The mean Pb in suspended particulates tended to increase with increases in stream sediment load. Samples from Six Mile (8.2 μg/l.), Fall Creek (8.3 μg/l.), and Cascadilla (7.0 μg/l.) were major sources of high Pb noted in the summer maximum (June–July) of particulate Pb (Table II).

The mean concentration of Cd, Zn, and Co in suspend-

Table II. Summary of Soluble Lead and Lead in Particulate Matter

	Soluble, μg/l.			Particulate fraction, μg/l.		
Sample source	**No. samples with detectable amounts**	**Mean**[a]	**Maximum**	**No. samples with detectable amounts**	**Mean**	**Maximum**
Primarily rural						
Canoga	4/8	1.17	2.67	5/8	1.37	2.06
Great Gully	6/8	0.62	1.33	8/8	1.38	6.17
Little Creek	4/7	0.57	1.00	6/7	0.66	1.85
Sheldrake	5/8	0.42	0.67	7/8	1.39	2.62
Taughannock	5/8	0.74	1.00	8/8	1.57	4.01
Salmon	5/9	2.99	16.1	8/9	0.91	2.62
Inlet	8/9	0.66	1.33	8/9	1.89	6.17
Buttermilk	3/8	0.40	0.67	6/8	1.45	3.09
Urbanized						
Trumansburg[b]	4/8	1.11	1.67	7/8	3.94	7.41
Six Mile	6/9	0.73	1.33	8/9	3.14	8.23
Cascadilla	5/9	0.50	1.00	9/9	3.88	6.99
Fall Creek	7/9	0.93	2.67	7/9	2.91	8.33

[a] Means are given for detectable amounts. [b] Sampling site located below sewage treatment plant.

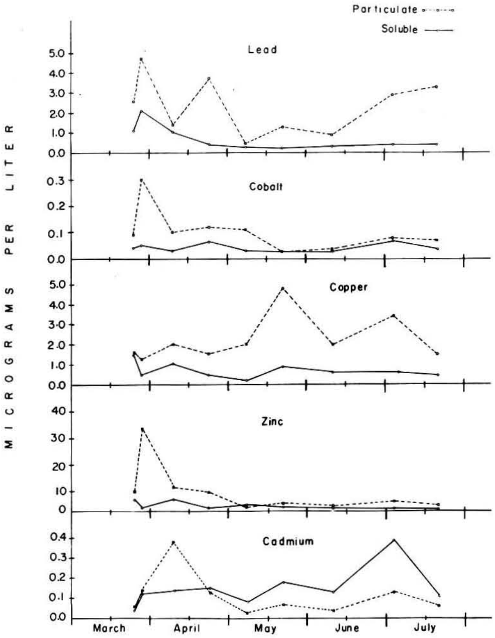

Figure 4. Seasonal transport pattern of Pb, Cd, Zn, Cu, and Co in waters and in suspended particulates of streams

ed particulates was also highest in early spring samples, but a peak load of Cu transport coincided more closely with periods of high stream flow following heavy summer rains (Figure 3).

The mean concentration of soluble Cd and Co increased with sampling date from March through June, unlike that of soluble Pb, Zn, and Cu. The increases in soluble Cd and Co tended to more nearly parallel increases in stream water temperature with sampling date (Figure 2). A similar seasonal rise in soil temperature might reasonably be expected during this period. Increased biologic and chemical activity in soils may account for the release of Cd and Co from the surrounding landscapes. High-volume stream flow does not appear to cause a dilution of Pb, Zn, and Cu in stream waters.

Variations Among Streams. A summary of the mean concentration of soluble Pb and Pb in suspended particulates is presented by streams in Table II. The concentration of soluble Pb did not differ consistently between streams flowing through rural areas from those flowing through an urbanized center. The soluble Pb concentrations in streams of rural areas provide an estimate of Pb release to water from geochemical processes and soil weathering. The data for Canoga Creek provide an estimate of soluble Pb in stream water that flows through calcareous glacial drift deposit.

The range of soluble Pb and particulate Pb reflects effects of sampling date. Over one half of the samples collected after April 9 had nondetectable amounts of soluble Pb. The maximum amounts reported (Figure 4) were found with few exceptions in samples collected on March 24 or March 27. Comparison of Pb in the suspended particulates is a better indicator of the impact of urbanization than soluble Pb. Fall Creek and Six Mile Creek consistently ranked among the top four streams with the highest concentrations of Pb in suspended particulates.

A summary of the mean concentration of Cd, Zn, Cu, and Co in suspended particulates is presented by streams in Table III. Most of the samples with less than detectable amounts of Cd were from the April 9, April 23, and June 10 sampling dates. The largest amount found in any sample during this period was 1.83 μg/l. of Cd. The mean concentration of Cd in suspended particulates in stream waters of rural areas was 0.09 μg/l., and that of urbanized areas, 0.21 μg/l. Suspended particulates of streams flowing through an urbanized area had about 50% more Zn, about 85% more Cu, and about 100% more Co.

The differences among streams in concentration of soluble Cd, Cu, Zn, and Co were small and did not consistently reflect an impact of urbanization (Table IV).

Evaluation of Sources of Trace Elements in Stream Particulates. Because soils of the surrounding uplands are sources of suspended particulates in stream waters, their trace element content was compared with that of stream suspended matter. For this purpose, 27 samples of soils from four nearby locations were fused with Na_2CO_3 and their trace element concentrations were determined according to the methods described earlier. The trace element data of stream particulates previously presented as concentration per unit volume (μg/l.) were recalculated on a dry weight basis (ppm) for this purpose.

Table III. Summary of Cd, Zn, Cu, and Co in Particulates Carried by Tributary Streams of Cayuga Lake

	Cadmium, μg/l.		Zinc, μg/l.		Copper, μg/l.		Cobalt, μg/l.	
Stream	No. samples with detectable amounts	Mean[a]	No. samples with detectable amounts	Mean	No. samples with detectable amounts	Mean	No. samples with detectable amounts	Mean
Primarily rural								
Canoga	5/8	0.09	8/8	6.40	8/8	1.69	8/8	0.08
Great Gully	6/8	0.06	8/8	10.28	8/8	1.35	8/8	0.07
Little Creek	1/7	≤0.05	6/7	2.91	7/7	1.72	7/7	0.05
Sheldrake	7/8	0.09	8/8	5.48	8/8	1.11	8/8	≤0.05
Taughannock	7/8	0.11	8/8	6.95	8/8	1.46	8/8	0.09
Salmon	6/9	0.10	9/9	3.94	9/9	1.37	9/9	0.10
Inlet	4/9	0.13	8/9	10.71	9/9	3.37	9/9	0.11
Buttermilk	5/8	0.10	7/8	8.96	8/8	1.64	8/8	0.13
Urbanized								
Trumansburg[b]	5/8	0.09	8/8	9.45	8/8	1.30	8/8	0.13
Six Mile	4/9	0.21	8/8	10.05	9/9	5.92	9/9	0.13
Cascadilla	6/9	0.10	8/8	14.67	9/9	2.43	9/9	0.15
Fall Creek	5/9	0.44	8/9	14.29	9/9	2.89	9/9	0.20

[a] Means are given for detectable amounts. [b] Sampling site located below sewage treatment plant.

Table IV. Summary of Soluble Cd, Zn, Cu, and Co in Tributary Streams of Cayuga Lake

	Cadmium, µg/l.		Zinc, µg/l.		Copper, µg/l.		Cobalt, µg/l.	
Stream	No. samples with detectable amounts	Mean[a]	No. samples with detectable amounts	Mean	No. samples with detectable amounts	Mean	No. samples with detectable amounts	Mean
Primarily rural								
Canoga	6/8	0.25	8/8	7.97	8/8	0.79	8/8	0.05
Great Gully	5/8	0.07	8/8	1.88	8/8	0.40	8/8	0.03
Little Creek	3/7	0.20	7/7	2.24	7/7	0.32	7/7	0.03
Sheldrake	6/8	0.10	8/8	1.61	8/8	0.53	8/8	0.04
Taughannock	4/8	0.28	8/8	1.17	8/8	0.53	8/8	0.05
Salmon	8/9	0.10	9/9	2.27	9/9	0.51	9/9	0.05
Inlet	6/9	0.28	9/9	2.71	9/9	0.39	9/9	0.05
Buttermilk	7/8	1.10	8/8	0.83	8/8	0.54	8/8	0.04
Urbanized								
Trumansburg[b]	6/8	0.07	8/8	3.20	8/8	0.77	8/8	0.03
Six Mile	6/9	0.25	9/9	1.57	8/9	0.88	9/9	0.04
Cascadilla	2/9	0.29	9/9	1.40	9/9	1.70	9/9	0.06
Fall Creek	7/9	0.17	9/9	3.51	8/9	0.75	9/9	0.04

[a] Means are given for detectable amounts. Sampling site located below sewage treatment plant.

Results of these comparisons are presented in Table V.

The mean concentration of Pb and Cd was appreciably greater in suspended particulates than in soils, Cu and Zn somewhat greater, and Co nearly the same. The concentration of Pb in suspended particulates fell within the range of Pb present in soils adjoining smelter plants (Djurić et al., 1971). The amount of Cd and Co in stream particulates of the Cayuga Lake watershed was nearly the same as that in Lake Michigan sediments (Shimp et al., 1970), but the amounts of Pb, Zn, and Cu were appreciably higher.

Trace element concentrations, expressed on a dry weight basis, provide a basis for making comparisons of stream particulates with soils of the surrounding areas, but give little information about the mineral carriers of the trace elements. Fractionation studies according to particle size separations of the particulates and by specific gravity separations may provide some definitive information. The undertaking of such a determination required appreciably larger amounts of suspended particulates than were available in this study.

The Co concentration in clay, silt, and sand particle sizes has been determined following fractionation of whole soils (Hill et al., 1953). Appreciably more Co (13 ppm) was present in clays than in sand (2.5 ppm). More sand might reasonably be expected in sediments of rapidly flowing streams. Maximum concentrations of Pb, Zn, Cd, and Co in suspended particulates found in early spring samples indicate a need to recognize sources other than soils to account for the amounts found. Particulates in streams of urban areas may represent confounded effects of inputs from industrial, automotive, and household uses. High Pb in river sediments has been attributed to snow dumped into local streams after its collection from streets (Oliver, 1973). The melting of snow from roads may also be a pathway by which Pb may enter a stream system during early spring thaws. Cadmium and Zn from wear and tear of tires (Lagerwerff and Specht, 1970) may have a similar pathway.

A summary of the soluble trace elements in water of Cayuga Lake, presented in Table VI, provides an insight into the possible fate of the trace elements transported by its tributary streams. The variations with sampling depths (surface, 5 meters, and 10 meters) and sampling stations (Figure 1) were appreciably smaller than were variations due to sampling dates. There was a general trend toward lower concentrations in samples collected in August (6 and 11) than in June and July. Lead was notable in this regard in that 11 of the 16 samples with nondetectable amounts were determined in samples collected in August. The mean temperature of the surface water on June 22 was 15°C, and 18°C on August 6; the temperature rise at the 10-meter sampling depth for the same sampling period was from 12–17°C.

An undetermined factor in the evaluation of the trace element concentrations is the mixing pattern of water in the lake. The mean retention time of water in Cayuga Lake is estimated to be about 12 years (Wright, 1969), and evaporation approximately equals precipitation. The input of trace elements from rainwater is largely not known.

Attempts to prepare an estimate of a trace element balance of the Cayuga Lake basin was limited further by the

Table V. Summary of Mean Concentrations of Pb, Cd, Cu, Zn, and Co in Soils of Upstate New York and in Suspended Particulate Matter of Streams

Trace element	Suspended particulate matter, ppm	Soils[a] (total), ppm	Ratio suspended particulates to soils
Pb	483.9	7.9	61.2
Cd	15.6	0.2	78.0
Cu	569.6	21.6	26.4
Zn	1044.2	79.9	13.1
Co	12.2	9.1	1.3

[a] Soil samples from Cayuga and Cortland counties.

Table VI. Summary of Concentrations of Soluble Pb, Cd, Zn, Cu, and Co in Water of Cayuga Lake, Sampled from Three Sampling Depths at Each of Four Sampling Stations in June, July, and August

	µg/l.		
Trace element	Mean	Median	Range
Pb	0.12	0.10	ND–0.93
Cd	0.54	0.16	ND–1.98
Zn	2.17	1.06	0.04–9.41
Cu	0.60	0.47	ND–1.57
Co	0.02	0.01	0.01–0.09

fact that the water discharged at the outlet (north end) is mixed with water from Seneca Lake by way of the Seneca River. There is a localized center of population with industrial plants, traffic, and housing along the banks of Seneca River. A notable observation, however, was that the mean concentration (μg/l) of Cd in Cayuga Lake water was slightly higher (0.54) than in waters of the tributary streams (0.17), and Pb slightly lower (0.12 against 0.91).

Discussion

The levels of soluble Pb, Cd, Zn, Cu, and Co are low in comparison with their levels in major rivers of this country (Kopp and Kroner, 1968) and well below minimum levels recognized for municipal drinking waters (Durfor and Becker, 1964). An absence of parallel increases in the soluble trace elements with increases in suspended particulates indicates that much of the trace elements in stream sediments probably end up in the lake in deltaic and lacustrine deposits.

The establishment of natural levels of trace elements in streams of rural areas will provide some basis for evaluating future changes resulting from increased urbanization and changes in land use within the Cayuga Lake basin. The changes may be important in affecting quality of lake water for drinking purposes as well as in the growth of aquatic plants and phytoplankton. Various workers have demonstrated a requirement by aquatic plants for Co, Cu, and Zn (Provasoli, 1961; Goldman, 1964), and increased phytoplankton photosynthesis with added trace elements to Cayuga Lake water has been observed (Mills and Oglesby, 1971).

While the relative changes in the soluble trace elements have been small, the direction of change indicating increases in concentrations of elements like Cd in the sediments may be important. Long-term ingestation of low levels of Cd have been associated with increased hypertension and decreased life span of experimental animals (Schroeder, 1965), and a detrimental effect of Cd movement in a food chain has been observed (Yamagata and Shigematsu, 1970). The possible movement of Cd through drinking water also suggests a need to safeguard open reservoirs located in areas with heavy traffic load (Johnson et al., 1966).

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Received for review October 6, 1972. Resubmitted July 20, 1973. Accepted November 7, 1973. Supported in part by the Office of Water Resources Research, U.S. Department of the Interior, Grant No. A-025-NY, and by a Federal Water Quality Administration Traineeship Grant (5T1-WP-212-02).

Characterization of Crude, Semirefined and Refined Oils by Gas-Liquid Chromatography

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■ A method is described for characterization of oils that is simple, requires comparatively little time and utilizes instrumentation and techniques that are available in most laboratories. Chromatograms are shown (combination flame ionization and flame photometric responses) of crude oils from different sources, artificially "weathered" samples of crude oils, samples of oil spills, and samples of lubricating oils removed from internal combustion engines. It is shown that crude oil may be laboratory "weathered" and will duplicate the chromatograms of materials extracted from oil spill samples. Furthermore, lubricating and fuel oils can be identified as to source by this procedure. The analysis of an oil sample, exclusive of artificial "weathering" and separation of some of its component fractions, can be accomplished in about 2 hr.

The ability to "fingerprint" and pinpoint the source of oil spilled in a river, harbor, or on a beach is essential to the control of water pollution. Oil from spills which occur many days prior to their discovery still retains many of its characteristics which the analyst is able to identify.

The present methods are time consuming (requiring days instead of hours) and complicated, involving techniques of metals analysis (Gamble and Jones, 1955), determination of sulfur content (ASTM, 1962), infrared absorption techniques (Kawahara, 1969), and others. With the proposed method, in most oil spills comparison of chromatograms—of the oil spilled and of oil from the suspected sources—is sufficient to determine the source. Only 4 or 5 hr are required to make identification. When gas-liquid chromatographic separation and dual response (flame ionization for hydrocarbons and flame photometric for sulfur-containing compounds) are employed, the identification of crude, semirefined, and refined oil is greatly simplifed.

The response of the flame photometric detector to sulfur-containing hydrocarbons depends on the concentration of individual compounds and separation on the gas chromatographic column. All oils contain different and varying amounts of sulfur-containing hydrocarbons; therefore, the chromatograms obtained with the 394-mμ filter vary in retention time, relative intensity, and peak configuration. This method utilizes these differences for the identification of oils. Brody and Chaney (1966), employing a flame photometric detector using the 394-mμ filter, noted differences of sulfur content and sulfur-containing compounds in different brands and grades of gasolines. Bowman and Beroza (1966 and 1967), Getz (1967), and others have successfully determined thiophosphate pesticides qualitatively and quantitatively, employing the flame photometric detector with a 526-mμ filter.

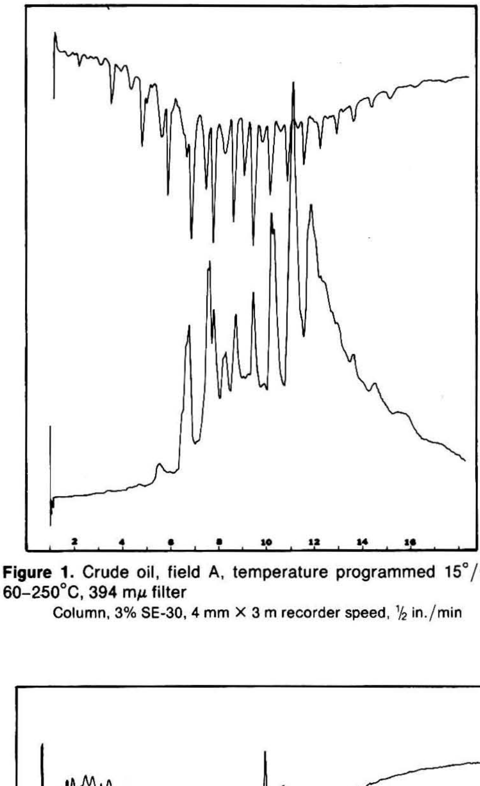

Figure 1. Crude oil, field A, temperature programmed 15°/min, 60–250°C, 394 mμ filter
Column, 3% SE-30, 4 mm × 3 m recorder speed, ½ in./min

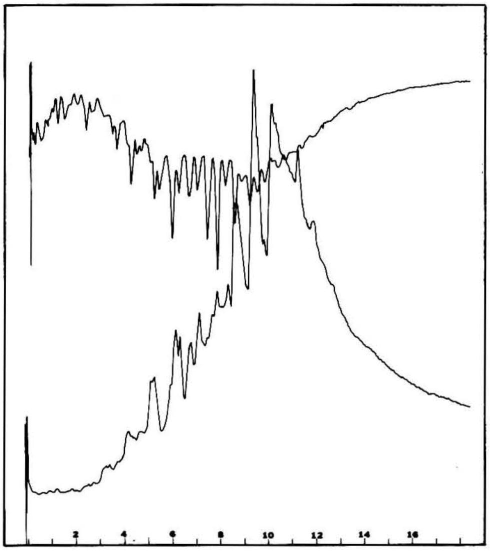

Figure 2. Crude oil, field B, temperature programmed 15°/min, 60–250°C, 394 mμ filter
Column, 3% SE-30, 4 mm × 2 m recorder speed, ½ in./min

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Results and Discussion

For all figures, the following conditions are true: detector, Melpar; carrier, N_2, 80 cc/min; air, 100 cc/min; H_2, 150 cc/min; O_2, 20 cc/min. The different columns and recorder speeds are noted under each caption.

