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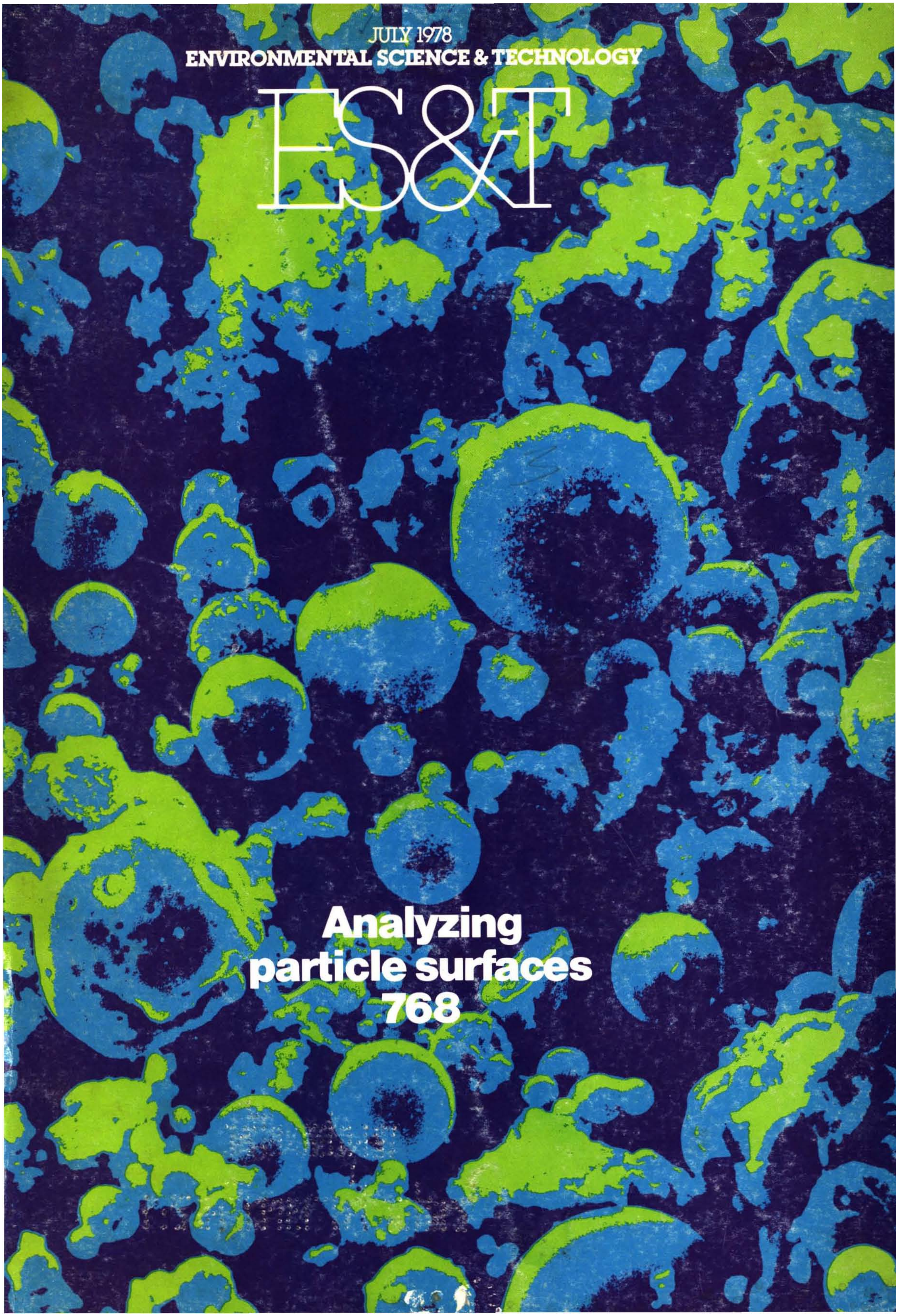

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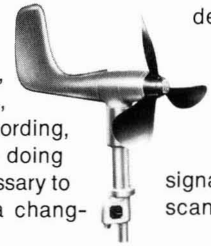
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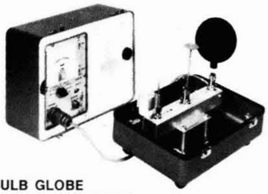
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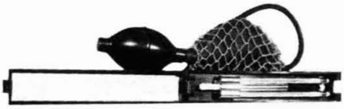
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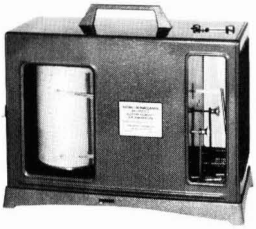
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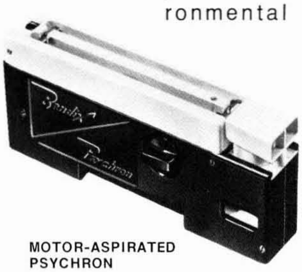

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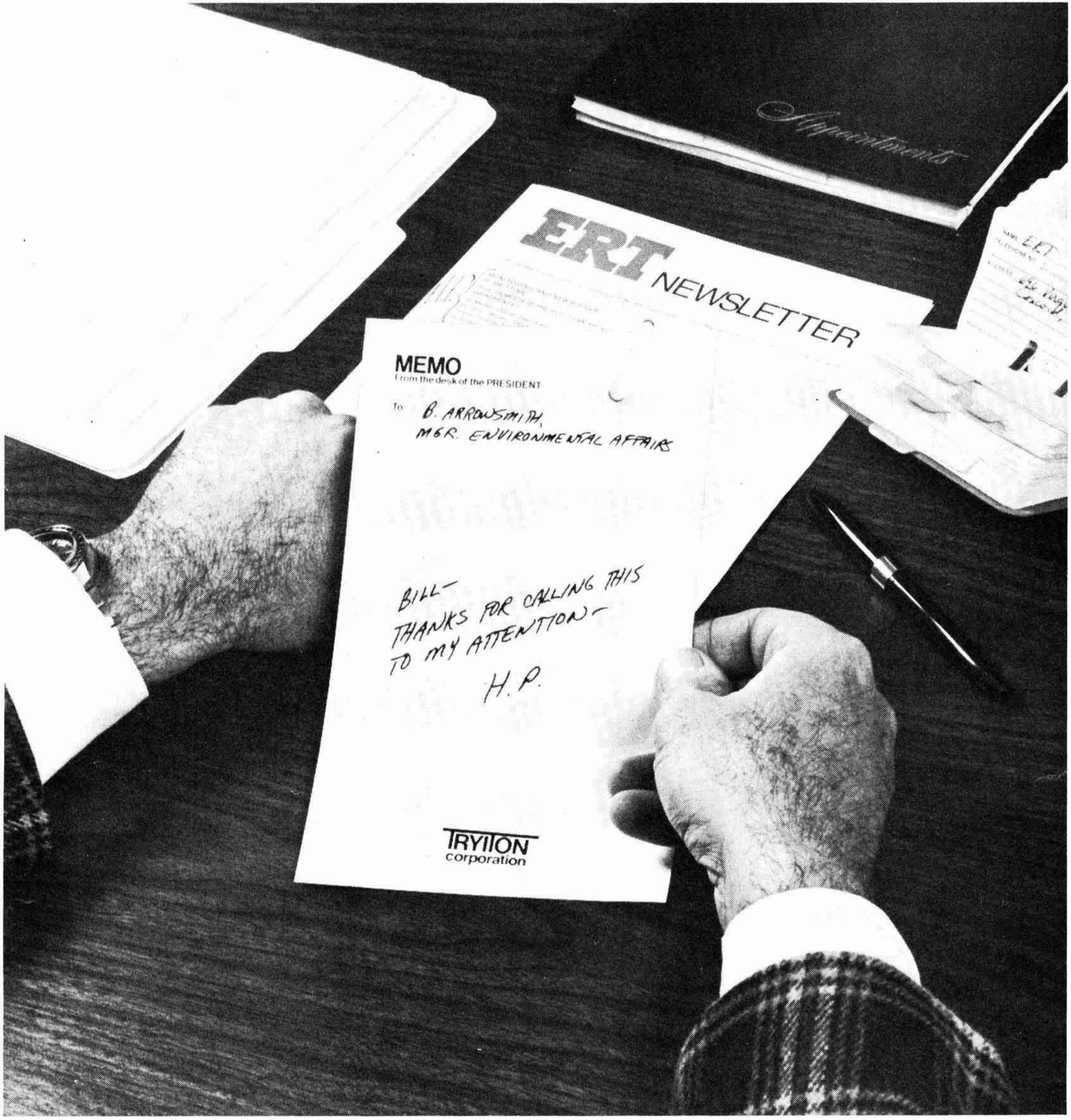
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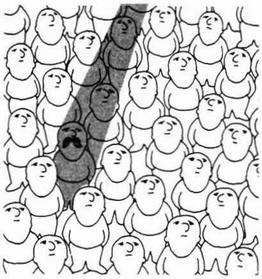

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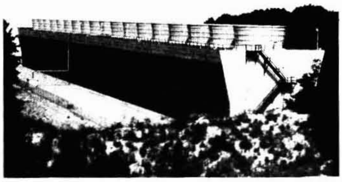

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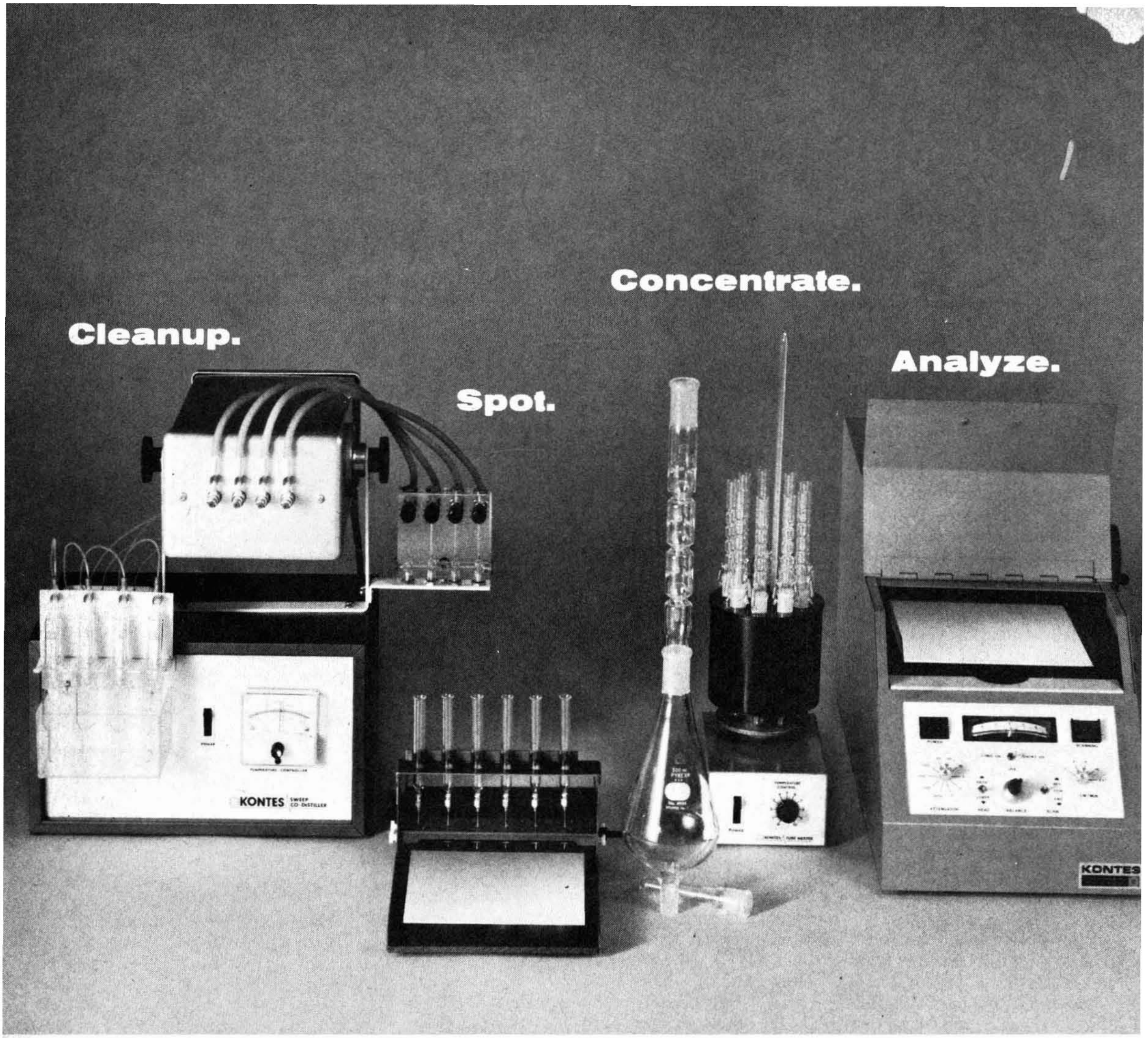
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Progress in water quality

Legislative achievements over the past decade have established the framework for the preservation of aquatic environments and the protection of human health. In the broadest terms our goal is now the maintenance of life—what Russell Train has referred to recently as the "bottom line" of our efforts in pollution control. We have seen an evolution of understanding in water quality over the past fifty years, from early concern with the major aquatic cycles of oxygen, carbon, and nitrogen in rivers, and with the control of waterborne diseases, to awareness of eutrophication of water by excessive discharge of nutrients such as phosphorus, and, during recent decades, to growing recognition of potential hazards for humans and ecosystems brought about by uncontrolled release of synthetic compounds and toxic metals.

Very recently, we have come to recognize that transformations in the environment, as in the example of mercury, and unanticipated side reactions in our treatment technologies, as in the chlorination of water supplies and wastewater effluents, can have very dangerous consequences. Thus, even with accomplishments of improved water quality in the "macroscopic" sphere of total suspended solids, organic carbon (BOD), nutrients, and the traditional pathogens, we now face very significant uncertainties in the "microscopic" sphere—a variety of carcinogens from many sources, chronic toxicants of several kinds, and possible contamination by viruses.

The challenge presented to scientists and engineers in the water-quality field is to sustain past accomplishments and to progress to a deeper understanding of the behavior of threats in the "microscopic" sphere. The problems in this sphere require far more scientific attention than they have received so far. From a scientific perspective, we need to continue to "get small", "get specific" and "get particular." In the field of air quality it has become more and more useful to define sources, transport, transformations, and exposure of receptors in terms of molecular forms and size distributions of particles. Developments along parallel lines are underway in aquatic chemistry. These need to be expanded.

Environmental lead contamination of the ocean illustrates sharply the need to "get small" in measuring levels of nanograms and less to define contamination levels. Arsenic, copper, trihalomethanes, mercury, and a variety of synthetic organics illustrate the importance of getting "specific" with respect to molecular forms in water. The fate of adsorbed trace metals and particulate organic pollutants is strongly influenced by coagulation and sedimentation processes in water. It matters a great deal where these substances are found with respect to particle sizes, both in the natural environment and in treatment processes.

It is sometimes said that our concern over pollutants at low levels has been brought about merely by analytical developments, but has little to do with real effects in the biosphere and with human hazards. Far from it. It seems more likely that for many potentially harmful species and particulate forms we have not yet attained the levels needed. The way to the criteria we need is through a deeper understanding of molecules and particles.

James J. Morgan

Dr. James J. Morgan *is currently professor of Enviromental Engineering Science and executive officer for the graduate program in Environmental Engineering Science at the California Institute of Technology, Pasadena, Calif.*

ES&T LETTERS

Aerosols & sulfate particles

The article "What are aerosols made of?" (*ES&T*, April 1978, p 374) covered progress in studies of aerosol composition reported at the mid-winter meeting of the American Meteorological Society. Related to that article, a March 20–22, 1978 Conference on Carbonaceous Aerosols at Lawrence Berkeley Laboratory in Berkeley presented a great deal of progress in this special area of aerosol research.

A major focal point of the latter conference was the possible importance of carbon soot particles in the conversion of SO_2 to sulfates and sulfuric acid. Gas-phase reactions of OH, HO_2 and similar photochemically produced radicals seem capable of accounting for the typical 1–2%/h conversion rate on warm, sunny days. Yet another mechanism must surely be important during Fall and Winter episodes, which are often accompanied by low temperature, haze and little sunlight. The "dirty water" mechanism, involving SO_2 oxidation by dissolved O_2 in droplets, catalyzed by Fe, Mn or V ions, has long been suggested, but as yet not quantitatively established as being important.

In 1973, Novakov et al. at Berkeley reported that SO_2 could be catalytically oxidized in the laboratory on carbon soot particles. The importance of this mechanism in the field, however, was not established.

Recently, at the 4th Conference on Environmental Sensing (New Orleans, November 1977) and at the Berkeley conference, Novakov et al. reported several observations that strengthen the case for the importance of the soot mechanism:

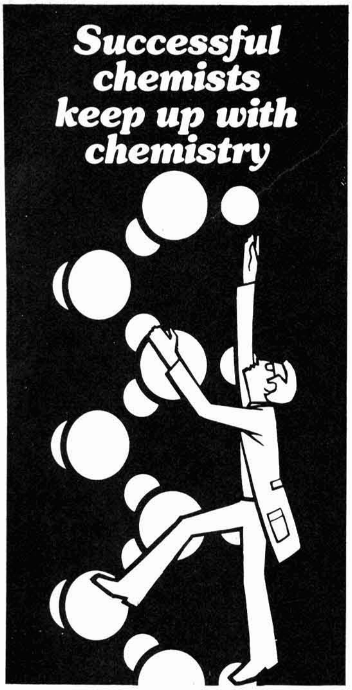
(1) Raman lines of soot are found in most ambient samples.

(2) Soot causes most of the blackness of filter deposits.

(3) Blackening correlates strongly with total carbon and the slope of the curve suggests that about half of the carbon under most conditions (photochemical and otherwise) is on primary soot particles.

(4) Soot suspended in sulfite solution catalyzes its oxidation.

(5) Sulfate/SO_2 ratios in Berkeley in Winter are comparable with those in Los Angeles in Summer, suggesting that high photochemical activity in the



latter case does not increase the oxidation rate.

Despite these advances, many controversies and uncertainties remain regarding the importance of the mechanism. For example, Daniel Grosjean (UC, Riverside) finds that the major fraction of carbon in Los Angeles area samples is soluble in organic solvents. This suggests that most of the carbon is condensed organic material (i.e., secondary) rather than primary soot, although even some primary diesel exhaust material is soluble.

There are also questions about the relative humidity (RH) at which the soot mechanism becomes active. Bruce Appel (Calif. Dept. of Public Health, Berkeley) found little sulfate to be produced on soot formed in combustion of acetylene at RH 90%. Novakov's group finds enhanced yields with increasing RH, but some yield at low RH. It's probably necessary that water be condensed on the particle, but this wasn't controlled in early experiments.

There are also many questions about the quantitative significance of the soot mechanism. How much soot is released by various sources? What is the capacity of soot, i.e., the maximum sulfate/carbon ratio? Is this enough to explain a substantial fraction of the sulfate formation in the field?

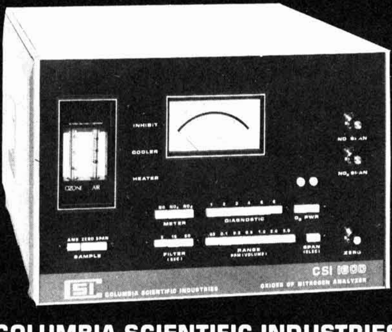
Thus, although many questions remain to be answered about this and other mechanisms for sulfate conversion, the information presented at the meeting represents a big step forward in this field. The field has at least progressed to the point that one knows the right questions to attack by further work. Proceedings of the conference will be available this Fall through NTIS.

Glen E. Gordon
University of Maryland
College Park, Md. 20742

Asbestosis

Dear Sir: Tens of thousands of people already have it; hundreds of thousands more may become afflicted. Lung diseases caused by asbestos dust are becoming one of the greatest health problems of all time. ABC News Closeup, Asbestos: The Time Bomb Explodes (Friday, July 14, 10:00–11:00 p.m.), examines the history of the disease; the steps that were, or were not, taken to protect asbestos workers, and the current enforcement of standards in industry and the United States Navy.

Phil Lewis
ABC News
New York, N.Y. 10023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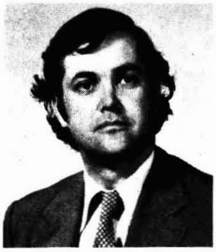
INTERNATIONAL

In a coordinated effort to clean up the Great Lakes, the U.S. and Canada have reached an agreement, not yet final, that revises the 1972 Great Lakes Water Quality Agreement. This new agreement, which has no force of domestic law, strengthens pollution control guidelines for phosphorus and toxic substances, and brings the entire Great Lakes Basin under surveillance. Under the agreement, a toxic substance is defined as any substance having a half-life of eight or more years that causes disease or death to an organism. The new phosphorus guideline calls for a reduction in phosphorus discharges to the lakes from 20 000 to 11 000 metric tons in 1978. Municipal sewage treatment plants must comply with the terms of the agreement by Dec. 31, 1982; industries must establish pollution prevention programs by Dec. 31, 1983.

WASHINGTON

The EPA issued final regulations on procedures by which it may veto issuance of state NPDES permits, and incorporate new effluent limitations, new source performance standards and pretreatment standards for 65 toxics from the 21 industrial source categories. These regulations incorporate the requirements of the consent decree in NRDC *v*. Train. The final regulations (40 CFR 124.46) clarify the criteria EPA will use in exercising its veto power under state-issued National Pollutant Discharge Elimination System permits. NPDES permits will now include "reopener clauses" to reflect new effluent limits on toxic pollutants.

Pending before the Justice Dept. are 10–12 criminal cases under the Clean Water Act and 5–6 criminal cases under the Clean Air Act. According to Angus MacBeth, chief of the Justice Dept.'s Pollution Control Section, the department is considering around 100 criminal cases referred by the Army Corps of Engineers on water pollution cases. MacBeth says that "The Government means business on the criminal side," but it will not adopt "a frivolous attitude toward the criminal law, nor one that strains to press the laws to the outer limits."


Justice's MacBeth

In the near future the focus of federal pollution control activities is expected to be on the disposal of toxic and hazardous materials, and on falsification of data and reports submitted to the government.

The EPA is conducting a 400-county, rural drinking water survey that will include interviews with individuals in these areas and analysis of household water samples. The survey is required under the Safe Drinking Water Act. On another matter concerning rural America, the EPA and the Dept. of Agriculture have reached an agreement on how to set up a new Rural Clean Water Program, which is authorized by the 1977 Clean Water Act. The program will provide federal cost-sharing assistance to farmers to help solve water pollution problems caused by agricultural activities. Under the Clean Water Act, Congress authorized $200 million in fiscal 1979 and $400 million in fiscal 1980 to enable the Agriculture secretary to enter into long-term contracts with rural landowners/operators for the purpose of installing and maintaining best management practices to control nonpoint source pollution.

DOE's report, "Voluntary Business Energy Conservation Progress Report 6," cites a 9.2% improvement in energy savings by 48 industrial and business groups for the first half of 1977 compared to 1972. Participating in the DOE program are over 3000 business firms, which represent more than 50% of the total U.S. industrial energy use. The report cites significant efficiency gains, despite the severe 1977 winter, in the chemicals and petroleum industries. Total improved efficiencies were equivalent to 667 000 bbl/day of oil. Donald A. Beattie, acting assistant secretary for Conservation & Solar Applications, said that he was impressed by the "disciplined approaches being used to achieve conservation goals." On another matter, DOE has established an Office of Nuclear Waste Management in the Office of the Assistant Secretary for Energy Technology.

The NBS has more than 50 Standard Reference Materials (SRM) and methods useful in air pollution measurements. EPA, whenever possible, requires that calibration methods used in air pollution reference methods be traceable to the National Bureau of Standards SRM's. SRM's have been developed for ambient air monitoring, stationary source monitoring, the automobile industry and for special measurement problems. In this latter area, the NBS has been working on SRM's and standard methods for monitoring chlorofluorocarbons and vinyl chloride. NBS developed a measurement standard in the form of an UV photometric instrument for monitoring ozone at ground level. The bureau is now developing SRM's for physical and chemical characteristics of atmospheric particulates 1 μm in size or smaller.

OSHA has directed its field staffs to continue to conduct workplace inspections using the method of scheduling in force prior to the

May 23 Supreme Court decision, but to seek a warrant whenever an employer refuses inspector's entry. Assistant secretary of labor for occupational safety and health, Eula Bingham, said that "compliance safety and health officers have been instructed to deal with such refusals in a courteous and responsible manner, leave the premises promptly, contact Labor Department attorneys, and obtain a warrant as quickly as possible." A recent GAO report stated that OSHA's and the States' workplace inspection programs are weak in detecting and correcting serious hazards.

STATES

Michigan now has a law that bans the disposal and storage of radioactive wastes. The bill became effective immediately after Governor William G. Milliken signed it. The bill was the state's response to the Dept. of Energy's search for a nuclear waste disposal site in Michigan. The state was concerned that a large groundwater aquifer was located near DOE's exploratory drilling site. Under the new law, exceptions to the radioactive ban include educational institutions, temporary storage, material stored at nuclear power plants, material used for medical purposes and material stored safely before January 1, 1970. A second companion law blocks federal designation of a Michigan disposal site.

Mich. governor Milliken

Virginia has abandoned plans to burn Kepone wastes in Hopewell, Va., because of strong public protest. The fate of the wastes is still undecided. An Allied Chemical Corp. plan to ship the wastes to Wales for incineration has been postponed because of objections from the British government. The EPA and the Army Corps of Engineers are studying Japanese dredging techniques to determine if they are suitable for Kepone removal from the James River.

Arizona reports a "dramatic" reduction in auto emissions which it attributes to its vehicle emissions inspection and maintenance (I/M) program. Tailpipe emissions in 1977, as compared to 1976, showed a 41% reduction in hydrocarbons, and a 25% reduction in carbon monoxide, both measured at idle. The average cost of repairs on a vehicle failing the initial test was $23.02; more than 1 million vehicles were tested last year. The report released by the Dept. of Health Services' Bureau of Vehicular Emissions Inspection estimates that gasoline consumption can be reduced by 30–35 million gallons/y as a result of improved vehicle maintenance. Because of this I/M program, the state expects to be in compliance with carbon monoxide standards in 1982, and by 1985 for other vehicular emissions pollutants.

Spending federal funds for secondary treatment projects in the St. Louis, Mo., area would "only minimally improve the quality of water in the Mississippi River," a recent GAO report declares. Planned expenditures for construction of two municipal secondary treatment facilities are pegged at $163 million. Secondary treatment of discharges to fresh water is required under the Clean Water Act; municipalities are required to fund secondary treatment projects before they may finance alternative pollution control projects, which may have greater potential for improving water quality and use of streams. The General Accounting Office, therefore, recommended that Congress amend the law to eliminate the mandatory requirement for secondary treatment.

The Metropolitan Denver Sewage Disposal District's project to turn sewage sludge into a marketable fertilizer will be funded 75% by federal funds, but it still must be approved by the Adams County Board of Commissioners, which is reluctant to approve it. The project, which involves transporting sludge by pipeline to a site 20 miles east of the Rocky Mountain Arsenal where it will be dried and prepared for sale, is estimated to cost $22 million.

MONITORING

What are ways of extracting toxicants from suspect wastes for analysis? EPA and the American Society for Testing and Materials (ASTM) D 19.12 subcommittee are helping to answer that question with a Toxicant Extraction Procedure now in draft stage. Instructions for processing and pH adjustments are very detailed. Analyses would be for toxicity and other hazards, mutagenicity, bioaccumulation, and whatever additional items are called for. Also, there would be degradation tests. An analytic option is now being developed, and the future will bring a bioassay option, and field simulation tests.

TECHNOLOGY

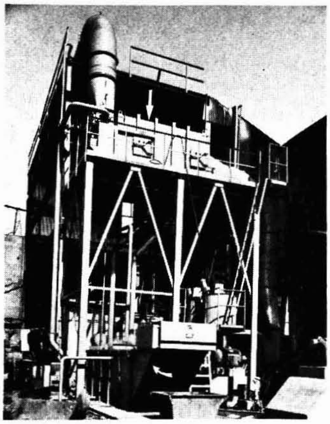
Irrigation of poplar, and other trees with oxidation pond effluent was tried at certain Michigan sites by the U.S. Forest Service. Generally, poplars, ash, and red oak did best. However, much of what tree mortality occurred was not so much from wastewater irrigation, as from a number of disease and pest infestations, and drought.