The flame ionization, flame photometric responses of crude oils from two different oil fields are shown in Figures 1 and 2. These crude oils on examination exhibit differences in relative intensities, retention time (rt) and peak configuration on both types of detectors.

Starting with the first significant peak at rt of 6 min, differences and similarities are noted throughout the chro-

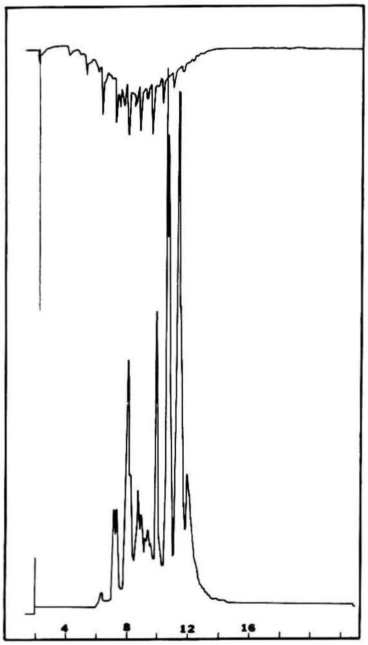

Figure 3. Co. A diesel fuel, temperature programmed 15°/min, 60–250°C, 394 mμ filter

Column , 3% SE-30, 4 mm × 2 m recorder speed, ¼ in./min

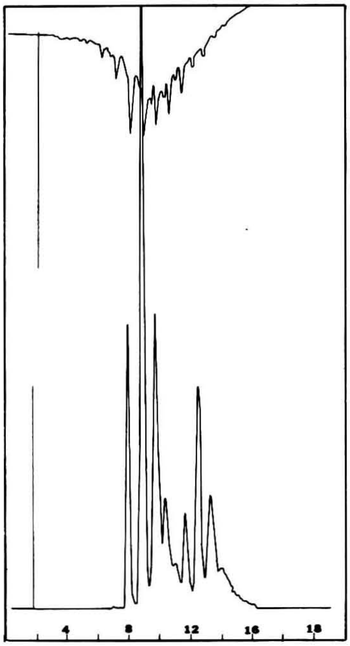

Figure 4. Diesel fuel Co. B, temperature programmed 15°/min, 60–250°C, 394 mμ filter

Column, 3% SE-30, 4 mm × 2 m recorder speed ¼ min./min

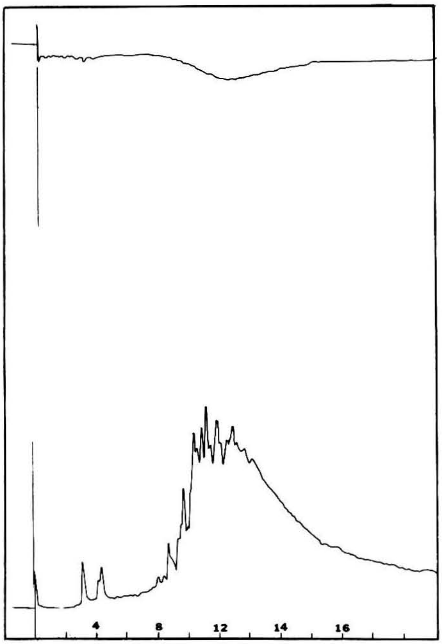

Figure 5. Crankcase oil from automobile in authors' parking lot, temperature programmed 15°/min 60–250°C, 394 mμ filter

Column, 3% SE-30, 4 mm × 2 m recorder speed, ¼ in./min

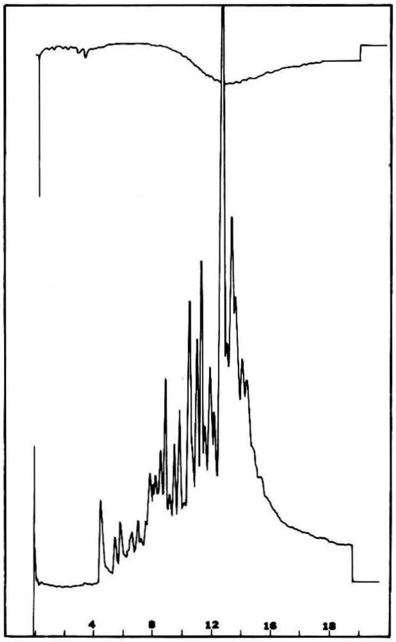

Figure 6. Crankcase oil in Figure 5, temperature programmed 15°/min, 60–250°C, 526 mμ filter

Column, 3% SE-30, 4 mm × 2 m recorder speed, ¼ in./min matograms. In general, these differences or similarities are sufficient to denote different or identical crude oils.

When the differences are not great enough to be obvious, intensity ratios of significant corresponding peaks may be used—i.e., the intensity ratios of the major peaks in the chromatograms at approximately rt of 12 min to the corresponding peaks at rt of 6½ min, are shown in Figure 1, 0.48 and Figure 2, 0.36. The intensity ratios of the two major peaks to the corresponding peaks at rt of 7½ min are Figure 1, 0.60 and Figure 2, 0.45. The intensity ratio of the major peaks to all other significant peaks in the chromatograms may be calculated to establish identity.

The techniques of ratioing the intensity of the major peaks and all other significant peaks in the chromatograms may also be employed in the chromatograms of the aromatic fractions (Figures 10 and 11) and the aliphatic fractions (Figures 12 and 13) of the samples. The same differences, Figures 3 and 4, were noted for semirefined oils processed by different companies.

Weathered oil spills present the greatest analytical problems in identification and source tracing by existing methods. The present method eliminates most of these problems by artificial laboratory "weathering" and direct visual examination of the weathered spill and the suspected source.

In weathered oil spills and unweathered suspected source samples, the flame photometric (394-mμ) responses are used in a screening process. Figure 7 (refuge oil spill) and Figure 8 (refinery crude oil) are good examples of the flame ionization, flame photometric responses of weathered and unweathered samples. Figure 8 exhibits a large

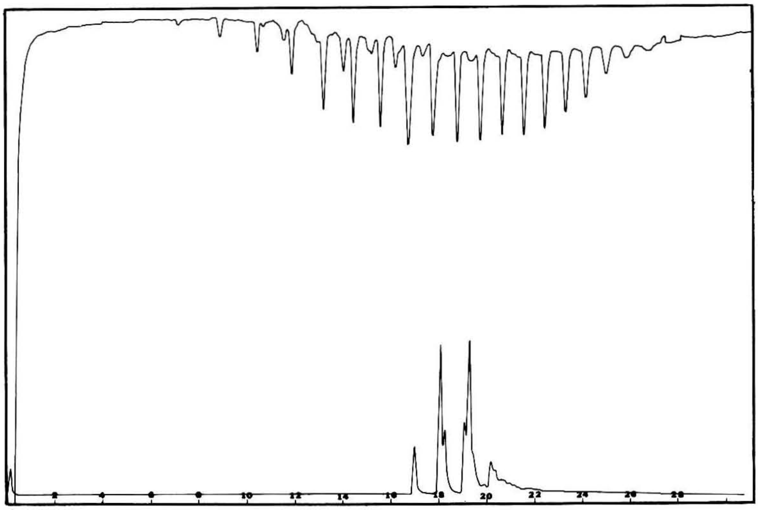

Figure 7. Refuge oil spill sample, temperature, programmed 10°/min, 60–300° C, 394 mμ filter
Column, 3% OV-1, 2 mm × 3.1 m recorder speed, ½ in./min

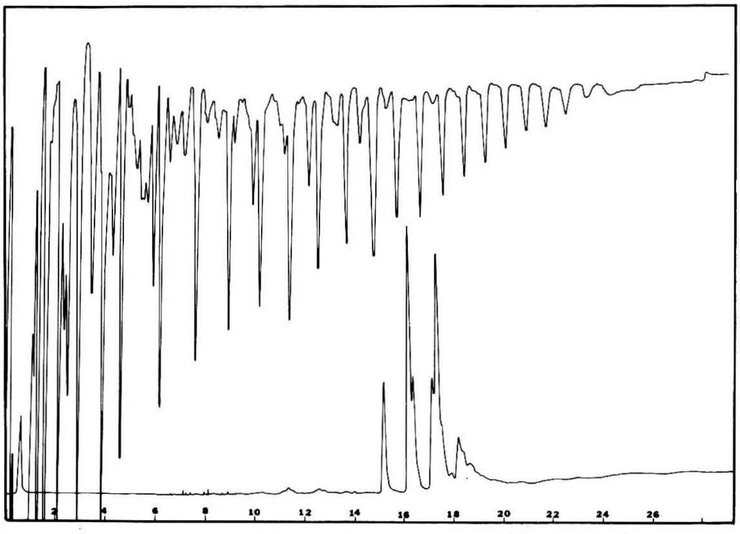

Figure 8. Refinery crude oil sample, temperature programmed 10°/min, 60–300°C, 394 mμ filter
Column, 3% OV-1, 2 mm × 3.1 m recorder speed, ½ in./min

number of low-boiling hydrocarbons on the flame ionization response, while the refuge oil spill sample of Figure 7 does not. The flame photometric response for both samples are identical, indicating that the refinery could be the source of the refuge oil spill.

The chromatograms of the laboratory "weathered" refinery crude, Figure 9 is nearly a duplicate of Figure 7, refuge oil spill, further indicating that the refinery was the source of the refuge oil spill.

Chromatograms of the aliphatic and aromatic fractions (see experimental section) of the refuge oil spill and the refinery crude oil samples supplies further evidence that the refinery was the source of the oil spill. The procedure employed on the refinery crude and the refuge oil spill samples yielded three different flame ionization responses and two different flame photometric responses of each sample for direct comparison (all sulfur-containing hydrocarbons noted were aromatic in nature).

Should additional information for direct comparison be desired, the 394-mμ filter may be replaced with a 526-mμ filter, a different flame photometric response is obtained (Figures 5 and 6).

The flame photometric and flame ionization responses of a variety of oils collected from 25 oil fields and other sources were examined to determine if gas–liquid chromatographic column separation and flame ionization and flame photometric responses could be used to distinguish differences in oils with reproducible results. Forty-nine different oils and oils from six spills were examined: In addition, two diesel fuels (different companies), six waste crankcase oils (brands unknown), 33 crude oils (25 different oil fields), one grease (outboard lower unit grease),

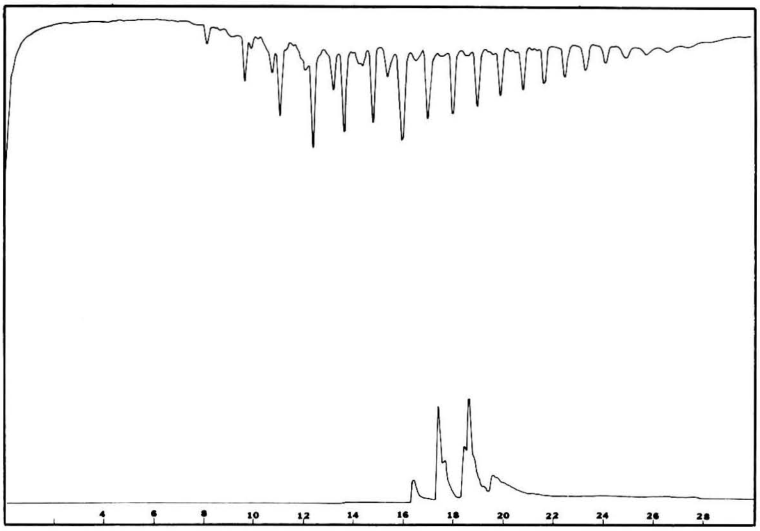

Figure 9. Laboratory-weathered refinery crude, temperature programmed 10°/min, 60–300°C, 394 mμ filter
Column, 3% OV-1, 2 mm × 3.1 m recorder speed, ½ in./min

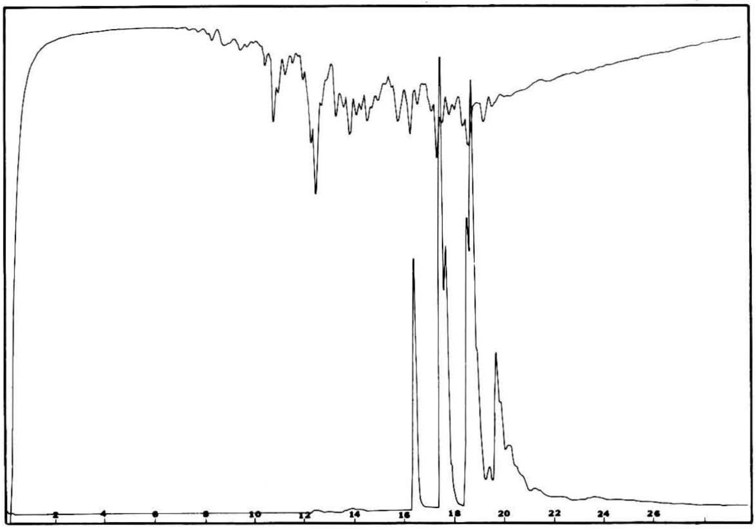

Figure 10. Aromatic fraction of oil spill sample, temperature programmed 10°/min, 60–250°C, 394 mμ filter
Column, 3% OV-1, 2 mm × 3.1 m recorder speed, ½ in./min

and 7 Bunker C oils were examined. This procedure identifies oil spill sources by direct comparison of flame ionization responses and 394 mμ and 526 mμ filter responses.

The weathering effect on oil spills by wind, water, sunlight, temperature, and other environmental factors has to be considered in order to apply this method to oil pollution problems. One significant effect of oil spill weathering is the rapid evaporation and loss of low-boiling hydrocarbon fractions.

Six oil spills in the Southwest, in fresh- and saltwater, during the years of 1968 through 1970, offered opportunities to test this method in its entirety and to determine its effectiveness. The oil spill samples collected were in varied forms—as slicks, emulsions, and thick viscous layers, affording a full range of sample conditions and weathering.

The Game Refuge pollution sample (Figure 7) was collected from the spill area. It was prepared for analysis as described in the experimental section. The resulting chromatograms of the flame ionization and flame photometric (394 mμ) responses eliminated all other suspected sources and pinpointed the refinery crude (Figure 8) as the source of the spill in the Game Refuge.

A portion of the refinery sample (Figure 8) was "weathered" as described in the experimental section. The resulting chromatogram (Figure 9) is identical in peak retention time, relative intensities, and configuration to the oil spill sample (Figure 7).

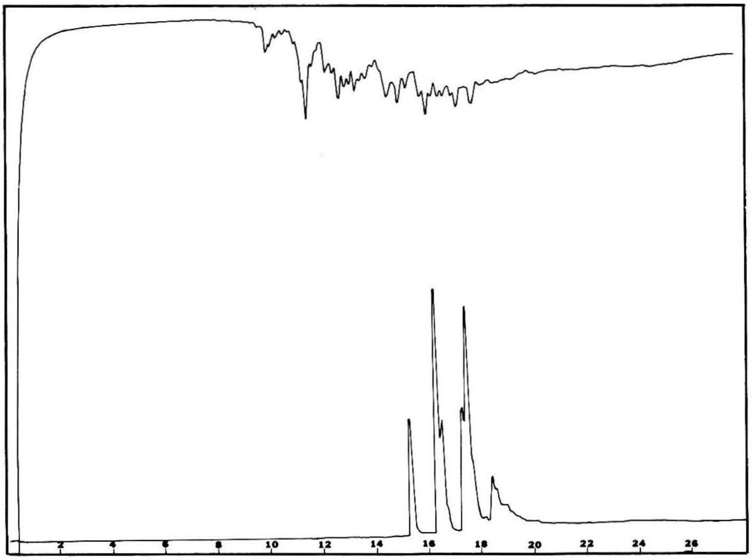

Figure 11. Aromatic fraction, laboratory-weathered refinery crude, temperature programmed 10°/min, 60–300°C, 394 mμ filter
Column, 3% OV-1, 2 mm × 3.1 m recorder speed, ½ in./min

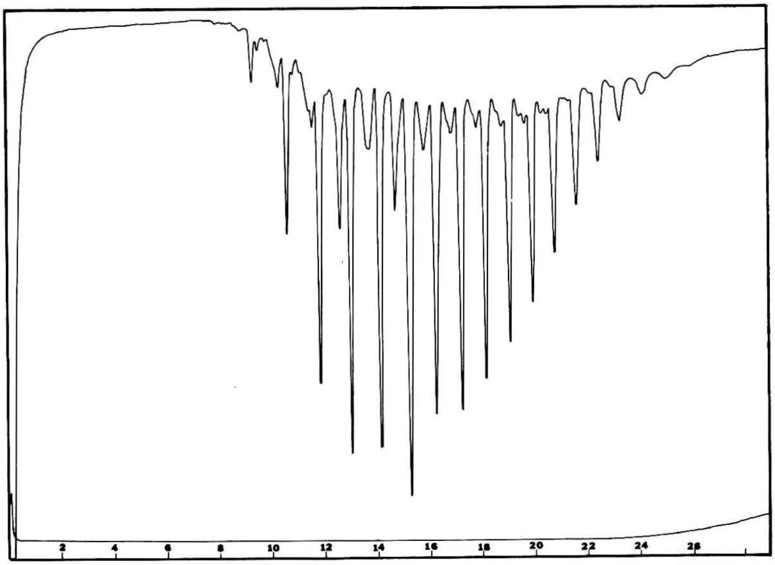

Figure 12. Aliphatic fraction of oil spill sample, temperature programmed 10°/min, 60–300°C, 394 mμ filter
Column, 3% OV-1, 2 mm × 3.1 m recorder speed, ½ in./min

As a further confirmation, the "weathered" sample and the oil spill sample were separated into aliphatic and aromatic fractions (see Experimental Section) and the corresponding fractions compared. (Figures 10–13). Again the fractions are identical.