An engine using no fossil fuels is the subject of U.S. Patent No. 3,977,191, granted to Powerlines Corp. (Wilmington, Del.). It uses lasers in the 10^{15}–10^{18}-Hz frequency range in pressure chambers containing all atmospheric gases except oxygen. The company calls the process the Atomic Expansion Reflux Optics Power Source.

A total solar electric village will be established for the Papago Indian Tribe at Schuchuli, Ariz., by the U.S. Health Service and NASA, with Dept. of Energy (DOE) funding. Power from the photovoltaic (3 kW peak) system should start flowing to Schuchuli's 96 residents by September.

Total water/air pollution control for industrial process exhausts was announced by Environeering, Inc., a subsidiary of the Riley Co. (Park Ridge, Ill.). A particulate scrubber captures particles in a water spray. Scrub liquor is then clarified and flocculated in such a manner that discharge to a sewer is unnecessary. Environeering says that particulate removal efficiency for difficult wastes needing disposal, such as


CYANIDE



Particulate scrubber system

sugar cane waste (bagasse), taconite waste, liquid waste, and many others, reaches 98%. Gas volumes of 1000-600 000 acfm can be accommodated, and water clarification tanks of 1000, 1500, 2500, or 4000 gal (more on special order) are available.

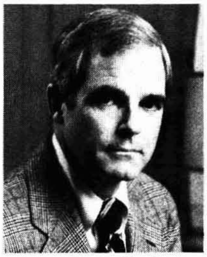
Electroplating with a 90% reduction in chemical waste, and a 97% cut in gaseous exhaust, has been announced by Bell Telephone Laboratories (Murray Hill, N.J.). Bell Labs also says that gold use is halved, and production output is increased by as much as 600%. The key is to carry out all plating jobs in small, totally enclosed cells, rather than in conventional open vats. Cells are in a straight line, and are coupled to a "mother tank" containing necessary chemicals and control devices. Most water is recycled. Cells can handle a number of jobs independently. Bell's Western Electric is using this technique at Dallas, Tex., and plans it for Kansas City.

The electric car may be a step closer, if the cost of lithium-metal sulfide batteries can be brought down. The aim is to have a 5.6-MW load-leveling battery module by 1984. Argonne National Laboratory (Ill.) let a $1.1 million contract to Eagle-Picher Industries (Joplin, Mo.) to build such an advanced battery. And as for conventional cars, a flywheel added to a 1976 Ford Pinto gave 50% better "gas" mileage in city driving, according to two University of Wisconsin (Madison) engineers. The flywheel stores energy normally wasted during braking, idling, and other operations of the car engine at low power, and can deliver 250 hp for acceleration purposes, after being easily primed to 9000 rpm.

One way that paper mills could get away from using mercury, which poses serious pollution problems, was with Du Pont's "Nafion" perfluorosulfonic acid membranes. These are used in electrochemical cells, such as those which produce chlorine at paper mills. The membranes separate the anolyte and catholyte, and provide selective passage to various chemical ions. This technique removes the need for mercury.

INDUSTRY

Among laws that could hamper the effort to bring about use of coal in a timely fashion, and at reasonable prices, are the new clean air and surface mining laws, Robert Quenon, president of Peabody Coal Co., told the National Energy Forum VI held at Washington, D.C. He said that the Administration, which supports these laws, while simultaneously advocating increased reliance on coal, must resolve this dichotomy, if coal is to play any meaningful part in the U.S. energy matrix. The Forum at which Quenon spoke was sponsored by the U.S. National Committee of the World Energy Conference (*ES&T*, December 1974, p 1069).



Peabody Coal's Quenon

The world's largest application of the Davy/Wellman-Lord SO_2 removal process was completed at the San Juan Power Plant of Public Service of New Mexico. The scrubbers, growing out of a $120 million pollution control project, will use sodium sulfite as the principal scrubbing medium. Treating 1.8 million scfm, they will produce elemental sulfur, sulfuric acid, and salt cake by-products from which PNM and Tucson Gas & Electric hope to realize $2.01 million/y in earnings by 1981. Moreover, scrubber sludge disposal costs would be eliminated. The system was developed by Davy Powergas (Lakeland, Fla.), and it will remove 90% of the SO_2.

Total wastewater treatment (wwt) equipment shipments should be about $1.5 billion by 1983-1985, according to William T. Lorenz & Co., management consultants of Boston, Mass. These shipments totaled $750 million in 1977. However, the firm foresees a sluggish period near-term, partly because of a "best available" (BAT) delay to 1984, and softened BAT requirements, except for toxics. However, shipments would pick up substantially during 1981-1984 as BAT deadlines come closer, and toxic pollutant standards must be met, according to Lorenz. The firm also sees more municipal spending on wwt equipment, as funding logjams break, say, by late 1979.

The present Administration is contributing to the nuclear industry's stagnation, Joseph Dietrich, chief scientist for Nuclear Power Systems, C-E Power Systems, told the National Energy Forum VI. C-E Power is a part of Combustion Engineering, Inc. Dietrich called for passage of a "good nuclear licensing reform bill," to reduce licensing times, and regain some of the capacity growth lost through cancellations and deferments of nuclear plants. He called for government policies to encourage the industry, and said that a "vigorously growing" nuclear power capability "is essential to the welfare of the nation."

No combination of conservation and alternative energy sources can supply New Jersey's energy needs through the year 2000, Robert Smith, chairman of Public Service Electric and Gas Co. (Newark, N.J.) warned. He said that coal and nuclear should meet part of the demand, and that nuclear was environmentally and economically more advantageous than coal. However, he also advocated pursuit of solar, but expressed little optimism for any important solar contribution in the immediate future. Smith also noted that his utility is active in power production from solid waste, and is looking into energy from landfill gas, and from cogeneration.

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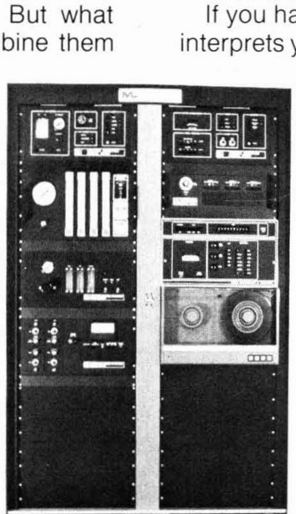

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OUTLOOK

Waste: a hot item these days!

At a photographic equipment company, a paper mill, and a wastewater treatment facility, heat from waste is reducing fuel bills

Industries of all types, and municipalities as well, are under heavy pressure to conserve energy. Apparently, they have been responding, for generally, industrial energy use today is less than what it was in early 1973. Indeed, one business publication quoted a 32% reduction. But even if that percentage may be somewhat exaggerated, conservation continually improves, and one method of bringing about such improvement is solid, liquid, and gaseous waste incineration.

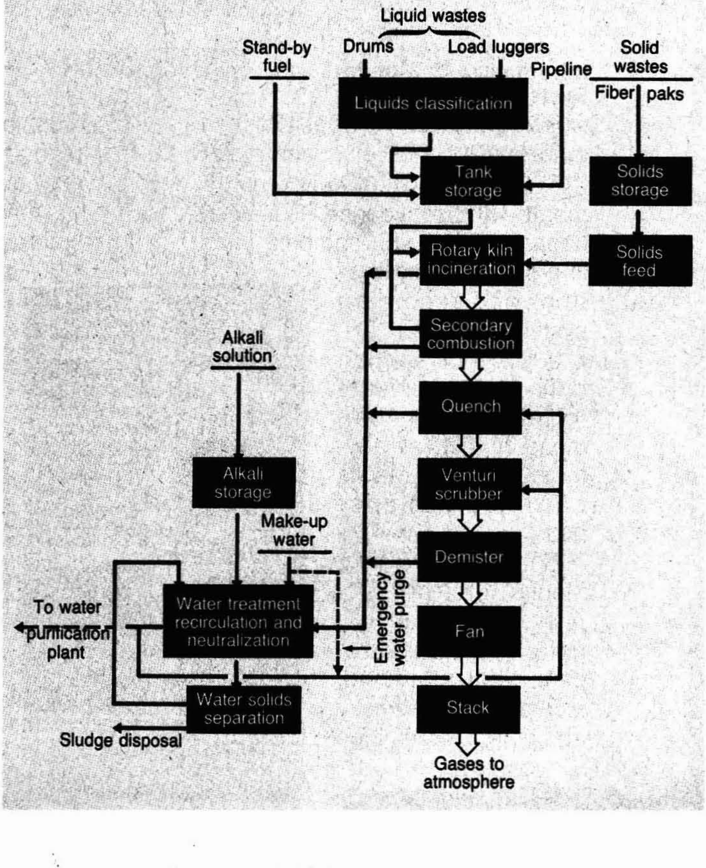
The use of waste to save energy has developed into a significant technology. On the occasion of the 8th Biennial National Waste Processing Conference and Exhibit, sponsored by the American Society of Mechanical Engineers, that technology was discussed and shown at Chicago, Ill. It is noteworthy that the conference's theme was, "Energy Conservation through Waste Utilization."

A variety of wastes

An installation at Eastman Kodak Co. (Rochester, N.Y.), which started up in January 1976, will give a picture of how the burning of liquid and solid wastes reduced No. 2 fuel-oil usage in just 2.5 years of operation. On a heat-value basis, this reduction was from 13% (1976) to 4% (1977). Kodak's Ron Bastian explained that the need to upgrade on-site chemical waste incineration facilities led the giant photographic firm to decide, during the early 1970's, to have a new thermal oxidation facility designed and constructed.

Accordingly, Kodak retained Hydroscience, Inc., a wholly-owned subsidiary of The Dow Chemical Co. (*ES&T*, January 1975, p 22), to provide such a facility. It was designed for a total heat-release rate of 90 million Btu/h. That heat-release rate translates into about 9 million gal/y of liquid waste, and 6 million lb/y of solid waste, Bastian said. Under full waste load, the facility operates with a venturi pressure drop of 65 in. of water, across the gas scrubber.

Energy-saving waste incineration with process wastes, at a photographic company . . .

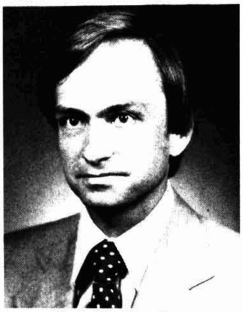


This technically advanced unit is called upon to handle a whole variety of wastes. For example, there are combustible liquid wastes consisting of various solvents, oils, and aqueous materials. Then, there are solid wastes comprising sludges, solvent-soaked filter media, and material from the laboratory. And when such wastes are burned, the incinerating unit must meet stiff requirements of the New York State air pollution laws and regulations (for example, a particulate emission limit of 0.05 gr/scf of dry gas).

A 12-digit code

Bastian said that at Kodak, wastes are not simply taken out and burned. On the contrary, each waste gets a 12-digit identification (ID) code. This ID tells where the waste was generated; gives a serial number for the waste; and charges a given department or account number for disposal. No waste is burned unless it is properly identified, and has a disposal ticket made for it.

In addition to devising the 12-digit code ID and ticket, Kodak conducted an internal survey, in order to obtain the fullest possible inventory of what wastes there are. For both solids and liquids, for example, sources, physical/chemical composition, heat value, disposal, and annual quantity and growth-rate data are compiled. Moreover, for liquid wastes, the number of layers or phases, and the composition and percent of each phase—light, water, heavy, and sludge—are cataloged. Other parameters for the waste data bank may comprise ash, water, chloride, sulfur, nitrogen, metals, and additional pertinent physical and chemical information.


Kodak's Bastian
the key is to know the waste profile

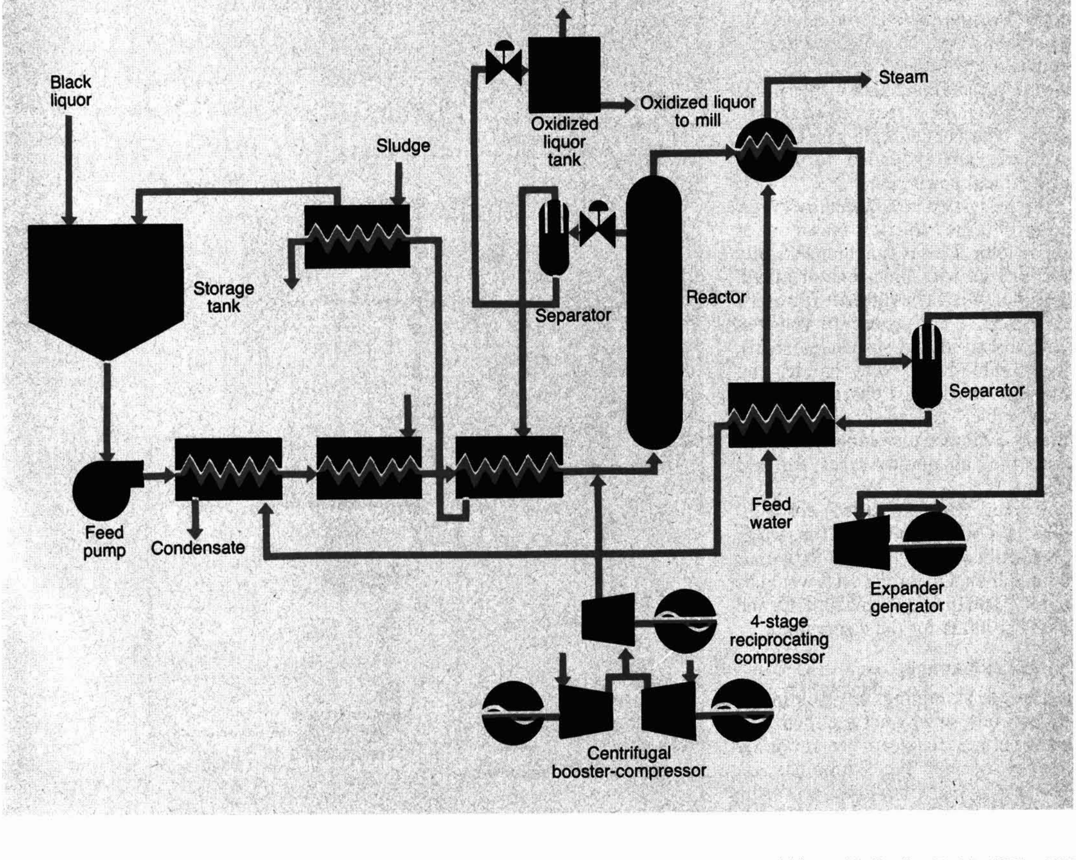
All of this cataloging seems like a great deal of effort. But it had great benefits. First of all, it led to improved incinerator design information. Secondly, it permitted computerization of waste information for easier data retrieval and manipulation. This computerization, in turn, made possible identification of a cross-section of waste materials to be test-burned in order to achieve the cleanest, most complete, and safest burnout possible.

Costs and performance

Since the waste incinerator unit started up, the average annual load has been 6–7 million gal (liquid), and 3.5–4.5 million lb (solid). Water from the demister, quench chamber, and other components, is neutralized with sodium hydroxide, and successfully recycled. Suspended and dissolved solids are controlled. Auxiliary fuel use, based on 1977 operation, should not exceed 150 000 gal/y, or 4% on a heat value basis; that figure was 13% in 1976.

Bastian and Bill Seeman of Hydroscience said that construction costs were approximately $11.3 million. Operating costs, excluding depreciation, come to $1.5 million/y, with 24 h/d, 7 d/wk operation, and 4 men/shift. Kodak is looking at reducing

. . . with wet air oxidation, at a paper mill . . .



operating costs by possibly operating the system with only one fan, and reduced scrubber venturi pressure drops, for certain selected waste profiles.

In any case, the unit that Hydroscience provided was chosen and designed specifically for Kodak's waste profile. Bastian cautions that for the design of a thermal oxidation system elsewhere, each waste profile must be evaluated separately.

Paperwork

One associates wet-air oxidation (WAO) with wastewater treatment (wwt), but not normally with energy conservation. However, Louis Pradt of Zimpro Inc. (Rothschild, Wis.) spoke of a WAO system that can be "quite competitive" with conventional steam boilers, or with fluidized-bed combustion systems. Here, waste sludges and liquors would be disposed of, concurrently with the burning of coal.

Zimpro installed similar WAO technology, of 303-gpm capacity, at a pulp and paper mill at Ontonagon, Mich. (*ES&T*, March 1978, p 249). It uses a black liquor/sludge slurry, with a stoichiometric quantity of compressed air. Heat of combustion is absorbed by water vapor leaving the reactor, together with non-condensable gases. Vapor heat is exchanged against boiler feedwater, to generate clean steam; meanwhile, most of the water condenses, and is recycled to the reactor. Non-condensable gases, under pressure, are expanded to recover mechanical power.

In the system introduced by Pradt, an ash-"brine" slurry is blown out of the reactor. This is stoichiometrically neutralized with limestone or alkali. The slurry is then filtered; filtrate is discarded. This procedure removes both dissolved and suspended solids, Pradt said. SO_x, NO_x, halide, and metal discharges are characterized as "negligible." Indeed, Pradt predicted that the Zimpro unit could be used in "pristine" air quality areas, for that reason.

Capital costs (installed) for a 50 000-lb/h WAO unit are estimated at \$4.8 million; for a 100 000-lb/h unit, \$7.4 million. Operating costs would be \$5.07/1000 lb for the smaller unit, and \$4.34/1000 lb for the larger one.

Steam and sewage

Sewage skimmings are rich in hydrocarbons, so why not use them as a source of heat for steam generation? It can be done if the skimmings are properly dewatered, and otherwise prepared. This is what Richard Petura and his colleagues at Malcolm Pirnie, Inc. (White Plains, N.Y.) designed for tertiary treatment at the Southerly Wastewater Treatment Plant (peak flow, 200 mgd) of the Cleveland (Ohio) Regional Sewer District. The design includes steam generation and associated air pollution control.

Normally, scum or skimmings from wwt plant settling tanks are incinerated, along with other wastes. However, in the Malcolm Pirnie design, skimmings (heat value of 16 000 Btu/lb) will be fired to provide the 425-psig saturated steam, at 2700 lb/h on a dry-weight basis, needed for the plant's thermal conditioning process. The skimmings themselves are mainly spent grease from soap, detergents, and service station discharges to sewers. They should furnish the bulk of the necessary heat; however, No. 2 fuel oil will always produce a minimum of 25%.

Nevertheless, the skimmings-fired boiler is expected to save 2.8 million gal/y of fuel oil. Its steam will contribute to thermal conditioning, non-potable water heating, skimmings and waste-tank farm heating, and numerous other functions. The boiler will provide up to 58% of the plant's total steam capacity. Fuel oil needs for the plant are reduced from 34.3 million lb/y to 14.3 million lb/y (oil density is 7.2 lb/gal).

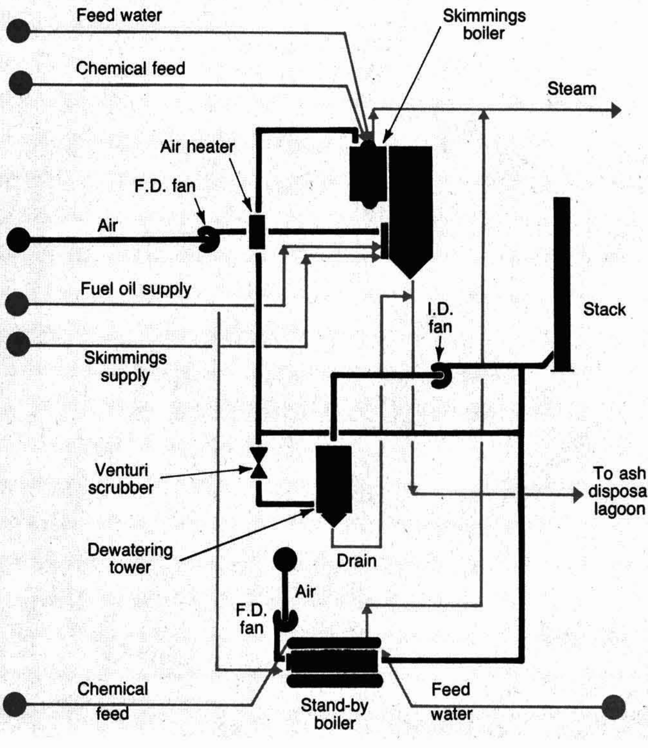
Expected advantages of skimmings as fuel are:

- elimination of the need to dispose of them, and of related liquid wastes
- ability to comply with all air emissions regulations
- elimination of oil-fired steam generators and skimmings disposal equipment; this can provide capital cost savings which, in turn, can be credited to reduce the skimmings-fired facility's capital costs.

Lessening the pain

To be sure, wwt, especially advanced wwt, will not be a low-cost item. It will require energy that is, to use a popular expression, "out of sight" these days. But development of a cost-effective technology to use liquid (or solid) wastes as a "home-made" energy source could contribute to lessening the pain in writing checks to pay fuel bills for wwt. JJ

. . . and with sewage skimmings, at a municipal wwt plant



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Trace organic analysis

This emerging discipline shows vast potential for quantifying environmental pollutants, and is likely to ease EPA's regulatory burdens

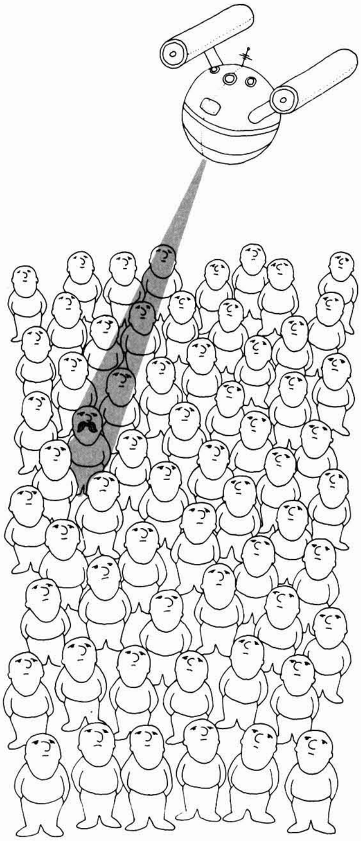
A UFO slowly circles the Earth. After several days of tracking, civilian and military aviation personnel report it hovering over a city in the Midwest. There it remains for days, seemingly poised over one particular house. Then, suddenly, it disappears, but not before it descends and engulfs the house. No trace of the house or its four occupants remains.

Out of a total world population of 4.2 billion, it would appear that the UFO searched for, found, and plucked out four people. A fantastic feat, you might think, but consider this: In chemical terms that translates to 1 ppb, and some of our most sophisticated analytical instruments are able to separate and identify a single component, present at that concentration (1 ppb), in a complex mixture of many substances.

At a recent National Bureau of Standards' (NBS) symposium on "Trace Organic Analysis: A New Frontier in Analytical Chemistry," scientists gathered to discuss the "state-of-the-art and future directions" of high-technology systems designed to detect trace levels of organic compounds in environmental samples, drugs in biological fluids and nutrients or contaminants in foods. Here the scientists spoke of spaceships, chromatographic methods, detection systems, and the male silk moth. Yes, the male silk moth.

To ward off scientific hubris, L. S. Ettre from Perkin-Elmer Corp. (Norwalk, Conn.), speaking on chromatographic methods and detector systems, described an early experiment in which a male silk moth became the very selective and sensitive detector for a gas chromatographic (GC) system.

The male silk moth was placed in a box that was connected to the GC. When trace amounts of the insect hormone, pheromone, emerged from the GC and wafted its way into the box, the male silk moth became very active. With wings aflutter, he searched wildly for the female. No other compound emerging from the GC sent the male moth into such frenzied activity. Lest man gloat over his technological wizardry, Ettre was saying, remember Nature did it first.



Despite the moth, man's analytical techniques have evolved to a state that would awe the general public. These techniques are continuingly being refined and coupled, when possible, to increase sensitivity and selectivity. And new techniques are constantly being developed.

NBS activities

In his opening remarks, NBS director Ernest Ambler explained that his agency, created in 1901 to perform research, has no regulatory function. This enables NBS to work well with other government agencies and industry.

Since 1901 the responsibilities of the agency have broadened; a fact which is reflected in its continuingly increasing budgets. This fiscal year, NBS' budget totals about $126 million. A portion of these funds, $1.1 million, will be used to support the research activities of the newly created Organic Analytical Research Division within the Center for Analytical Chemistry, which itself is part of the National Measurement Laboratory.

The Organic Analytical Research Division, headed by Harry Hertz, will certainly ease EPA's regulatory burdens by developing adequate measurement techniques, many of which do not now exist, for the more than 100 organic materials EPA must regulate.

According to Philip LaFleur, director of the Center for Analytical Chemistry, interest in trace organic analysis has increased because of the growing recognition of the:

- action and potentially adverse impact of organic materials at trace levels
- large and ever-increasing number of organic materials produced by industry.

Organic compounds of interest run the gamut: natural toxins, nutrients, hormones, pesticides, emissions from the combustion of fossil fuels, and trace levels of substances in drinking water.

The state of the art

Trace organic analysis (TOA) is now in an early stage of evolution. According to LaFleur and others at the meeting, current analytical methods are not so accurate or fully exploited, nor are they standardized.

A step toward improving the accuracy of TOA methods is the use of standard reference materials (SRM). These materials can be used to calibrate systems and assure quality control. The NBS, LaFleur said, will issue its first SRM for TOA this year. The candidate: polynuclear aromatic hydrocarbon in water.

There are seven steps in TOA—collection, storage, extraction, concentration, isolation, identification and quantification. The last three steps can be automated by using chromatography.

To improve the detection limits of current TOA methods, Harold McNair of Virginia Polytechnic Institute (Blacksburg, Va.) explained that one or all of the following must be done:

- concentrate by adsorption, partitioning, condensation or ion exchange
- inject more sample
- maximize the signal or increase the sensitivity of the detector (to achieve a high signal-to-noise ratio)
- reduce extraneous signals (noise).

Ideally, increasing the sample size would solve many problems, but this measure is not often feasible.

MS, GC/MS, LC/MS

These analytical systems are very sensitive; femtogram (10^{-15}) quantities can be detected. They are also unique in the types of samples they can handle: these may be universal or specific. The systems are available, but they are expensive, especially GC/MS (gas chromatography/mass spectrometry).

NBS' LaFleur
"a challenging area"

MS is the preferred system for TOA because of its high sensitivity and the fact that it can be universal or specific in the types of samples it handles. If there is no interference from other components in the matrix (as there would not be if the sample were sewage effluent), MS is satisfactory alone.

However, when air, water or biological samples are being analyzed, MS alone will not suffice and some type of chromatographic system linked to the MS must be considered. One such coupling is GC/MS, which is ideal for volatile compounds.

There is now one LC/MS (liquid chromatography/mass spectrometry) system commercially available (Finnigan Corp., Sunnyvale, Calif.), and McNair feels that continuous LC/MS will rapidly become available. This system is nearly universal in the type of samples it can handle, and it can be designed to handle very concentrated samples on small-volume columns. In the future, LC may be coupled to FPD (flame photometric detector) and AA (atomic absorption spectrometry).

For GC, the sample components must be volatile. Sample size must be 0.1-1.0 mg (therefore, ppm-ppb), which is this technique's major disadvantage. While the system is very sensitive, ppb analyses cannot be performed routinely. With the following detectors, these minimal detectable quantities are feasible: thermal conductivity (TC), 10^{-9} g; flame ionization detector (FID), 10^{-11} g; electron capture (EC), 10^{-13} g; nitrogen/phosphorus detector (N/PD), 10^{-12} g; flame photometric detector (FPD), 10^{-9} g (sulfur), 10^{-11} g (phosphorus). GC is, of course, readily available.

Of all the GC detectors, FID and TC are universal for organics, while all the others are very selective for the type of compounds they will detect.

The future is brightest for LC techniques. Here the sample size is not a limiting factor as it is with GC. Coupled to the various detectors, the minimal detectable quantities for LC are: UV, 10^{-9} g; electrochemical, 10^{-10} g; and fluorescence, 10^{-12} g. Sample sizes must be in the mg-g range (sub-ppm).

The UV detector is almost universal for organics, while the electrochemical detector is selective and the fluorescence detector is even more selective. LC systems are readily available.

Less promising systems

Atomic absorption spectrometry (AA) is an available system that is selective for organics, but it requires derivatization of the sample. Sample size is in the ppm range. Atomic fluorescence spectrometry (AF) can handle sample sizes in the ppm-ppb range, requires derivatization and is also selective for organics. It is not readily available, however.

Some analytical systems

Most useful

MS[a] GC/MS LC/MS
GC[b]
LC[c]

Should be considered

AA[d] AF[e] AA/GC AA/LF
NMR[f]

Not so widely used

Fluorescence
Radiochemical
Electrochemical
Plasma chromatography

[a] mass spectrometry; [b] gas chromatography; [c] liquid chromatography; [d] atomic absorption spectrometry; [e] atomic fluorescence spectrometry; [f] nuclear magnetic resonance
Source: H. M. McNair

GC could be coupled directly to AA. The resulting system, AA/GC, would be very selective—only volatile compounds could be analyzed. Such a linkage is now not commercially available.

A more promising linkage would be AA to LC. The resulting system would also be selective, but the compounds would not have to be volatile, which most organics are not. Because larger samples could be analyzed, the AA/LC system could detect sub-ppm quantities, while the AA/GC could detect only ppm. An AA/LC system is not commercially available.

Nuclear magnetic resonance (NMR), while available, is not very useful for TOA. McNair, however, feels that this technique is very promising.

VPI's McNair
ranked the systems for TOA

Another available technique is fluorescence, which is very sensitive, but very selective. The technique is applicable only to planar, highly conjugated ring molecules, and as such is not generally applicable to TOA.

Radiochemical methods, while sensitive, are not applicable to the samples of interest, because these are usually not radioactive. Radioimmunoassay (RIA), however, should be considered promising because it can be used to analyze any substance for which an antibody can be made, which is almost any substance if it is coupled to a large protein.

Other very promising techniques are electrochemical systems and plasma chromatography, especially when the latter is coupled to GC. Two additional techniques, GC-IR and FT-IR (Fourier transform infrared spectroscopy), are rapidly developing technologies that hold much promise for TOA.

Lest mother nature be forgotten, biological (especially insects) and microbiological systems can be coupled to man's high technologies (GC and LC) to act as sensitive detectors for these systems.

(Cont. on p 760)

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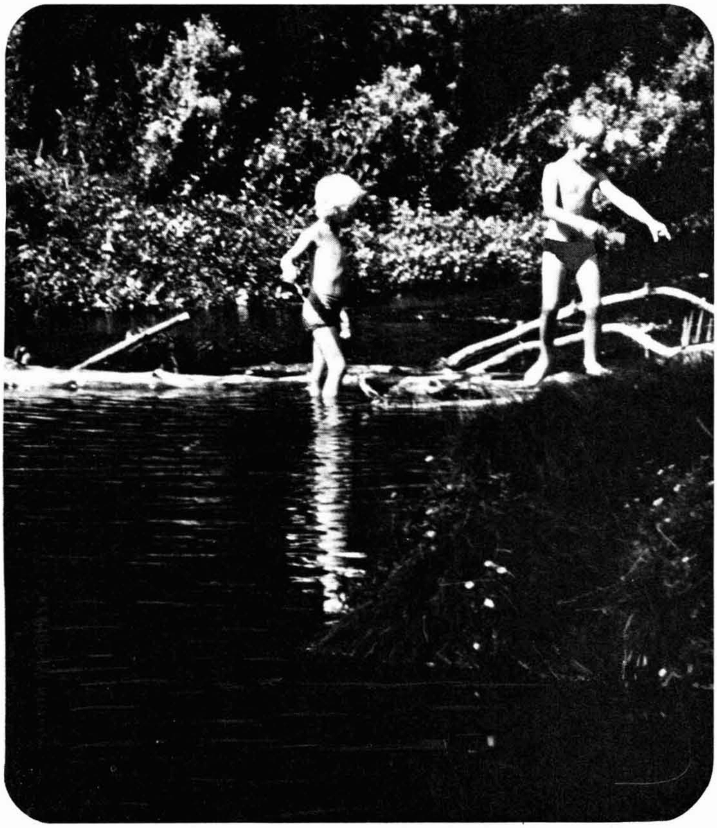

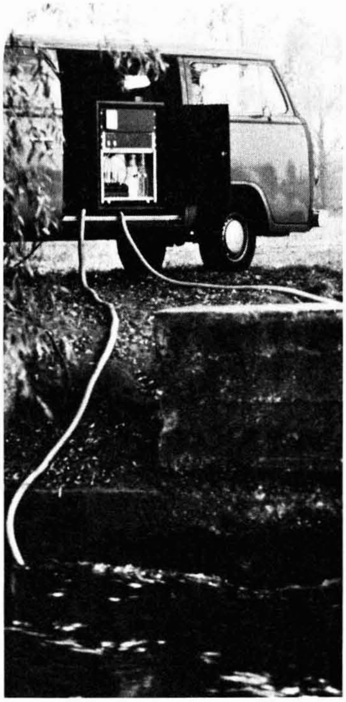

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According to McNair, the various analytical systems can be ranked in the order of their usefulness for TOA. In his opinion, this order is: GC/MS, LC/MS, GC, LC, GC/AA or LC/AA and, in some cases, NMR; GC/MS is the most useful.

And the permutations

Leslie Ettre described how the chromatographic method GC could be coupled to different detectors to make the resultant system universal or specific in its detection capabilities. For example, if an FID is coupled to a GC the resulting system has universal capabilities. Detectors other than FID can be added that are selective and detect specific substances.

For example, the first truly selective detector developed was the EC detector, in 1959, for pesticide analysis. Other selective detectors are FPD, electrochemical and nitrogen/phosphorus detector (N/PD). The latter is widely used with GC to detect drugs of abuse.

These are all classical GC detectors. Their greatest drawback is that they exhibit no selectivity for oxygen-containing compounds. However, spectrometric detectors (MS, UV, IR, and fluorescence) are able to detect oxygen-containing groups.

For liquid chromatographic systems, especially the most modern one, high performance (pressure) liquid chromatography (HPLC), the detectors are: the electrochemical detector, MS, UV, fluorescence and AA.

Since most samples to be analyzed for their trace components are complex, it is advantageous to separate components by a chromatographic method and then use detectors in tandem. One example: GC with the universal detector FID, followed by the specific detector N/PD.

Ettre believes that the greatest development in the next couple of years will be in the area of selective detectors. He also believes that there will be a greater utilization of spectrometric detectors, especially for LC.

According to another speaker, Milos Novotny of the University of Indiana (Bloomington), the future will witness the replacement of conventional packed chromatographic columns by capillary columns. Methods of directly introducing the sample into capillary columns have already been devised, which make them useful tools for TOA.

Novotny feels that analytical systems are moving toward the use of efficient, short capillary columns at lower, more reasonable temperatures (around 240 °C). In fact, he is developing a micro-capillary column for LC that can withstand higher pressures while accepting small volumes.

In short, Novotny feels that the most rapid developments in GC are "approaching a plateau." He sees some promising developments in HPLC/MS and HPLC/FT-IR. And in the future, he feels that ion-pair chromatography will be developed to the point of being useful for TOA.

But what of future directions for TOA? Novotny sees "improvements but nothing drastically new." Some of the developments will include computer-control instrumentation, and improvements in selective detectors, micro-manipulation techniques and data-treatment methods. He feels that analytical chemists have neglected the fractionation of very large molecules, and that chromatographic research should head in this direction.

On the horizon

There are other techniques that were discussed at the symposium that, when refined, would be sensitive methods for TOA. Among several promising systems discussed were bioprobing systems and laser-induced fluorescence techniques.

Jeffery Richardson of Lawrence Livermore Laboratory, University of Calif. (Livermore), told the symposium that, at present, laser-induced fluorescence lacks selectivity for many types of compounds, but as more reliable lasers are developed, the technique will find more use in TOA.

Garry Rechnitz from the University of Delaware (Newark) told the symposium of bioselective membrane electrodes that, in the future, may be used as bioprobes for TOA. While the electrodes that have been developed to date are selective, they are not sensitive. Rechnitz admits that much work needs to be done to adopt these bioprobes to TOA.

One bioprobe that Rechnitz described was an ammonia electrode onto which bacteria were coated. Rechnitz explained that this electrode decays with use as bacteria die, but it can be regenerated by placing it in a growth nutrient medium. The concept of bioselective membrane electrodes is exciting because, as in the example above, the scientist not only has a living electrode but a reproducing one.

The future for trace organic chemistry is expansive. Not only is TOA a new frontier, but as LaFleur told the symposium, it will be "one of the most challenging and important areas in the next couple of decades." LRE

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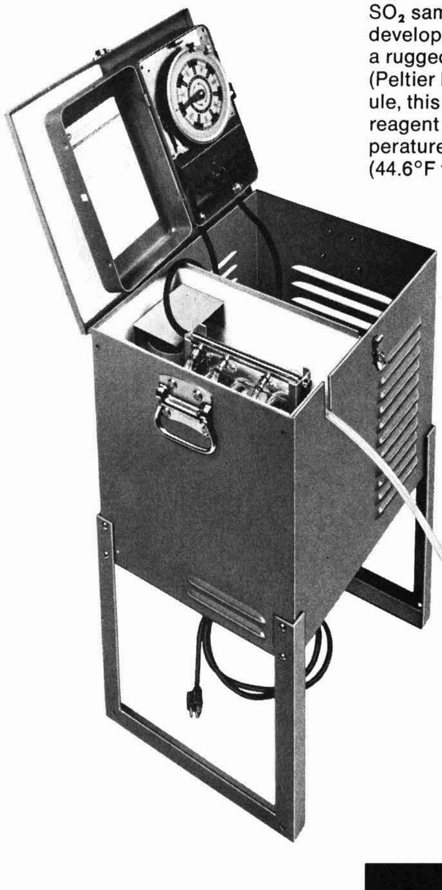
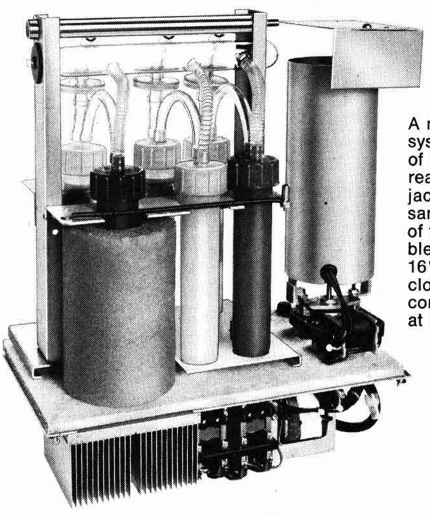


Outdoor model of RAC 3-Gas Sampler, with top opened to show installation of an optional 7-day skip timer. An optional 24-hour timer also is available.



A new thermoelectric system controls temp of bubbler with SO_2 reagent (in insulating jacket) for maximum sample stability. Temp of the other two bubblers is kept above 16°C (60.8°F) by enclosed thermostat-controlled heater, at right.

***Modification kit is available to adapt new cooling-heating module to existing RAC 5-Gas Samplers (outdoor models).**

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CIRCLE 13 ON READER SERVICE CARD

William Harrison on clean coal

A pioneer in the field of SRC, **William Harrison,** *senior vice president of Southern Co. Services, Inc. (SCS), explains to* ES&T's *Julian Josephson how, with a certain amount of flexibility and reasonableness in the enforcement of the Clean Air Act Amendments of 1977, clean coal could be a viable energy option.*

Dr. Harrison, could you please describe some of the advantages of solvent refined coal [SRC], especially with respect to scrubbers, fluidized bed combustion [FBC], or other clean fuels from coal. In comparison with scrubbers, SRC has the advantage that one can provide a storable, relatively clean fuel at the power plant, just as today, one would provide oil or coal. The capital and the operating problems associated with the whole spectrum of scrubber technology could thereby be avoided.

I don't mean to overstate the problems of scrubber technology, but the comparison is really very simple, and favorable to SRC. You do not require the large installation of hardware to clean up the stack gas. You do not require the logistics related to supply of scrubber reactant materials to the site, or to disposal of wastes generated by the scrubbers at the site.

With regard to FBC, that comparison is more difficult to make, because FBC requires so many innovations in the design and operation of the power plant, which has not yet been demonstrated in a commercial utility boiler. And for that reason it is somewhat speculative at this moment to make a comparison. But my presumption is that SRC will still be competitive in terms of ease of use, overall plant efficiency and certain other factors that would be meaningful to the utility operator.

Do you see the provisions of the Clean Air Act Amendments of 1977 [CAAA 1977], especially with regard to New Source Performance Standards [NSPS], as severely hobbling, or even foreclosing future development of SRC or any nonscrubber options? The language of the amendments would not have such an adverse impact on the future of SRC, but the *manner* in which EPA proposes to implement those those amendments could very well have a bad impact. In particular, EPA has proposed to implement the provision for a percentage of emission reduction by requiring that the percentage be set at 90. Now in some of the coal materials that we have used, we have achieved 90% emission reduction. That has not been our objective, however, since we were merely trying to achieve sulfur limits below that which would comply with present NSPS that limit the emissions to 1.2 lb SO_2/million Btu. Selecting a number as high as 90% will have the effect of either reducing the raw coal supply that would lend itself to solvent refining, or increasing the processing costs. And both of these effects I judge to be contrary to the national interests. In fact, it appears to me that EPA's case for qualifying scrubbers to achieve 90% is very weak.

What modifications to CAAA 1977 would you advocate, in order to retain the viability of SRC and other nonscrubber options? I don't believe that modifications are needed in the language of the amendments, so much as in the inclination of EPA for implementing these amendments. All I am proposing is some degree of reasonableness in the EPA response to the amendments. In particular, that means that the percentage of emission reduction should not be greater than 85%, and perhaps it should be even less.

As you know, there is speculation that EPA may relax its proposed sulfur emission reductions from 90% to a more realistic 85%. This reduction would maintain the SRC option, with all its merit, for most of the coal reserve; and it would, in addition, maintain FBC and other promising technologies as viable options.

Do you foresee markets for by-products from the SRC process; that is, the mineral matter and sulfur that would maybe otherwise go up the flue? The principal by-products of the SRC process are, as you mentioned, the sulfur and the mineral matter. There are also some combustible gases, comparable to synthetic natural gas, and light liquids that have market value. Among this slate of by-products, I doubt that the mineral matter will be marketable. However, I believe that everything else will be; that is, the sulfur, gases, and light liquids, as well as the SRC itself.

Despite the apparent regulatory setback in the Clean Air Act and EPA's subsequent rules, does your company intend to pursue the development of SRC, and other nonscrubber approaches? Let me assure you that if it becomes clear that SRC cannot be a compliance fuel—that is, a fuel which would enable us to operate generating facilities without the requirement of additional flue gas desulfurization [FGD]—then I believe our corporate interests would disappear for all types of purposes. The battle is not lost, however. I think that the Congress, the Department of Energy [DOE], and others who understand these issues will surely bring some pressure to bear on EPA to avoid what I would call environmental overkill. And once this reasonableness is restored to the regulating process, then I am satisfied that SRC does have an important future as a part of our energy supply.

Please understand that this is not an anti-scrubber position. Because, although our company has been developing SRC, we are also active in advancing the art of FGD. But we are simply trying to keep options open, so that a given utility can make the most cost-effective choice to meet its requirements at any point in time.

What do you consider to be the main problem with SRC—is it mostly the problem of residual organic sulfur, or are there others you can name? Well the process works, so in one sense, one can say that the major problems have been resolved. This is not to say that there is no room for improvement. For instance, I am quite sure that we would be pleased for a new process modification to be feasible that would eliminate filtration, because filtration is not a perfect unit operation by any means. It is expensive both in terms of capital and operating costs, and, it is the filtration step that gets most of the adverse attention when others attempt to appraise SRC technology.

However, our position is that we have shown, at the project at Wilsonville, Ala., that filters can be made to work, and that until, or unless something better comes along, we are quite willing to live with them. And we believe that the technology can be commercialized on the basis of using filters. Now as you probably know, there are some very promising alternatives being developed, and we expect to try out some other process options at Wilsonville.

And this would even improve the removal of organic sulfur? No, this would not improve the removal of organic sulfur, but we do see ways to do that, if it becomes necessary to do so, at greater processing expense. Let's realize that our objective has been to produce the least expensive coal-derived boiler fuel that would meet the NSPS. We have done that with respect to the existing NSPS. We must remember that SRC is a very significant technical achievement in the context of the current NSPS. Its importance could, however, be lessened by the threat of extreme and unnecessary regulations that may prevent some of its applications in our industry.

> *"The problem is not so much the language of the law, as it is the proposed manner of enforcement."*
>
> **SCS' Harrison**

Some major questions that were being asked early in the development of SRC were, could the filters be made to work, and could you make as much solvent as you use? Could you operate the process in what is called solvent balance? The work at Wilsonville has proved that both of those problems can be inadequately resolved. We do make sufficient solvent to stay in solvent balance. And we have made the filters work. I believe those are key achievements that I could cite.

The Navajo plant [*ES&T*, January 1970, p 41] is a 2250-MW power plant, and burns approximately 24 000 tpd of coal. And, by way of comparison, your total generating capacity at the Southern Co. is 22 000 MW. This would require something like 240 000 tpd of coal, or something in that area. Could you foresee that for such large systems as your own, or, say, for such a large plant as Navajo, that it could be economical to supply the entire needs with SRC? Could you see this happening one day? Let's imagine a situation like this: If our industry must double in size in the next 10–15 years, that growth must be based in large part on coal or coal-derived fuel. Therefore, I can easily visualize supply systems as large as ours, in the future, with SRC, because the choice is going to be either to burn clean fuel, or to burn raw coal and equip the plant with scrubbers. We also presume that within the next decade, there are going to be other competing alternatives, such as coal-derived liquids, and perhaps FBC.

But the point of my remarks is that our company or our system is like the industry at large, in the sense that we are going to have the same options available to us that everybody else has. And probably they will all have to be based in a large part on coal, or coal-derived fuel. So I don't have any

SRC test burn site. *The world's first, it's near Albany, Ga.*

problem at all conceiving of the rapid proliferation of a coal-refining industry, much like the present-day oil-refining industry, to be able to meet these needs.

But if you can see this happening, would this not assume a certain reasonableness on the part of those that frame the clean air laws and regulations, and perhaps certain recommendations on the part of the National Air Quality Commission that must be put together in order to make so-called mid-course corrections downstream? Yes, a degree of reasonableness is necessary for SRC to proliferate as I have imagined. But there are other markets besides the utility industry, which may justify growth in solvent refining, regardless of the eventual outcome of environmental regulations. The basic point is, however, that there will be more expensive options, if these less expensive options are foreclosed. And it is simply a matter of national priority to see how these costs and benefits are ultimately analyzed.

Some other views on SRC

Should draft revised NSPS become final in their present form, they would have "only minimal impact" on the cost and commercialization of "emerging" pollution control technologies, Stephen Gage, EPA's acting administrator for research and development, told a Congressional subcommittee. This would be the case, even if a 90% sulfur reduction from uncontrolled coal-burning levels were mandated. However, Gage also said that SRC would not meet the draft standards "without excessive cost."

Meanwhile, A. Joseph Dowd, general counsel for the American Electric Power Service Corp., said, "Emerging technologies such as SRC and FBC may provide more reliable, economic, and environmentally acceptable methods of control than the current generation of lime-limestone scrubbers. But he warned that the 90% removal requirement for sulfur would obstruct the development of "promising" alternatives to scrubbers. In fact, he even said that the 90% removal standard "would probably eliminate limestone scrubbing, and require every utility to use lime as the scrubber absorbent."

Hach Chemical's Cliff & wife Kitty

Clifford Hach, *chairman of the board and technical director of the company, tells* ES&T's *Stan Miller that his wife Kathryn, president of the Hach Chemical Co., runs the day-to-day business. First in water analysis, Hach Chemical was founded in 1948, went public in 1968, and, last month, opened the new instrument manufacturing facility and Hach Center for Applied Analytical Chemistry near Loveland, Colorado. In 1977 (fiscal year ending April 30, 1978), Hach Chemical reported a $16.7 million sales volume with nearly 500 personnel and having 1500 shareholders. Known worldwide for innovation, the company makes instruments and reagents for the water or wastewater analytical lab with a philosophy of providing the general public with economical and efficient analyses.*

What are the plans for the new facility? About a year and a half ago, we decided to expand our overall company but to carry out the expansion in an area that is more conducive to the younger scientists and engineers who want to be in an area with skiing, cultural events, and the like. The HACH Center for Applied Analytical Chemistry is a group of organizations that will work on the practical application of existing methods of analysis. The Center has a budget of well over $1 million and has more than 50 people on the staff of the technical center. In addition, the entire instrumentation manufacturing facility is now located in Loveland, as well as the corporate headquarters. Remaining in Ames, Iowa is the chemical manufacturing activity and the new agricultural analysis division, now about 1½ years old with a small group of five—a director of marketing, a senior agronomist, an analytical chemist, a technician, and an administrator.

FIRST IN WATER ANALYSIS

How did the company reach this decision to enter the water analysis area? What companies are in competition with Hach Chemical? Our initial policy was to become a laboratory supply company that would supply everything that was needed in the laboratory of a water or wastewater treatment plant. In 1948, there was no single comprehensive supplier of chemical reagents, lab apparatus, and instruments. We saw an opportunity and also a need in providing these materials. We chose both markets—water and wastewater analysis—because in many smaller towns the two laboratories were operated by the same person.

Is the company unique in the water and wastewater analysis area? There is no company exactly like ours. Yes, there are three of four companies that have portions of the Hach product line. For example, there are two or three chemical testing kit companies that have been around a very long time that make portable testing kits for swimming pool water and pH tests and the like. By far, Hach Chemical's line is the most broad. We have laboratory reagents and procedures for carrying out the tests that are oriented toward the practical user. In addition, process control analyzers are continually being developed to automate the water treatment plant.

Please comment on recent acquisitions to give the firm a broader base in the

chemical analysis area and the analytical chemistry area? For many, many years the company has been very jealous of not diverting its attention outside the field of water analysis. The reasons were that we did not have our product line fully developed and that we did not dominate the field. At that time any diversion would simply weaken our achieving a total objective. In the past years we have done very little outside the field. But now that many of the products are of such exceptional quality, well received, and with the unique features the company can move into other closely allied areas of analysis.

We acquired the Fann Instrument Company in 1976. It's a company that manufactures viscosity measuring instruments used primarily in the oil-well drilling business. In oil-well drilling, approximately 50% of the cost goes for drilling mud. These muds require a great deal of testing and the water analysis part of drilling mud is an area we have been involved with for a long time. This company plans to merge together the physical testing of the drilling muds with all of the oil field water analysis as a single product line. It's a fine growing business with a marvelous future.

In what product areas does the company concentrate? The instrument product line of the Hach Chemical Co. consists of two broad classes of products—first, laboratory instruments, some 30 different models, that are on table tops and perform manual analyses. Second, continuous monitoring analyzers for on-line monitoring and automatic control and recording. The basic needs of the water analysis laboratory include a number of photoelectric colorimeters, spectrophotometers, pH meters, conductivity meters, BOD respirometers, flocculation testers, turbidimeters and the like. We are always adding and intend to have a rather complete set of instruments.

In the process control area, we have continuous automatic chlorine analyzers, using DPD reagents, hardness analyzers, and silica analyzers along with a number of others. These silica analyzers, for example, are used principally for determining very low amounts of silica in boiler feed water and condensate analysis.

We have three broad types of turbidimeters. A low-range instrument measures very small amounts in filter effluents in water plants. A second, a surface scatter unit—a patented device—measures turbidity from above the surface of water. It is used in surface-water monitoring in sewage plants and has a range up to 5000 turbidity units. This instrument has been on the market for nearly 15 years. It's one of our major products and is distributed worldwide. It measures river water, surface water, raw sewage, and the like wherever dirty water turbidity is to be measured.

A third, a falling stream turbidimeter, measures the light absorption by a stream of water that is descending from a nozzle. It measures sludge blanket levels in clarification plants.

The turbidimeter area is one of continual development. We have developed an instrument that will have the least stray light and will be able to read the lowest turbidity values ever achieved. We are also developing new units of expression that will be more versatile than the Jackson turbidity unit. The final design on any of these products has not yet been reached in meeting absolute perfection.

We intend to continue to work very hard in the continuous-monitoring area, and are always improving our colorimetric analyzers. Soon, we will be introducing a new line of colorimetric analyzers that will have broad applications for literally all tests of water by continuous analysis.

STANDARD ANALYSES

How do the Hach methods compare with other standard methods? In the very beginning there was, more or less, only one text book—the APHA (American Public Health Association) Standard Methods for the Examination of Water and Wastewater. There was also in the beginning an ASTM methods manual that was oriented more toward industrial wastewater. There were no other sources of procedures for the laboratory.

We took a quick look and determined that this standard methods manual was written to provide authoritative reference-type methods of analysis. These methods were not at all sensitive to the capabilities and practical uses or requirements for the average water treatment plant in regard to cost, equipment, time and ease of operation.

We didn't invent any new methods. Rather we took the known methods, DPD for chlorine, and EDTA for hardness, for example, and reformulated the reagents to be the most practical, economical, and easy to use, consistent with accuracy.

Can you make a distinction for the *ES&T* reader regarding the Hach method of analysis, which does not require highly skilled Ph.D. analytical chemists? One of our greatest problems is continually describing or explaining the fact that the Hach methods are easier, more rapid, more economical, and require less equipment. The popular conception is therefore they must not be as accurate. This misconception is a very serious thing. There is no relationship between absolute accuracy and ease or time required in conducting analysis.

The last item in the criteria list (see box) is that the method gives accurate results. These methods have been worked out in every case to provide identical accuracy with APHA standard methods. We do not admit for a moment that there is any difference in accuracy in tests using Hach formulated reagents or Standard Methods reagents. Because precisely the same chemical reaction occurs in both cases, the results are identical.

The company has recently published two new handbooks on water analysis. The first on drinking water contains a side-by-side comparison of the chemical reagents and laboratory apparatus for the drinking water tests. The EPA method appears on the left-hand pages. On the right-hand side is the Hach method. Also listed are the equipment and chemicals used in the specific tests. The methods have been rewritten in an understandable fashion—by the numbers, do this, then that—for the complete analysis.

The drinking water analysis handbook, with about 220 pages, has been available for one year. The EPA approved methods, on blue pages on the left side, contain all tests requested by EPA for reporting requirements under the Safe Drinking Water Act. A companion publication on wastewater analysis became available last month; it contains 700 pages.

STANDARD ADDITIONS

Would you elaborate on what you mean when you say (the last criteria item) "includes a means of proving that the results obtained in the tests are correct?" This proof is something that has never been in "Standard Methods". The most fundamental and single quality of a system of analysis is to know that the analysis is correct. Standard additions is an old technique; it has been in the literature for many years. It's a very powerful tool which, in my view, in the long term, will supplement or surpass all other endeavors toward accuracy.

What happens? Simply described, an analysis is made on one portion of the original unknown sample for the substance, in the usual way. The results are noted. A second portion is taken and an addition of a standard quantity of the substance is added to it, and this spiked sample is analyzed as before. The difference in the results is the recovery of the standard addition. Ideally, 100% of the addition should be recovered, in which case one can be almost positive that the original analysis was correct.

On the other hand, if significantly less than the standard quantity of the substance is recovered, one can be sure that the original analysis is in error. A system has been developed to systematically check the entire analytical system, step by step, to locate the source of the malfunction so that corrective action can be taken. Some of the sources of error are improperly calibrated instruments, faulty reagents, poor laboratory technique, contamination of the glassware, interferences in the sample, etc. Until three years ago, when Hach introduced our product, there was no convenient way to prove correct sample results. Now, with the Voluette® Ampule Standards System, it's both practical and easy to check accuracy every time you run a test. With this system Hach restored a well-established analytical technique to water and wastewater testing.