Experimental

Examination of all oils was performed on a Micro-Tek MT-220 gas chromatograph equipped with FPD detectors. The gas chromatographic columns employed were a glass "U" type 2 m × 4 mm i.d., packed with 3% SE-30 on 60/80 mesh Chromosorb W, and a stainless steel coiled "U" type 3.1 m × 2 mm i.d., packed with 3% OV-1 on 80/100 Chromosorb W, AW, DMCS High Performance. The operating conditions were as follows: column temperature programmed from 60–250°C at 15°/min and 60–300°C at 10°/min. The detector temperatures were 170° and 220°C; the injection port temperatures were 225° and 300°C. The gas flows were: nitrogen carrier gas 80 ml/min, hydrogen flow 150 and 200 ml/min, oxygen flow 20 ml/min, and air flow of 100 and 120 ml/min. Electrometer sensitivities were: FID, 4×10^{-10} through 64×10^{-10} amp full scale; FPD, 3.2×10^{-8} amp full scale.

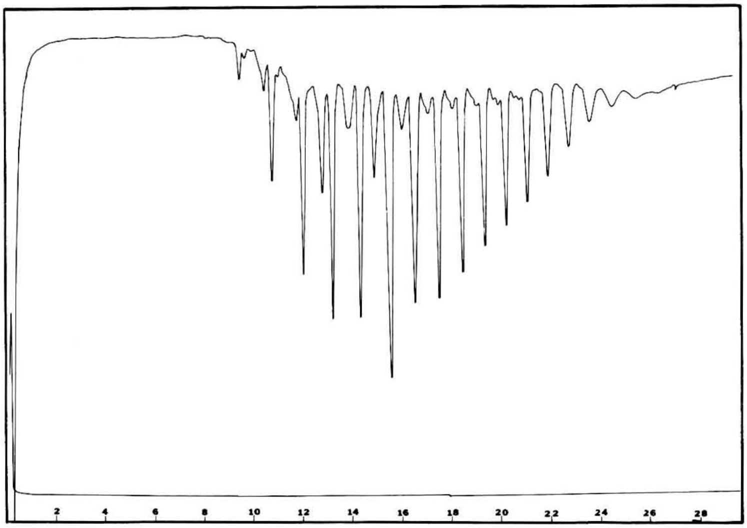

Figure 13. Aliphatic fraction, laboratory-weathered refinery crude, temperature programmed 10°/min, 60–300°C, mμ filter
Column, 3% OV-1, 2 mm × 3.1 m recorder speed, ½ in./min

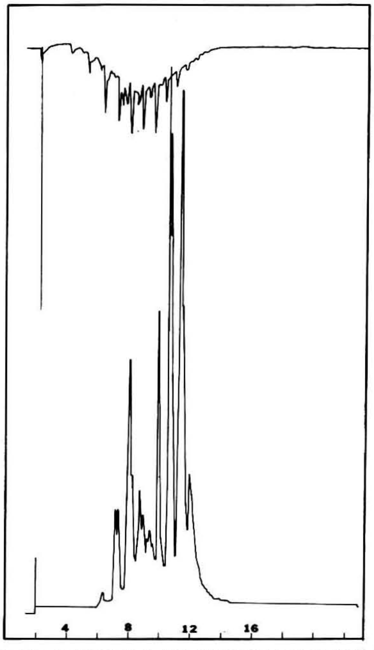

Figure 14. Co. A diesel fuel, temperature programmed 15°/min, 60–250° C, 394 mμ filter
Column, 3% SE-30, 4 mm × 2 m recorder speed, ¼ in./min

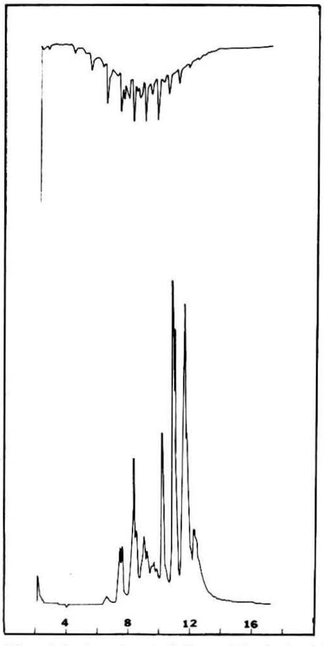

Figure 15. Diesel fuel extracted from Mississippi River water, temperature programmed 15°/min, 60–250°C, 394 mμ filter
Column, 3% SE-30, 4 mm × 2 m recorder speed, ¼ in./min

The recorder used was a Westronics MT-22, dual pen having 1 mV full-scale sensitivity.

Samples of oil, each 100 μl, were diluted with *n*-hexane in ratios of 1 to 25 and 1 to 50. The amounts injected for examination ranged from 1-5 μl.

Portions (100 μl.) of the pollution and suspected source samples were cleaned and dried by dissolving them in *n*-hexane and passing them through a 1-in. column of anhydrous sodium sulfate. The volumes of each were reduced to 5 ml on a water bath at 70°C, and aliquots ranging from 1-5 μl. were injected into the gas chromatograph.

Water Partitioning. Three 1-ml samples were obtained from each "standard" oil sample and added to 800 ml of Mississippi River water in clean 1-qt glass jars. The samples and 800 ml of Mississippi River water blank were stirred for 1 hr with the aid of 2-in. Teflon-coated magnetic stirring bars and magnetic stir-jacks. The samples and the Mississippi River water blank were then extracted with 30 ml of *n*-hexane and dried on a 5-cm, column of anhydrous sodium sulfate.

"Standards" of each oil were prepared by diluting 100 μl. of the oil to a volume of 5 ml with *n*-hexane.

The *n*-hexane extracts of the samples and Mississippi River water blank were reduced to a volume of 25 ml on a water bath at 70°C and aliquots, ranging from 1-5 μl., of the extracted samples, blank and corresponding "standard," were injected for analysis. The gas chromatographic responses were compared for reproducibility (Figures 14 and 15).

Weathering. One gram of the refinery sample (Figure 8) was laboratory "weathered" by placing the sample in a water bath at 70°C for 4 hr to remove the more volatile components and reduce the sample 25% by weight by evaporation. A 100-μl. portion of the "weathered" sample was diluted to a volume of 5 ml with *n*-hexane and 5 μl. were injected into the gas chromatograph for analysis.

Aliphatic, Aromatic Separation. Another portion of the "weathered" refinery crude oil sample and a similar amount of the oil spill sample were each dissolved in 5 ml of ethyl ether and transferred to columns containing 2.5-cm layers of silica gel. The ethyl ether was evaporated from the column with the aid of a small reverse flow of prepurified nitrogen gas. The columns were eluted with 75 ml of isooctane, then with 75 ml of benzene, collecting the eluates separately. The two eluates collected from each sample contained the aliphatic and aromatic fractions, respectively. The eluates were reduced to a volume of 25 ml on a water bath and 5 μl. of each eluate were injected into the gas chromatograph for analysis.

The use of a proprietary product is for information and does not necessarily imply endorsement of the product by the U.S. Environmental Protection Agency.

Acknowledgments

The authors thank Micro Tek Instrument Corp., a subsidiary of Tracor, Inc., for the use of a Micro Tek MT 220 gas chromatograph equipped with a Melpar detector.

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Received for review December 23, 1971. Resubmitted October 26, 1973. Accepted November 7, 1973.

Migration and Redistribution of Zinc and Cadmium in Marine Estuarine System

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• A survey of trace-element levels in the estuarine sediments of Texas shows that Corpus Christi Bay has anomalously high concentrations of zinc and cadmium. Maps of elemental abundance within the bay indicate large concentration gradients, the highest values being near the harbor entrance. Seasonal determinations of metal levels in the harbor and bay waters also revealed variations with time. During summer, stagnation of the harbor water increases the concentration of metals so that significant quantities precipitate in the reducing environment of the bottom water. In winter, the exchange of water between the bay and the harbor increases, and metals are redissolved from harbor deposits, washed into the bay, and adsorbed by particles settling to the bottom.

During a survey of the trace-element distribution in the sediments of Texas bays and lagoons, anomalous zinc and cadmium levels were found in Corpus Christi Bay. Because zinc has been found to be detrimental to fish and other aquatic life (Pettyjohn, 1972) and because cadmium is a known toxin to man, these elements pose a threat to the estuarine system. Although zinc does not appear to be highly concentrated in the marine food chain (IDOE, 1972), it may pose a greater hazard in the dissolved state where it can interact freely with nectonic life. Cadmium, on the other hand, does become concentrated in the food chain and is therefore a hazard in any chemical state. This report presents data on the distribution of these elements in the sediments, their seasonal variations, and the pathways by which they move within the estuarine system.

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Corpus Christi Bay is approximately 4 meters deep and nearly equidimensional, covering an area of approximately 300 km^2 (Figure 1). In the saucerlike central part of the bay, the sediments consist of fine silts and clays; sands composed mainly of shell debris rim the bay on shallow shelves. A dredged ship channel 15 meters deep and 123 meters wide nearly bisects the bay and terminates in a narrow, 13-km-long, landlocked harbor, along which petrochemical and other industries are located. Current measurements and drogue studies at the entrance of the harbor show a significant inwardly directed current below 6 meters; outflow occurs in the surface zone. The strength of both currents is much greater than can be accounted for by industrial uptake and discharge or by the movement of the tidal prism.

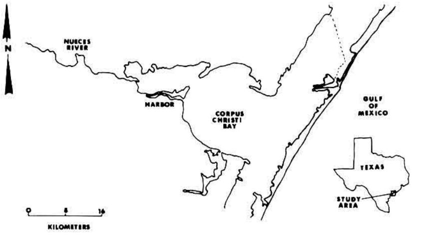


Figure 1. Location of study area

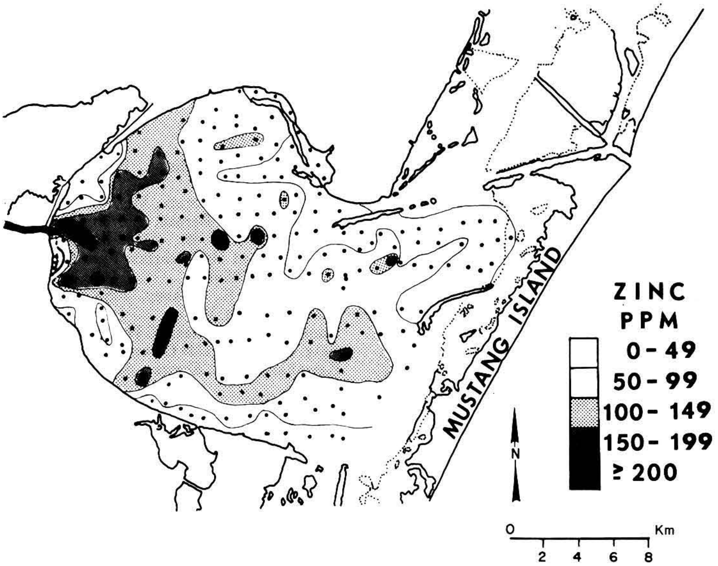


Figure 2. Distribution of zinc in the sediments of Corpus Christi Bay (dot = sample locality)

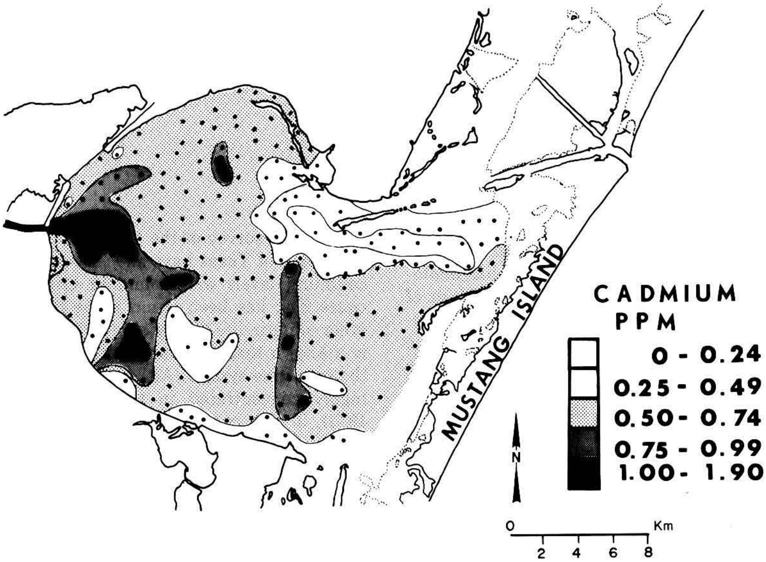


Figure 3. Distribution of cadmium in the sediments of Corpus Christi Bay (dot = sample locality)

Methods

In the initial phase of the study, 287 sediment samples were taken from the bay and harbor with a clamshell sampler designed to obtain a $\frac{1}{50}$ m^3 sample. In addition to these, 156 water samples were taken with a PVC water sampler.

The sediment samples were air dried, ground to less than 200 mesh, and leached with boiling 16N HNO_3 until NO_2 fumes ceased; they were then analyzed for zinc and cadmium by atomic absorption spectrophotometry. The deviation in this procedure determined on replicate samples was found to be less than 10%. Subsequent analyses on replicate samples by a spectrographic method (Grimes and Marranzino, 1968) demonstrated that this digestion procedure accounted for approximately 85% of the zinc and cadmium in the sediments. These results roughly agree with those of Jones (1973), who reported that 75% of the zinc and 60% of the cadmium in the bottom sediments of Cardigan Bay, Wales, were acid soluble.

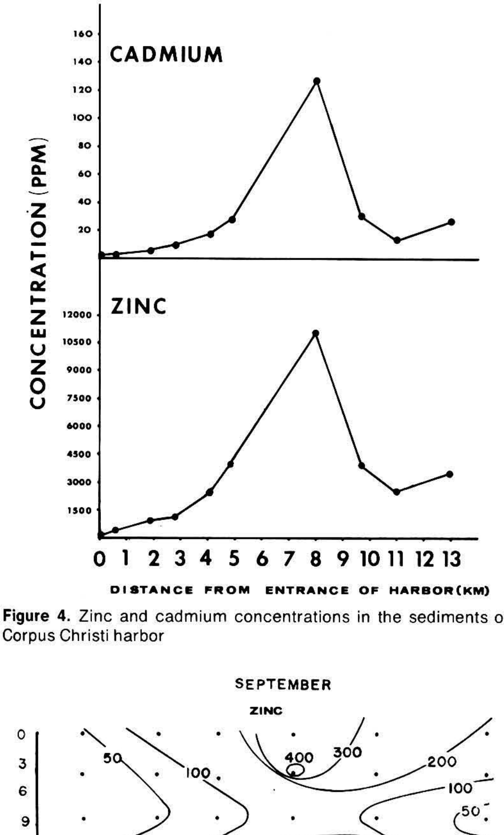


Figure 4. Zinc and cadmium concentrations in the sediments of Corpus Christi harbor

Zinc concentrations in the water were determined by chelating and extracting the metal with an ammonium pyrrolidine-dithiocarbonate (APDC) methyl-isobutylketone (MIBK) mixture and subsequent atomic absorption analysis (Brooks and others, 1967). The deviation determined on replicate samples by this procedure was approximately 20%. Cadmium in the water was determined directly by anodic stripping voltammetry (ASV) (Matson, 1968), with a deviation on replicate samples of less than 8%.

In an attempt to determine the mineral association of the zinc in the bay and harbor sediments, 18 representative samples were analyzed for the metal-mineral associations. These samples were shaken for approximately 1 hr in a solution of 1M hydroxylamine-hydrochloride and 25% (v/v) acetic acid, a procedure which dissolves nonsilicate ferromanganese minerals and carbonate minerals and extracts the adsorbed trace elements but has no effect on the silicate or authigenically formed sulfide minerals (Chester and Hughes, 1967). Subsequent leaching of the residual material with 16N HNO_3 allowed for an estimation of the amount of zinc and cadmium bound with organic or sulfide compounds. Replicate analyses of these samples established the analytical deviation to be less than 10%.

The pH of the sediment and water was determined with a combination glass electrode calibrated against commercially available buffer solutions. The Eh (redox potential) was measured with a combination platinum electrode calibrated with "Zobell" solution (Langmuir, 1971). The temperature and salinity were determined by an *in situ* induction salinometer.

Results and Discussion

In the sediments of the bay, zinc concentrations ranged from a maximum of 235 ppm near the entrance of the harbor to a minimum of 6 ppm in the northeastern part of the bay (Figure 2) and cadmium concentrations ranged from a high of 1.9 to a low of 0.1 ppm (Figure 3). In the harbor sediments, zinc ranged from a maximum of 11,000 ppm, approximately 8 km from the harbor entrance, to a minimum of 235 ppm at the entrance, cadmium ranging from 130 ppm to 2 ppm (Figure 4). Correlation between the zinc and the cadmium concentrations in the bay and harbor sediments was calculated to be 0.80, indicating an identical source and their chemical similarity.