It is not entirely as simple as one is first led to believe. The application of standard additions for each analysis is perhaps somewhat different. It requires a development for each test—how you apply it and how you interpret it. Standard additions are routinely used in other areas of analytical chemistry, namely atomic absorption analysis, and analyses using specific ion electrodes, but has never been written up as a formalized procedure. I think it is just through neglect.

INNOVATIONS

Hach Chemical has come up with a number of innovative solutions to the problems of the analytical chemist. Would you elaborate on some of these? In the early years almost all colorimetric methods of analysis were conducted using a visual color comparison with standards. In 1948 there was no photoelectric instrument in the water analysis industry. It occurred to us to make a simple economical photoelectric colorimeter that would be more accurate than visual comparison. A visual comparison provides about ±10% accuracy, a photoelectric instrument ±2–3% accurate, and a high-quality photoelectric instrument is better than 1% accurate.

Our innovation was to insert a card scale right into the instrument. Then the analyst, without having to refer to calibration tables, or graphs, makes the reading from the meter scale. There is a card for each test. All told about 60 cards come with the instrument. They are all precalibrated. An operator simply installs a card, develops a test such as chlorine, phosphate, silica, or whatever, puts the test tube into the instrument and reads his answer directly in ppm on the scale card.

One of the products that we are working on and for which we have great anticipation of major growth is

Criteria for the foundation, objectives, and design of the Hach product line, at a glance

Aimed at a comprehensive system of analysis, the product line includes written procedures, analytical (chemical) reagents, measuring instruments and kits that

- anyone can use if he can read
- uses reagents that do not deteriorate, cannot be contaminated and are safe to handle
- uses reagents that are accurately premeasured for quantity and that can be shipped by all means of transportation to all parts of the world
- is economical, gives accurate results and is rapid and easy to use
- includes a means of proving that the results obtained in the tests are correct.

a digital titrator. Every year, many millions of titration analyses are carried out in all fields, including water and wastewater analysis. We have developed and patented a disposal cartridge titration system with a dispenser that has a digital-type readout. This titrator gives the results directly in ppm (mg/L). It's remarkably accurate, easy to use, light, portable and economical. So, one lofty objective is to replace all the glass burrettes in the world with the Digital Titrator. It's a major task, but at the same time a great opportunity.

Hach has also introduced a system of packaging reagents. Known simply as pillows, this product line has grown remarkably. Unit doses of almost any chemical powder or solution can be packaged to meet user specification in segments of heat-sealed plastic tubing.

Last year we passed the 50 million mark in pillows, which translates to about $2 million business. This concept has certainly caught on.

Acceptance of our products seems to be increasing. The Hach products are being more widely used now than at any other time. I have real confidence that the company will be able to supply its products for even more general use.

VISUAL COMPARISON

What are the basic objectives of the Hach Chemical test procedures? The needs for chemical measurements in society are broad, and modern colorimetric analysis is one aspect of that. Common types of measurement include soil fertility, irrigation water, swimming pools, drinking water, wastewater, power plants, boiler water, and the like. Our methods are sufficiently mechanized to allow the general public to conduct the test as precisely and as accurately as a fine laboratory. What's more, our methods allow the public to conduct the analysis on-the-spot and quite economically.

Twenty-five years ago, an amateur photographer who developed his pictures would need a dark room, a balance for weighing, bottles of pure chemicals such as acetic acid, and sodium sulfite, graduated cylinders for measuring volumes, and brown storage bottles. He would make up the developer, the fixer, use them to develop film, and store the solutions that would eventually deteriorate and finally be discarded.

Later came the packet system. The amateur photographer would then buy a sealed packet, open it, and dissolve it in a quart of water, develop the film and when it was all done he would throw away the solution and start afresh next time.

Then came the Polaroid system—the film is in the camera with the developer. Now, a child can take a picture. Push the lever, out comes the fully developed picture.

In a fashion this is the path that Hach Chemical keeps working toward: more or less totally mechanical methods of testing—dispensing, mixing and reading—that the general public can produce useful and accurate analytical results.

PERSONAL ASIDE

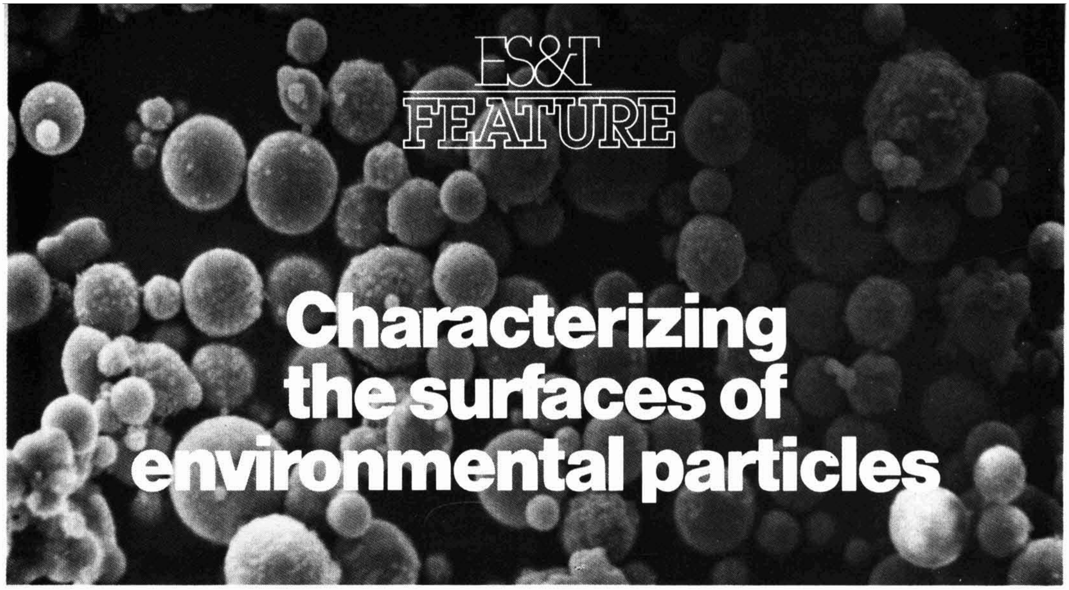
What are your backgrounds, interests, and aspirations? I graduated from Iowa State University in 1947. Kitty and I were married while we were still in school, and we never got out of town. The conference room in which you are conducting this interview served at one time as a family living room. The fire place there was the center of the house in the early days.

(Kitty) I came to Iowa State from a farm in Missouri, and majored in Home Economics. My pet statement is that it gives me enough chemistry not to talk about it but just to listen! On outside interests, I have been flying for 25 years. I have a multi-engine instrument rating, a commercial license instrument rating, a multi-instrument rating. I fly regularly.

(Cliff) I have no hobbies. I enjoy lab work as much as anything else. To me the greatest sport is inventing.

(Kitty) Cliff looks at everything with a questioning eye. He is continually looking at ways to do something better and easier. Cliff accepts very few things at face value. He always wants to know more about it and from this comes the ideas for better techniques. Cliff has an expression for this—having a seminar in the dark. Often in the morning Cliff will tell me that he had a seminar in the dark last night. He woke up in the middle of the night, did some thinking about something that he is going to do.

(Cliff) One of the most pleasant times I have is actually getting into the field for an extended period, going to an actual water plant and working with those folks. A multitude of products come to the fore that they need in their work. I plan to continue to go into the field working at actual treatment plants to determine what they need in order to provide better equipment for the water analysis laboratory.



ES&T FEATURE

Characterizing the surfaces of environmental particles

A most important generalization from such studies is that most trace elements are all concentrated on the surface of particles

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Many of the processes that determine the chemical transformations and adverse effects of pollutants, and that influence their transfer between environmental compartments take place at an interface or surface. For example, the so-called surface microlayer present on ocean and freshwaters accumulates both organic and inorganic pollutants and controls their aquatic-atmospheric exchange. Likewise, adsorption of pollutants onto airborne and waterborne particles is a primary factor in determining the transport, deposition, reactivity, and potential toxicity of these particles.

Interfacial phenomena are just as important in the biosphere; membrane transport characteristics can play a controlling role in determining pollutant toxicity.

Conventional studies of environmental systems involve the collection of bulk samples of air, water, soil, or of atmospheric and aquatic particles followed by the determination of the average concentrations of pollutant species in the samples. While the utility of such measurements is beyond dispute, they do not provide information about the identities and amounts of pollutant species present in the microscopically small regions that constitute environmental interfaces.

This article, therefore, will consider some of the methods that can be used to obtain information about surface chemistry, and will illustrate how such information can provide an understanding of the behavior and effects of certain environmental pollutants. Attention will be focused on particulate materials whose surface chemistry is important for the following reasons:

- A number of potentially toxic trace metal and organic species are highly enriched at the surfaces of many types of environmental particles.
- It is the surface of a particle that is directly accessible to extraction by aqueous leaching in the natural environment, and by body fluids following inhalation or ingestion.
- It is the surface chemistry of a particle that governs its heterogeneous reactivity with gaseous or solution species.

Methodology

Two types of analytical measurements are normally performed in surface studies of particulate material: *surface analysis* to determine the elemental and, in some cases, the molecular composition of the outermost atomic layers; and *depth-profile analysis* to determine the variation of chemical composition with depth below the original surface.

Both types may be performed on a single particle or on a field of particles, although individual particle analysis requires microprobe capabilities. Microprobe capabilities further enable generation of compositional maps that establish the lateral distribution of an element.

From an analytical standpoint there are four problems, not normally encountered in conventional analyses of bulk material, which are associated with surface measurements. First, quantitative analysis is extremely difficult because of the uncertainty in defining a precise analytical volume. Second, a truly representative measurement is difficult to obtain because of considerable variations in sample composition even within a set of apparently similar particles. Thus, in achieving the specificity associated with characterization of a single particle, one sacrifices statistical information unless a large number of particles are investigated serially, or a field of particles is studied in a single measurement.

The third problem area is associated with sensitivity. Surface analytical techniques must be extremely sensitive owing to the very small analytical volumes sampled. Indeed, unless a given species is highly surface enriched it is frequently undetectable unless the bulk concentration is greater than 0.1–1.0%.

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Finally, since surface analytical techniques involve bombardment with charged particles, there is a danger of changing the sample because of chemical reactions, selective volatilization of elements or migration in the solid. In general, it is difficult to obtain authentic depth profiles of volatile species such as chlorine, and mobile species such as the alkali metals.

Instrumentation

At the present time there are a large number of analytical techniques that can be used for surface analyses. However, those that are most used are electron microprobe X-ray emission spectrometry (EMP), electron spectroscopy for chemical analysis (ESCA), Auger electron spectrometry (AES), and secondary ion-mass spectrometry (SIMS).

The electron microscope (EM) and microprobe (EP) bombard the sample with a focused beam of electrons to stimulate emission of X-rays characteristic of the elements present. The technique is useful for analyses of individual micrometer-size particles, and has a lateral and depth resolution of about 1 μm determined by the X-ray emission volume.

Surface analysis capabilities of EM and EP are poor since the depth resolution is very much greater than the thickness of the surface layer normally of interest. Indeed, information about elemental surface predominance can be obtained only be varying the energy of the electron beam (depth penetration) or by ion etching of the outer surface and by comparing elemental ratios for inner and outer surfaces.

The ESCA technique irradiates the sample with X-rays and records the energy (depth penetration) of the electron beam by analyzing before and after ion etching, or by comparing elemental ratios obtained by bulk and EMP analyses.

The ESCA technique employs an x-ray source to eject core-level electrons from the sample. Energy analysis of the resulting photo electrons provides chemical bonding information since the bonding energies of the core electron are sympathetic to changes in the electronic structure of the valence level. Elements present at levels greater than one atom percent in the uppermost 20 Å are detected. Depth profiling is achieved by etching the surface with an ion beam between analyses.

The utility of ESCA for individual particle analysis is limited because of the difficulty of focusing X-rays to a beam diameter smaller than 1 mm,

FIGURE 1

Auger electron spectrometry is useful for depth probing as well as surface analysis

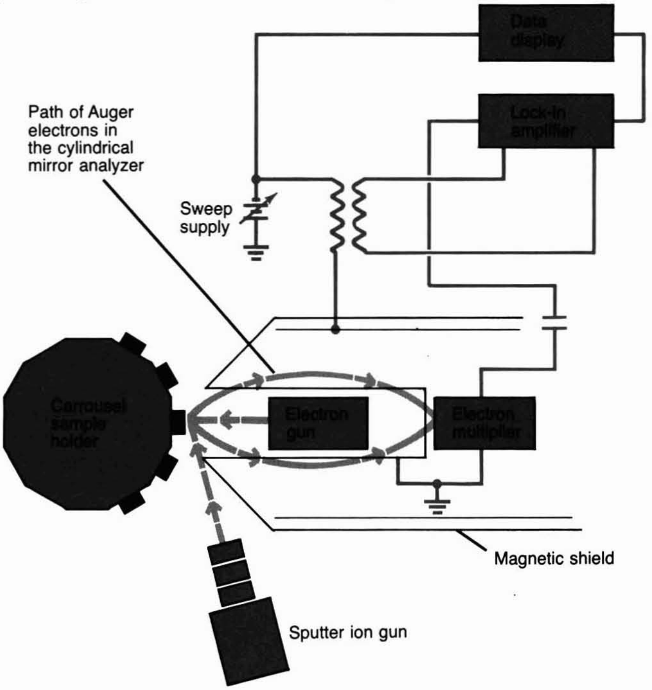
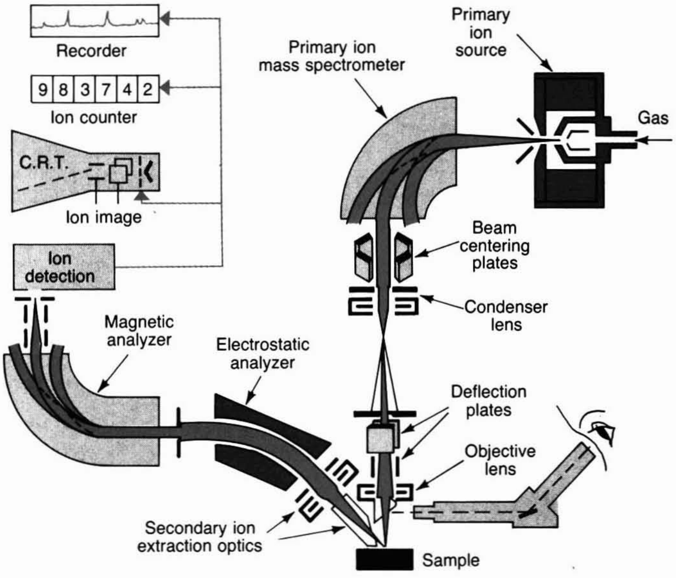
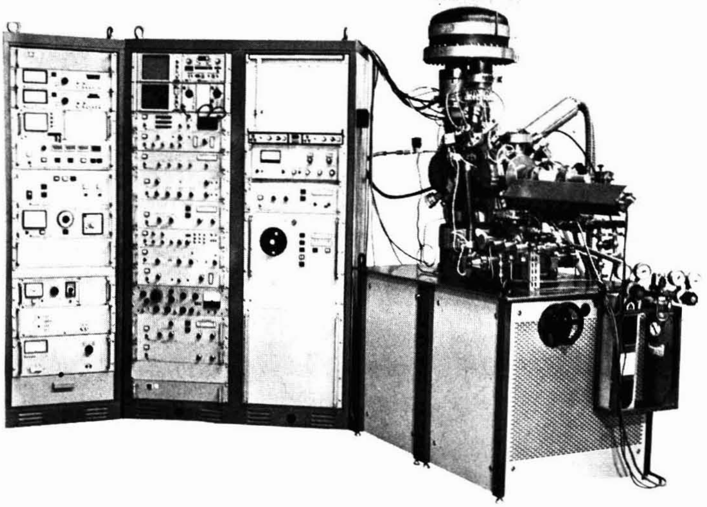


FIGURE 2

Secondary-ion mass spectrometry's high sensitivity permits studies of pollutants present at trace levels





Surface analysis system. *This system combines ESCA, SIMS and AES capabilities*

although recent advances indicate that lateral resolutions of $\sim$10 μm are feasible. Normally the sensitivity of ESCA is insufficient to enable observation of trace constituents unless considerable surface enrichment is encountered.

In AES the emission of Auger electrons is stimulated by bombarding the sample with a beam of electrons. The energy of the secondary Auger electrons is characteristic of the emitting element and is determined by using a cylindrical mirror analyzer (Figure 1). Spectra are recorded in the first derivative mode to discriminate against a background of inelastically scattered electrons. Elemental detection limits lie in the range 0.1–1.0% (atomic) within the analytical volume (depth $\sim$20 Å); variation in sensitivity is less than a factor of 10. Depth profiling is achieved by etching the sample surface with an ion beam (normally Ar$^+$) as in ESCA. Most AES spectrometers possess microprobe capabilities with incident beam diameters of 1–5 μm.

In SIMS the sample is bombarded with a stream of ions (most commonly, negative oxygen ions) and surface material is physically removed. About 1–10% of the sputtered material is in the form of secondary ions that are mass analyzed by a conventional mass spectrometer (Figure 2).

Suppliers of surface analysis equipment

Environmental Sciences Associates, Inc.
Inficon Leybold-Heraeus, Inc.
Instruments SA, Inc.
The Kearns Group
Physical Electronics Industries, Inc.
Spectro Products, Inc.
Varian Associates, Industrial Equipment Group

Source: Lab Guide, 1977–78

The ion microprobe represents a special configuration of SIMS in which the primary ion beam can be focused to a diameter of about 3–5 μm. Both individual particle analysis and elemental mapping capabilities are thus available and depth profiling constitutes an integral part of the process of secondary ion generation.

A major advantage of SIMS is its extremely high sensitivity, with elemental detection limits ranging from 10^{-2}–10^{-6}% atomic depending on the element and the primary ion used. Typically, it is possible to observe as little as 1 μg/g in the analytical volume, thereby enabling studies of species present at trace levels.

SIMS is, however, subject to several types of interferences and artifacts. In particular, spectral interferences from molecular and multiply charged ions make the high resolving power of a double-focusing mass spectrometer desirable. Also, volatilization losses and migration of sample ions under the influence of the primary ion beam can give rise to spurious depth profiles. Such effects are often difficult to identify in SIMS since removal of surface material is an integral part of the detection process.

Of the above techniques, AES and SIMS are generally most useful for surface analysis and depth-profiling studies owing to their sensitivity and good lateral and depth resolution. ESCA, however, has the important advantage of providing information about the identity of molecular species present.

With all the techniques, difficulties are encountered in establishing even semiquantitative depth scales, which are normally attempted by calibrating the rate of removal of surface material against that obtained for a standard having a surface layer of known thickness. The main problem, however, lies in matching the matrix composition of the standard to that of the material being studied. In the case of environmental particles, matrix and surface compositions are not, in general, well defined.

Studies of environmental particles

Most man-made particulate matter entering the environment contains higher specific concentrations (μg/g) of several potentially hazardous trace elements that are normally found in natural crustal dusts, soils, and sediments. In many cases these elements—As, Cd, Co, Cr, Mn, Ni, Pb, S, Sb, Se, Tl, V, and Zn—are preferentially associated with particle surfaces as a result of condensation from the vapor phase or adsorption from solution. Such surface association is of special environmental significance since it leads to preferential enrichment of small particles that are least effectively collected by pollution control devices, have long atmospheric and aquatic residence times, and can deposit in the pulmonary region of the human respiratory tract when inhaled.

Several of the surface analytical techniques described earlier have been used to study airborne particles, and particles derived from specific sources. The results of such studies are presented here to illustrate the types of information that can be obtained.

Airborne particles

The most definitive surface studies of composite airborne particulate matter have used ESCA and have emphasized the capability of this technique to identify the chemical compounds present. Sensitivity limitations do not enable detection of trace species; however, it has been established that the elements C, N, Pb and S are surface predominant.

Most aerosol sulfur is in the form of sulfate, and most nitrogen is present as the ammonium ion. Quantitative measurements of these species indicate their association as ammonium bisulfate and sulfate. In addition, however, there are substantial amounts of amine nitrogen.

ESCA has proved especially useful

for following the surface chemistry of sulfur and nitrogen compounds with changes in meteorological conditions. Using ESCA, scientists have demonstrated the catalytic role of atmospheric carbon (soot) particles in heterogeneous reactions involving NH_3, NO, and SO_2.

Coal flyash particles

Flyash derived from combustion of coal in a conventional power plant is composed primarily of an impure aluminosilicate glass together with small amounts of several crystalline minerals. Only about 1-3% of the bulk material is soluble in water.

Depth profiling studies that used EMP, AES, and SIMS have established that a number of elements including C, Cr, K, Mn, Na, Pb, S, Tl, V, and Zn are substantially surface enriched, whereas Al, Ca, Fe, Mg, Si, and Ti are not. This observation supports the hypothesis that the more volatile elements, or their compounds, are vaporized during combustion and then condense on the surfaces of coentrained flyash particles at lower temperatures.

Depth profiling studies of flyash have also demonstrated the utility of using instrumental techniques in conjunction with solvent leaching to remove soluble surface material. An example of this approach is presented in Figure 3 for the elements Pb and Tl.

The results show that extraction of flyash with water or dimethyl sulfoxide removes the surface layer of both elements. Determination of the amounts of Pb and Tl in solution then enables estimation of the amounts present in the surface layer. If one assumes this layer to be 300 Å thick, then one obtains average concentrations of 2700 μg/g for Pb and 920 μg/g for Tl in the surface layer as compared to bulk particulate concentrations of 620 μg/g and 30 μg/g for these elements, respectively.

Solvent leaching can also provide some insight into the chemical forms of elements present. For example, although AES and SIMS indicate little surface enrichment of iron, aqueous leaching rapidly removes this element from the surface region, thereby indicating its presence there in a readily soluble form.

The comparison of the leaching and depth profiles of K, Fe, Na, and S suggests that these elements may be associated in the surface layer—possibly as alkali-iron sulfates. Further support of the existence of simple and/or complex sulfates is provided by ESCA studies that show that the oxidation states of Fe and S in the surface region are +3 and +6, respectively.

Auto exhaust particles

Scanning electron microscopic investigations show that automobile exhaust particles occur in two distinct morphological forms. The first involves quite large particles (>10 μm cross-

Environmental ramifications of coal flyash research

- Since a number of toxic elements are highly enriched in soluble form on flyash surfaces, their potential toxicological impact may be significantly greater than that predicted from bulk analysis. Such enrichment will be greatest in small, pulmonary-depositing particles, and will give rise to high localized trace metal concentrations in the microregions of the lung, where the particles are deposited.
- The surface enrichment of alkali metals, which determine the resistivity of flyash particles, will enhance the ability of the particle surface to hold a charge and, in turn, improve the efficiency of electrostatic precipitation.
- The presence of acid sulfates on flyash particle surfaces may, of itself, enhance their toxicity.
- The existence of sulfate on flyash surfaces indicates the ability of flyash to function effectively as a catalyst for the heterogeneous oxidation of SO_2. Flyash may, therefore, be important in determining the extent of SO_2 to SO_4 conversion in power-plant plumes.

FIGURE 3

Depth profiling of flyash by using SIMS plus solvent extraction permits an estimation of the surface layer concentration of Pb^+ and Tl^+

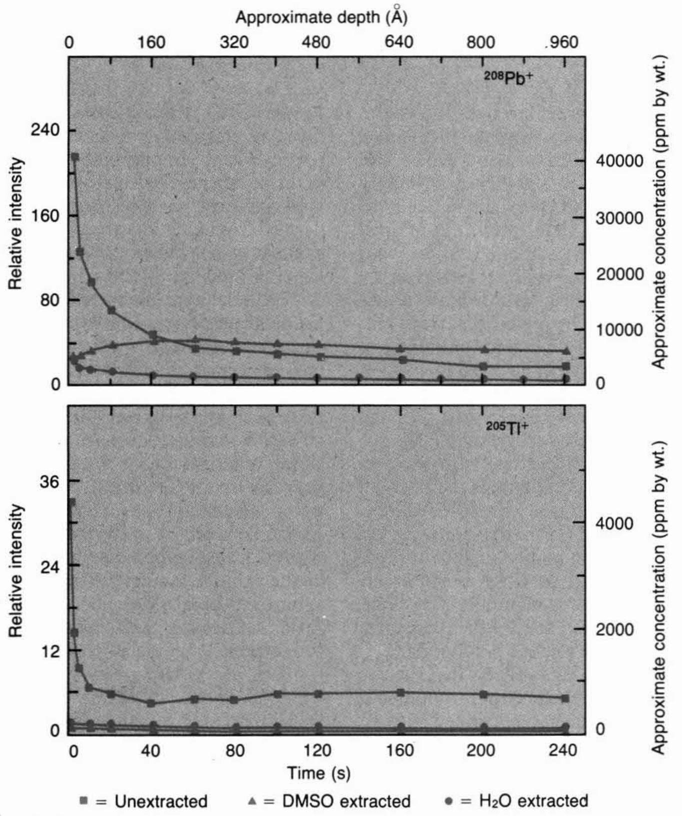
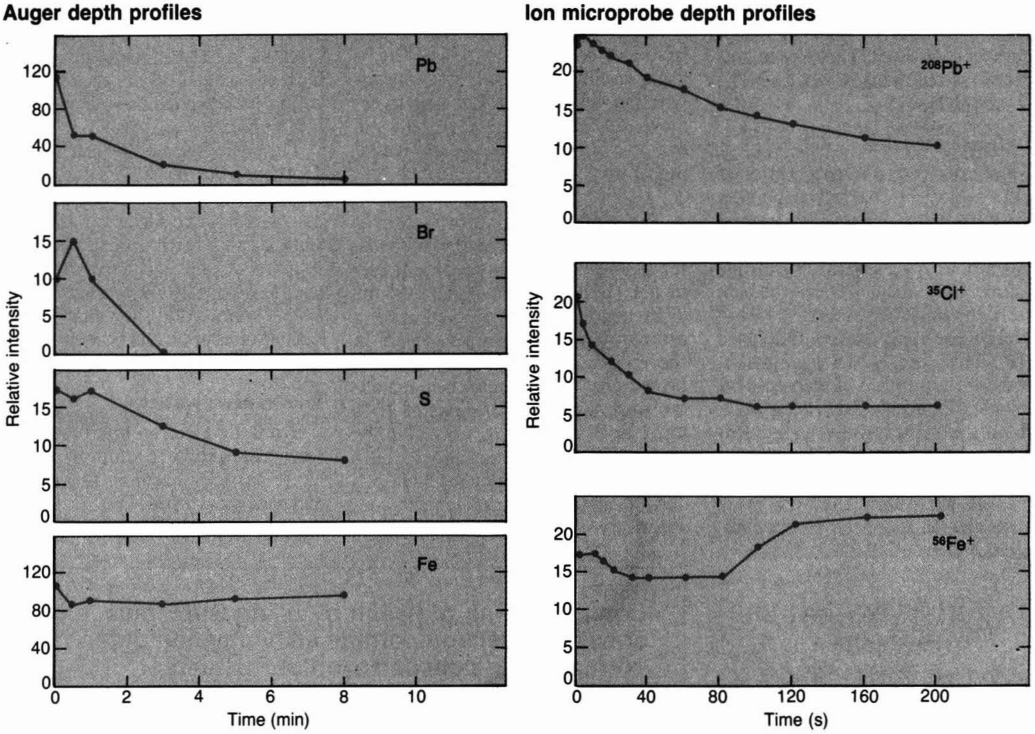


FIGURE 4

The surfaces of large auto exhaust particles are enriched with Pb, Br, Cl, and S but not Fe



section) of irregular size. Individual (EMP) particle analyses indicate that the predominant elements are Fe, Pb, Br, Cl, and S together with highly variable amounts of Ca and Si.

Elemental depth profiles obtained by using AES and SIMS indicate that Pb, Br, Cl, and S are enriched at the particle surface but that Fe is not (Figure 4). The region of surface predominance is estimated to extend less than 1000 Å into the particle interior. It is also interesting to note that SIMS shows the trace elements Cr, Ni, and Tl to be highly surface enriched.

The second particle type involves small (<1 μm diameter) spherical particles that are composed almost exclusively of Pb, Br, and Cl, but which contain no Fe. Surface analysis of such small particles is extremely difficult; however, preliminary indications are that none of the constituent elements are surface predominant.

These findings suggest that the two types of particles present in automobile exhaust emissions are formed by quite different processes. The surface predominance of Pb, Br, Cl and S on large particles is attributed to deposition of volatile lead and sulfur species (probably PbBrCl and SO_2) onto the surfaces of refractory iron-containing particles as the temperature decreases in the automobile exhaust system. The iron-rich host particles are probably derived from ablation of iron from the exhaust system. The small amounts of Cr, Ni, and Tl observed probably originate as impurities introduced with the lead gasoline additive or, in the case of Cr and Ni, are derived from engine wear. In either event, their surface predominance strongly indicates their vapor-phase history.

The homogeneous nature of the small spherical exhaust particulates suggests that their formulation occurs by a nucleation process in which PbBrCl condenses to form quite pure molten droplets when the temperature of the exhaust system falls below the saturation point. There is, however, little supporting evidence for this suggestion.

Coal conversion catalysts

While not strictly an environmental example, it is illustrative to demonstrate the utility of surface analytical techniques for studying catalyst poisoning effects. The example chosen is an experimental $CoO/MoO_3/SiO_2/Al_2O_3$ pelletized catalyst used in coal liquefaction.

Comparison of AES spectra of fresh and spent catalyst shows that the spent catalyst is highly surface enriched in C, Fe, and S, with lesser enrichment of Ca and Ti. AES depth profiles of the catalyst constituents show that the active constituents (Co and Mo) are significantly depleted at the surface of the spent catalyst. Interpretation of the behavior of the Al and Si constituents is difficult since the spent sample may contain appreciable amounts of these elements owing to contamination derived from mineral components in the coal.

AES depth profiles of the primary surface contaminants (C, Fe, S) show that carbon contamination extends well into the catalyst interior indicating penetration of organic material. The major inorganic contaminants (Fe and S) are concentrated close to the particle surface, but they do not appear to diminish the concentrations of Co and Mo in this region. Poisoning of this catalyst, therefore, is primarily due to pore blockage or conversion of CoO and MoO_3 to their sulfides. In this regard it is interesting to note the similarity of the Fe and S depth profiles, which suggests the presence of iron-sulfur compounds. Owing to the reducing conditions involved, these are probably iron sulfides. A similar conclusion has been reached using EMP analysis.

Open-hearth furnace dusts

Baghouse dusts derived from the open-hearth smelting of iron provide an interesting example of the operation of several of the artifacts associated with instrumental surface analysis. These dusts consist of three morphological forms: large (>60 μm cross-section) irregular slag particles; gray black spheres of varying size; and small (<2 μm cross-section) grains of red iron oxide that adhere to the large particle surfaces.

EMP analysis shows that the predominant elements in the slag are Ca, Mg, and Si, whereas Ca, Cl, Fe, K, S, and Zn are predominant in the black spheres. AES surface analysis indicates that Ca, K, P, Pb, and Zn are enriched near the particulate surface. Iron and oxygen, on the other hand, are apparently depleted near the surface.

It is apparent from visual observation of these dusts following EMP and AES analysis that considerable sample modification occurs as a result of both electron and ion bombardment. In particular, exposure to constant electron bombardment in AES results in changes in the intensity of the Cl and S signals. These changes are attributed to volatilization in the case of Cl and to either migration or simply increased exposure owing to removal of Cl in the case of S. Under high-electron beam energies, Si is observed to decrease with time and K to increase, thus indicating additional disturbance of the surface chemistry. These effects lead one to suspect the validity of depth-profile analyses, but is is necessary to perform several tests to distinguish real effects from artifacts. Such tests include variation of electron-beam intensity, minimization of irradiation time, solvent leaching, and sequential heating of the sample in an inert atmosphere.

It is interesting to note that, as in the case of coal flyash, the surface-associated elements (in this case Ca, Cl, K, P, Pb, S, and, to some extent, Zn) are quite soluble in water even though the bulk matrix is essentially insoluble.

In summary

Consideration of the foregoing examples indicates two important points. First, a great deal of new information about the physical and chemical characteristics of particulate surfaces can be obtained by using the techniques discussed. Second, most of the insights provided are highly speculative. It is suggested, therefore, that surface analytical results should be used primarily for formulating hypotheses about probable surface chemistry, mechanisms of particle and surface layer formation, and potential environmental effects. Such hypotheses are then best substantiated by additional independent experiments in which surface analysis may or may not be used for monitoring purposes.

Further development of environmental surface analysis seems likely to proceed via two distinct pathways. The first involves combined (ideally simultaneous) use of several techniques. For example, combined use of SIMS and AES or ESCA provides the capability of observing both material removed from a surface (SIMS) and that freshly exposed (AES or ESCA) as the analysis proceeds. Such an approach would help in identifying changes that occur as a result of charged-particle bombardment.

A second approach, which shows considerable promise, involves so-called time-resolved-solvent leaching in which the sample is leached with selected solvents in a continuous flow configuration, and the leachate analyzed as a function of time. The advantages of this approach are:

- It enables utilization of the most sensitive analytical methods for determining all species entering solution.
- It provides information both about the surface distribution of a species and about its identity.
- It establishes which chemical species can be mobilized in solution and thus have an environmental or toxicological impact.
- It is applicable to organic species that are normally removed from surfaces under the high-vacuum conditions associated with instrumental techniques.
- It is inexpensive, thereby making the field of surface analysis available to most scientists.

Overall, therefore, it appears that surface analysis has provided, and will continue to provide, valuable insights into the characteristics, formation, reactivity, and eventual impact of environmental particles. Perhaps, above all, such analysis has indicated the very real significance of surfaces in determining a wide variety of environmentally important processes.

Additional reading

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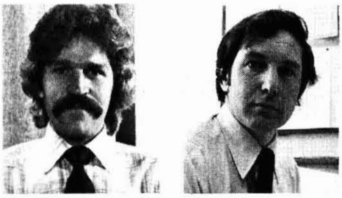

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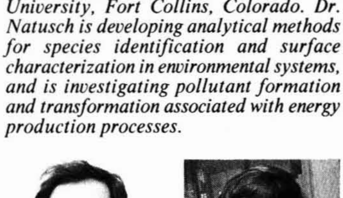

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Coordinated by LRE

Siting air monitoring stations

Careful selection for spatial scale and specific sources assures that the collected data "actually represent what they are interpreted to mean"

F. L. Ludwig
SRI International
Menlo Park, Calif. 94025

It does not require an extensive review of the literature to conclude that air pollution measurements are used for a wide variety of purposes. In fact, it sometimes appears that the number of purposes exceeds the number of stations. It is very seldom that any attempt is made to show that the physical characteristics of a given sampling location are appropriate to the problem being addressed by the data that are collected there—a coherent scheme is needed for classifying sites and relating their characteristics to intended data usage.

Most monitoring stations will be expected to operate for many years. Tens of thousands of dollars will be spent for equipment and installation and, additionally, for maintenance and data processing during the period of operation. It would be foolish to locate a station where its data would not be appropriate to the intended uses. The costs of poor siting procedures can extend well beyond the actual costs of establishing and operating the stations. Whenever data are used as bases for large-scale programs such as air quality improvement projects, there are likely to be great economic and social impacts, making the siting of air monitoring stations even more important.

The uses of air pollution data can be broadly categorized (box). Each of the broad categories contains several narrower subcategories, but at no level of classification is this kind of system directly related to physical factors.

A site-classification system that can be used to define an appropriate set of physical characteristics for each site type should be tailored according to the physical factors that influence the data. For example, different uses of data usually have different degrees of spatial smoothing that are appropriate. Sometimes, many closely spaced measurements are needed to reveal small-scale features of the pollutant distribution in space; at other times the requirement is for measurements to typify large areas within a city, or perhaps even a large region.

Siting concepts

Those uses of data that are related to the development of air quality control measures illustrate the variety of spatial scales that can be of concern within a single, broad category of use. Measurements that are typical of a street canyon or a freeway corridor will be suitable for formulating control plans to reduce emissions along the specific roadway, or along a limited number of similarly congested streets, but they will not necessarily be useful for the formulation of plans that are citywide in scope. Plans of the latter type hequire data that represent much larger areas.

The concept of spatial representativeness provides a useful basis for classifying stations, and the uses to which their data are put. Furthermore, the concept of representativeness has a physical basis that can serve to define station characteristics. In general, the measurement scales (box) of greatest importance are: microscale; middle scale; neighborhood scale; urban scale and regional scale.

The concept of scale can be extended upward to national and global scales, but for routine regulatory monitoring, the scales enumerated above are sufficient. In fact, the discussion can be limited to the middle, neighborhood, and regional scales and still cover most general-siting requirements.

Urban-wide conditions cannot usually be specified with a single station representing middle or neighborhood scales, but when the latter two scales are well represented at several locations, it will not be necessary to find the ideal urban-scale site. Microscale measurements are often made only for short time periods and for very specialized research purposes that make a generalized set of siting criteria nearly impossible to devise.

Scale of representativeness is not the only factor important to classification of monitoring site types and to the definition of siting criteria. Health effects are a pervasive motivation for much air quality monitoring and must be incorporated into the system.

The basis for most of EPA's air quality regulation is the amelioration of adverse health effects; hence, regulatory monitoring is usually health oriented and siting criteria must be such that exposures of the population to pollutants will be realistically represented.

Differences among the various air pollutants must be considered in any site-classification scheme, especially when that scheme is translated into the corresponding siting criteria. The differences are of several types.

Some pollutants are chemically inert; others are highly reactive. Some pollutants are emitted directly to the atmosphere; others are formed by chemical reactions within the atmosphere. Some pollutants come almost exclusively from many small, individual sources. Other pollutants come from large, individual sources, which are responsible for an appreciable fraction of the total emissions.

Total suspended particulates (TSP) differ from other pollutants in that all fractions of the atmospheric aerosol are not equally noxious, so there may be some justification for selecting sites that are biased toward respirable or toxic materials.

In summary, a system of siting based exclusively on spatial representativeness is not sufficient, but must be modified in its application to different kinds of pollutants. For pollutants that have large, individual sources, provisions must be made for sites specifically oriented to the assessment of the impact of those sources. For particulates, recognition must be given to the fact that not all subfractions of te aerosol fraction are of equal importance. And, finally, for pollutants such as ozone that are products of atmospheric chemical reactions, there must be some provision for locating monitoring sites to represent stages of the oxidant transport and production processes when the concentrations are greatest.

We can begin with the basic concept of classifying sites according to their spatial representativeness by using carbon monoxide monitoring as an example. Carbon monoxide is the only major pollutant for which the concept of spatial representativeness can be applied to the siting problem without modification or extension. The modifications in the basic system that are required for monitoring other pollutants will be discussed later.

Siting for carbon monoxide

In proceeding from the concept of spatial representativeness to the concrete requirements of siting, several decisions are required. Among these is the selection of an appropriate height for the sampling. Most routine air quality monitoring is related directly or indirectly to health effects and, therefore, samples taken at breathing level are most appropriate. Inlets at breathing level will constitute an obstacle in many locations and will also be subject to vandalism.

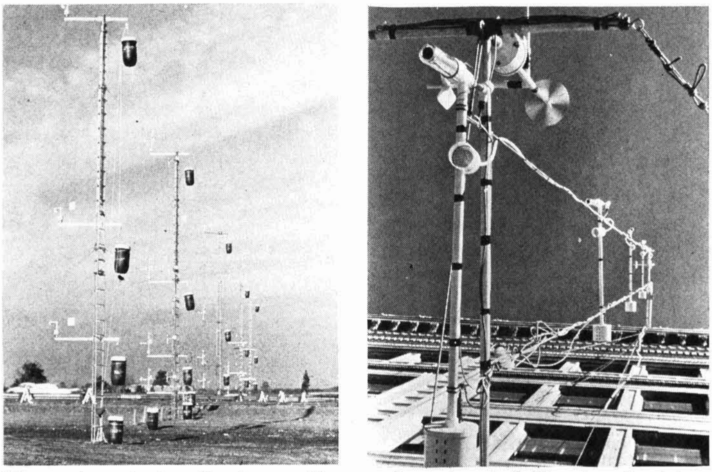
W. R. Ott, at the 1975 meeting of the Air Pollution Control Association, suggested a height of 3 m ± 0.5 m as a compromise. The adoption of Ott's inlet height provides consistency, and consistency, in turn, allows data from different locations to be compared with the assurance that any differences in the data sets will reflect something other than anomalous site characteristics. The site standards that Ott has proposed were derived from a combination of empirical evidence, and practical requirements, but the representativeness concept, not surprisingly, leads to similar results.

In deriving the appropriate physical characteristics for a site of a given type, representativeness can be ensured if the site is located so that no individual source is likely to contribute unduly to the measured concentrations. This means that some equivalence must be provided to relate maximum allowable influence (in units such as $mg/m^{3)}$ to minimum separations between the monitor and certain kinds of sources. For instance, regional sites should be far enough removed from cities so that the concentrations arising from emissions within the city will be less than typical rural background concentrations. In the case of CO, a figure 0.2 mg/m^3 might be used.

Analogous guidelines could be used for selecting maximum acceptable

Measurement scales

- **Microscale** measurements define concentrations in volumes with dimensions on the order of meters to tens of meters.
- **Middle-scale** measurements will generally be used to define concentrations that are typical of areas with dimensions of tens to hundreds of meters. This câtegory can include measurements that define concentrations along streets and roads, so typical areas can be elongated, measuring tens of meters by hundreds of meters or even kilometers.
- **Neighborhood-scale** measurements are among the most widely used. They define concentrations within some extended area with dimensions on the order of kilometers that has relatively uniform land use.
- **Urban-scale** measurements, to define the overall citywide conditions on a scale of tens of kilometers, will usually require more than one site.
- **Regional-scale** measurements provide a measure of concentrations typical of large, usually rural areas of reasonably homogeneous geography, extending for tens to hundreds of kilometers.



Microscale monitoring. *Closely spaced bag samplers in barrels* (left) *and monitor inlets* (right) *provide detailed concentration distributions*

influences for other pollutants and other types of sites. For example, neighborhood sites should not be so close to large roadways that emissions from the roadway affect the measured concentrations by more than some reasonable amount. For CO, 10% of the 8-h standard might be reasonable, so an appropriate setback would prevent individual sources from contributing more than about 1 mg/m^3 to the measured concentrations.

Smaller streets are less important contributors to the overall neighborhood concentrations so they should be allowed to influence the observed concentrations less than the major roadways.

Middle-scale sites may be heavily influenced by an individual source, but the source itself must be selected to represent some class of sources.

Ludwig and Kealoha and others (EPA Report 450/3-75-077, Sept. 1975; EPA Office of Air Programs Pub. No. AP-26, 1970) have estimated vehicular emission rates and citywide average emissions to define minimum separations for the various types of monitoring. These reports, or the EPA guidelines—*Guidance for Air Quality Monitoring Network Design and Instrument Siting—CO Siting,* Office of Air Quality Planning and Standards Report 1.2-012, Suppl. A, Sept. 1975—can be consulted.

The major point is that a classification system based on scale of representativeness allows one to specify some acceptable level of influence for individual sources and then derive specific criteria for locating sites so that those levels will not be exceeded. When practical considerations dictate that a less than ideal site be used, there are some criteria for deciding just how much less than ideal it really is and how great the undesired effects might be.

The summaries of the physical characteristics of the monitors given by Ludwig and Kealoha and by Ott make mention of traffic on certain roadways, of homogeneity of land use, and of other considerations that imply that it is not sufficient simply to place an inlet 3-m high at some arbitrary location. In general, some areas are preferable and, within the preferred areas, some specific sites are better than others. A step-by-step procedure has been derived for locating each type of CO monitoring site.

Before any procedure can be used, it must be decided what the uses of the data are to be, and what type of monitor will provide the right kind of data. This obvious fact is often overlooked. A common example of a mismatch between data and application is the development of an air quality control plan for an entire region to eliminate a pollution problem recorded at a station whose data may only be representative of conditions within a few hundred meters of the site.

The site-selection process begins by identifying the most important monitoring purpose and matching that to the most appropriate scale of representativeness for the site. After selection for the appropriate type of site, the next step will be to gather emission data, traffic data, land-use data, topographic maps, and climatological information. The information is used to identify generally desirable areas so that a final selection can be made. When a site has been selected in this way, the data should be reasonably representative of the desired conditions.

Siting for sulfur dioxide

The selection of sites for monitoring sulfur dioxide concentrations has one complication not present in the selection of CO monitoring sites: large individual sources of SO$_2$ are common. This adds one more dimension to the classification system. There must still be those types of sites that represent average conditions over various sized areas, but there must also be some provision for sites oriented toward determining the impacts of an individual source. R. J. Ball and G. E. Anderson (EPA Report 450/3-77-013, April 1977) added this dimension to the basic scale of representativeness system; they call the source-oriented site a "proximate" site.

Locating the appropriate place for a source-oriented monitor follows almost the exact opposite of the procedures for locating spatially representative sites. The areas of maximum source effects are sought, rather than avoided. The methods for finding these areas of maximum influence are based on Gaussian descriptions of diffusion and wind-tunnel studies of airflow in complex terrain and around large buildings.

For source-oriented SO_2 monitoring, the site-selection procedures are fundamentally different from those used for finding appropriate locations for CO monitoring. For more general SO_2 monitoring, there are many more similarities. Nevertheless, there are some important differences that reflect differences in the nature of the sources. Most CO sources are at ground level, while major SO_2 sources are elevated. Thus, by the time SO_2 is mixed down to the "breathing zone," its distribution in the vertical is more uniform, and much more relaxed criteria for the placement of the inlet are possible.

In procedures for selecting CO sites, considerable emphasis is given to the avoidance of streets and highways. For SO_2, the analogous role is assumed by areas where sulfur-containing fuels are burned in relatively large quantities.

Siting for TSP

The monitoring of particulates is very similar in many respects to that for SO_2. In fact, in many instances, the major sources are the same for both pollutants. However, total suspended particulates (TSP) have some features that distinguish them from the other pollutants. Principally, the differences are related to particle size.

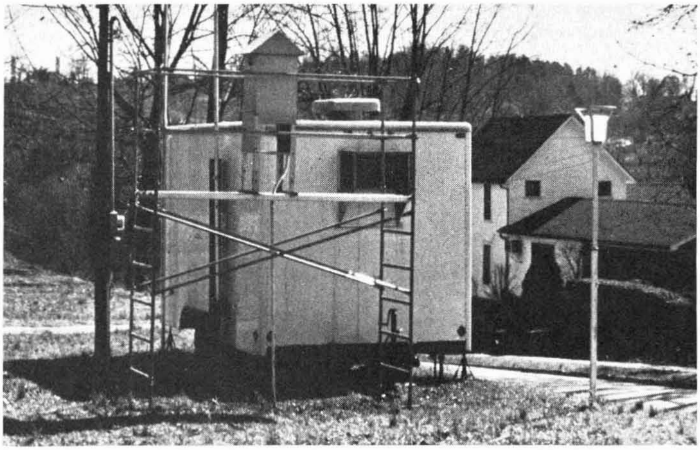
The distribution of urban particulate mass with particle size is bimodal; one of the modes consists largely of material respirable by humans, and the other mode contains mostly nonrespirable material.

G. M. Hidy and coworkers have suggested [*J. Air Pollut. Control Assoc.*, **25,** 1106 (1975)] that the larger sizes are dominated by relatively innocuous minerals and that the smaller sizes contain most of the lead compounds, sulfates and nitrates. Taking into account the health motivations of the air quality regulations, routine TSP monitoring should be conducted, if possible, at sites where the aerosol concentrations are representative of the smaller, somewhat more toxic fraction, and special care should be taken to avoid areas where large-particle fugitive dust can dominate the sampling.

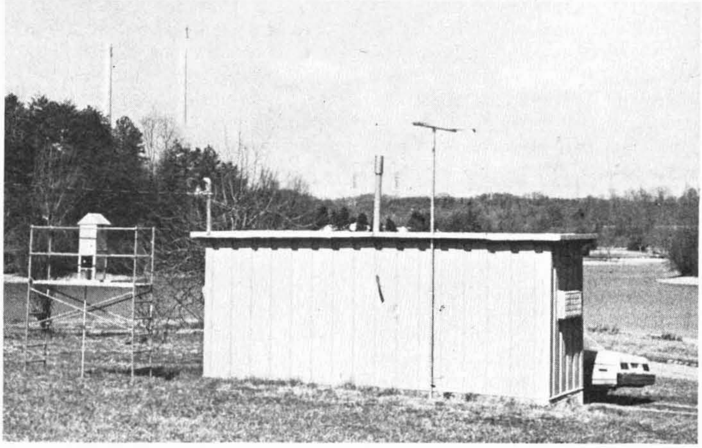
Another reason for finding a location where the larger particles are less dominant is that the smaller particles tend to be related more to primary anthropogenic sources rather than resuspended natural and unnatural dusts.

The siting criteria that have evolved for TSP are similar to those for SO_2, but with consideration also given to the avoidance of large particles for most kinds of monitoring. The TSP site-selection procedures treat source-oriented monitoring and spatially representative monitoring as do the SO_2 site-selection procedures.

Much emphasis must also be given to the avoidance of streets and roads in TSP monitoring because of the concentrations of large resuspended particles of road dust in their vicinity. Sampling only a few of the large roadside particles can completely obscure the more representative sample of smaller particles. It takes a million respirable particles of 0.5 μm diameter to equal the mass of one 50 μm diameter particle.



Neighborhood monitoring. *This well-placed monitor in Harriman, Tenn., monitors for TSP and SO_2*



Source-oriented monitoring. *The monitor, in the vicinity of Kingston, Tenn., is operated to detect high SO_2 concentrations from TVA's power-plant stacks* (in background)

Siting for photochemical pollutants

The monitoring of pollutants most important to the photochemical smog processes—the nonmethane hydrocarbons (NMHC), the oxides of nitrogen ($NO + NO_2 = NO_x$), and ozone (O_3)—will follow most of the same scale-based, site-selection principles already enumerated. Also, there may be reasons for source-oriented monitoring of NO_x or NMHC, but other factors must also be incorporated into a system for classifying monitoring sites for the photochemical pollutants. There are differences related to the pollutants' roles as reactants and as products in the smog-forming process.

The air quality guidelines for

Uses of collected air quality data

- Determination of compliance with air quality standards
- Enforcement and implementation of air quality regulations
- Development, application, and evaluation of control measures
- Public health
- Scientific research
- Evaluation of the impact of specific sources
- Miscellaneous purposes

NMHC emphasize their role as reactants, but the oxidant standard is differently oriented. Even though the scales of interest might be similar for air quality monitoring of NMHC and O_x, the site-selection processes will be quite different because of the intrinsic differences between reactants and products.

The fact that photochemical processes proceed over rather extended periods of time must affect the site classification. In general, the small-scale features in the distribution of the pollutants, whether reactants or products, will be of little interest because they will have been subjected to considerable large-scale mixing during the photochemical processes in which they take part. Except for special purposes, the monitoring of photochemical pollutant concentrations will use sites representative of the neighborhood and larger scales.

The selection of appropriate neighborhoods and regions for monitoring inert pollutants depends to a large extent on the assumption that concentrations and emissions are closely related, and that the latter can serve as a surrogate for the former. In the case of photochemical pollutants, the problem is more complex. If one wants to monitor in neighborhoods where oxidant concentrations are likely to be high, several questions must be answered. For example:

- What meteorological conditions are conducive to oxidant formation?
- Where are the most important sources of the precursors to the oxidants?
- Where will the precursors be, under conditions conducive to oxidant formation, when the high concentrations are reached?

The guidelines for selecting monitoring sites for the photochemical pollutants (F. L. Ludwig and E. Shelar, EPA Report 450/3-78-013) provide some suggestions for answering the above questions and finding suitable areas for monitoring oxidants. As a rule-of-thumb, it has been suggested that the wind directions for days when the air temperature is above 20 °C will serve to define the likely movement of the precursors under photochemically active conditions. This suggestion is based on the observed positive correlations between ozone concentration and the temperature of the air during the time that the ozone was forming.

The other photochemical pollutants are important because of their participation as reactants in the photochemical process. Therefore, the important siting questions are different than for oxidant monitoring. The meteorological conditions conducive to photochemical activity still must be identified. Then those regions where precursors are likely to lead to high-ozone concentrations, especially in a sensitive, populated area, must be located. Although the basic information required is much the same, the interpretations must be different for reactants and products.

The selection of sites representative of certain spatial scales involves some different considerations for the two kinds of pollutants also. The reactants, especially NMHC, are much like the nonphotochemically active pollutants in that a location must be found where nearby sources do not exert undue influence. However, ozone does not have important primary sources at ground level, but it does have important sinks. Therefore, ozone monitors must be sufficiently far away from surfaces and NO sources so that ozone concentrations are not reduced to unrepresentative levels.

Other aspects of site selection

There are two reasons why monitoring sites must be classified and uniform physical criteria established for each type of site. First, such a classification system will allow comparisons among sites and give some assurance that differences in observations reflect something more fundamental than local anomalies.

The second, more important reason for uniform siting criteria, is that such a system will provide guidance for the proper use of the data that are collected. The physical concepts entailed in the classification system, especially that of spatial representativeness, should help users to avoid gross mismatches between what the data actually represent and what they are interpreted to mean.

The importance of site selection leads to a paradoxical situation with regard to the prescription of site-selection procedures. One is apt to believe that such an important topic requires rigorous, complex specifications. However, rigorous, complex procedures are very apt to be ignored, especially by people with other responsibilities who must work within the practical constraints of money, safety, and accessibility. Fortunately, the procedures do not have to be complex to be effective.

A grasp of the underlying philosophy of monitoring and some common sense will avoid the worst errors. A day or two spent in data acquisition and interpretation along the lines suggested in the different guideline reports would ensure selection of high-quality sites.

If carefully considered selection of monitoring sites could prevent one instance where a large-scale air quality control plan is designed to cure a small-scale problem, that single instance would justify the effort required for proper selection of monitoring sites.

Additional reading

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Ludwig, F. L., Shelar, E., Selecting Sites for Monitoring the Photochemical Pollutants, EPA Report 450/3-78-013, April 1978.

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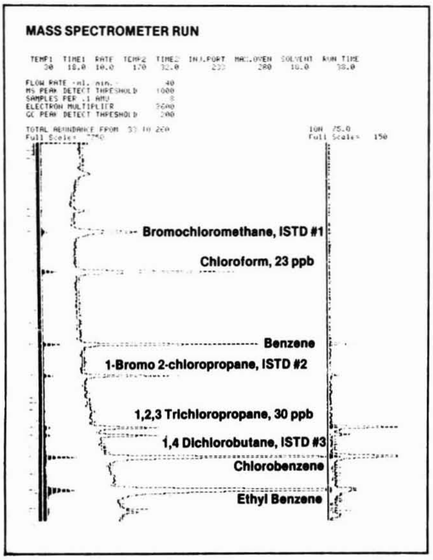

MASS SPECTROMETER RUN

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 TEMP1  TIME1  RATE  TEMP2  TIME2  INJ.PORT  MAN.OVEN  SOLVENT  RUN TIME
   30    18.0  10.0    170   32.0       [illegible]      280     10.0      38.0

FLOW RATE (ml. min.)           40
MS PEAK DETECT THRESHOLD     1000
SAMPLES PER .1 AMU              8
ELECTRON MULTIPLIER          2600
GC PEAK DETECT THRESHOLD      200

TOTAL ABUNDANCE FROM  33 TO 260                   ION  75.0
Full Scale= [illegible]                                     Full Scale=   150
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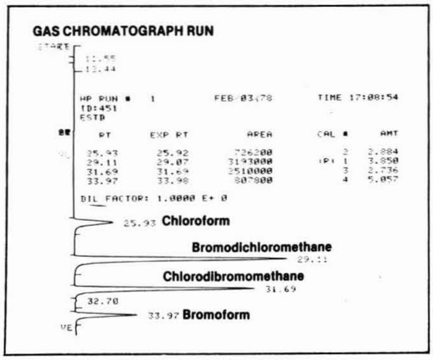
Volatile Organic EPA Indicators in 50 ml water.
Run on HP 5992 GC/MS.