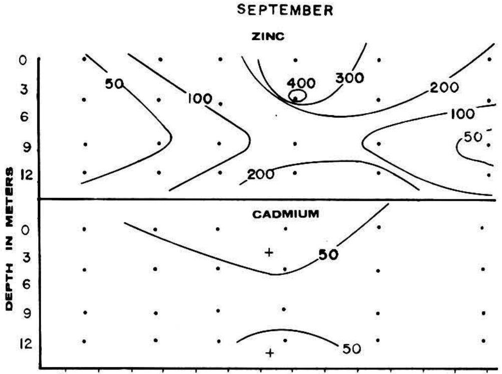


Figure 5. Zinc and cadmium concentrations in the water during summer conditions for Corpus Christi harbor (concentration in ppb [μg/l.] Dot = sample site)

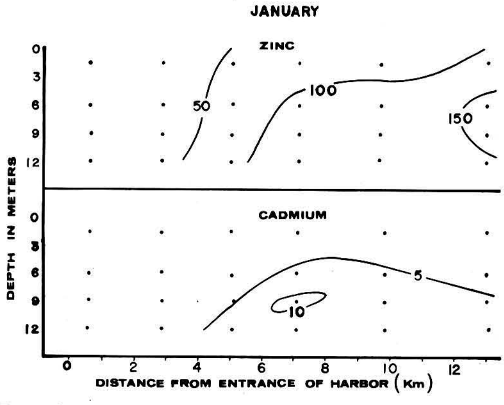
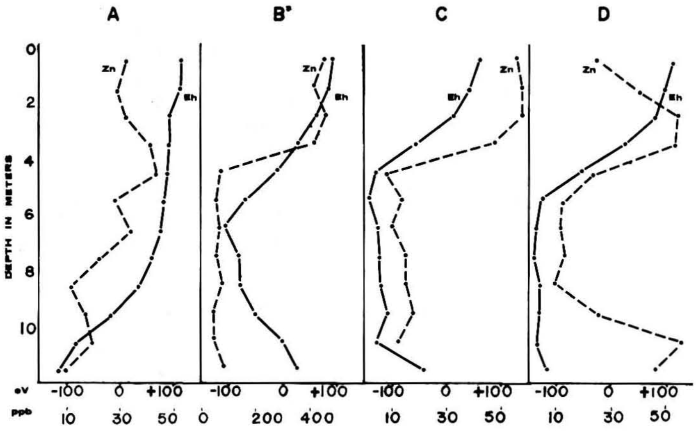


Figure 6. Zinc and cadmium concentration in the water during winter conditions in Corpus Christi harbor (concentration in ppb [μg/l.] Dot = sample site)



*Note Scale Change

Figure 7. Vertical summer distribution of zinc and Eh in the water at four stations in Corpus Christi harbor, June 1972
Station A is 4.2 km from harbor entrance, station B is 7.4 km, station C is 11 km, and station D is 13 km

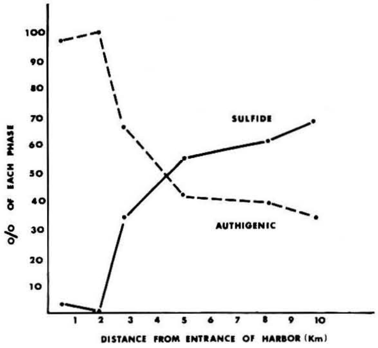


Figure 8. Correlation of sulfide and authigenic phases of zinc in the sediments of Corpus Christi harbor

Figure 9. Aerial photograph taken from an altitude of 3600 meters on December 23, 1968. The dark, clear water originated in the harbor at the upper left and is discharging into the open bay. Mixing with light-colored turbid bay water can be seen taking place, especially in the gyre near the center of the photo (NASA photo)

Determination of zinc and cadmium dissolved in the harbor waters revealed significant spatial and temporal variations. In September, zinc and cadmium ranged from a high of 480 ppb and 78 ppb, respectively, in the harbor (Figure 5) to a low of 6 ppb and 3 ppb in the bay. At the time of this traverse, the highest concentrations were near the surface, and secondary concentrations were at the sediment-water interface, a distribution characteristic of conditions during the summer (June to October). The January pattern was simpler (Figure 6). Zinc ranged from 182–4 ppb and cadmium from 10 to less than 2 ppb. This pattern was characteristic during winter (November to May).

Temperature, salinity, dissolved oxygen (Hahl and Ratzlaff, 1970), and Eh and pH measurements in the harbor showed that the bottom water is more saline, anoxic, and slightly more acidic during the summer period. When these parameters were monitored bimonthly, the boundary between the oxygen-rich and oxygen-poor water was seen to rise during the summer, enlarging the anoxic zone. Hydraulic configuration is the probable result of the combination of the predominant and nearly constant southeasterly winds which inhibit circulation in the harbor and of increases in the microbial activity. Because of these factors, the anoxic water mass at its maximum extent (late in the summer) is wedge-shaped, increasing in thickness from the entrance to the upper reach of the harbor.

During the summer when water in the harbor is most stagnated, the zinc and cadmium concentrations, introduced from industrial effluent, are increased in the oxidizing surface waters. In these waters, the zinc exists in the ionic state (Zn^{2+}), whereas cadmium is present as an ion pair with chlorine ($CdCl^{+}$) (Goldberg, 1963). Below the surface water, zinc and cadmium react with the sulfide ions present and are precipitated, probably according to the following reactions:

$$Zn^{2+}{}_{(aq)} + HS^{-} \rightarrow ZnS_{(s)} + H^{+}{}_{(aq)}$$

$$CdCl^{+}{}_{(aq)} + HS^{-} \rightarrow CdS_{(s)} + Cl^{-}{}_{(aq)}$$

This precipitation process is accelerated as the redox boundary rises and more metals diffuse into the reducing layer. The end result is a metal-rich oxidized upper layer, a metal-poor reduced lower layer, and a metal-sulfide-rich sediment (Figure 7). Figure 8 illustrates the relative partitioning of zinc between the adsorbed (authigenic) phase and the sulfide (HNO_3 leached) phase and diagrammatically shows that the sulfide-entrapped metal increases with distance from the harbor entrance. This is good evidence that the proposed chemical reactions do in fact occur.

Table I. Amount of Zinc and Cadmium Leached by Shaking Selected Samples 30 Min in 0.5*M* NaCl

Distance from harbor entrance, km	Zinc			Cadmium		
	In sediment, ppm	Leached, ppm	% leached	In sediment	Leached, ppm	% leached
3	1,400	60	4.2	20	6	30.0
8	11,000	75	0.6	130	15	11.5
13	3,700	15	0.4	31	1	3.1

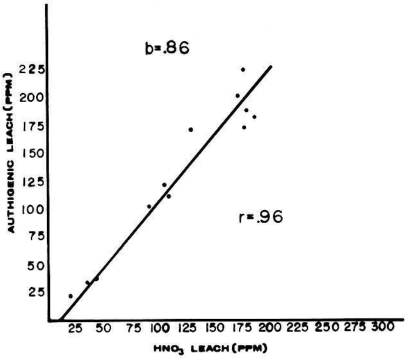


Figure 10. Adsorbed (authigenic) vs. total zinc content of bay sediments

r = correlation coefficient, *b* = slope of line based on data presented

When the seasons change, significant hydraulic changes occur within the harbor. High winds associated with the passing of cold fronts mix the waters in the harbor and increase circulation between the harbor and bay. The increased flow of oxygen-rich water into the previously stagnant areas results in desorption of some of the precipitated metals. Similar desorption of zinc has been noted in Chesapeake Bay sediments when sediments previously deposited in fresh to brackish water come in contact with salt water (Bradford, 1972). Experimental data also demonstrated significant desorption of zinc and cadmium from harbor sediments by a 0.5*M* NaCl solution (Table I). The data from this experiment suggest that the metals are more tightly bound with increasing distance from the harbor entrance; a situation that would be expected since more of the metals are associated with the sulfide phases in the upper reaches of the harbor.

Thus, by a "conveyor belt" type of circulation set up by the hydraulic conditions, metal-poor water enters the harbor along the bottom, is enriched in these metals by desorption, and leaves on the surface where it joins the normal bay circulation (Figure 9). As a result of this mixing, the metals are adsorbed onto the suspended sediment and are transported through the bay by the currents. Figure 10 illustrates the one-to-one relationship of the adsorbed metal to the total metal content of the sediments, showing that most of the metals are adsorbed onto the sediments. Further supporting data were obtained by measuring the adsorption of ^{65}Zn and ^{109}Cd on suspended material in the laboratory, which demonstrated that more than 99% of the zinc and an average of 79% of the cadmium were rapidly (within 1 hr) adsorbed onto suspended material (Table II).

Table II. Adsorption of ^{109}Cadmium and ^{65}Zinc by Corpus Christi Bay Sediments

^{109}Cd

Sample	Total ^{109}Cd in sample, cpm[a]	^{109}Cd in sediment, cpm[a]	Total ^{109}Cd in sediment, %	^{109}Cd in supernate, cpm[a]	Total ^{109}Cd in supernate %
C-11	496,376	383,432	77	112,944	23
G-128	488,522	393,751	81	94,771	19

^{65}Zn

Sample	Total ^{65}Zn in sample, cpm	^{65}Zn in sediment, cpm	Total ^{65}Zn in sediment, %	^{65}Zn in supernate, cpm	Total ^{65}Zn in supernate, %
C-11	7763	7750	99.8	13	0.2
G-128	8112	8102	99.9	10	0.1

[a] Cpm, counts per minute. The experimental data suggest that equilibrium was reacted within 1 hr.

In conclusion, the zinc and cadmium concentrations in Corpus Christi Bay are the result of the interactions between the waters of the harbor and the bay; these interactions take place predominantly during the winter when this exchange is the greatest. This significant transfer into the bay of the metals previously deposited on the floor is seen as a danger long after the effluent from industrial processes is stopped. This is a consideration which must be taken into account in coastal management.

Acknowledgments

We wish to acknowledge the aid of Allyn Lopez and Ronald Miller in the collection of the samples. John J. Dillon and Ramiro Trevino performed the laboratory analyses. The manuscript benefited from helpful criticism of Ralph E. Hunter and Joseph H. Murphy.

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Received for review July 30, 1973. Accepted November 12, 1973.

Poisoning of Vehicle Emission Control Catalysts by Sulfur Compounds

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■ The effects of sulfur combustion products on particulate base metal vehicle emission control catalysts have been studied. Some of the factors controlling the degree and rate of deactivation of one type of UOP exhaust gas control catalyst, namely, copper–chromium alumina, are discussed. Data are presented which show how sulfur alters the chemical composition of these catalysts; how sulfur-poisoned catalysts may be regenerated in situ; and that low levels of sulfur accumulation on the catalyst are more detrimental to catalyst performance than small accumulations of lead or phosphorus. Under certain automotive operating conditions, sulfur poisoning can be minimized to the point that copper–chromium alumina catalysts offer the potential to meet 1976 EPA hydrocarbon and carbon monoxide standards for 50,000 miles. Emissions from a slave vehicle, using one such catalyst after prior use for 52,000 vehicle miles on fuel containing sulfur, were 0.34 and 3.16 grams per mile of hydrocarbon and carbon monoxide, respectively, using the 1975 EPA test procedure.

Pollution from the internal combustion engine (ICE) is a problem that has concerned the automobile industry for many years. Such items as utilization of mechanical modifications (the PCV valve), manifold air injection, high air-fuel ratios, spark advance–retard, and exhaust gas recirculation (EGR) have reduced emissions from the ICE such that 1973 federal standards (Table I) for vehicle emissions for hydrocarbon (HC), carbon monoxide (CO), and oxides of nitrogen (NO_x) have been met. With introduction of the 1975 and 1976 federal vehicle emission standards shown in Table I, additional or alternative emission control systems are required. Use of a catalytic converter is one such alternative.

The maximum temperature at which catalysts for vehicle emission control applications will function without major loss of activity or physical degradation is dependent on the nature of the support and the active ingredient. Loss in activity following exposure to high temperature is generally caused by one or more of the following effects: structural collapse of the support and any associated burial of active ingredient, crystal growth of the active ingredient, and reaction between the support and the active ingredient.

There are two general categories of active ingredients: base metal oxides and noble metals. Although the latter are more active, concern over their availability in some quarters has led to the expenditure of considerable effort in the development of base metal catalysts. The most commonly used base metals are the oxides of the first transition series, specifically the oxides of chromium, manganese, iron, copper, and nickel. The subject of vehicle emission control catalysts has been recently reviewed by Dwyer, 1972.

In the development of base metal oxidation catalysts, the HC and CO emissions from a Chevrolet Bel Air test vehicle using such catalysts increased rapidly, even after limited mileage accumulation, as shown in Table II.

Initial evaluation of the physical and chemical analyses of used catalysts from vehicles (Table III) did not point to any single cause for this deactivation. Hence, detailed investigations of the effects of S, P, and Pb were initiated.

This paper discusses the deleterious effects of sulfur combustion products on catalysts in vehicle exhaust environments, first reported by Hunter, 1972, and how these may be eliminated.

Experimental

Catalyst Preparations. Copper–chromium alumina catalysts in the form of approximately ⅛-in. diameter spheres were prepared conventionally from the metal salts and the composites calcined in a flowing stream of dry air at 650°C. Catalyst A, as prepared, has a copper-to-chrom-

Table I. Federal Vehicle Emission Standards ($G \cdot Mile^{-1}$)[a]

Year	HC	CO	NO_x
1973[b]	3.4	39.0	3.0
1975[c]	0.41	3.4	3.1
1976	0.41	3.4	0.4[d]

[a] As of January 15, 1973, these standards were to be met for 50,000 miles using the EPA durability cycle.
[b] Emissions for 1973 models to be determined using 1972 EPA testing procedures.
[c] After completion of this work the 1975 Federal HC and CO standards were relaxed to 1.5 and 15 $g \cdot mile^{-1}$, respectively.
[d] The EPA may recommend to Congress that this standard be relaxed to 1.5–2.0 $g \cdot mile^{-1}$ in September 1973, to be effective in 1976.

Table II. 1975 EPA Emissions ($G \cdot Mile^{-1}$) for Catalysts A and B

	Catalyst A[a]	
Catalyst miles	HC	CO
0	0.14	1.21
1500	0.19	4.32
3600	0.17	3.98
	Catalyst B[a]	
0	0.10	1.07
500	0.32	4.56
1000	0.35	2.23
3600	0.55	7.63

[a] Catalysts A and B are Cu–Cr–Al–O materials.

Table III. Chemical Analyses of Catalyst B, Fresh and After 3600 Miles of Vehicle Use

	Fresh	Used
Total S, wt %	...	0.86
Total SO_4^{2-}, wt %	...	2.42
Pb, wt %	0.001	0.067
P, wt %	...	0.0085
CO 50% conversion temp, °C	238	412
HC 50% conversion temp, °C	324	346
Relative CO oxidation activity	124	33
Surface area, $m^2 \cdot g^{-1}$	111	92
Pore volume, $m \cdot g^{-1}$	0.28	0.27
Mean pore diameter, A	101	117

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ia weight ratio of 0.2–1; catalyst B has a weight ratio of 1–1. These are the only two catalysts formulated. Catalysts C through I are catalyst-A treated as specified in Tables VII and XIII.

Determination of 50% CO and HC Conversion Temperatures. Fifty percent conversion temperatures for CO and HC oxidation were obtained by treating catalysts with a gas blend of the following composition: CO, 1.0; C_3H_6, 0.025; O_2, 2.5; H_2O, 10.0; and N_2, 86.475 mol %. The gas flow rate was 5000 $ml \cdot min^{-1}$ over the catalyst (20 ml), resulting in a gas hourly space velocity (ghsv) of 15,000 hr^{-1} at STP. Reactors were constructed of 304 stainless steel with bed dimensions of 5.26 cm by 2.2 cm in diameter.

Catalysts were brought to 595°C inlet temperature in dry N_2 and held in the feed gas for at least 30 min. HC and CO conversions (100%) were observed at these conditions. After thermal equilibrium was reached, power was cut, furnaces were opened, and a temperature-conversion curve was obtained as the catalyst cooled. Temperatures for 50% conversion were then read directly from temperature-conversion plots. Catalyst temperature is measured at a point one fourth of the bed length from the inlet.

NO_x Testing. Nitric oxide conversion data were obtained at 480°C and a ghsv of 300,000 hr^{-1} at STP. The catalyst (1 ml) with γ-Al_2O_3 (19 ml) was contained in the same reactor used for the determination of the 50% CO and HC conversion temperatures described above. At an equivalence ratio (ER) of 2.22 (equivalance ratio is defined as $[CO] + [H_2]/2[O_2] + NO]$) the gas blend composition was NO, 0.2; O_2, 0.35; H_2O, 10; CO_2, 10; CO, 1.56; H_2, 0.44; N_2, 77.45 mol %.

Relative CO Oxidation Activity Test. Relative CO oxidation activities were obtained on a laboratory screening unit at a ghsv of 75,000 hr^{-1} at STP with a gas composition of H_2O, 10; CO, 1.5; O_2, 1.1; N_2, 87.4 mol % with a 300°C inlet temperature. Activities were determined with the catalyst in a quartz reactor having bed dimensions of 1.8 cm by 2.6 cm in diameter. The catalyst bed consisted of the catalyst test sample (3cc as $\sim$⅛-in. spheres) and α-Al_2O_3 (7cc, 14/20 mesh) diluent, separately shown to be inert. Inlet and outlet gas streams were analyzed by gas chromatography, and the CO conversion was compared to that of a standard, catalyst A. Relative CO oxidation activities are expressed as *V* (standard) 100/3, where *V* (standard) is the volume of catalyst A required to give the same conversion as the test sample. By definition, standard catalyst A possesses a relative CO oxidation activity of 100 (i.e., catalysts possessing relative CO oxidation activities >100 are more active under the conditions of the experiment for CO oxidation than catalyst A).

Laboratory Thermal Aging. Catalysts were temperature cycled in the laboratory under the following conditions: catalyst sample (50 ml) was loaded into a quartz tube (2.5 cm o.d.) and heated to 950°C, then cycled between 950° and 850°C (time for one complete cycle, 20 min) for three cycles under flowing N_2 (3.75 $l. \cdot min^{-1}$).

Laboratory SO_2 Treatment. SO_2 treatment was carried out in the laboratory with catalysts contained in a quartz reactor at 480°C for 1 hr using a blend gas composition of SO_2, 1.7; air, 32.3; and N_2, 66 mol % at a flow rate of 210 $l. \cdot hr^{-1}$. The catalyst volume used was either 20 or 100 ml.

Sulfur and Sulfate Analyses. The sulfate ion was determined gravimetrically by precipitation as barium sulfate. Catalyst samples were dissolved by refluxing in concentrated HCl under a N_2 blanket to prevent oxidation of other sulfur species to SO_4^{2-}.

Total sulfur was determined by combustion, employing the Leco Model 521 sulfur analyzer. Combustion products were bubbled through a slightly acidic solution containing a small amount of NaN_3. The amount of sulfur in the solution as H_2SO_3 is then measured by an automatic iodometric titration.

Pb Analyses. Catalyst samples were digested by refluxing with concentrated HCl. Portions of the dissolved sample were aspirated into the burner of a Jarrell-Ash Model 82-500 solid state atomic absorption spectrometer and Pb was determined at 2833 A by the method of standard addition.

P Analyses. Catalyst samples were fused with Na_2O_2 in a Ni crucible and the melt was neutralized with HCl. Na_2MoO_4 and $SnCl_2$ were added to PO_4^{3-} containing solutions, resulting in the formation of a molybdenum blue color, the absorbance of which is determined photometrically (λ = 725 nm).

Vehicle Testing. 1975 EPA HC, CO, and NO_x emissions were obtained from a 1971 Chevrolet Bel Air equipped with a V-8 engine (350 CID), a fuel evaporative emission control system, manifold air injection [air being supplied from a Saginaw pump (19.3 $in.^3$, drive ratio 1.55:1)], and a downflow converter (260 $in.^3$). Sufficient air was added to ensure oxidizing conditions in all modes. The front of the converter was located in such a way that it was directly below the front of the transmission housing.

Base emissions (without converter) from this vehicle were HC, 0.96; CO, 20.53; and NO_x, 3.35 $g \cdot mile^{-1}$. Constant volume sampling (CVS) test procedures were carried out according to the requirements laid down in the *Federal Register,* except that the 12-hr soak time prior to the test was not necessarily carried out in the specified temperature range of 20–30°C and the fuel evaporative emission control system was disconnected.

Mileage accumulation on the catalysts was carried out with a 13-mode driving cycle (Table IV), using either a 1970 Ford Galaxie or a 1971 Buick LeSabre on a CT-200 Clayton Chassis Dynamometer equipped with adjustable inertia flywheels. The Ford was equipped with a V-8 engine (351 CID), a Saginaw pump (19.3 $in.^3$, drive ratio 1.7–1) supplying air immediately prior to the converter. The Buick had a V-8 engine (455 CID), and an air supply from a Saginaw pump (19.3 $in.^3$, drive ratio 1.7–1) to the manifold. Converters were removed from the latter vehicles and transferred to the Chevrolet slave car for CVS testing so that any deterioration in the operation of these vehicles, and hence higher base emissions, would not influence the performance of the catalyst. Indolene fuel (typical analysis, Pb, 0.017; P, 0.01 $g \cdot gal^{-1}$; S, 110 ppm) and Shell XL-100 lubricating oil were used in all cases.

Table IV. 13-Mode Vehicle Durability Test Cycle

Mode no.	Speed, mph	Time, sec.
1	Idle, 1	15
2	1–35	14
3	35	13
4	35–17	11
5	17–46	21
6	46	44
7	46–23	17
8	23	10
9	23–1	8
10	1	10
11	1–60	17
12	60	40
13	60–1	20
		4 min

Engine Pb and P Poisoning Experiments. Catalysts were loaded into a segmented, six-compartment converter (120 ml per segment) and inserted into the exhaust train of a Labeco CLR single cylinder engine (42.5 CID). The engine was run at 2000 or 2500 rpm and air-fuel ratios in the range of 13.5–14.6 on isooctane fuel containing either Pb or P added as tetraethyllead plus halogen scavenger or benzyl dicresyl phosphate, respectively. Secondary air was added to the converter to ensure an oxidizing atmosphere in the catalyst bed. Bed temperatures of 480°C (for the Pb studies at 2000 rpm) and 540°C (for the P studies at 2500 rpm) were obtained by use of a heat exchanger prior to the converter. Catalysts were removed, analyzed for Pb or P, and tested for oxidation activity on completion of the test.

Results and Discussion

Exposure of catalysts containing Cu, Cr, Al, and O to various gaseous sulfur species resulted in a substantial decline in CO oxidation and NO removal activities while the HC oxidation activity was only slightly affected (Table V). These observations confirm results regarding oxidation activity reported previously (Hunter, 1972). The extent of deactivation due to "sulfur poisoning" was far worse than after thermal aging in the laboratory (Table V). Analysis of these catalysts showed that the sulfur was present as SO_4^{2-} in all cases where a final oxidation step was carried out. Attempts to determine the nature of the sulfur component(s) by X-ray diffraction were inconclusive; however, $CuSO_4$ was identified for γ-Al_2O_3-supported catalysts containing CuO or $CuAl_2O_4$ after exposure to a SO_2/air/N_2 blend (see Table VI).

Oxidation activities for a 10% Cu on UOP γ-Al_2O_3 catalyst, typical of several prepared, were 50% HC conversion temperature $T_{HC}^{50\%}$, 332°C; $T_{CO}^{50\%}$, 291°C; relative CO oxidation activity (rel, CO), 107. Activities for a typical 10% Cr on UOP γ-Al_2O_3 catalyst were $T_{HC}^{50\%}$, 274°C; $T_{CO}^{50\%}$, 466°C; rel, CO, 17. From these data the assumptions were made that under simulated and actual exhaust gas conditions, the active sites for CO and HC oxidation on a Cu-Cr-Al-O catalyst were primarily associated with the copper and chromium, respectively.

The oxidation of CO over a metal oxide catalyst may proceed via the following type of mechanism (Shelef et al., 1968):

$$\begin{aligned} CO_{gas} &\longrightarrow CO_{ads} \\ CO_{ads} + MO &\longrightarrow CO_{2_{ads}} + M \\ CO_{2_{ads}} &\longrightarrow CO_{2_{gas}} \\ O_{2_{gas}} &\longrightarrow O_{2_{ads}} \\ O_{2_{ads}} + 2M &\longrightarrow 2MO \end{aligned}$$

Table V. Comparison of Effects of Laboratory Temperature Cycling and "Sulfur" Treatment at 480°C for Catalysts A and B

Treatment	Catalyst	Total S, %	SO_4^{2-}, %	50% conv. temp, °C		Rel. CO oxidation activity	NO conv., %	NH_3 sel.
				HC	CO			
Fresh catalyst	A			308	259	100	58.2[a]	48.2[a]
	B			324	238	124	54.1	31.8
	B						84.0[a]	75.0[a]
SO_3/air	A	1.46		312	374	60		
	B	2.53	7.2	334	396	6	19.8	25.6
Vehicle exhaust, 3600 miles on Indolene fuel, S, 110 ppm	B	0.86	2.42	346	412	33	10.0	40.4
Lab temp cycling	A			319	285	81		
	B			339	262	90		

[a] Inlet temperature, 540°C; ghsv, 150,000 hr^{-1} at STP.

Table VI. Activities of Catalysts Containing CuO and $CuAl_2O_4$

Catalyst	Treatment	50% conv. temp., °C		Species identified by X-ray
		HC	CO	
Cu on Al_2O_3 (1)	Fresh	313	277	γ-Al_2O_3 and CuO
(1)	SO_2/air	338	456	γ-Al_2O_3 and $CuSO_4$
Cu on Al_2O_3 (2)	Fresh	272	307	Expanded γ-Al_2O_3 and $CuAl_2O_4$
(2)	SO_2/air	338	427	Expanded γ-Al_2O_3 and $CuSO_4$

Table VII. Activity Data for Fresh, SO_2/Air Treated, and Regenerated Catalyst A

Treatment	Treatment temp, °C	Total S, wt %	SO_4^{2-}, wt %	50% conv. temp, °C		Rel. CO oxidation activity
				HC	CO	
Fresh catalyst A				308	259	100
SO_2/air (catalyst C)	480	1.46		312	374	60
Catalyst C + air for 1 hr	650	0.70	2.22	317	352	43
Catalyst C + air for 1 hr	760	0.29	1.02	293	288	80
Catalyst C + air for 1 hr	870	<0.03	0.10	303	268	91
Catalyst A + 8 cycles consisting of following treatments: SO_2 at 480°C for 30 min followed by air at 870°C for 1 hr Final treatment with SO_2 at 480°C for 30 min (catalyst D)				309	421	
Catalyst D + air for 1 hr at 870°C				298	275	

Table VIII. Results of Treatment of 3600-Mile Vehicle-Used Catalyst B in Flowing Gas for 1 Hr

Atmosphere	Treatment temp, °C	Total S, wt %	SO_4^{2-}, wt %	50% conv. temp, °C		Rel. CO oxidation activity	NO conv., %	NH_3 sel.
				HC	CO			
Fresh catalyst				324	238	124	54.1	31.8
Vehicle-used[a]		0.86	2.42	346	412	33	10.1	40.5
Air	650	0.77	2.20	342	416	40		
Air	760	0.40	1.12	318	318	76	15.9	38.1
Air	815			324	315	83		
Air	870	0.05	0.10	321	262	107	40.3	41.2
N_2	870	0.08	0.15	329	286	98		
90% air, 10% H_2O	870	0.39	1.03	335	340	50		
0.5% H_2, 0.5% CO, 99% N_2	650	0.75	0.25	333	347	49	47.2	20.3
0.5% H_2, 0.5% CO, 99% N_2	760	0.25	0.21	325	296	60	53.6	18.8
0.5% H_2, 0.5% CO, 99% N_2	870	<0.03	0.04	327	277	102	67.7	25.8

[a] Pb (670 ppm) and P (85 ppm) were also found on this catalyst.

In light of the above, although $CuSO_4$ is a known oxidation catalyst, it would be expected that the rate of CO oxidation over $CuSO_4$ would be slower than over CuO. Therefore, if CuO on a catalyst were converted to $CuSO_4$, a decline in the CO oxidation activity would be expected. Decomposition of $CuSO_4$ to form CuO via the intermediate basic sulfate should result in an improvement in the CO oxidation activity. Thus, attempts were made to reactivate SO_2-treated catalysts in the laboratory by decomposing the metal(s) sulfate(s). The results in Table VII show that the oxidation activity (mainly CO) of catalyst A improves on heating in air. With increasing temperature of exposure, a concomitant improvement in the CO oxidation activity and a decline in the SO_4^{2-} content were observed. Repetition of sulfur poisoning followed by regeneration did not adversely affect the resultant catalyst's activity.

Similar results were observed when a vehicle-used catalyst (described in Table III) was regenerated in the laboratory. The extent of regeneration could be correlated to the atmosphere, temperature, and time of treatment (Table VIII). At 870°C with air, N_2 or a H_2-CO-N_2 mixture, sulfur concentrations on the catalyst were reduced to <0.10%, resulting in the equivalent of fresh HC oxidation activity and essentially fresh CO oxidation activity.

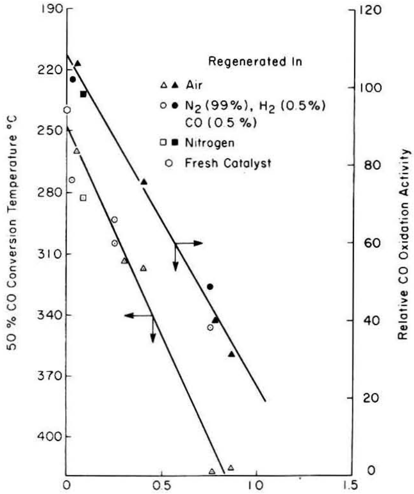

Figure 1. Relationship between CO oxidation activity and sulfur concentration on regenerated vehicle-used Catalyst B

The CO oxidation activity of catalysts regenerated at these three conditions varied somewhat owing to a probable difference in the oxidation state of the metal components on the final catalyst. Failure to attain fresh CO oxidation activity on regenerated vehicle-used catalysts may be the result of one or more of the following: Pb poisoning, P poisoning, loss in surface area, and burial of active ingredient. It should be pointed out that Hunter, 1972, was unable to obtain complete sulfur removal from a poisoned Cu-Cr-Al-O catalyst at 870°C. Treatment conditions and/or catalyst nature may explain these different results.

Partially regenerated samples of vehicle-used catalyst showed a direct relationship between CO oxidation activity and sulfur content regardless of the atmosphere used in the regeneration, as shown in Figure 1. When the standard deviations for the results obtained from the activity tests are taken into account, the time required for regeneration at 820°C in air appears to be less than 15 min (see Table IX). At ~870°C it is believed that complete sulfate decomposition on these catalysts in exhaust gas environments can be achieved in a matter of seconds.

Data in Table VIII indicate that sulfur attack decreases NO removal activity and increases the fraction of NO converted to NH_3. As in the case of CO and HC oxidation activity, the deactivation is reversible. When regenerations were carried out in a reducing atmosphere (Table VIII),

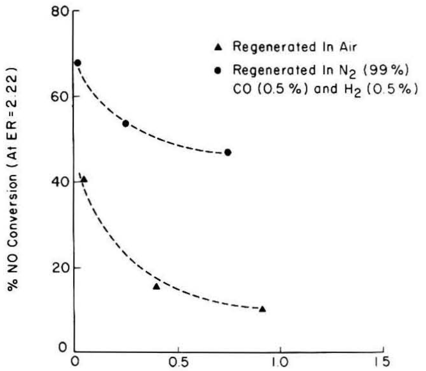

Figure 2. Relationship between NO removal activity and sulfur concentration on regenerated vehicle-used catalyst B

activities exceeded the fresh activity, indicating that a reduced form of the catalyst is more active than the oxidized form. Correlations between sulfur and sulfate concentrations and NO removal activities are shown in Figures 2 and 3, respectively. Although the relevance of obtaining NO_x removal data on catalysts that have operated solely in oxidizing atmospheres is questionable, linear relationships in Figure 3 may indicate that it is specifically SO_4^{2-} formation that causes the decline in NO removal activity, whereas apparently any form of sulfur adversely affects CO oxidation activity.

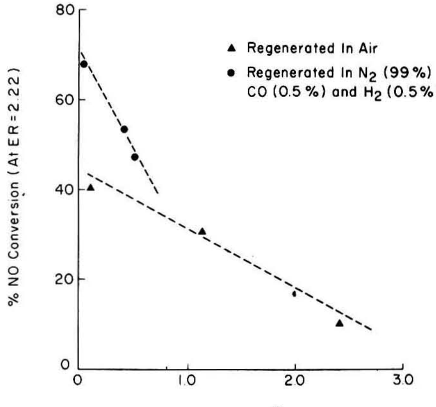

Figure 3. Relationship between NO removal activity and sulfate concentration on regenerated vehicle-used catalyst B

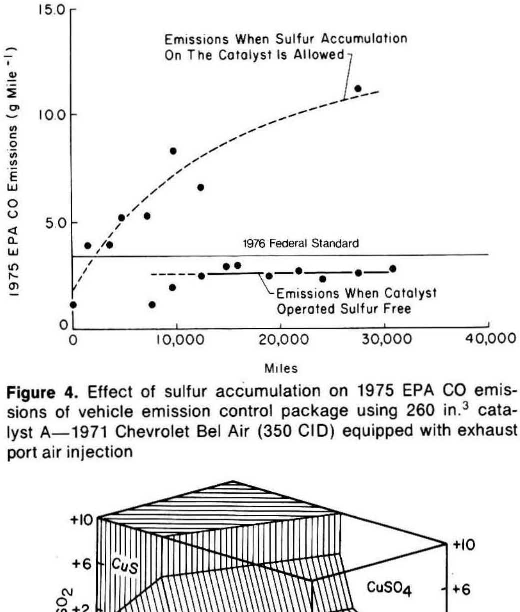

Figure 4. Effect of sulfur accumulation on 1975 EPA CO emissions of vehicle emission control package using 260 in.^{3} catalyst A—1971 Chevrolet Bel Air (350 CID) equipped with exhaust port air injection

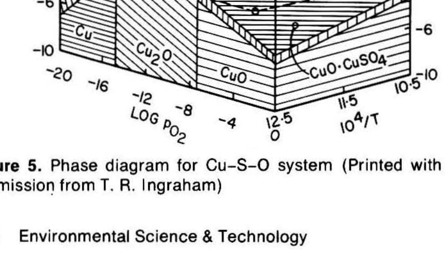

Figure 5. Phase diagram for Cu–S–O system (Printed with kind permission from T. R. Ingraham)

Table IX. Dependence of Regeneration of Vehicle-Used (3600-Mile) Catalyst B at 820°C in Flowing Air on Time

Treatment time, min.	50% conv. temp, °C HC	CO	Rel. CO oxidation activity
0	346	412	33
15	311	318	71
30	322	337	66
45	318	309	76
60	324	315	83
Std Dev, σ	5	4.5	8.3

Following the successful attempts to regenerate sulfur-poisoned Cu–Cr–Al–O catalysts in the laboratory, it appeared feasible to regenerate similarly sulfur-poisoned catalysts on a vehicle. Attempts were made to regenerate in situ a catalyst A sample which, after 7200 miles of vehicle use, showed a substantial decline in CO oxidation activity, as indicated in Table X. Regeneration was accomplished by using the durability cycle described previously (Table IV), except that periodically (15 min every 2 hr), the bed temperature was raised to 790–900°C by accelerating and decelerating between 65 and 70 mph. After this treatment, 1975 EPA HC and CO emissions at 7700 miles were 0.08 and 1.15 g·mile^{-1}, respectively, compared with 0.15 and 5.25 g·mile^{-1} at 7200 miles.

During the period from 7700 to 9800 miles, the normal durability cycle was used and bed temperatures were in the range 510–565°C, where sulfur poisoning of the catalyst is expected. At 9800 miles, 1975 EPA HC and CO emissions were 0.48 and 8.27 g·mile^{-1}, respectively.

After a 15-min in situ regeneration, when we used the procedure described above, the emissions were reduced to HC 0.18 and CO 2.12 g·mile^{-1}. An additional regeneration period of 15 min did not result in any further improvement. The CO emissions from the CVS test vehicle equipped with catalyst A when sulfate formation was permitted, and then prevented by use of elevated temperatures, are summarized in Figure 4.

Although it was shown that these catalysts could be regenerated in situ on a vehicle, the feasibility of carrying out such an operation in practice was questionable; however, if conditions in the catalyst bed could be maintained such that attack by sulfur combustion products could be prevented, the sulfur-poisoning problem would be eliminated. The obvious solution to this situation is to remove the sulfur from gasoline during processing, as has been suggested previously (Hunter, 1972). The cost of reducing the sulfur level in most straight-run naphthas to <1 ppm is currently estimated to cost 15¢/bbl (approximately $0.0033/gal) for a 10,000-bbl/d refinery (Parker, 1973).