GAS CHROMATOGRAPH RUN

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HP RUN #    1          FEB/03/78          TIME 17:08:54
ID:451
ESTD
    RT       EXP RT        AREA        CAL #       AMT

  25.93      25.92       726200            2     2.884
  29.11      29.07      3193000        (P) 1     3.850
  31.69      31.69      2510000            3     2.736
  33.97      33.98       807800            4     5.057

DIL FACTOR: 1.0000 E+ 0
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CIRCLE 23 ON READER SERVICE CARD

Chlorine knocks out slime, but can be toxic in high dosages, and is therefore regulated. Two utility scientists tell how the rules can be made more effective

POWER PLANT CHLORINATION

Ibrahim H. Zeitoun
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Consumers Power Company
Jackson, Mich. 49201

Intermittent chlorination is practiced at steam-electric power plants to control the development of biofouling on the walls of cooling system tubes. The composition of the organisms that contribute to the biofouling problems of power-plant cooling systems varies with the type of water used (marine or freshwater systems), and with the productivity of the waters. In general, these biofouling organisms produce an insulating layer that retards the heat exchange process, thereby lowering the efficiency of power generation. Also, biofouling promotes the corrosion of the condenser tubes, as exhibited by pitting, and by loss of wall thickness. Pitting could lead to the leakage of cooling water, as well as contamination of pure steam that is used to drive the turbines.

In freshwater systems, the biofouling organisms are slime formers. Slime-forming organisms in condenser pipes are primarily prolific bacteria, fungi, protozoa and algae. Algae, however, are also predominant in lighted areas such as cooling towers. Therefore, cooling-tower water systems encounter two sources of fouling problems—condenser biofouling and cooling-tower biofouling.

On the other hand, power plants located near marine or estuarine waters encounter more types of potential biofouling. These water systems are characterized by a greater variety of organisms that may contribute to the reduction of heat-transfer efficiency, and even to the reduction of the flow of water through cooling system conduits. Moreover, in addition to the slime-forming organisms that are present in saline water, molluscs and barnacles are involved. The growth and development of these organisms, if severe enough, could lead to the complete blockage of the cooling system.

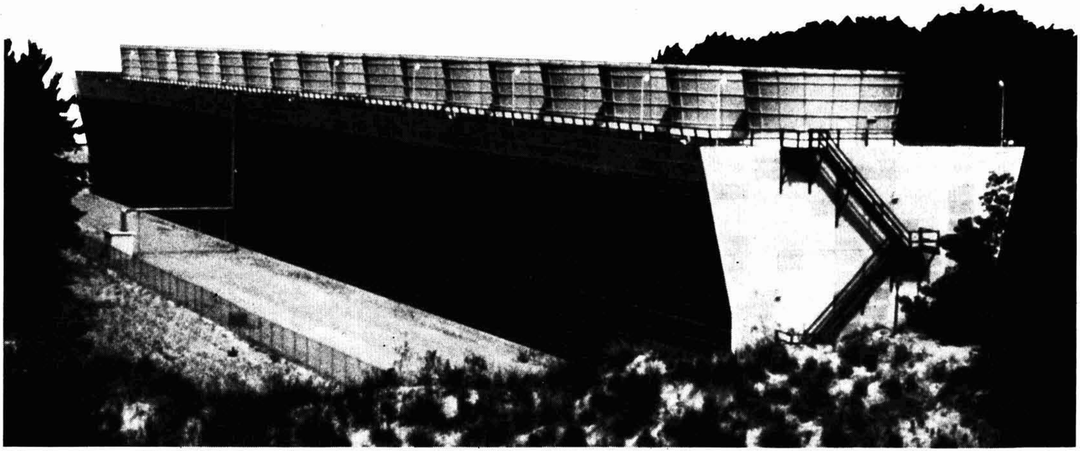
Inorganics are the "heavies"

Although the fouling of cooling systems is of biological origin, the fouling composition may not be totally organic in nature. Slime-forming organisms, which develop a gelatinous layer over the inner walls of the condenser tubes, trap suspended inorganic materials such as silt and sand. The combination of gelatinous materials and inorganic compounds are the constituents of slime.

It is believed that the inorganic content comprises the largest portion of the total weight of the slime. Furthermore, carbonates in the water, and in the presence of certain bacteria, often form complex carbonate depositions (scaling). Therefore, for effective power generation, the development and proliferation of these biofouling organisms must be inhibited.

Chlorine—the No. 1 biocide

Chlorine is the predominant biocide used in power-plant condenser systems throughout the U.S. Chlorine is highly preferred as a defouling chemical because of its greater effectiveness and practicality, and lower costs, as compared to other biocides. It is normally injected into the condenser tubes for



Cooling towers. *The idea is to solve slime and effluent problems at the same time*

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short periods as a shock defouling treatment. In marine situations, however, mussel and barnacle control may require continuous chlorination during the breeding seasons, since these organisms can tolerate higher chlorine concentrations.

Thus, it is evident that the frequency, duration, and quantity of chlorine applications for defouling purposes are dependent upon the composition of the fouling organisms, the severity of fouling of the cooling system, and the inorganic and organic content of the water. In general, chlorine is added to the circulating cooling water as a gas, or as a hypochlorite salt solution. Frequency of application varies widely, but typically could occur up to three times daily for approximately 30 min each time. At power plants where cooling water is not highly productive of fouling organisms, such as Lake Michigan, chlorination may take place only once daily for 30 min, as a typical maximum. Essentially, no chlorination is required in some instances, such as during winter periods, and when entrained sediment may keep the condenser tube surface well scoured.

Chlorine is a potent oxidizing chemical that diffuses into cells, disrupting their enzymatic system, and killing them on contact. The oxidizing activity of chlorine is dependent largely upon the amount of free available chlorine in the form of hypochlorous acid (HOCl).

Gauging the effectiveness

The effectiveness of chlorination at power plants, and in turn, the quantity of chlorine required for biofouling control, is related to the amount of materials prone to oxidation in the water. The presence of inorganic reducing agents such as ferrous and manganous ions, and organic products and compounds such as ammonia and those possessing unsaturated linkages, will reduce the oxidizing capacity of HOCl against biofouling organisms.

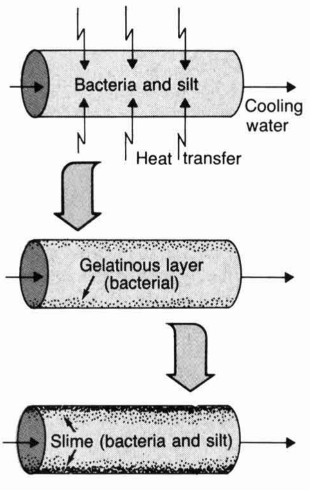
The amount of chlorine that is used in oxidizing the naturally-occurring reducing compounds is called the chlorine demand of the water. Accordingly, the essential point in condenser defouling is to add enough chlorine to the cooling water to satisfy the chlorine demand, as well as to provide a sufficient quantity of HOCl for oxidation of biofouling organisms. Thus, the quantity of chlorine injected is dependent upon the local conditions.

The amount of chlorine that combines with organic products, such as ammonia, to form chloramines is known as the combined chlorine. Chlorine is also capable of reacting with organics in cooling waters to form chlorinated organics. These reactions are highly activated by added heat, ultraviolet irradiation, or both factors combined. The slow reaction of chlorine with acetone or methanol to form the volatile chloroform is a good example. Free available chlorine together with chlorine combined with the various substances form the total residual chlorine (TRC).

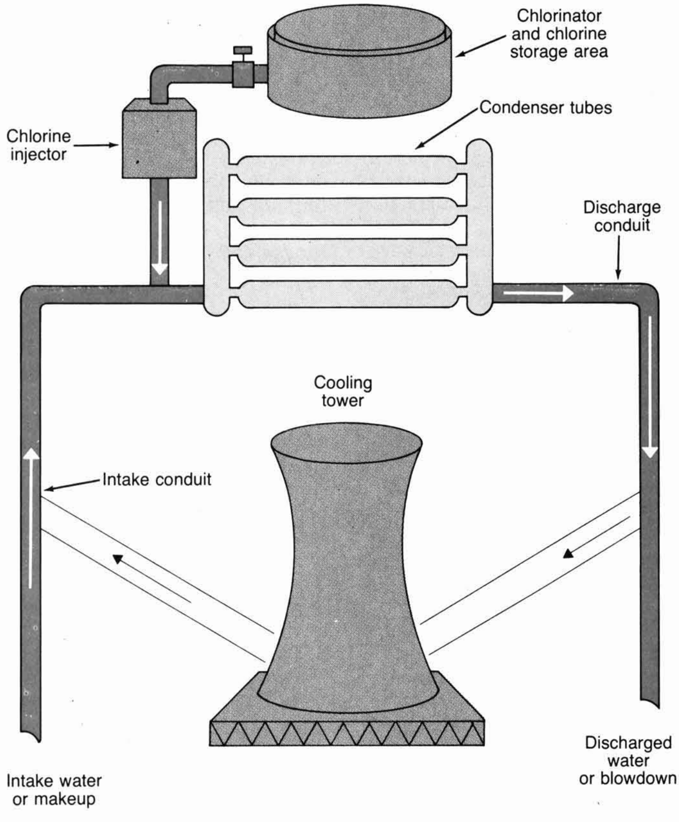
The effectiveness of chlorination is controlled by two important factors—the concentration of chlorine used, and the period of application. In other words, similar defouling effects may be obtained if the concentration of chlorine is increased while the exposure period decreases, or conversely, if the chlorine concentration is decreased while the exposure period is increased.

Theoretically, the effectiveness of chlorination can be monitored on a periodic basis in the power plant by noting changes in turbine back pressure. In practice, however, because of normal load variations in generation, and of the relatively severe economic consequences of a small change in efficiency, it has not been possible to

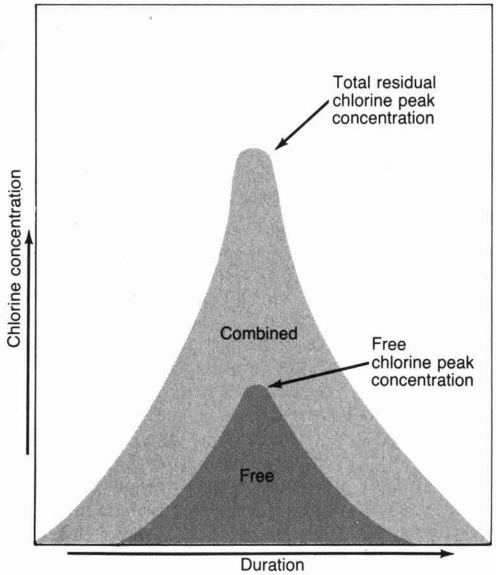
How slime forms



How chlorine goes through the system

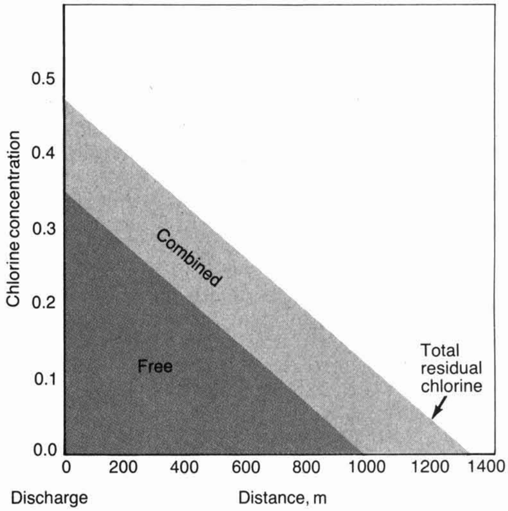


Shape of a typical chlorine pulse



Reduction of peak chlorine concentration with distance

Based on data collected at J.H. Campbell Plant, Consumers Power Company, Mich.



provide adequate on-line detection of biofouling and chlorination effectiveness. On the other hand, potentially adverse results of biofouling have historically led power-plant operators to err on the conservative side, in attempting to keep condenser tube surfaces clean.

Chlorination practices

Intermittent power-plant chlorination in this manner has been proved to be an economically justified practice, when one considers the potential effects of reduced efficiency of power generation, and possible shutdown of a plant. However, the environmental consequences may not always be justifiable.

Also, chlorination practices differ with the type of cooling system of concern. In an open, once-through system, for instance, the chlorine injected into the condenser inlet will be discharged directly with the heated effluents. By comparison, chlorination of a closed-cycle circulating water system, such as cooling towers, is a cumulative chlorine treatment, since most of the combined forms of chlorine would remain from previous chlorinations in the recirculating water cycle. Generally, chlorine concentrations in the discharge effluent, or the cooling tower blowdown, when plotted against time, exhibit a bell-shaped curve, or a chlorine pulse at any point in the receiving water.

The magnitude of free and total chlorine pulses are related to the amount of organic and inorganic reducing compounds present in the water. Moreover, hypochlorous acid is capable of releasing its oxygen—this reaction is catalyzed by ultraviolet rays—and of reacting with chloramines, to liberate chlorine ions through the breakpoint reaction. These reactions are also accelerated by temperature. Thus, the peak concentrations or magnitudes of the pulse of both forms of chlorine will become smaller as the point of measurement proceeds further away from the point of discharge.

Bioassays and other analyses

Many bioassays have been conducted by using various species of aquatic organisms, mainly fish, to establish a maximum safe chlorine concentration for these biota. The inconsistency of the results has been confusing, and there is reason for serious concern over the reliability of the measurement and testing techniques, life stages of species tested, kinds of bioassays adapted, phenotypes of the species used, and influences of water quality.

During the second Conference on Water Chlorination, held in Gatlinburg, Tenn., October 31–November 4, 1977, it was evident that the techniques used to measure the chlorine forms in water are still crude (*ES&T*, January 1978, p 14). The DPD (N,N-diethyl-*p*-phenylenediamine) method was reported to measure no chlorine, although it was detected amperometrically, because the latter procedure measures all oxidants in water. Thus, the results of amperometric titrations, the best available procedure, should be reported as total oxidants. And it should be borne in mind that water constituents could be critical in data interpretation.

Some investigators have found that the smaller the fish, the more sensitive they are to chlorine. Other investigators have derived opposite conclusions.

Also, development of chlorine-resistant strains among fish has also been reported. Genetic adjustment and adaptation to chlorine situations have also been suggested. Finally, the type of bioassays used to extrapolate limitations are mostly laboratory tests in which the organisms are exposed to a continuous peak concentration for a certain specific time.

Problems with testing

The concentration at which 50% of the test animals die within a specific time, usually 96 hours, is known as the LC_{50}. This LC_{50} has been multiplied by a factor to establish a safe concentration. This type of exposure and data extrapolation are not reasonable for direct application to field situations, since fish are often overexposed to chlorine in the laboratory.

On the other hand, results from field studies are not always fully satisfactory. In the field, test fish (presumably caged fish) are exposed to various environmental conditions, such as continuous temperature alteration and gas supersaturation, as well as intermittent chlorination. These factors are stressful, and special attention must be given in data interpretation, in order to ascribe mortalities to the proper variables.

Regulations and practices

Because of the toxic nature of reactive chlorine, it is generally recognized that discharges should be regulated to be adequately protective of aquatic life. At the same time, because of the beneficial application of chlorine in power-plant operation, and the lack of substitutes that have been proven to be effective, reliable, economical and safe, regulations and practices should be based on the best scientific evidence. They should adequately consider the costs and risks associated with alternative approaches.

The development of chlorine discharge regulations has occurred through the process of standard setting common to many pollutants. This process has generally involved the establishment of water quality criteria, based on scientific evidence, with consideration of available technology and mixing-zone phenomena, in development of discharge limitations. The current Environmental Protection Agency (EPA) effluent limitation guideline is 0.5 mg/L maximum, and 0.2 mg/L average free available chlorine, with a limit of two hours per day for any unit. Many states have adopted different limits. For instance, Michigan (until July 1, 1977) imposed a maximum limit of 0.5 mg/L TRC.

The initial scientific work to derive suitable criteria that would be protective to aquatic life concentrate on continuous discharges that would be characteristic of municipal wastewater chlorination practices. Because of this emphasis, the criteria have lacked provisions for cases involving intermittent discharges, and have been conservatively directed to be protective of aquatic life under constant exposure, including consideration of reproductive functions. Criteria published by the EPA in 1976, for instance, are 0.01 mg/L and 0.002 mg/L TRC limit for warm water and cold water species, respectively, in freshwater, and 0.01 mg/L for all marine species.

As noted above, it has been clearly established that separate criteria for intermittent exposure to chlorine are needed. The time-dependent nature of chlorine toxicity, as well as site-specific factors, such as water quality and species potentially affected, must also be considered in applying criteria in a realistic manner. Recent investigations have confirmed that species behavior, such as avoidance reactions and seasonal migration patterns, can be considered in establishing site-specific limits that would be protective of important aquatic life.

Nevertheless, it is possible to establish conservative limits, by ignoring these factors, while still considering possible interactions with other water-quality factors that may be stressful to sensitive species. For example, criteria have been proposed that are merely time-dependent extrapolations based on paradoxical laboratory bioassays as described above. Further refinement could readily accommodate additional evidence demonstrating dependence on temperature- and species-sensitivity.

Site specificity

As a general rule, however, a discharger should be allowed the opportunity to demonstrate that site-specific factors are appropriate; that would allow for a less conservative approach, but still be protective of the important aquatic life. In some cases, for instance, the rapid dissipation of reactive chlorine results in such a relatively small area of potential effect, that exclusion of fish from consideration may be possible. In other cases, the frequency of chlorination, in combination with a limited area of effect, may provide for development of probability estimates of lethal effects on fish, that would warrant different limitations from what might otherwise be applied.

Other factors may also temper the application of limitation on a site-specific basis. Maximum limitations, as a single value, are probably of little direct importance when the peak value may only occur for a few minutes. The true toxicity is obviously a function of the shape of the chlorine pulse, and of the relative composition of the different forms of chlorine.

Dechlorination techniques

It has been recognized that a readily available method for meeting restrictive chlorine limits is through the application of dechlorination chemicals. This would involve the stoichiometric application of a strong reducing agent, such as sodium sulfite, sodium thiosulfate, sodium metabisulfite, and sulfur dioxide, at the point of discharge.

The question then becomes one of determining the need and value of adding these additional chemicals to receiving waters in which the evidence may not indicate any harmful effects of the chlorine. For example, field bioassay tests with Lake Michigan water have shown that a maximum limit of 0.3 ppm TRC for a normal 30-min chlorination dosage will not cause toxic effects in rainbow trout, a species that is recognized as being highly sensitive to chlorine toxicity. Other observations have not shown observable effects at 0.5 ppm TRC, maximum, under similar conditions.

In view of these results, it is apparent that arbitrary decisions to add conservatism to discharge limits should consider costs. They should also take into account potential adverse environmental effects of techniques that might be used simply to meet such limits, with no perceptible environmental benefit.

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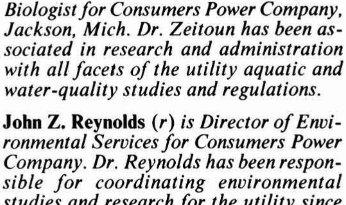

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John Z. Reynolds (*r*) *is Director of Environmental Services for Consumers Power Company. Dr. Reynolds has been responsible for coordinating environmental studies and research for the utility since 1969 and has been active in industry affairs dealing with water quality and related regulations. Currently he is on loan to the Ecological Assessment Program of the Electric Power Research Institute (Palo Alto, Calif.).* Coordinated by JJ

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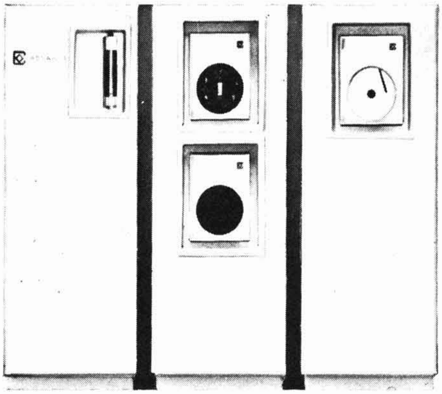

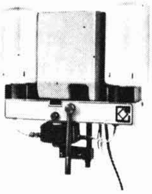

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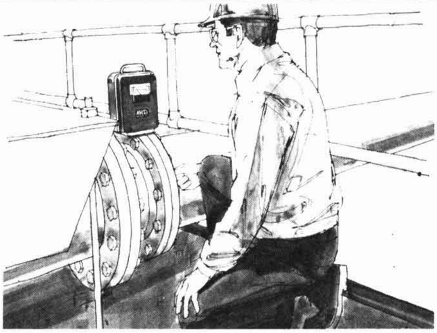

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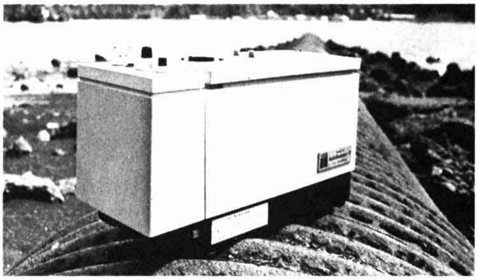

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ES&T RESEARCH

Multielement Analysis of Animal Feed, Animal Wastes, and Sewage Sludge

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■ Animal excreta and sewage sludge are currently being used as animal feed ingredients on an experimental basis. The levels of 30 elements are reported for a typical cattle feedlot diet, two dried cattle manures, a commercial cattle waste product, two dried poultry manures, and a metropolitan sewage sludge. The analyses are conducted using neutron activation analysis, induction coupled plasma spectroscopy, atomic absorption spectroscopy, and anodic stripping voltammetry. The levels of most inorganic elements are considerably higher in animal wastes and sewage sludge than in traditional animal feeds. For most elements the levels determined by several techniques are in good agreement. Problems of loss of lead with precipitate formation, accurate quantitation of elements present at high levels, and obtaining homogeneous samples for analysis are discussed.

Solid waste from farm animals has traditionally been used as cropland fertilizer. In recent years municipal sewage sludge is also being increasingly used as crop fertilizer. The safety with respect to animal and human health of cropland application of sewage sludge is currently the subject of considerable research activity (*1–5*). The broader aspects concerning management of sludge use on land to assure safety and wholesomeness of the food supply have also been discussed (*6*).

A large amount of undigested protein and high levels of several nutrient elements are found in solid wastes from animal feedlot operations and municipal waste treatment plants. These wastes are currently being considered as animal feed ingredients to be mixed with the more traditional grain and forage animal feeds.

The practice of feeding "wastelage" (derived from ensiling ground grass hay and manure), or mixtures of dried animal waste and feedlot diets appears to be commonplace (*7–9*). Although several states have approved the use of animal waste as a feed ingredient for meat producing animals sold in intrastate commerce, the U.S. Food and Drug Administration recently decided to delay issuing proposed guidelines for the safe use of animal waste in feed because legitimate questions about safety remain unanswered (*10*). While sewage sludge has not been formally approved for use in feed by any governmental agency, several federal and state-supported projects are studying the effects of feeding sewage sludge to animals on an experimental basis (*11*).

Numerous papers have appeared in the literature reporting the elemental content of animal wastes and sewage sludges for various numbers of elements (*1–5, 12–17*). Most feeding studies in which animal wastes or sewage sludge are fed to animals have been conducted with the objective of showing the nutritive value of the material being fed, and not for the purpose of determining possible effects on human or animal health (*12*). Bhattacharya and Taylor's (*12*) review indicates that little work has been done to determine typical trace element content of animal wastes for a number of important elements. Nor has much work been done to determine whether trace elements accumulate in edible tissue, or edible products, from animals fed diets containing animal wastes.

The purpose of our study was to determine the levels of as many elements as possible in typical dried animal wastes having a documented history and to compare these levels with those of the same elements in animal feeds and sewage sludges. These data should be useful in future studies or to other groups in arriving at conclusions about the desirability or relative safety of using animal wastes and sewage sludges as animal feed ingredients. Such data should also be considered in choosing among the various possible alternatives for beneficial use of animal wastes and sewage sludge, including cropland application, conversion to methane, and animal feed ingredients.

Experimental

Samples Analyzed. The samples analyzed were all received from the same source (Colorado State University) and included: (I) a typical feedlot diet without animal waste products added (the dry weight composition of this ration was 70% corn, 3% hay, 5% beet pulp, 20% corn silage, and 2% mineral supplement); (II) oven-dried cattle manure from feedlot heifers fed a low fiber diet containing 59% corn, 2% alfalfa hay, 3% molasses, 33% corn silage and 3% mineral supplement; (III) oven dried cattle manure from feedlot heifers fed a high fiber diet containing 24% corn, 29% alfalfa hay, 3% molasses, 41% corn silage, and 3% mineral supplement; (IV) a commercial high-protein feedlot animal waste product similar to (III) in which a portion of the fiber and ash was removed and the product was pelletized; (V) dried poultry waste with litter consisting of wood shavings mixed with excreta from hens fed a layer ration; (VI) dried poultry waste from caged laying hens without any litter; (VII) dried sewage sludge from Metropolitan Denver Sewage Disposal District No. 1 (Metro Denver). These samples correspond to columns I–VII, respectively, in Table I. Samples (V), (VI), and (VII) are being used as feedlot diet ingredients at Colorado State University.

Sample Homogenization. The feedlot diet was analyzed as received without further homogenization. Portions of the animal waste and sludge samples (100 g) were initially blended with a Waring Blendor (hereafter referred to as "blended" samples), and subsamples were analyzed by neutron activation analysis (NAA), flame atomic absorption spectrometry (AAS), and anodic stripping voltammetry (ASV) as described below. However, because most of the waste samples were still visibly inhomogeneous, additional portions of the as-received unhomogenized and unblended waste and sludge samples

(70–105 g each) were mixed in the ratio of 4 parts distilled deionized water to 1 part dry material and homogenized at high speed with a Model PCU-2 Polytron homogenizer (hereafter referred to as "homogenized" samples) equipped with a PT-35 K sonic probe-type generator until a homogeneous slurry was obtained (usually about 5 min). The slurries were then freeze dried in a VirTis Model 10-MRTR freeze drier. The resulting homogenized dry samples were analyzed by using AAS, ASV, NAA, and induction coupled plasma optical emission spectroscopy (ICP) in conjunction with the appropriate procedures described below.

Sample Mineralization. Dry samples for AAS, ASV, and ICP analyses were mineralized by acid digestion and analyzed following the procedures detailed below. Sample sizes for analysis were 1.00 g "blended" animal wastes and sewage sludge, 2.00 g for "homogenized" animal wastes, 0.20 g for "homogenized" sewage sludge, 2.00 g for unhomogenized feedlot diet, and 1.00 g for NBS Standard Reference Materials.

Samples for AAS, ASV, and ICP analyses were weighed into 100-mL micro-Kjeldahl flasks and digested with 25 mL HNO_3 and 5 mL $HClO_4$. Sample digests were transferred to 50-mL volumetric flasks and diluted to volume with deionized water.

As routine practice at least one 1.00-g sample of an NBS Standard Reference Material (Orchard Leaves, Bovine Liver, or Spinach) and one reagent blank were also carried through the entire analytical procedure for each set of 10 samples. "Blended" animal wastes and sewage sludge samples were digested and analyzed in duplicate, while "homogenized" samples and the unhomogenized, unblended feedlot diet were digested and analyzed in triplicate.

AAS Determination of Pb, Cd, Cu, Zn, Fe, Mg, and Mn. A Perkin-Elmer Model 403 or Model 503 AAS instrument with an air–acetylene flame was used for determining these elements. The following analytical lines were used: Pb 2833.1, Cd 2288.0, Fe 2483.3, Zn 2138.6, Cu 3247.5, Mg 2852.1, and Mn 2794.8, all in angstroms. Sample solutions were diluted when necessary to achieve elemental concentrations within the following ranges: 0.2–15 μg Cu/mL, 0.5–2.0 μg Zn/mL, 2.0–10.0 μg Fe/mL, 0.1–2.0 μg Mn/mL, and 0.1–0.5 μg Mg/mL. A 10% (v/v) $HClO_4$ concentration was maintained in diluted solutions. Sample solutions for Mg determinations contained 0.6% (v/v) La to prevent refracting oxide formation.

Sewage sludge was analyzed for Pb and Cd, and NBS Orchard Leaves were analyzed for Pb by AAS. These were the only samples with concentrations of Pb and/or Cd high enough for AAS analysis for the sample sizes analyzed.