Ingraham, 1965, has determined stability regions for all the phases that constitute the Cu–S–O system, Figure 5. The equilibrium temperatures for the decomposition of $CuSO_4$ to $CuO{\cdot}CuSO_4$ and $CuO{\cdot}CuSO_4$ to CuO were estimated from this information for O_2 and SO_2 concentrations that would be experienced in vehicle exhaust. Some of these data are summarized in Table XI. The effects of H_2O and CO were ignored despite their obvious importance (Table VIII). For an exhaust gas containing 10% O_2 and 10 ppm SO_2 (typical concentrations in exhaust gas, after air has been added), CuO would be the stable phase, provided temperatures are held above 580 ± 15°C. If the assumption is made that these estimated equilibrium decomposition temperatures for bulk $CuSO_4$ and CuO·-

Table X. Vehicle Durability Test Results for Catalyst A

Miles	1975 EPA emissions, g·mile^{-1} HC	CO	NO_x	Approx operating bed temp range, °C	Treatment
0	0.14	1.21	3.25	...	
1,500	0.19	4.32	2.10	510–565	
3,600	0.17	3.98	2.22	510–565	
4,900	0.14	4.86	2.55	510–565	
7,200	0.15	5.25	2.52	510–565	
7,700	0.08	1.15	(2.48)	510–565 + high temp	For 15 min every 2 hr, bed temp raised to approx, 790–900°C by accelerating and decelerating between 65 and 70 mph
9,800	0.48	8.27	1.88	510–565	
9,800	0.18	2.12	2.55	...	Catalyst bed temp raised to approx 815°C for 15 min
9,800	0.23	1.67	3.21	...	Catalyst bed temp raised to approx 815°C for 30 min
12,400	0.23	6.58	2.76	510–565	
12,400	0.37	4.24	3.03	...	
12,400	0.21	2.49	2.64	...	Catalyst bed temp. raised to approx 815°C for 30 min
14,800	0.15	2.40	2.48	650–760	
15,875	0.30	2.90	3.00	650–760	
18,900	0.20	2.44	2.65	650–760	
21,800	0.20	2.64	2.57	650–760	
24,100	0.20	2.90		650–760	
27,550	0.22	11.03	3.53	510–565	Catalyst deliberately sulfur poisoned
27,550	0.26	2.53	1.86	...	Catalyst bed temp raised to approx 815°C for 15 min
30,400	0.26	2.73	3.41	650–760	
32,000	0.27	3.95	2.66	650–760	
35,000	0.18	3.28	2.79	650–760	
40,750	0.21	2.16	3.21	650–760	
47,700	0.40	3.49	3.51	650–760	
48,100	0.42	3.29	3.69	650–760	
52,000	0.34	3.16	2.76	650–760	

Estimated standard deviations, HC, 0.10 and CO, 1.0 g·mile^{-1}.

Table XI. Equilibrium Sulfate Decomposition Temperatures

Estimated from data reported by Ingraham

$-\text{Log } p_{SO_2}$ (atm)	6	5	6	5	
$-\text{Log } p_{O_2}$ (atm)	2	2	1	1	
$MO = MO \cdot MSO_4$	525	565	540	580	°C, ±15°
$MO \cdot MSO_4 = MSO_4$	480	530	495	545	°C, ±15°

$CuSO_4$ are similar for dispersed copper sulfates, then sulfur poisoning of catalysts A and B in a vehicle emission control system should be inhibited, providing bed temperatures are held in excess of 600°C.

In an attempt to prevent sulfur poisoning, the catalyst A vehicle durability test was continued from 14,800 to 24,100 miles with bed temperatures held in the range 650–750°C by partially activating the choke on the Buick test vehicle. Throughout this testing, HC and CO emissions from the Chevrolet slave car were below the 1976 HC and CO federal standards (Table X), indicating that no detectable sulfur poisoning had occurred and that the assumptions made regarding the equilibrium decomposition temperatures were correct.

Continuation of the durability test from 24,100 to 27,550 miles was deliberately conducted with bed temperatures in the range where sulfur poisoning would occur, namely 510–565°C. The HC and CO emissions at 27,550 miles were 0.22 and 11.03 g·mile^{-1}, respectively. After the test, catalyst (100 ml) was removed for analysis. Inert diluent (100 ml) was added and the converter subjected to temperatures in the range 790–900°C on the vehicle using methods described previously. The HC and CO emissions after this high-temperature treatment were 0.26 and 2.53 g·mile^{-1}, respectively. Another catalyst sample (100 ml) was removed from the converter for analysis and replaced with inert diluent. The durability test was continued to 52,000 miles, at which point the HC and CO emissions from the Chevrolet slave car were still below the 1976 federal standards.

Analytical and activity data for fresh and vehicle-used (at 27,550 miles) catalyst A are given in Table XII. At 27,550 miles after the deliberate sulfur poisoning (S, 0.50; SO_4^{2-}, 1.04%) the CO oxidation activity was poor, as expected. After nearly complete removal of the sulfur (carried out in situ on the vehicle), the CO oxidation activity improved sufficiently to meet 1976 EPA CO emission standards (Table X), but did not approach the fresh laboratory activity (Table XII). This loss in activity is probably due primarily to partial collapse of the support and burial of the active ingredients. Although structural collapse and decline in the activity as determined in the laboratory was limited during the period 27,550–52,000 miles,

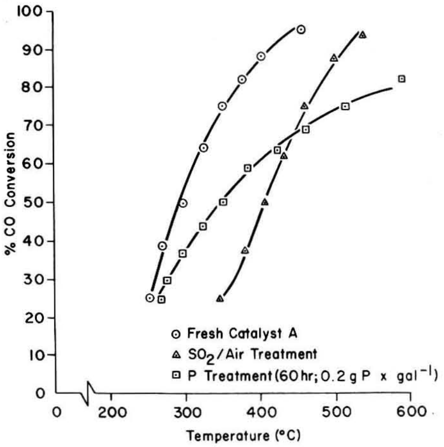

Figure 6. Percent CO conversion (at 30,000 ghsv) vs. temperature for fresh and treated catalyst A samples

the loss of 161 grams of catalyst of the original 2177 grams loaded probably caused channeling in the converter, hence higher vehicle emissions (Table X). No loss of copper or chromium due to vapor transport was observed.

The degree of sulfur poisoning of a catalyst will be determined by a number of factors including: Sulfur concentration in the fuel and hence p_{SO_2} and p_{SO_3} in the exhaust gas; p_{CO}, p_{O_2}, and p_{H_2O} in the exhaust gas; catalyst formulation; gas flow rates (Ingraham, 1965); and catalyst temperature.

Ideal catalyst formulations would contain a catalytically active ingredient(s) which either does not form a sulfate or forms a sulfate that decomposes to form the oxide at low temperature. From a recent survey of the chemistry of 47 M-S-O systems, which includes decomposition data for $M_x(SO_4)_y$ compounds (Lowell et al., 1971), it is apparent that very few base metal oxides are potential candidates. Noble metals are not directly affected by sulfur combustion products at the temperatures experienced in catalytic converters, but deactivation of supported noble metals may occur if constituents of the substrate form stable sulfates—e.g., Al_2O_3 (Papazian et al., 1972). Many noble metal-promoted base metal catalysts have been prepared on a variety of supports in these laboratories and each has shown some activity decline as a result of exposure to SO_2 at 480°C; the deactivation observed, particularly for noble metal catalysts, however, is much less severe than for the Cu-Cr-Al-O catalysts. Snyder et al., 1972, claimed that noble and noble metal-promoted base metal catalysts do not lose any activity on exposure to the equivalent of 5000 miles of operation on fuel containing 0.1 wt % S added as $(t\text{-BuS})_2$.

Data in Table XIII show the effects of Pb, P, and S combustion products on the oxidation activity of catalyst A. High Pb and P concentrations in the fuel were used in the CLR studies to simulate the effect of low concentrations for extended periods. Twenty-five, 50, and 75% HC and CO conversion temperatures were determined in a manner similar to that previously described but at a ghsv of 30,000 hr^{-1}. From the limited number of experiments carried out, it is not possible to compare the effects of Pb, P, and S on an absolute basis. However, in light of the proposed 1975 EPA restrictions on the Pb and P content of gasoline, 0.05 and 0.005 g·gal^{-1}, respectively, and a typical S content of 1 g<gal^{-1} (~0.04 wt %), some qualitative conclusions regarding the effects of these poisons at the above levels may be drawn. In the preparation of catalyst C (Table XIII), 5.3 grams of S, as SO_2/SO_3, was passed over the catalyst compared to 1 gram of Pb in the preparation of catalyst E—i.e., S-Pb is 5.3-1. Although this ratio is substantially less than that projected for 1975 fuels (20-1), the S combustion products have caused greater decline in the oxidation activity than those arising from the Pb.

Table XII. Analytical and Activity Data for Fresh and Vehicle-Used Catalyst A

		Vehicle-used		
	Fresh	Sulfur poisoned at 27,550 miles	After regen. at 27,550 miles	After 52,000 miles
Av. crush strength, kg	6.3		2.8	2.0
BET surface area, m^2·g^{-1}	158		65	46
Pore volume, ml·g^{-1}	0.39		0.14	0.09
Pore diameter, A	99		86	78
Rel. CO oxidation activity	100	17	66	71
50% HC conv. temp, °C	301	354	342	351
50% CO conv. temp, °C	260	457	298	302
1975 EPA HC emissions, g·mile^{-1}	0.14	0.22	0.26	0.34
1975 EPA CO emissions, g·mile^{-1}	1.21	11.03	2.53	3.16
P, wt %		0.062	0.062	0.11
Pb, wt %				0.36
S, wt %		0.50	0.07	0.06
SO_4^{2-}, wt %		1.04	0.23	

Table XIII. Effects of S, Pb, and P on Oxidation Activity of Catalyst A (Conversion temp obtained at a ghsv of 30,000 hr^{-1})

		Temp, °C for X% HC or CO conv.					
		HC			CO		
Treatment	Poison concn, wt %	X = 25	50	75	25	50	75
Lab SO_2 treatment for 1 hr at 480°C (catalyst C)	1.46	317	368	422	348	409	460
Exhaust from CLR engine Fuel, iso-C_8 + 0.2 gram Pb·gal^{-1}, temp., 480°C, 60 hr at 2000 rpm (catalyst E)	0.5	277	338	393	249	307	365
Exhaust from CLR engine Fuel, iso-C_8 + 0.22 gram P·gal^{-1}, temp., 540°C, 60 hr at 2500 rpm (catalyst F)	0.93	310	391	504	271	352	515
Catalyst F heated in flowing air for 1 hr at 870°C (catalyst G)	0.90	310	379	590	274	335	590
Exhaust from CLR engine Fuel, iso-C_8 + 3.0 grams Pb·gal^{-1} temp., 480°C, 60 hr at 2000 rpm (catalyst H)	6.8	327	471	599	274	377	593
Catalyst H heated in flowing air for 1 hr at 870°C (catalyst I)	6.5	345	477	...	318	415	585

The effect of S and P combustion products on the CO oxidation activity are shown in Figure 6. Comparisons of the plots for fresh and SO_2-treated catalysts show that the slopes are similar but a shift to higher temperatures is evident for the SO_2-treated catalyst. Since the slope of a temperature vs. conversion plot is relatable to the activation energy (E_{act}), it appears that for these SO_2-treated catalysts the frequency factor, A (a function of the number of active sites in the expression $K = Ae^{-E(act)/RT}$), has been reduced. The corresponding plot for a P-treated catalyst shows a change in the slope, indicating that the number of active sites is essentially the same as on the fresh catalyst but that the activity of these sites has declined.

From the activities of catalysts C and F (Table XIII), it would appear that P-combustion products have a more adverse effect on the activity of catalyst A at a S-P value of approximately 4.5 than S-combustion products. The S-P ratio for proposed 1975 fuels, however, will approach 100-200, and at these levels, the same as used in the 52,000-mile durability test, it is apparent that any effects due to P-poisoning were not sufficiently adverse to hinder the catalyst's ability to meet 1976 federal HC and CO standards.

Heating both the P-treated catalyst F and Pb-treated catalyst H samples in flowing air at 870°C for 1 hr resulted in only slight removal of the poisons and a further decline in activity (Table XIII). This is consistent with the pore-mouth poisoning mechanism recently proposed by Dwyer and Morgan, 1972, for Pb-poisoning of copper chromites. Scanning electron microscope/microprobe studies of catalysts G and I show that the Pb penetration on catalyst I is greater than on catalyst G. Unlike the case of sulfur poisoning, apparently Pb and P poisoning of catalyst A is irreversible under oxidizing conditions at least at $\leq 870°C$.

Conclusions

The oxidation activity of Cu-Cr-Al-O catalysts is adversely affected by Pb-, P-, and S-combustion products. However, at their proposed levels in 1975 fuels, S-combustion products far outweigh the effects of Pb- or P-combustion products. Unless these S levels are reduced, vehicle operating conditions and, hence, catalyst environment, will have to be strictly controlled, such that SO_4^{2-} formation on the catalyst is prevented.

Vehicle durability results do not infer that 1976 federal standards can be met on a production vehicle equipped with an emission control package that includes catalyst A, but it does indicate, given the optimum operating conditions, that: The physical stability of catalyst A is sufficient to allow appreciable mileage accumulation without excessive catalyst loss and the activity stability of the catalyst is sufficient to enable 1976 federal HC and CO standards to be met for a meaningful period of time.

Acknowledgments

The authors wish to express appreciation to R. L. Herbold and A. D. Wilks for assistance with the experiments; G. R. Lester, Dorothy Darling, and J. R. Polk for catalyst activity test development; T. V. DePalma, J. E. Thoss, and G. M. Hutter for the automotive work; and J. R. Deering for analyses carried out. Thanks are due to V. Haensel and Hertha Skala for their helpful discussions and encouragement.

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Received for review July 2, 1973. Accepted November 16, 1973. A paper based on this material was presented at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973.

NOTES

Aqua Regia for Quantitative Recovery of Mercuric Sulfide from Sediments

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■ A digestion procedure consisting of a 2:1 concentration of H_2SO_4:HNO_3 plus $KMnO_4$-$K_2S_2O_8$ oxidation (Iskander et al., 1972) proved to be inadequate for quantitative recovery of HgS, a Hg compound that may be present in reduced materials such as river and lake sediments and waste sludges. Since HgS or Hg(II) associated with metal sulfide phases may be a significant fraction of the total Hg in these substances, incomplete dissolution of these Hg(II) sulfide phases during sample digestion will cause total Hg concentrations to be underestimated. An aqua regia digestion procedure which quantitatively recovers HgS from sediments is described, and is recommended for total Hg analyses of sediments. The authors found that $KMnO_4$ and $K_2S_2O_8$ must be included with aqua regia to obtain complete recovery of five other Hg compounds implicated in Hg transformations and pollution in the environment. Nonaqua regia procedures being used to analyze sediments or sludges for total Hg should be tested for quantitative recovery of HgS.

During an investigation of Hg transformations in river sediments, we observed a significant decrease with time in the total Hg content of Hg-amended sediments incubated in situ within closed vessels. Because no obvious loss of Hg from these vessels could be postulated, we evaluated the total Hg procedure (Iskandar et al., 1972) for possible sources of error. In anaerobic sediments where H_2S is being produced, HgS and/or Hg(II) associated with metal sulfide phases will likely be formed owing to the low solubility of metal sulfides. Therefore, pure HgS was analyzed by the Iskandar et al. (1972) procedure. Results of the recovery test showed that this procedure recovered only 10-

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20% of the Hg added as HgS. The low and variable recoveries indicated that any HgS present in the sediments was not being completely dissolved during acid digestion.

Consequently, other digestion procedures were evaluated with respect to their effectiveness in completely dissolving HgS. Aqua regia (Dow Chemical Co., 1970) was the best digestion reagent, and the procedure finally adopted is described. In addition to HgS, the recoveries of several other Hg compounds were also evaluated.

Recommended Procedure for Sediments

Lower the water content of a wet sediment by centrifuging and decant the interstitial water. Weigh an amount of sediment, equivalent to approximately 1 gram of oven-dry material, into a 250-ml beaker. Weigh separate samples for moisture determination. Wet sediment is used since Iskandar et al. (1972) noted that significant losses of Hg compounds occurred on drying of sediments at 60°C.

Slowly and cautiously add 25 ml of aqua regia with stirring. (CAUTION: Aqua regia is an unstable mixture which should not be stored or put into a stoppered container. Prepare just prior to use by carefully adding 1 part concentrated HNO_3 to 3 parts concentrated HCl and allowing the mixture to stand for approximately 5 min. Use only in a fume hood.) Heat the sample to boiling and boil for 1 min, stirring occasionally to prevent excessive frothing. Rinse down the sides of the beaker with a few ml of deionized water and allow the sample to cool to room temperature. Carefully add 25 ml of 5% $KMnO_4$ and 2 ml of 5% $K_2S_2O_8$. Slowly stir the solution to avoid frothing, cover the sample, and allow to stand about 16 hr.

Reduce the residual $KMnO_4$ with a 20% solution of hydroxylamine hydrochloride to a faint pink color and transfer the sample quantitatively to a 100-ml volumetric flask. Make further dilutions where appropriate and determine total Hg^{2+} by flameless atomic absorption as described in an earlier procedure (Iskandar et al., 1972).

Results and Discussion

To compare the recovery of various Hg compounds using the recommended digestion with the recoveries obtained with the H_2SO_4-HNO_3-$KMnO_4$ digestion of Iskandar et al. (1972) or aqua regia without $KMnO_4$ and $K_2S_2O_8$, replicated samples of wet sediment (2 grams) containing various Hg compounds were digested by these digestion procedures and analyzed for total Hg. Enough salt of each compound was weighed to give approximately 1 mg of Hg, an amount equivalent to the Hg present in 1 gram (oven-dry) of sediment containing a 1000-ppm concentration. This concentration would rarely be exceeded except in sediments or soils located near ore deposits. Sediment near the discharge point of a chloralkali plant in Wisconsin was 700-800 ppm of Hg (Konrad, 1971).

The recoveries of several Hg compounds obtained by the digestion procedures evaluated are listed in Table I. In addition to HgS and the three compounds tested by Iskandar et al. (1972), two other compounds implicated in Hg transformations were checked for recovery, namely methoxyethylmercuric chloride (Jernelöv, 1969) and diphenyl mercury (Matsumura et al., 1971). Results show the necessity of using aqua regia for complete dissolution of HgS—i.e., hot H_2SO_4-HNO_3 mixture was not adequate.