ASV Determination of Pb and Cd. Those sample solutions prepared for AAS analyses which could not be quantitated for Pb and/or Cd by AAS were analyzed for these elements by using ASV. This included all sample solutions except those of sewage sludge and NBS orchard leaves. One-milliliter aliquots of the sample solution were buffered at pH 4.3 with a sodium acetate/acetic acid buffer and analyzed with a Princeton Applied Research (PAR) Model 174 polarographic analyzer equipped with a PAR Model 315 automatic electroanalysis controller, a hanging mercury drop electrode, SCE reference electrode, and platinum counter electrode. The technique of standard additions and the instrumental parameters previously reported (*20*) were used for quantitating the Pb and Cd present.

Hydride Generation–AAS Determination of As, Sb, and Se. All samples were analyzed for As, Se, and Sb by using the hydride generation–AAS procedure and apparatus reported by Fiorino et al. (*21*).

ICP Determination of 17 Elements. A Jarrell-Ash Model 975 Plasma Atomcomp was used to simultaneously analyze for 25 elements (Al, As, B, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Te, Ti, Tl, V, and Zn) in the same solutions prepared for AAS analysis. Operating parameters for ICP were 1100 W forward power; less than 5 W reverse power; plasma observation height 17 mm above the load coil; sample solution aspiration rate 1.2 mL/min.

The high and variable salt content of the sample solutions caused slight aspiration problems. Occasionally, the solution would clog the nebulizer and stop aspiration. Because the undiluted sample solutions contained levels of Fe and Ca beyond the linear range of the instrument, they had to be diluted 1–5.

NAA Determination of 22 Elements. The dry powdered samples were analyzed in three parts: a long irradiation-decay for long-lived radionuclides, a short irradiation-decay for short-lived radionuclides, and a chemical separation for Hg analysis. All irradiations were carried out at the FDA NAA facility, which uses the National Bureau of Standards (NBS) reactor in suburban Washington, D.C.

Long-Lived Radionuclides. Approximately 300 mg of the dry material was weighed into clean, high-purity quartz vials, sealed, and irradiated together with standards in the high flux position (6×10^{13} neutrons/cm^2/s) of the NBS reactor for 6 h. These were allowed to undergo radioactive decay for 2–4 weeks and then counted by using the automated data acquisition system described elsewhere (*22*). Briefly, this consists of an Ortec Ge(Li) detector (2.2 keV resolution, 15% efficiency) in an automatic sample changer (modified Nuclear Chicago Unit) connected to a Nuclear Data 4410 analyzer (16K memory). The data are collected and stored on magnetic tape for later reduction using the program MLTELMT (for Multielement) developed at FDA. Under these conditions ^{65}Zn, ^{82}Br, ^{51}Cr, ^{59}Fe, ^{140}La, ^{152}Eu, ^{46}Sc, ^{86}Rb, ^{131}Ba, ^{60}Co, ^{75}Se, and ^{124}Sb were determined.

Short-Lived Radionuclides. Approximately 400 mg of dry sample was weighed into cleaned polyvials and heat sealed. These samples and standards were irradiated in the low flux position (1×10^{13} neutrons/cm^2/s) of the NBS Reactor for 15 s and then counted after a 5-min decay. The Ge(Li) detector was the same as described earlier, but was connected to a Nuclear Data ND-100 analyzer with 2K memory. Again, the data were collected, stored on magnetic tape, and reduced later. Under these conditions ^{38}Cl, ^{28}Al, ^{56}Mn, ^{42}K, ^{52}V, ^{49}Ca, ^{27}Mg, ^{66}Cu, and ^{24}Na were determined.

Hg Analyses. Mercury was determined by irradiating the samples, which were sealed in high-purity quartz, in the high flux position (6×10^{13} neutrons/cm^2/s) of the NBS reactor for 1 h. The samples and standards were then allowed to undergo radioactive decay for about 3 days before separating the Hg by the Rook et al. (*23*) volatilization procedure. The samples were counted with an Ortec low-energy photon detector connected to the Nuclear Data ND-4410 analyzer. This counting procedure was previously described by Friedman et al. (*24*). Concentrations were calculated on all three peaks (67, 68.8, and 77.3 keV) and then averaged for the final concentration.

Results

The analytical results from determination of 30 elements in the animal feedlot diet, animal wastes, sewage sludge, and the NBS Standard Reference Materials are reported in Table I. Values are reported only for those elements with concentrations within the reliable quantitation range for the method indicated. For the highly toxic elements Be and Hg, "less-than" values are reported when quantitation was not possible. The mean levels of the same elements in sewage sludges from the 16-city study reported by Furr et al. (*15*) are also tabulated in Table I for comparison with the data obtained in this study. These mean values also compare well with the results of Sommers (*17*).

Table I. Elemental Content of Animal Feed, Animal Waste, Processed Waste Pellets, Sewage Sludge, and Reference Materials[a,b]

		Concentrations, ppm in dried samples										
										Reference materials[d]		
Element	Analytical method	I Feed lot diet	II Cattle manure low fiber diet	III Cattle manure high fiber diet	IV Processed cattle waste pellets	V Poultry waste with litter	VI Poultry waste without litter	VII Metro Denver sewage sludge	16 Cities[c] average sewage sludge	NBS Orchard Leaves	NBS Bovine Liver	NBS Spinach
As	AAS	0.10	0.88	2.2	0.60	0.57	0.66	8.1	14.3	10.8	0.50	0.16
										(11 ± 2)	(0.055)	(0.15 ± 0.05)
Ba	NAA	18.	105.	305.	70.	54.	57.	1066.	621.	45.	<30.	<45.
										NV	NV	NV
Be	ICP	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.25	<8.5	<0.06	<0.06	<0.06
										NV	NV	NV
Br	NAA	10.	34.	29.[d]	66.	9.[d]	31.	30.[d]	45.5	11.	11.	48.
										(10)	NV	(54)
Cd	AAS	NA	NA	NA	NA	NA	NA	26.0	104.	NA	NA	NA
	ASV	0.05	0.28	0.24	0.14	0.42	0.58	NA		NA	NA	1.32
	ICP	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	25.4		<2.5	<2.5	<2.5
										(0.11 ± 0.02)	(0.27 ± 0.04)	(1.5)
Co[e]	NAA	0.10	1.7	2.2	1.1	2.0	1.2	7.1	9.6	0.13	0.29	1.41
										(0.2)	(0.18)	(1.5)
Cr[e]	NAA	0.75	20.	31.	5.	6.	4.9	280.	1441.[f]	2.7	<0.4	4.8
										(2.3)	NV	(4.6 ± 0.3)
Cu	AAS	3.0	24.0	21.0	18.7	30.7	20.0	816.	1346.	11.6	185.	12.6
	ICP	2.6	22.3	19.5	15.9	30.6	18.1	905.		11.4	210.	12.3
										(12 ± 1)	(193 ± 10)	(12 ± 2)
Eu	NAA	0.012	0.12	0.4	0.06	0.03	0.07	0.6	3.7	<0.05	0.003	<0.2
										(0.027)	NV	(0.02)
Hg	NAA	<0.01	0.05	<0.03	<0.09	0.06	<0.04	7.8	8.6	NA	NA	NA
La	NAA	0.5	5.0	18.6	3.2	5.5	9.	56.	35.7	1.2	0.07	<.7
										(1.2)	NV	(0.37)
Mn	AAS	16.8	117.	161.	100.	166.	242.	220.	194.	81.3	10.4	155.
	ICP	17.2	111.	158.	90.	167.	246.	222.		80.0	9.7	157.
	NAA	17.	115.	185.	92.	176.	273.	262.		85.0	11.5	171.
										(91 ± 4)	(10.3 ± 1.0)	(165 ± 6)
Mo	ICP	<2.5	29.9	49.2	15.6	5.0	7.2	84.9	14.3	<5.	<5.	<5.
										NV	(3.2)	NV
Pb	AAS	NA	NA	NA	NA	NA	NA	950.	1832.	52.6	NA	NA
	ASV	0.36	2.10	3.28	3.29	2.08	3.45	NA		NA	NA	1.25
	ICP	<2.5	3.6	5.9	4.5	2.5	5.8	885.		44.9	<3.5	<3.5
										(45 ± 3)	(0.34 ± 0.08)	(1.2 ± 0.2)
Rb	NAA	2.3	17.	46.	15.	7.0	12.	42.	32.6	10.5	17.8	10.
										(12 ± 1)	(18.3 ± 1.0)	(12.1 ± 0.2)
Sb	AAS	<0.08	<0.08	<0.08	<0.08	<0.08	0.10	7.07	10.6	NA	NA	NA
	NAA	<0.03	0.14	0.26	0.10	0.10	0.19	11.		2.5	<0.02	0.05
										(2.7)	NV	(0.04)
Sc	NAA	0.065	0.54	1.41	0.44	0.21	0.44	2.6	2.5	0.067	<0.004	0.16
										NV	NV	(0.16)
Se	AAS	0.19	0.35	0.32	0.36	0.38	0.66	4.57	3.1	0.07	1.06	0.025
	NAA	0.21	0.5	0.6	0.7	0.5	0.9	7.2		0.20	1.1	<0.6
										(0.08 ± 0.01)	(1.1 ± 0.1)	NV
Sn	ICP	<0.8	4.73	7.40	3.74	2.04	4.05	93.5	216.	<1.5	<1.5	3.1
										NV	NV	NV
Ti	ICP	8.1	54.9	129.	50.0	12.1	27.4	398.	2331.	7.6	<0.15	16.5
										NV	NV	NV
V	NAA	0.57	3.2	8.0	3.0	3.9	4.3	20.	40.6	0.8	0.46	1.7
										NV	NV	NV
Zn	AAS	20.0	115.	86.	76.7	155.	158.	1672.	2132.	25.9	145.	59.7
	ICP	20.9	101.	79.2	69.2	142.	143.	1717.		23.1	135.	48.
	NAA	19.0	114.	110.	80.	133.	141.	1978.		23.	124.	48.
										(25 ± 3)	(130 ± 10)	50 ± 2)
		% (or ppm if noted) in dry weight sample										
Al	ICP	0.023	0.17	0.38	0.18	0.047	0.07	1.12	1.83	157. ppm	<15 ppm	482. ppm
	NAA	0.065	0.51	1.56	0.28	0.087	0.20	1.96		383. ppm	65. ppm	881. ppm
										(420) ppm	NV	(870 ± 50) ppm
Ca	ICP	0.46	2.03	2.16	2.32	4.88	9.42	5.90	3.62	2.63	140. ppm	1.62
	NAA	0.31	1.85	1.78	1.90	3.70	7.10	4.50		2.15	309. ppm	1.46
										(2.09 ± 0.3)	(123. ppm)	(1.35 ± 0.03)
Cl	NAA	0.17	1.01	0.85	0.71	0.35	0.65	0.71	0.38	675. ppm	2530. ppm	6290. ppm
										(700. ppm)	(2600. ppm)	(6400. ppm)

(Continued on page 788)

Table I. Continued

		Concentrations, ppm in dried samples										
										Reference materials[d]		
Element	Analytical method	I Feed lot diet	II Cattle manure low fiber diet	III Cattle manure high fiber diet	IV Processed cattle waste pellets	V Poultry waste with litter	VI Poultry waste without litter	VII Metro Denver sewage sludge	16 Cities[c] average sewage sludge	NBS Orchard Leaves	NBS Bovine Liver	NBS Spinach
Fe	AAS	0.023	0.22	0.51	0.20	0.073	0.18	1.51	3.06	246. ppm	253. ppm	494. ppm
	ICP	0.024	0.22	0.48	0.20	0.071	0.17	1.61		235. ppm	254. ppm	478. ppm
	NAA	0.025	0.27	0.65	0.21	0.077	0.18	1.73		259. ppm	257. ppm	510. ppm
										(300 ppm)	(270 ± 20) ppm	(550 ± 20) ppm
K	NAA	0.80	1.94	4.70	2.80	1.80	2.30	1.40	1.22	1.42	7420 ppm	3.73
										(1.47 ± 0.03)	(9700 ± 600) ppm	(3.56 ± 0.03)
Mg	AAS	0.156	0.46	0.42	0.50	0.26	0.46	0.35	0.60	0.53	566 ppm	0.84
	ICP	0.155	0.45	0.41	0.50	0.26	0.43	0.35		0.49	613 ppm	0.70
	NAA	0.180	0.55	0.63	0.68	0.28	0.65	0.74		0.63	949 ppm	0.98
										(0.62 ± 0.02)	(605 ppm)	NV
Na	NAA	0.088	0.69	0.91	0.47	0.21	0.57	0.44	0.44	155. ppm	2438. ppm	1.44
										(82 ± 6) ppm	(2430 ± 130 ppm)	NV
P	ICP	0.29	0.61	0.39	0.41	0.89	1.34	1.46	1.56	0.156	0.98	0.45
										(0.21 ± 0.01)	NV	(0.55 ± 0.02)

[a] Abbreviations: AAS, Atomic absorption spectroscopy; ASV, anodic stripping voltammetry; ICP, induction coupled plasma; NAA, neutron activation analysis; NA, not analyzed; NV, no NBS value available. [b] All values for samples I–VII are average of triplicate analyses. [c] Calculated mean from ref. *15* values. See ref. *15* for method used. [d] NBS values in parentheses. [e] "Blended" samples. Co and Cr contamination from homogenizer prevented analysis of "homogenized" samples. [f] Milwaukee 14 000 ppm value excluded in calculating 16-city mean for Cr.

Among the animal wastes, the low fiber diet manure has a slightly lower content of most metals than the high fiber diet manure. The processed waste pellets, which are derived from a high fiber diet manure, also had a lower content of most metals than did the high fiber diet manure. During processing of the pellets, some of the fiber and ash was removed from the manure, which probably accounts for the lower metals content (*25*). In general, the poultry waste without litter contains higher levels of most elements than the poultry waste with litter. The lower levels in waste with litter probably are due to dilution by the litter (mostly wood chips).

The order of magnitude of the levels of elements found in the Metro Denver sewage sludge compares well with the average level calculated from the 16-city study by Furr et al. (*15*). With a few exceptions the levels of elements found in the NBS Reference Materials agree well with the certified or uncertified NBS values.

Whenever the levels found in the same sample by different determinative step techniques could be compared, the results are generally in good agreement. Two exceptions are the lower Se and Sb values obtained by AAS compared to NAA. Only the acid-soluble portion of the sample is analyzed by AAS; these results indicate that part of the Se and Sb is associated with the acid-insoluble portion of the samples.

Several observations and related experiments were made during the analyses. The "homogenization" of the waste and sewage sludge samples resulted in measurably higher levels of Co, Cr, and Ni compared to the "blended" samples. This is probably due to contamination from abrasion of the probe blade caused by the shearing action of the probe acting on the solid material in the sample. This shear action is not present with the Waring Blendor. The values for Co and Cr in Table I are for the "blended" samples. Ni was below the quantitation limit but sufficiently above the detection limit to observe the increase noted above. Due to data acquisition limitations of the ICP, those solutions containing high levels of Ca and Fe required dilution.

However, for the purpose of making comparison, all solutions were analyzed before and after a fivefold dilution. The levels of Al, Mg, P, and Zn in all samples and Ca and Fe in those not requiring dilution showed about a 10% increase in concentration in the diluted over the undiluted samples after accounting for the dilution factors. The AAS results for Fe, Mg, and Zn agreed more closely with the ICP results on diluted samples. Thus, the levels reported in Table I for Al, Ca, Fe, Mg, P, and Zn are from the diluted solutions. The cause of these dilution discrepancies is not fully understood, but was not seen with other elements present at lower concentrations. A 1.00-g digested sample of sewage sludge showed a decrease in Pb concentration with time as shown in Figure 1. For this reason, a 0.20-g sample was digested to provide a more dilute solution for analysis. The Pb concentration in the dilute sample was stable with time. Cd did not show a time decrease, nor did any of the other samples show this problem with Pb or Cd. With animal waste and sludge samples, a sand-like residue remained after the nitric-perchloric and the nitric-perchloric-sulfuric acid digestions. One set of residues from the nitric-perchloric digest was filtered out, treated with HF, diluted to 25 mL with 4% HCl (v/v), and analyzed by AAS for Zn and Cu. No detectable Zn or Cu was found in the animal residues, and the amount of these elements in the sludge residue was very low, less than 0.4% of that in the original acid soluble portion. One set of filtered residues of the nitric-perchloric-sulfuric digest was analyzed by NAA for As, Sb, and Se. These elements were detected, but not quantitated in the residues.

Considering the gross inhomogeneity of the samples as received by the laboratory, including the wood chips, feathers, undigested grain, small rocks, and other identifiable particles

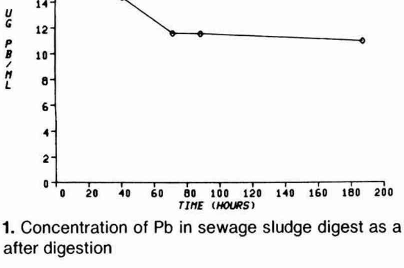

Figure 1. Concentration of Pb in sewage sludge digest as a function of time after digestion

Table II. Analytical Precision for Selected Elements in Animal Sewage Sludge[a]

Element	Determinative[b] instrument	Coefficient of variation %[c]	
		Blended	Homogenized
Al	NAA	13.3	4.9
	ICP		2.9
As	AAS	3.0	5.2
Ca	NAA	11.5	5.8
	ICP		4.8
Cd	ASV	69.6	9.2
Cu	AAS	4.6	1.4
	ICP		2.7
Fe	NAA	8.6	5.9
	ICP		1.7
	AAS		2.1
K	NAA	28.8	28.6
Mg	NAA	27.3	28.0
	ICP		1.1
	AAS		1.3
Mn	NAA	22.0	5.5
	ICP		2.2
	AAS		3.9
Na	NAA	22.7	4.1
Pb	ASV	23.3	5.9
Se	AAS	7.6	7.1
Zn	NAA	7.3	4.6
	AAS	1.4	2.2
	ICP		1.8

[a] Based on analyses of five animal wastes and one sewage sludge listed in Table I. [b] Abbreviations: AAS, atomic absorption spectroscopy; ASV, anodic stripping voltammetry; ICP, induction coupled plasma; NAA, neutron activation analysis. [c] Based on duplicate analyses for blended samples and triplicate analyses of homogenized samples.

normally present in animal waste and sewage sludge, the precision of the analytical results and the agreement of analyses of a given sample by several techniques are quite good. The extensive amount of data does not permit reporting precision data for individual elements by all techniques. However, representative precision data are reported in Table II, and it can be seen that the homogeneity of the samples was improved for most elements after "homogenization" compared to "blending".

Discussion

Table III compares the levels of several elements found in the feedlot diet analyzed in this study with the mean levels of the same elements reported in the literature for alfalfa hay, corn, barley, and wheat (*18*). These data show that the feedlot diet closely approximates these traditional animal feeds. Table III also compares the mean elemental level in both animal wastes analyzed in this study and the sewage sludge results of Furr et al. (*15*) with those in the feedlot diet. Both animal wastes and sewage sludge show about a fivefold increase for the macronutrient elements compared to the feedlot diet. However, for the micronutrient, toxic, and nonessential elements the increases are generally considerably higher, with roughly a tenfold increase of these elements in animal wastes compared to animal feed, and as high as a several hundredfold increase for sewage sludge compared to animal feeds. Thus, the potential for accentuated accumulation of trace elements in animal tissues exists when animal wastes or sewage sludge is used as diet ingredients.

The levels of the macroelements Ca, Cl, Mg, P, K, and Na, and of the microelements Co, Cu, Fe, Mn, Se, and Zn found in the animal wastes and sewage sludge are considerably above the levels of these elements reported in the literature (*18*) as being necessary for normal growth in cattle, horses, sheep, swine, rats, and dogs. The levels of As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Sn, Ti, V, and Zn are all at least a factor of 5 higher in animal wastes than in the feedlot diet. The levels of some of these may be high enough to raise concern about continuous use of animal wastes as an animal feed ingredient. The levels of Al, As, Cd, Co, Cr, Cu, Eu, Fe, Hg, Pb, Sb, Sn, Ti, and Zn are all at least a factor of 100 higher in sewage sludge than in the feedlot diet. Toxicity could be expected to occur in some animals fed the levels of Cd, Cr, Cu, Fe, Mn, Pb, Se, and Zn shown in Table I for sewage sludge (*19, 26, 27*). Whether any of the above elements would concentrate in animal tissues, similar to that demonstrated in previous studies (*1, 6, 13, 14*) sufficiently to present a human health hazard can only be determined by appropriate feeding studies with animal wastes or sewage sludge as feed ingredients. Cd accumulates in beef liver and kidney (*28*), and the current level of Cd in the American food supply already approximates the World Organization maximum tolerable intake (*6*).

Multiple recycling of animal wastes should also be studied for the effects on animal health and tissue elemental levels. Assuming a more or less constant concentration factor for each element with each pass through the animal and a more or less constant fractional absorption of each element during each pass, the potential exists for significantly elevated absorption for most elements after only a few passes. Whether multiple

Table III. Comparison of Elemental Levels in Animal Feeds, Animal Wastes, and Sewage Sludge[a]

Elements	FLD/AF	AW/FLD	SS/FLD
Macronutrients			
Ca	0.84	9.6	9.4
Cl	1.2	4.2	2.2
K	0.96	3.4	1.5
Mg	0.82	2.8	3.7
Na	1.3	6.5	5.0
P	0.78	2.5	5.4
Mean	0.98	4.8	4.5
Micronutrients			
Co	1.1	16.4	96
Cr		17.4	1920
Cu	0.33	7.9	481
Fe	2.5	10.3	128
Mn	0.52	9.4	11.4
Mo		>8.6	>5.7
Se		3.0	15.5
Sn		>5.5	>270
V		7.9	71.2
Zn	1.2	5.7	107
Mean	1.1	>9.2	>311
Toxic elements			
As		9.8	143
Cd		6.6	2080
Hg		>5	>860
Pb		10.1	5089
Sb		>5.3	>353
Mean		>7.4	>1705
Nonessential elements			
Al		8.1	28
Ba		6.6	34.5
Br		3.4	4.6
Eu		11.3	308
La		16.5	71.4
Rb		8.4	14.2
Sc		9.4	38.5
Ti		6.8	288
Mean		8.8	98.4

[a] All numbers are ratios of elemental levels (ppm on air-dried weight basis) in materials being compared. FLD, feedlot diet, sample I, Table I; AF, animal feed (ref. *18*); AW, animal wastes, samples II–VI, Table I; SS, sewage sludge (ref. *15*).

recycling of animal wastes actually results in elevated tissue elemental levels can only be determined by appropriate studies.

Any widespread use of animal wastes or sewage sludge as animal feed ingredients could be expected to be accompanied by a need for periodic multielement and multiresidue organic analysis of the mixture being fed. Because of the gross variability, both with time and location, of animal wastes and especially sewage sludge, obtaining representative samples for analysis, which accurately reflect the average level of each element or residue being fed, would be a difficult problem. The cost of such representative analyses would detract from the economic gain of using these waste products as animal feed ingredients.

The results of this work indicate that the levels of most inorganic elements are considerably higher in animal wastes and sewage sludge than in traditional animal feeds. These findings suggest that the safety of using animal wastes, sewage sludge, and multiple recycled animal wastes, both with respect to animal and human health, should be thoroughly investigated.

Acknowledgment

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Monitoring of Polynuclear Aromatic Hydrocarbons in Water
II. Extraction and Recovery of Six Representative Compounds with Polyurethane Foams

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■ Flexible polyurethane foam plugs effectively concentrated trace quantities of the six representatives of the polynuclear family from large volumes of finished and raw waters when the water was heated to 62 ± 2 °C and passed through foam plugs at a flow rate of 250 ± 10 mL/min. The retention efficiencies of the individual PAH on the foams were no less than 88% from finished water and 72% from raw water. The purification of the concentrate was achieved by solvent partitioning and column chromatography on Florisil. The recovery of PAH from the cleanup procedure varied between 90–100%. Thin-layer chromatography coupled with fluorometric detection was more sensitive and selective than gas-liquid chromatography–flame ionization detection. The technique described detected as low as 0.1 ng/L of an individual PAH.

In a previous publication (*1*) the preconcentration of benzo(a)pyrene from water with polyurethane foam plugs as sorbent was reported. It was determined that benzo(a)pyrene retention was almost quantitative from water spiked with the radioactive compound when the water temperature was maintained at 62 ± 2 °C and the flow rate at 250 ± 10 mL/min. The use of radiolabeled benzopyrene eliminated the need for any chemical cleanup procedure for its quantification. Establishing the general validity of the method toward other polynuclear aromatic hydrocarbons (PAH) requires the determination of the retention efficiencies of other PAH and thus the development of an analytical method involving cleanup of the foam extract and a selective detection method to aid their quantification.

The choice of procedure for the separation of PAH from the interfering classes of compounds depends largely on the type of sample to be analyzed. No satisfactory method exists for the analysis of PAH in drinking waters and their respective raw waters, although abundant references are available for their analysis in other types of samples (*2–6*).

In this paper, collection efficiencies of foam plugs for mixtures of benzo(a)pyrene, fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, and benzo(ghi)perylene from water are reported. A cleanup procedure is described which is capable of removing impurities introduced from water and foam plugs to the extent necessary for their interference-free detection. The compounds selected are regarded as representatives of the whole polynuclear family, and examination of drinking waters for the presence of these PAH has been recommended by the World Health Organization (*7*).

Experimental

Materials and Reagents. The PAH compounds, benzo(j)fluoranthene (BjF) and benzo(k)fluoranthene (BkF), were obtained from J. F. Monkman, Air Pollution Control Directorate, Ottawa, Canada. Fluoranthene (FL), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IP), and benzo(ghi)perylene (BPR) were obtained from Aldrich Chemical Co., Inc. Each compound was at least 99% pure as verified by gas chromatographic and TLC–fluorometric analysis. All the solvents used were "Distilled in Glass" grade, and other chemicals were either chromatographic or analytical grade. Polyurethane foam plugs (referred to as Identi plugs by the manufacturer) were obtained from VWR Scientific Co.

Water Samples. Laboratory tap water was used as a representative finished water. Water from Onondaga Lake (Syracuse, N.Y.) was chosen in retention studies with raw water since it would represent a worst possible case of raw drinking water source (total suspended = 102 mg/L; total dissolved solids = 2.4 g/L.

PAH Separation and Analysis. PAH analysis was performed using two techniques: gas-liquid chromatography–FID detection and thin-layer chromatography–fluorescence detection. A Hewlett-Packard 5730A gas chromatograph with a dual-flame ionization detector and a linear temperature programmer was operated in a differential mode. The matched columns consisted of 6 ft × ⅛ in. stainless steel packed with 3% Dexsil-300 on chromosorb W (AW, DMCS treated, 100–120 mesh). The chromatograph was programmed in the following manner: initial temp: 200 °C; initial delay: 2 min; program rate: 4 °C/min; final temp: 290 °C; final delay: 8 min.

The stainless steel injection port liner was kept at 250 °C and the detector block at 300 °C. To avoid ghost peaks, the use of aluminum foil backed septa (Metasep, Altech Assoc., Inc.) was found necessary. For injection of samples, a solvent flush technique (*8*) was used to prevent injection error. The GLC conditions used failed to separate the isomers—benzo(j)-fluoranthene and benzo(k)fluoranthene—and therefore combined values are presented. The quantification of these PAH was based on the response obtained with 1:1 mixture of the two compounds.

Thin-layer chromatography was performed using aluminum oxide:acetylated cellulose plates which were prepared as described by Borneff and Kunte (*9*) except that 2% (w/v) $CaSO_4 \cdot 2H_2O$ (200 mesh) was added to the slurry to increase binding of the layer to the surface. The plates were developed in two dimensions: *n*-hexane:benzene (4:1, v/v) and methanol:ether:water (4:4:1, v/v).

The emission and excitation spectra used for identification of the suspected PAH spots were run directly on the plates at room temperature with an Aminco thin-film scanner attached to an Aminco-Kiers spectrophotofluorometer. This procedure eliminated the losses usually encountered during removal of PAH spots for fluorescence measurement in solvents and the interferences arising due to solvent interactions.