To our knowledge, only two published papers recommend the use of aqua regia for sediment or sludge analysis, namely the Dow Chemical Co. (1970) and the Analytical Quality Control Laboratory (AQCL) of EPA (1972). The AQCL has revised its original provisional method for Hg in sediments and sludge-like materials (published in 1970) by recommending the use of aqua regia instead of the H_2SO_4-HNO_3 mixture, although it still recommends the latter for water and fish analyses. No reason was given in the sediment method for this change, but low recoveries of Hg, similar to those reported in this paper, probably warranted a change to aqua regia.

Table I. Average % Recovery of Various Hg Compounds Using Recommended Digestion Compared to Other Digestion Procedures

	Average % recovery		
Hg compound	Iskandar et al. procedure	Aqua regia	Aqua regia[a] w/ $KMnO_4$-$K_2S_2O_8$
Methoxyethylmercuric chloride	...	92	99 ± 7
Methylmercuric chloride	103[b]	86	104 ± 9
Phenylmercuric acetate	100[b]	98	103 ± 4
Diphenyl mercury	...	96	101 ± 8
Mercuric chloride	102[b]	92	106 ± 4
Mercuric sulfide	10–20	97	96 ± 8

[a] Recommended procedure showing ± standard deviations for 6 or more samples.
[b] Recovery percentages previously published by Iskandar et al. (1972).

Another important part of the recommended procedure is the inclusion of $KMnO_4$ and $K_2S_2O_8$. These oxidants appear to be necessary for complete recovery of various organic Hg compounds as the data in Table I suggest. The AQCL (1972) recommends using $KMnO_4$ with aqua regia in their procedure, but Dow Chemical (1972) does not. The authors feel that $KMnO_4$ and $K_2S_2O_8$ should be used with aqua regia to ensure complete oxidation and dissolution of the six Hg compounds listed in Table I.

Many procedures have been published recently for the determination of Hg in various biological materials and soils with a wide variety of oxidants being used for sample digestion. However, few procedures are concerned specifically with reduced materials such as sediments and sludges. Consequently, many other procedures, including that of Iskandar et al. (1972), have been adopted for total Hg determinations in sediments and sludges without consideration of HgS recovery. While the Iskandar et al. (1972) procedure and others are adequate for the digestion of most soils, the total Hg content of materials which may contain significant amounts of HgS—e.g., sediments and sludges, will likely be underestimated.

Acknowledgment

We thank Ronald T. Checkai for technical assistance.

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Received for review May 2, 1973. Accepted November 8, 1973. This research was supported by the College of Agricultural and Life Sciences, University of Wisconsin, Madison, and by the State of Wisconsin Department of Natural Resources (Project, 133-8233).

INDUSTRY TRENDS

Research-Cottrell, Inc., will acquire Multi-Amp Corp., Dallas, Tex., in an exchange of stock. Multi-Amp produces equipment for testing nuclear and fossil-fueled electric power plant protective systems and other safety devices. The merger is subject to Multi-Amp stockholder approval at meeting this month.

Dravo Corp. will do the preliminary engineering on water management improvements at Weyerhaeuser Co.'s pulp and paper mill at Longview, Wash., to design a "best value" waste discharge treatment facility and recycle much of the process water.

Ethyl Corporation's subsidiary, Air Monitoring, Inc., has designed and built a $1-million, 4-unit quality control system for audit-testing catalytic converters for auto emission control.

The Foxboro Co. said that no corporate relationship or joint venture with Computer Sciences Corp. is being negotiated or considered.

Zurn Industries, Inc. agreed to sell its heavy construction division to Pascal and Ludwig, Inc., of California for an undisclosed amount of cash and notes.

Mercedes-Benz of North America started up its $250,000 exhaust emission sampling laboratory (Carson, Calif.) to monitor pollution control performance of Mercedes cars sold in southern California.

Dames & Moore (Los Angeles, Calif.) was retained by the Southwest Florida Water Management District to do a $179,000 study of the Alafia and Little Manatee Rivers.

Universal Oil Products Co. has completed arrangements for $50 million in short-term credits for 1974. Ten banks will grant the credit.

Ionics, Inc. has acquired the assets and business of Olin's Custom Analytical Instrument Venture. No plant or facilities were involved. Terms were not disclosed.

The National Center for Resource Recovery, Inc. (Washington, D.C) received two contracts totaling $181,600 from New York State and Westchester County, N.Y., in the field of solid waste resource recovery.

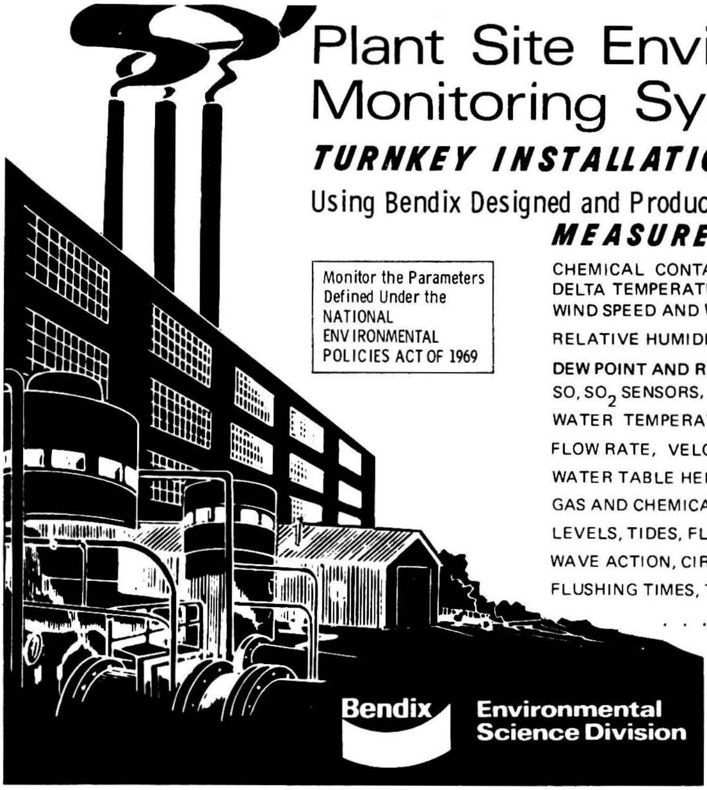
Dow Chemical U.S.A. has begun a $2-million expansion for product safety research, and will complete a major new toxicology laboratory early in 1975.

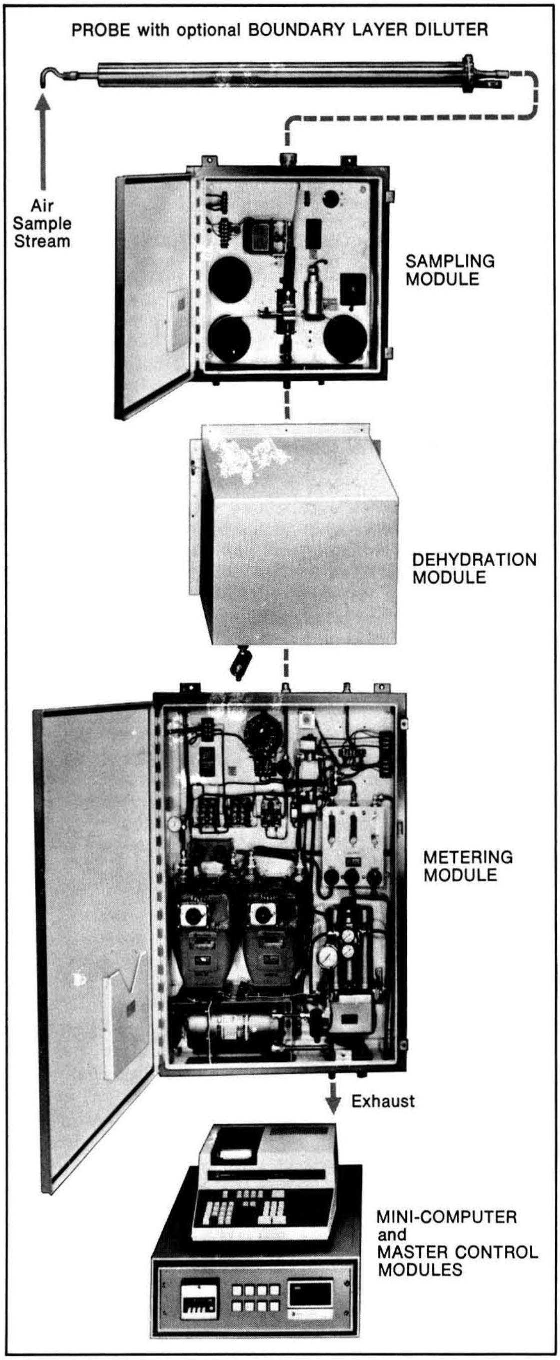
Westinghouse Electric Corp. will build a cooling tower for 160,000 gpm of water at Florida Power & Light Company's 500-MW plant to be built near Palatka, Fla.

Poly Con Corp. will build a major gas scrubbing system for Rollins Environmental Services (Houston, Tex.), as part of a chemical waste incineration scheme.

Met-Pro Water Treatment Corp. will manufacture and supply a 50,000-gpd independent physical-chemical compact advanced sewage treatment plant for the Wionkhiege Valley Waste Treatment Co. (Smithfield, R.I.).

International Telephone & Telegraph Corp. has signed an agreement with Romania for cooperation in telecommunications, electronic and electrochemical components, industrial products, consumer products, and publishing.

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Precast sewage plant

System for erecting precast concrete sewage treatment plants without the need for on-site forms can save developers as much as 50% in both construction and expansion costs, according to the manufacturer. Plants consist of 500 psi precast concrete sections. They can be installed within 14 weeks. The one prerequisite is that a concrete base slab be poured on site. Marolf, Inc. **143**

Waste water sampler

Automatic waste water sampler features a simple, single-stroke displacement action, controlled by an adjustable timer. The device is of heavy duty corrosion resistant construction and can handle raw wastes without plugging. It is available in both 110-V and battery-operated models and is readily adapted to flow proportional sampling. Environmental Marketing Associates **108**

Oven rate controller

Ultrahigh, autofeed system is designed to improve combustion and reduce smoke emissions from Dutch oven boilers by automatically controlling feed rate and height of hog fuel, sawdust, and shavings. Components of the system include a thermocouple sensing probe, solid state transducer, and relay. Requires little or no attendance. Easy to install. Union Heating Inc. **141**

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Cooking device fries, roasts, boils, broils without wasting energy or polluting the environment. It converts from a rectangular aluminum enclosure measuring 17″ × 19″ × 3″ into an umbrella-like, self-standing unit measuring a little over 3 ft in diameter. Best results, of course, are possible on clear, sunny days. Intercontinental Enterprises Co. **110**

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Butterfly valves

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Fuel oil additives. Booklet narrates how the use of Alken treatments can improve combustion efficiency, reduce fuel consumption, and control particulate emissions and SO_3. Alken-Murray Corp. **168**

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Digital recorders. Bulletin 37A describes use of environmental data monitoring servosystems for punched tape recording of temperature, conductivity, pH, dissolved oxygen, and pressure. Leupold & Stevens, Inc. **170**

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Environmental system. Report 88-050 outlines applications of data acquisition system in electric utilities, industries, and municipalities. Each key component of the Adviser is illustrated. Westinghouse Electric Corp. **171**

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Analyzers. Illustrated bulletin details combustible and toxic gas monitors, and gas analyzers for process control. Mine Safety Appliance Co. **178**

Oil spill equipment. Brochure covers alarm systems for inland spills on water and on land. Drawings and specifications are included. Illinois Chemical Corp. **179**

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Piping. Booklet G-24 describes polyvinyl pipes which minimize corrosion worries, speed up installation time, reduce maintenance problems, and lower overall costs. Application histories are included. B. F. Goodrich Chemical Co. **187**

Instruments. Bibliography lists ultraviolet and fluorescence applications in air and water pollution studies. Perkin-Elmer Corp. **191**

BOOKS

Patterns and Perspectives in Environmental Science. National Science Foundation. xiii + 426 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1973. $7.30, hard cover.

Prepared as a companion volume to the National Science Board's "Environmental Science—Challenge for the Seventies." It is a compendium of the views and judgments of a large number of scientific leaders. It addresses a broadly representative array of topics that serve to illustrate the scope and nature of environmental science today.

Radioecology. V. M. Klechkovskii, G. G. Polikarpov, R. M. Aleksakhin, editors. xii + 371 pages. Halsted Press, 605 Third Ave., New York, N.Y. 10016. 1973. $35, hard cover.

Attempts to satisfy the need for a monograph review of the current status of radioecological problems. In doing so, it deals both with radioecology of land biogeocenoses and aquatic biocenoses. Shows how the atmospheric source of radionuclide fallout on the soil-plant cover of the earth is the starting stage of migration in many contamination situations.

Solid Waste Disposal, Vol. 1: Incineration and Landfill. Bernard Baum, Charles H. Parker. xvi + 397 pages. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1973. $22.50, hard cover.

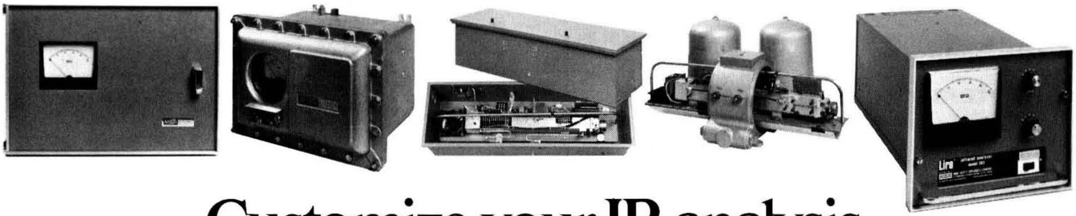
Treats the practice of incineration in terms of its history and its design criteria for municipal and industrial wastes, capital and operational costs, instrumentation, and the control of air pollutants. Landfill practices and the design, construction, administration, and economics of sanitary landfill operations are discussed.

Environmental Pollution and Mental Health. John S. Williams et al. xi + 136 pages. Information Resources Press, 2100 M St., N.W., Washington, D.C. 20037. 1973. $9.50, hard cover.

Seeks to demonstrate how pollution and degradation of the physical environment have complex and varied consequences for man's mental health. Book provides material for elucidating the mechanisms through which mental health is affected, on the one hand, by the external world, and, on the other hand, by the inner world as it is experienced conceptually by each particular human being.

Sourcebook on the Environment: The Scientific Perspective. Charles ReVelle, Penelope ReVelle. ix + 332 pages. Houghton Mifflin Co., Educational Div., 110 Tremont St., Boston, Mass. 02107. 1974. $4.95, paper.

Attempts to provide a better understanding, from a scientific perspective, of the principal environmental issues that confront civilization. Book sees the various needs of man, such as mechanical and electrical energy, water and food, and raw materials, as interrelated. It says the balancing of these costs against the benefits of a healthy environment is everybody's concern.



Name your Poison. Bill Mauldin. 80 pages. New Mexico Citizens for Clean Air and Water, 500 Camino Rancheros, Santa Fe, N.M. 87501. 1973. $3.95, paper.

A collection of 76 Bill Mauldin environmental cartoons, which first appeared in the Chicago *Sun-Times.* Drawn over a period of 15 years, the cartoons employ the same props (dead fish, poisonous drainpipes, filthy chimneys) to whack away graphically at the people and institutions that have been polluting our air, water, and lives.

Adverse Effects of Environmental Chemicals and Psychotropic Drugs: Quantitative Interpretation of Functional Tests. Vol. 1. Milan Horvath, editor. 292 pages. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N.Y. 10017. 1973. $20, hard cover.

Concerned with current approaches and methodological practices for evaluating functional impairment resulting from exposure to chemical agents. This volume centers on the use of functional tests and on the quantitative interpretation of test results in two well-defined research areas; experimental toxicological criteria and the influence of drugs in work and transport safety.

Forty Years of Landscape Architecture: Central Park. Frederick Law Olmsted, Jr., Theodora Kimball, editors. xviii + 575 pages. MIT Press, 28 Carleton St., Cambridge, Mass. 02142. 1973. $4.95, paper.

Edition is produced from Volume 2 of "Frederick Law Olmsted, Landscape Architect, 1822–1903." Contains statements, by the designers, of the reasons underlying the development of Central Park's design, and opinions as to its possibilities for deep-rooted usefulness in the life of New York City. Shows the park as a single "work of art."

Instrumentation for Environmental Monitoring. Vol 3: Radiation. Technical Information Division, Lawrence Berkeley Laboratory, University of California, Berkeley, Calif. 94720. 1973. $25, notebook.

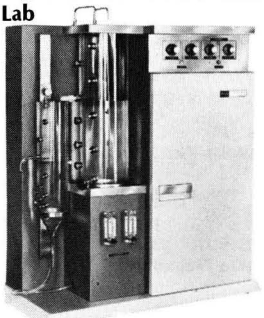
This volume investigates those instruments useful in measuring radiation environmentally. Consideration is given to instruments and techniques presently in use, and to those developed for other purposes that have possible applications. The survey results include descriptions of the physical and operating characteristics of available instruments, critical comparisons among instrumentations, and recommendations.

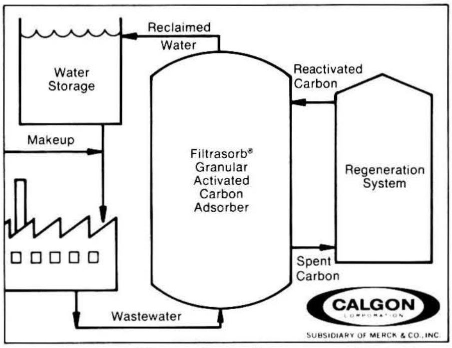
A Guide to Air Quality Monitoring with Lichens. William C. Denison, Sue M. Carpenter. vii + 39 pages. Lichen Technology, Inc., P.O. Box 396, Corvallis, Ore. 97330. 1973. $3, soft cover.

Written to acquaint the general public about the possibilities of monitoring the quality of the air using lichens. The book is aimed at the high school and undergraduate levels. It demonstrates that lichens are sensitive to very low levels of air pollution and serve as a measuring device that is cheap, can be used anywhere, and responds immediately.

Environment and Society: A Book of Readings on Environmental Policy, Attitudes, and Values. Robert T. Roelofs, Joseph N. Crowley, Donald L. Hardesty, editors. x + 374 pages. Prentice-Hall, Inc., Englewood Cliffs, N.J. 07632. 1974. $11.95, hard cover.

Collection of articles offers an interdisciplinary approach to the historical, social, policy-making, and value dimensions of environmental problems. The collection goes beyond the factual data of such problems as population and pollution, and embodies the interrelated viewpoints of the social sciences and the humanities.

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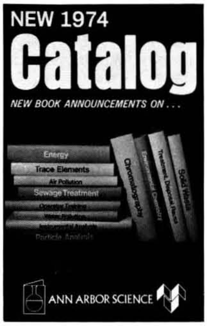
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MEETING GUIDE

March 18–20 Salt Lake City, Utah
Physiological and Toxicological Aspects of Combustion Products. National Academy of Sciences, Committee on Fire Research and other

Contact: I. N. Einhorn, Div. of Materials Science and Engineering, U. of Utah, 2020 Merrill Engineering Bldg., Salt Lake City, Utah 84112

March 20–22 Houston, Tex.
Artificial Reefs Conference. Texas Coastal and Marine Council and others

Covers experiences and opportunities in enhancing the marine environment. *Contact:* Joe C. Moseley, Executive Director, Texas Coastal and Marine Council, Box 13407, Austin, Tex. 78711

March 25–27 Rochester, N.Y.
Agricultural Waste Management. Cornell University

Write: Agricultural Waste Management Program, 207 Riley Rd., Cornell U., Ithaca, N.Y. 14850

March 26–27 Champaign, Ill.
Fourth Illinois Water Resources Conference. American Water Resources Association

Theme is "A Decade of Progress in Water Resources." *Contact:* Z. A. Saleem, 2456 SES, U. of Illinois, Box 4348, Chicago, Ill. 60680

March 26–27 Columbus, Ohio
Land-Use Planning. Battelle Columbus Laboratories

Contact: J. M. Griffin, Battelle, 505 King Ave., Columbus, Ohio 43201

March 27 Washington, D.C.
APCA Government Affairs Seminar. Air Pollution Control Association

Theme is "Clean Air and Energy—What Next." *Write:* APCA, 4400 5th Ave., Pittsburgh, Pa. 15213

March 29 Honolulu, Hawaii
April 19 Memphis, Tenn.
Quality Control Conference. Professional Engineers in Private Practice

Write: NSPE/PEPP, 2029 K St., N.W., Washington, D.C. 20006

March 31–April 3 Denver, Colo.
Thirty-Ninth North American Wildlife and Natural Resources Conference. Wildlife Management Institute

Theme is "Balancing Environmental and Economic Goals." *Write:* WMI, 1000 Vermont Ave. N.W., 709 Wire Bldg., Washington, D.C. 20005

April 1–3 Austin, Tex.
Virus Survival in Water and Waste Water Systems. University of Texas

Write: Engineering Institutes, c/o Division of Extension, P.O. Box K, U. of Texas, Austin, Tex. 78712

April 1–4 Detroit, Mich.
1974 WWEMA Industrial Water and Pollution Conference and Exposition. Water and Wastewater Equipment Manufacturers Association

Contact: Robert Hughes, WWEMA, 744 Broad St., Newark, N.J. 07102

April 2 Valley Forge, Pa.
Annual Industrial Air Pollution Control Seminar. Rossnagel & Associates

Write: R&A, 1999 Rt. 70, Cherry Hill, N.J. 08003

April 2–4 Pittsburgh, Pa.
Joint Railroad Conference. American Society of Mechanical Engineers and others

Write: ASME, 345 E. 47th St., New York, N.Y. 10017

April 7–9 Lake Geneva, Wis.
Mid-Western Regional Conference. Environmental Management Association

Western Regional Conference will be held April 22 at Monterey, Calif. *Write:* EMA, 1710 Drew St., Clearwater, Fla. 33515

April 7–11 Chicago, Ill.
Scanning Electron Microscopy 1974. IIT Research Institute

Tutorials will be held before and during symposium. *Contact:* Om Johari, IITRI, 10 W. 35th St., Chicago, Ill. 60616

April 8–10 Athens, Ga.
Identification and Transformation of Aquatic Pollutants. EPA and others

Write: Wayne Garrison, S.E. Environmental Research Lab, College Station Rd., Athens, Ga. 30601

April 8–10 Boston, Mass.
Symposium on Fabric Filtration for the Collection of Fine Particulates. EPA and other

Write: L. M. Seale, GCA/Technology Div., Burlington Rd., Bedford, Mass. 01730

April 9–15 Pacific Grove, Calif.
Stack Sampling and Monitoring. Engineering Foundation

Write: Engineering Foundation, United Engineering Center, 345 E. 47th St., New York, N.Y.

April 16–19 Monterey, Calif.
Fifth National Food Processing Waste Symposium. EPA and others

Emphasizes recycling of food processing wastes to abate air, water, or soil pollution. *Write:* National Canners Association, 1950 6th St., Berkeley, Calif. 94710

April 16–19 New Orleans, La.
1974 TAPPI Environmental Conference. Technical Association of the Pulp and Paper Industry

Write: J. E. Doherty, TAPPI, 1 Dunwoody Park, Atlanta, Ga. 30341

April 18 Washington, D.C.
Congressional Views on Pollution Control. International Association for Pollution Control

Write: IAPC, 4733 Bethesda Ave., Suite 303, Washington D.C. 20014

Courses

March–December New York, N.Y.
Seminars: Plastics, Metals, Packaging. New York University

Three or five days in length. *Write:* NYUSCE, Registration Office, Rm. 3700, 600 3rd Ave., New York, N.Y. 10016

March 20–21 San Francisco, Calif.
Managing and Monitoring Environmental Impact Statements. University of California Extension

Fee: $100. *Write:* Continuing Education in Engineering, U. of Calif., 2223 Fulton St., Berkeley, Calif. 94720

March 25–27 Dallas, Tex.
Data Communications Interface 74. Data Communications Interface

Fee: $40/day or $80/3 days. *Write:* William Saxton, Data Communications Interface, 160 Speen St., Framingham, Mass. 01701

March 25–29 Richmond, Va.
Eighth Institute on Noise Control Engineering. Institute on Noise Control

Fee: $400. *Contact:* James Botsford, Director, Institute on Noise Control, Inc., P.O. Box 3164, Bethlehem, Pa. 18107

March 26–29 Washington, D.C.
Management of Municipal Solid Waste. George Washington University

Fee: $310. *Write:* G.W.U., Washington, D.C. 20006

April 1–5 North Wales, Pa.
Liquid Analysis Instrumentation, Control and Applications. Leeds & Northrup

Fee: $325. *Write:* D. S. Luppold, L&N, North Wales, Pa. 19454

April 1–5 Columbus, Ohio
Introduction to Vibration and Shock Testing, Measurement, Analysis and Calibration. Tustin Institute of Technology, Inc.

Fee: $340. *Contact:* TIT, 22 E. Los Olivos St., Santa Barbara, Calif. 93105

April 1–5 Cleveland, Ohio
Industrial Noise Control Seminars. B&K Instruments, Inc.

Other noise courses offered at different dates. Fee: $200. *Write:* B&K Instruments, 5111 W. 164th St., Cleveland, Ohio 44142

April 1–5 Nashville, Tenn.
Development of Design Criteria for Wastewater Treatment Processes. Vanderbilt University

Fee: $300. *Write:* W. W. Eckenfelder, Box 6222, Station B, Vanderbilt University, Nashville, Tenn. 37235

April 1–5 Research Triangle Park, N.C.
Atmospheric Sampling. Air Pollution Training Institute

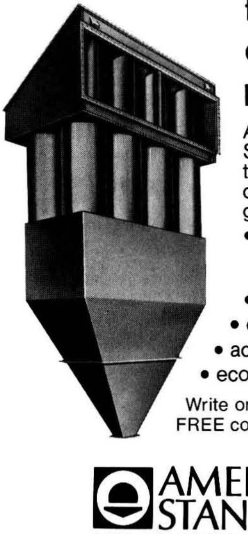
Other courses are offered during April. *Write:* APTI, Research Triangle Park, N.C.

April 4–5 Pittsburgh, Pa.
Stack Sampling. Research Appliance Co.

Other courses held at different times. *Write:* R. J. Bulger, RAC, Rt. 8, Gibsonia, Pa. 15044

April 16–18 Washington, D.C.
Problems of OSHA Compliance. George Washington University

Fee: $250. *Contact:* Continuing Engineering Education Program, G.W.U., Washington, D.C. 20006



International

March 25–29 Paris, France
Pollution Control Equipment Exhibition. Department of Commerce, U.S. Trade Center

American manufacturers and suppliers of equipment for the control of air and water pollution, noise abatement, sewage treatments and solid waste disposal can display their products to the French market. *Write:* John L. Wolf, U.S. Department of Commerce, Room 1009, Washington, D.C. 20230

March 28–29 London, England
Recent Analytical Developments in the Petroleum Industry. Institute of Petroleum

Contact: C. H. Maynard, Assistant General Secretary, IP, 61 New Cavendish St., London, W1M8AR, England

April 2–5 Montreux, Switzerland
Second European Electro-Optics Conference. Mack-Brooks Exhibitions Ltd.

Write: Mack-Brooks, 62–4 Victoria St., St. Albans, U.K.

April 17–19 Lincoln, Neb.
International Livestock Environment Symposium. American Society of Agricultural Engineers and others

Contact: Roger Castenson, ASAE, 2950 Niles Rd., St. Joseph, Mich. 49085

April 22–26 London, England
International Heating, Ventilating and Air Conditioning Exhibition. Heating, Ventilating and Air Conditioning Manufacturers' Association

Write: British Information Services, 845 3rd Ave., New York, N.Y.

April 23–24 Washington, D.C.
Seventh International Water Quality Symposium. Water Quality Research Council

Theme is "Declining Quality of Life." *Contact:* DXM Co. Inc., 237 E. Rocks Rd., Norwalk, Conn. 06851

Call for Papers

April 1 deadline
Fourth Mineral Waste Symposium. IIT Research Institute and other

Conference will be held May 7–8, in Chicago. Emphasis is on recovery, utilization, and disposal of wastes. *Write:* S. A. Bortz, IITRI, 10 W. 35 St., Chicago, Ill. 60616

April 15 deadline
Inter-Noise 74. Institute of Noise Control Engineering

Conference will be held in Washington, D.C. from September 30–October 2. *Contact:* J. C. Snowdon, Applied Research Lab., Penn State University, P.O. Box 30, State College, Pa. 16801

April 30 deadline
1974 Earth Environment and Resources Conference. IEEE and others

Conference will be held in Philadelphia, Pa., from September 10–12. *Write:* E. P. Mercanti, 12415 Shelter Lane, Bowie, Md. 20715

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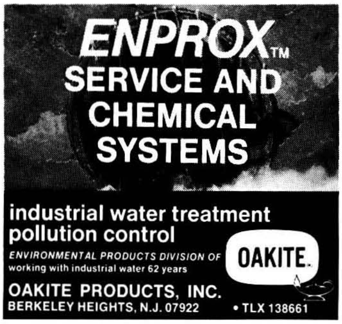

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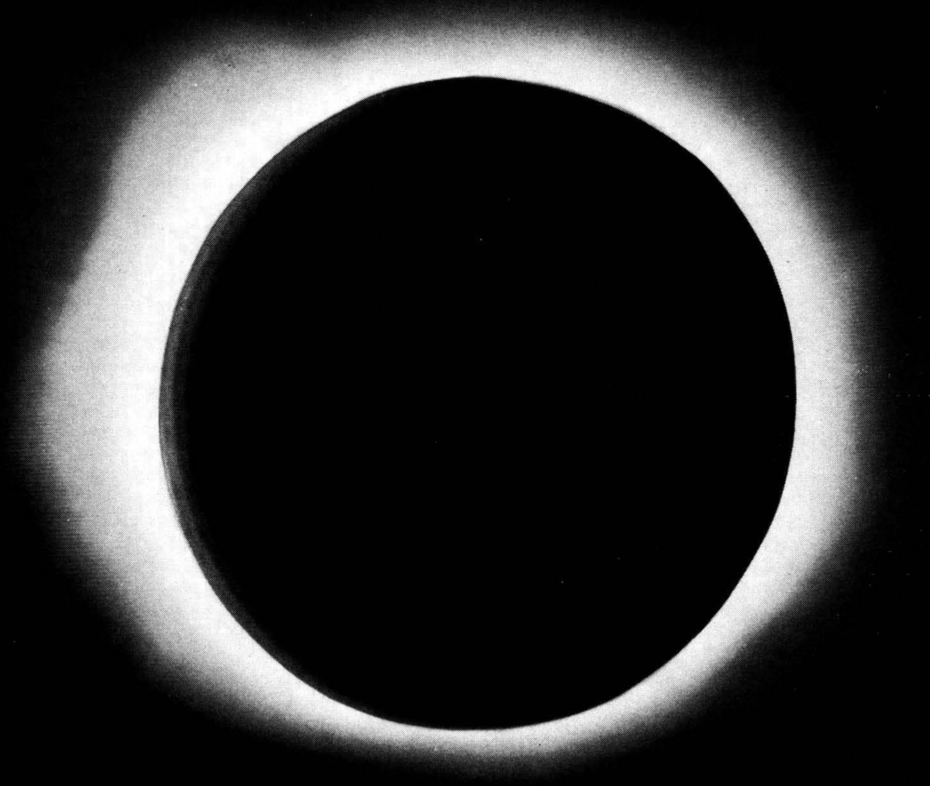

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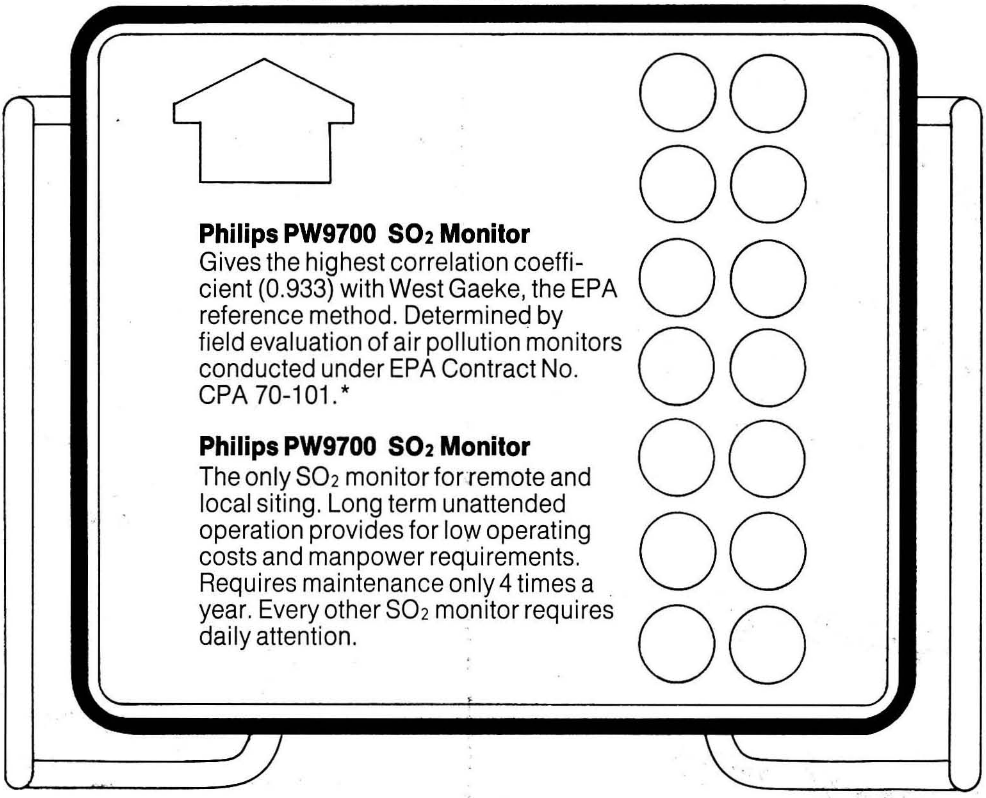

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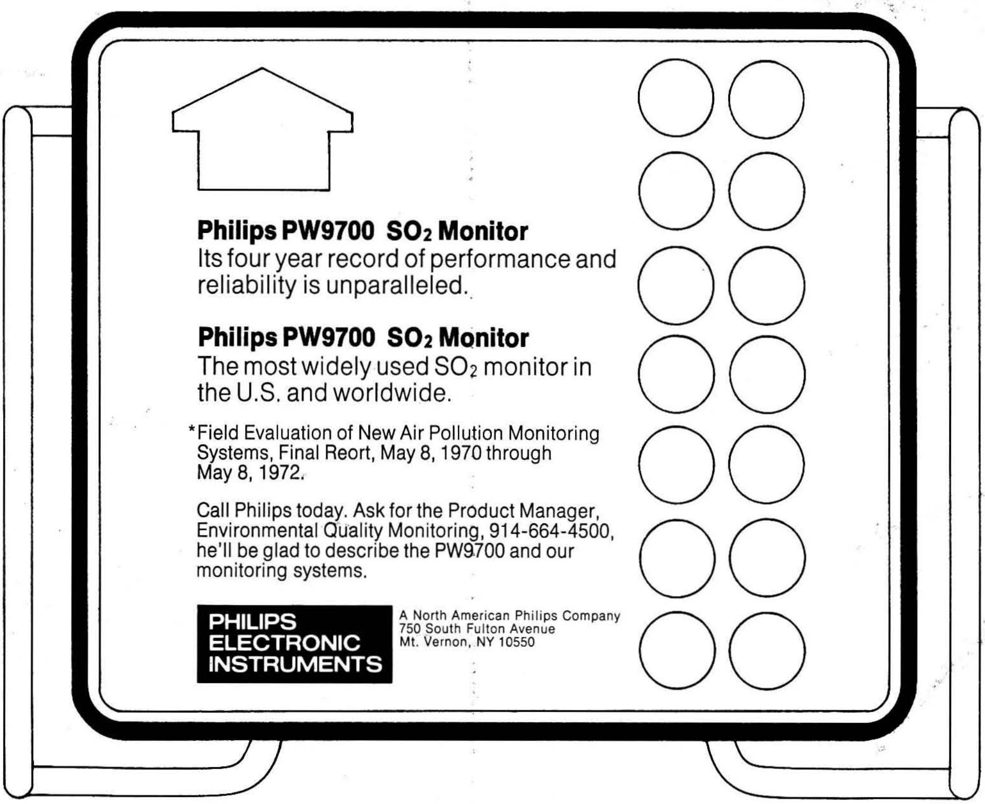

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