For quantification of the spots, the excitation wavelength was fixed at 365 nm, and the fluorescence intensities were measured at the following wavelengths (nm): FL:458, BjF:427, BkF:428, BaP:427, IP:467, and BPR:416. During quantification, any day-to-day variation in the intensity of the light source was corrected by measuring the intensity with a standard quinine sulfate spot.

Cleanup Procedure. During the concentration of PAH from water on foam plugs, several other contaminants were also concentrated and some of these got eluted during PAH elution. In addition, several impurities belonging to foam were also leached during the elution process. The latter impurities could be partially eliminated only by precleaning of the plugs

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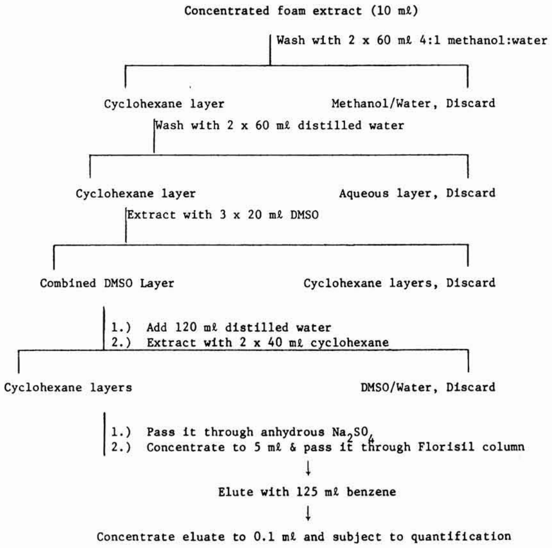

Figure 1. Flow chart of cleanup method

with cyclohexane and/or benzene by batch or soxhlet extraction. The impurities interfered with the analysis of PAH; therefore, efforts were directed to devise a cleanup procedure. The levels of impurities and subsequently the extent of cleanup necessary are directly dependent upon the sample volume and number of foam plugs employed for concentration. Our estimates based on the available data concerning the levels of PAH in drinking water (*7, 9*) showed that a sample volume of 60 L would be adequate for detection of PAH. Earlier studies (*1*) showed that four foam plugs would effectively concentrate PAH from 20 L of finished water. In view of this information, studies were undertaken to devise a cleanup procedure to remove interfering substances, introduced from 60 L tap water and those leached from 12 foam plugs.

Sixty liters of unspiked finished water was passed through six precleaned (*1*) foam columns each containing two plugs, in three successive steps maintaining the water temperature at 62 ± 2 °C and flow rate of 250 ± 10 mL/min. Each column was eluted with 30 mL acetone and 125 mL cyclohexane. The combined extract was concentrated (*1*) and subjected to cleanup. At no time was the PAH mixture allowed to proceed to complete dryness since this has been shown to result in loss of PAH (*6*).

The first cleanup step consisted of a solvent partitioning procedure of Hoffmann and Wynder (*1*) as modified by Acheson et al. (*11*). However, this procedure alone was inadequate, and additional cleanup involving a short Florisil column was found to be necessary for further separation from impurities. Chromatographic grade Florisil (60–100 mesh) was washed with methanol and 1:1 hexane:benzene and activated for at least 4 h at 130 °C. The Florisil was cooled to room temperature, and 8 g was transferred to a glass column (1.5 × 30 cm) with benzene by slurry method and washed with an additional 100 mL of benzene prior to passing sample concentrate through it. The flow chart illustrated in Figure 1 depicts the complete cleanup procedure.

The recovery of PAH from the cleanup procedure was determined by spiking the eluate prepared from the foam plugs exposed previously to finished water, and subjecting it to the full cleanup procedure. The PAH recovered were quantified by GLC–FID analysis. The contribution of the PAH from finished water was below the detection limit of FID.

Determination of Retention Efficiencies of PAH on Foam Plugs. The retention efficiency of the foam plugs for the PAH was determined with spiked water contained in a glass bottle. Initially, the retention efficiency was determined at a concentration of 25 μg/L for each PAH that could be detected by GLC–FID. Experiments were later conducted to evaluate the retention efficiency at lower PAH concentrations; concomitantly, large sample volumes and the more sensitive TLC–fluorometric detection method were employed.

In experiments with higher concentrations, 4 L of spiked-finished water was passed through one foam plug, and the plug was eluted. To account for the PAH adsorbed on the walls of the bottles holding the spiked samples, the bottle was washed with acetone and benzene and the washings were added to the foam eluate. The combined extract was concentrated, and PAH determined by GLC–FID. Purification of the concentrate was unnecessary because of relatively higher added PAH concentrations and lower levels of impurities.

Retention of PAH on foam plugs from large volumes of water was examined with both raw and finished waters. The sample volume was 60 L for finished water and 30 L for raw water. Water was spiked with a PAH mixture in a 12-gal Pyrex glass bottle to a concentration of 500 ng/L for fluoranthene and 100 ng/L for all others. Following mixing for an hour with a Teflon magnetic stirrer, the spiked water was passed through foam columns maintaining optimum conditions for retention. Foam columns were changed after every 20 L in the case of finished water and every 10 L for raw water (*1*). Foam plugs were eluted, and the eluate was concentrated and subjected to the full cleanup procedure. Quantification of PAH in the eluate was performed by the TLC–fluorometric method.

The actual PAH concentration in the aqueous phase (as contrasted with the amount added) was determined by extracting two 1-L aliquots of spiked water, one at the beginning and the other at the end of the PAH preconcentration pro-

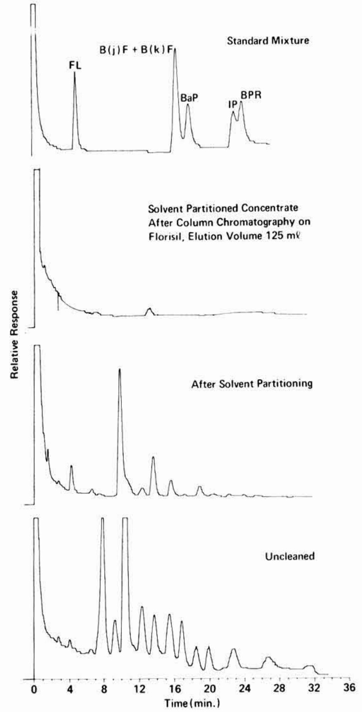

Figure 2. Purification efficiency of cleanup procedure

cedure. The extracted cyclohexane layers from the two steps were combined and concentrated. Following cleanup, the extract was concentrated to 0.1 mL and subjected to TLC–fluorometric analysis for the quantification of the six PAH. The determination of PAH concentration in the aqueous phase eliminated the need for quantification of PAH losses due to adsorption to the holding bottle and determination of the background PAH concentration in the unspiked water. Results are expressed as averages of duplicate analyses.

Results and Discussion

The chromatogram of the uncleaned foam eluate shown in Figure 2 points out that a cleanup procedure was required prior to quantification. During the development of the cleanup method, considerable effort was devoted to justify the necessity and verify the reliability of each step. Since PAH are known to form charge-transfer complexes, DMSO was selected to obtain an aromatic hydrocarbon enriched mixture largely separated from alkane impurities. Acheson et al. (*11*) have shown that extraction efficiency for the six PAH from cyclohexane by DMSO is almost quantitative. The gas chromatogram of the foam eluate after purification by solvent partitioning is shown in Figure 2. Several impurity peaks remain in the PAH region, suggesting the necessity of further cleanup. These impurity peaks were eliminated by chromatography on a short Florisil column. The recovery of PAH from the entire cleanup procedure obtained on PAH-spiked foam eluate is presented in Table I. The data show quantitative recovery for each PAH.

The cleaned-up eluate, when subjected to thin-layer chromatography, showed three fluorescent spots. Since these impurities could be seen in the foam eluate without exposure to finished water, they originated either from the foam or eluating solvents. Thin-layer chromatography of the concentrate from solvent blank proved that these impurities were contributed from the foam plugs and not from solvents. The impurities were not detected by gas-liquid chromatography since only a small portion of the total concentrate was injected.

Thin-layer chromatography of the cleaned-up foam eluate spiked with the standard PAH mixture showed that one of the impurity spots did not cause any interference. Of the other two spots, one remained unresolved with BPR and the other with FL. Matching of the fluorescent emission and excitation spectra of the impurities with the spectra of the model PAH compounds (Figure 3) revealed that one spot was BPR and the other a composite of an unidentified compound superimposed on a spot recognized as FL. The unidentified compound exhibited its emission minimum at FL emission maximum and thus presented no problem in quantification of FL. The presence of trace amounts of FL and BPR in plugs necessitated running a foam blank with each batch of foam plugs and correcting the values of BPR and FL obtained in samples. The foam plugs used in this study contained 70 ng FL and 10 ng BPR per 12 foam plugs.

PAH have a tendency to adsorb to solid surfaces including on the surface of the glass bottle used for holding the spiked sample. In evaluating the retention efficiency of foam plugs for PAH, it was necessary to account for these losses. Table II shows the amount of each PAH actually added and that recovered from the aqueous phase. The PAH losses amount to as high as 77.4% in the case of BPR. Similar losses have been noted by Acheson et al. (*11*). Direct leaching of the bottle with solvents and quantification of the leachate showed that over 90% of these losses could be accounted for by bottle adsorption alone. To account for these losses in foam retention studies, two different approaches were used depending upon the sample volume and the size of the bottle used. In experiments with sample volumes that could be contained in a 5-L bottle, it was possible to eluate the adsorbed PAH from bottle surface and thus correct for these losses. Similar leaching of adsorbed PAH was not feasible with a 12-gal bottle which was used to hold larger sample volumes. In these experiments, therefore, the actual concentration of PAH in the aqueous phase of the spiked samples was experimentally determined following equilibration with the holding bottle.

Table I. Recovery of Overall Cleanup Method Determined by Gas-Liquid Chromatography

Compound	Amt of std added (μg)	Amt of std recovered (μg)	% Recovery
FL	10.0	8.97	89.7
B(j+k)F	20.0	20.2	101.0
BaP	10.0	10.0	100.0
IP	10.0	8.93	89.3
BPR	10.0	9.15	91.5

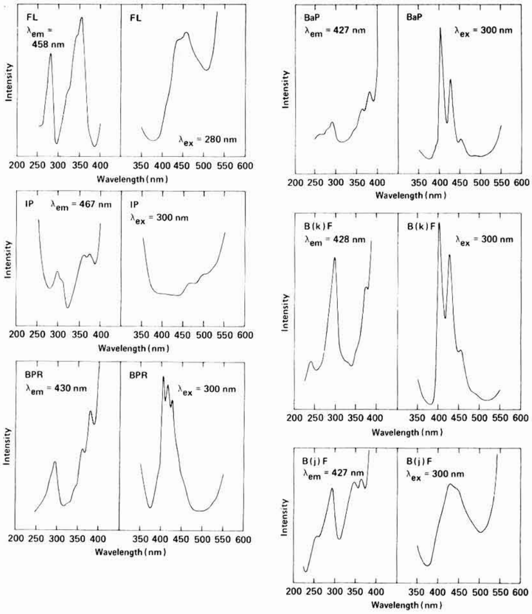

Figure 3. Fluorescence emission and excitation spectra of model PAH compounds obtained directly on plate

Table II. Amount of PAH Unaccounted for as a Result of Mixing with Water in a Glass Bottle. Water Volume: 60 L; Bottle Capacity: 12 Gal

Compound	Concn on basis of amt added to water (ng/L)	Concn found in aq phase (ng/L)	% PAH losses
FL	500	278.6	44.3
BjF	100	48.3	51.7
BkF	100	51.7	48.3
BaP	100	36.4	63.6
IP	100	25.5	74.5
BPR	100	22.6	77.4

Foam retention efficiencies of the six PAH from spiked laboratory tap water at 25 ppb are shown in Table III. The data confirm that polyurethane foam plugs under suitable conditions not only effectively concentrate benzo(a) pyrene

Table III. Foam Retention Efficiencies for PAH from Treated Water. Water Source: Laboratory Tap Water; Water Volume: 4 L; Concn of Each PAH: 25 ppb; Detection Method: GLC–FID

Compound	Amt added to water (μg)	% Retention
FL	100	100
BjF	100	88[a]
BkF	100	
BaP	100	81
IP	100	89
BPR	100	91

[a] Combined value given since the compounds could not be separated on the GLC column.

Table IV. Foam Retention Efficiencies for PAH from Treated Water. Water Source: Laboratory Tap Water; Water Volume: 60 L; Concn of Fluoranthene: 500 ppt; All Others: 100 ppt; Detection Method: TLC–Fluorometric

Compound	Concn in aqueous phase (ng/L)	Amt retained by foam from 1 L of water (ng)	% Retention
FL	278.6	260.4	93.5
BjF	48.3	47.4	98.1
BkF	51.7	50.6	97.9
BaP	36.4	33.6	92.3
IP	25.5	23.9	93.7
BPR	22.6	19.8	87.6

Table V. Foam Retention Efficiencies for PAH from Raw Water. Water Source: Onondaga Lake; Water Volume: 30 L; Concn of Fluoranthene: 500 ppt; All Others: 100 ppt; Detection Method: TLC–Fluorometric

Compound	Concn in aqueous phase (ng/L)	Amt retained by foam from 1 L of water (ng)	% Retention
FL	289.1	343.7	118.9
BjF	77.6	94.0	121.1
BkF	66.1	55.6	84.1
BaP	74.5	59.7	80.1
IP	85.2	61.2	71.8
BPR	23.9	28.3	118.4

Table VI. Limit of Detection of PAH with Foam Preconcentration Coupled with TLC–Fluorometric or GLC–FID Method

	TLC–fluorometric detection		GLC–FID detection	
Compound	Absolute limit (ng)	Limit in 60 L water (ng/L)	Absolute limit (ng)	Limit in 60 L water (ng/L)
FL	140.0	2.3	13.6	4.5
BjF	7.5	0.1	10.1[a]	3.4[a]
BkF	5.0	0.1		
BaP	10.0	0.2	11.9	4.0
IP	10.0	0.2	14.7	4.9
BPR	20.0	0.3	14.9	5.0

[a] Combined values given since the compounds could not be separated on the GLC column.

but other PAH as well. Foam plugs concentrated PAH almost quantitatively from finished water at lower concentrations also (Table IV). The high PAH retention efficiencies were also maintained with heavily polluted surface waters (Table V). It is unclear why the retention values for FL, BjF, and BPR are well above 100%. A possible explanation for this may be the inability of cyclohexane extraction to quantitatively recover these PAH from the heavily polluted water; this will give rise to lower PAH concentration in the aqueous phase than actually present. In this context, it is of interest to mention that Acheson et al. (*11*) have noted a difference in the extraction efficiency of dichloromethane for the two PAH–pyrene and benzo(ghi) perylene from waters containing suspended solids.

Recovery studies with the mixture of six PAH could not be undertaken at concentrations lower than 100 ppt because of the difficulty in PAH quantification in the aqueous phase by direct extraction. Experiments with radiolabeled BaP (*1*) have shown that retention is quantitative at concentrations as low as 2 ppt; thus, it is not unlikely that other PAH will also be efficiently retained at such low concentrations. The ability of foam plugs to effectively retain PAH at such a wide concentration range is valuable from the point of view of field monitoring where large fluctuations in concentrations may be encountered.

Table VI shows the detection limits of the six PAH using the polyurethane foam preconcentration method with GLC–FID or TLC–fluorometric analysis. The detection of FL and BPR in TLC–fluorometry is restricted by the background levels of these compounds contributed from the foam plugs. Their detection limit is assumed to be twice the background fluorescence level. In the case of the GLC–FID method, the detection limits for PAH are based on a minimum output response of five times the background noise level and a maximum sample loading volume of 5 μL from a total of 100 μL concentrate.

Conclusions

Polyurethane foam plugs are excellent for preconcentration of the six representatives of the polynuclear family from finished and raw waters. The cleanup procedure devised is capable of separating PAH from the impurities introduced from water and polyurethane foam. Thin-layer chromatography coupled with fluorometric detection is more sensitive and selective, and possesses a much larger sample capacity than gas-liquid chromatography–FID. The overall method is convenient and suitable for routine monitoring of PAH in waters.

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Polynuclear Aromatic Hydrocarbons in Selected U.S. Drinking Waters and Their Raw Water Sources

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■ A portable sampler, which allowed control of optimum conditions for collection of polynuclear aromatic hydrocarbons on polyurethane foam plugs at water distribution/treatment sites, was assembled. This instrument was employed for monitoring PAH in treated and raw waters at 10 selected water supplies in the eastern U.S. PAH were detected in the ng/L range in all the waters sampled. While the sum of the concentration of six representative PAH in drinking waters was small (0.9–15 ng/L) in all cases, the value determined for a raw water was as high as 600 ng/L. A considerable reduction of PAH was noted as a result of water treatment. Whether the PAH are actually removed or transformed to some other compounds was not determined.

In recent years concern has been expressed over the possible occurrence of certain carcinogenic compounds in drinking water. A group of compounds that has received particular attention is the polynuclear aromatic hydrocarbons (PAH). The levels of PAH in the water environment have been extensively studied by many European researchers (*1–3*), but data regarding their levels in U.S. drinking waters and their respective raw waters are virtually nonexistent.

Although there is no epidemiological evidence to prove that PAH in drinking water are related to the incidence of cancer, the investigation of Poel (*4*) indicates that the potential danger of continuous exposure to carcinogenic PAH through drinking water should not be overlooked, even at low concentration. Borneff (*5*) recommends that raw waters containing 0.1–1.0 μg/L of PAH should be adequately treated to reduce their levels to the lowest possible concentration and that raw waters containing over 1.0 μg/L PAH are unsafe for drinking purposes even after treatment.

Although PAH levels in a few polluted (*6, 7*) and relatively unpolluted (*8*) U.S. river waters have been reported, no published study is available to demonstrate their degree of removal in U.S. water treatment plants. The anticipated levels of PAH in such water samples are very low and require a preconcentration and special analytical method for their quantification. The potential of polyurethane foam plugs for concentration of PAH from treated and raw waters and the subsequent method of cleanup of foam eluate for quantification of PAH have been reported earlier (*9, 10*). The present investigation utilizes this method for the monitoring of these compounds in a few selected treated waters and their respective raw water supplies in the eastern U.S. The information generated on the levels and nature of PAH has been related to raw water source and the treatment provided.

Experimental

Selection of Sampling Sites. In selecting sampling locations, several factors, such as the source of raw water, wastes/discharges entering raw water and the treatment provided, were taken into consideration. Ground water, in general, has been found to contain low PAH (*11*), and inclusion of one of this source as a site was to check this expectation. Several researchers (*12, 13*) have indicated that activated carbon filtration is a good treatment method for PAH removal from water. Four of the selected sites include waters subjected to such a treatment process. Also included in the selected sites are water supplies of five major urban centers, each of which serves a large number of consumers. Table I identifies the different monitoring sites and provides information about the raw water and the treatment provided.

Sampling Procedure. Earlier studies (*9, 10*) showed that foam plugs can effectively concentrate PAH from water at 62 ± 2 °C and a flow rate of 250 mL/min. Four foam plugs—two in each column—were adequate for sampling 20 L of water. Sixty liters of drinking water and 30 L of raw water were sampled with a portable sampling unit assembled from a combination of custom-made and off-the-shelf hardware available commercially. The equipment allowed maintenance of proper conditions for concentration of PAH in the field.

The unit consisted of the following five parts: (a) variable water pumping unit, (b) thermostated water circulator, (c) unit containing the column system, (d) temperature monitoring device, and (e) flow meter. The variable pumping unit consisted of two oscillating pumps connected in series and controlled by a variac. The pumping system allowed water from the sample source to be pumped through a thermostated water circulator to the foam columns at a controlled rate of 250 ± 10 mL/min. A Haake thermostated circulator with a custom-made helical glass coil (25 cm × 6 mm) immersed inside the reservoir housing through the cover plate was used to bring the water temperature to 62 ± 2 °C. Foam plugs were held in two 25-mm i.d. Chromaflex extender-type columns connected in series with the help of tapered glass adapters and double-bent Pyrex tubing. The temperature of the water passing through the columns was monitored by introducing a water trap equipped with a thermometer. A Gilmont flow meter calibrated to measure the flow rate of water at 62 °C was placed at the end of the sampling unit. The connections were made with glass tubing as much as possible and only where necessary with Tygon tubing.

The column stands, pump, variac, water trap, and flow meter were firmly fixed on an 18 × 12 × ½ in. piece of plywood. The whole unit weighing about 10 lb was transported to the sampling site along with the thermostated circulator, an electric timer, a 20-L Jerrican and other detachable items, such as Chromaflex columns, thermometers, clamps, "O" rings and connecting tubes. The purpose of the calibrated 20-L Jerrican was to collect the effluent from the sampler and thereby keep an exact record of the volume of water passed through the columns. The electric timer was used to indicate the running time of the sampler.

At the sampling location, the unit was assembled and water from a 1-L beaker placed under a continuously running

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Table I. Details of Water Supply Systems Used as Sample Site

Location	Supply system	Water source	Type of pollution, if any	Treatment provided [a]	Date(s) sampled	Sample no.
Syracuse, N.Y.	City of Syracuse Water Works, Skaneateles, N.Y.	Lake Skaneateles	Uncontaminated lake water	Copper sulfate addition, chlorination, and fluoridation	12-16-76	1
Buffalo, N.Y.	Ward's Pumping Station	Lake Erie	Contaminated with industrial discharge	Coagulation, activated carbon addition, chlorination, and fluoridation	12-26/27-76	2
Pittsburgh, Pa.	Hays Mine and E. H. Aldrich Purification Station	Monongahela River	Contaminated with coke oven effluent	Lime, ferric sulfate addition, activated carbon addition [two stages: (1) powdered carbon,[b] (2) granular carbon], chlorination, and fluoridation	1-19-77	3
Huntington, W.Va.	Huntington Water Corp.	Ohio River	Downstream from coke oven plants	Lime, ferric sulfate and granular carbon addition, chlorination, and fluoridation	1-20-77	4
Endicott, N.Y.	Endicott Village, Dept. of Public Works	Ground water	Uncontaminated ground water	Chlorination and fluoridation	2-22-77	5
Hammondsport, N.Y.	Hammondsport Village, Dept. of Public Works	Keuka Lake	Contaminated with agricultural and vinery waste	Chlorination	2-28-77	6
Philadelphia, Pa.	Torresdale Water Treatment Plant	Delaware River	Contaminated with municipal waste	Ferric chloride, lime, activated carbon ammonia addition, chlorination, and fluoridation	3-5/6-77	7
Name withheld at request of plant official			Uncontaminated upland water	Copper sulfate addition, aeration, corrosion control, chlorination, and fluoridation	3-17-77	8
Lake George, N.Y.	Lake George Village, Dept. of Public Works	Lake George	Contamination from recreational sources	Chlorination	3-26-77	9
New Orleans, La.	Tap water from a motel in downtown New Orleans	Mississippi River	Downstream from industries on Mississippi River	Chemical treatment to control alkalinity, hardness and organics, coagulation, ammonia addition, and chlorination	5-1-77	10

[a] Not necessarily in the proper order of treatment, & filtration steps wherever used during the treatment are not shown. [b] Used temporarily.

treated or raw water tap was pumped through two foam columns under the previously specified conditions. Since residence time for water in the beaker was very short, the losses of PAH due to adsorption were assumed to be insignificant. Both foam columns were changed after every 20 L in the case of finished water and every 10 L in the case of raw water, and the sampling was continued to the desired volume. At the end of sampling, the columns wrapped in aluminum foil and cooled in ice were transported to the laboratory for analysis.

PAH Elution and Analysis. The procedure for elution of PAH from foam plugs, cleanup, and quantification of fluoranthene (FL), benzo(j)fluoranthene(BjF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)-pyrene (IP), and benzo(ghi)perylene (BPR) has been described elsewhere (*10*).

Addition of Internal Standard and Determination of Recovery Factor. The efficiency of PAH elution and purification procedure for each analysis was evaluated by addition of ^{14}C-benzo(a)pyrene as an internal standard to the foam plugs prior to initiating any sample workup. A known amount of the radiolabeled material (approximately 600 dpm) was added to foam plugs, PAH eluted, purified, and concentrated as described before. A 10-μL aliquot of the concentrate was assayed for radioactivity by liquid scintillation counting. The recovery factor was determined from the amount of radioactivity initially added to the foam plugs.

Results and Discussion

The results of analyses of 10 treated and 4 raw water samples are presented in Table II. Data regarding the precision and accuracy of the results are not given, since a single analysis of each sample was performed. However, incorporation of a cleanup recovery factor for each analysis greatly increased the accuracy of the presented values. Although both TLC–spectrofluorometric and GLC–FID methods were employed in PAH analysis, the latter method in most cases failed to detect PAH. The GLC–FID values in most cases were higher than TLC–fluorometric values. This would indicate incomplete resolution of the compounds on the GLC column. Also, the GLC–FID values were susceptible to an error due to the large multiplication factor involved, since only 2 μL of the total 100-μL concentrate was subjected to the analysis. The GLC column used (*14*) failed to resolve benzo(j)fluoranthene and benzo(k)fluoranthene. Consequently, the sum of the values presented in Table II is derived from a standard chromatogram obtained by the injection of a 1:1 mixture of the compounds. The combined values are uncertain, since the ratio of the two compounds and their individual response factors could not be incorporated in the results.

PAH were detected in the nanogram per liter range in both raw and finished water at all locations sampled. Whereas the combined concentration of PAH in drinking waters was small, the value found in a raw water was as high as 600 ng/L. Among the waters sampled, a few showed all the six PAH listed. The compounds benzo(a)pyrene and benzo(ghi)perylene were among the most frequently detected PAH occurring 100 and 90% of the time, respectively, in all the drinking waters monitored. The next most abundant PAH in drinking waters were benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene, occurring in 70% of all the water monitored. In spite of its relatively high water solubility, fluoranthene was not widely detected. Water samples derived from Buffalo with Lake Erie as the source showed surprisingly lower levels of PAH. It is difficult to explain the reason for the lower levels of PAH at this location than those determined in ground water at Endicott. In this regard, it should be mentioned that the Buffalo samples were collected during the severe snowstorm period in that area.

Figure 1 represents typical spectra of PAH identified in water samples along with the spectra of the model compounds. In each case, the solid line represents the spectra of the model

Table II. Results of Analyses of Field Samples (Values Corrected for Recovery Factor, and Traces of PAH Contributed by Foam Plugs)

Sample no.[a]	1	2	2A	3	3A	4	4A	5	6	7	7A	8	9	10[b]
Recovery factor	0.80	0.81	0.61	0.82	0.67	0.85	0.75	0.89	0.83	0.73	0.72	0.79	0.66	0.66
FL concn (ng/L)	X	X	X	X	408.3[c] 405.9	2.4	23.5 38.0	4.3 5.5	X	8.9 9.0	114.3 124.8	X	X	X
BjF concn (ng/L)	X	X	X	0.3	35.7 50.2[d]	0.3	5.0	0.2	0.3	X	42.6 71.3[d]	1.2	0.3	X
BkF concn (ng/L)	0.4	X	0.6	0.2	19.1 50.2[d]	0.2	3.6	X	0.1	X	33.0 71.3[d]	0.7	0.1	0.6
BaP concn (ng/L)	0.3	0.2	0.3	0.4	42.1 77.1	0.5	5.6	0.2	0.3	0.3 [e]	41.1 [e]	0.5	0.3	1.6
IP concn (ng/L)	X	X	X	1.2	60.4 80.6	1.2	9.5	0.7	0.9	1.7	72.4 105.6	2.2	0.9	X
BPR concn (ng/L)	0.4	0.7	3.8	0.7	34.4 49.8	2.5	10.7	2.9	1.9	4.0	48.4 66.2	1.8	2.6	X
Total concn (ng/L)	1.1	0.9	4.7	2.8	600.0 663.6	7.1	57.9	8.3	3.5	14.9	351.8	6.4	4.2	2.2

[a] The samples designed by numeral only are the drinking water, and those followed by the letter "A" are the corresponding raw water. [b] Values subjected to error because the adsorbent layer on TLC plate was accidentally scraped. [c] The lower values indicate the concentration determined by GLC–FID. [d] These values are the sum of unresolved concentrations of these two isomers as determined by GLC–FID. [e] These concentrations could not be determined because of lack of separation from an impurity peak.

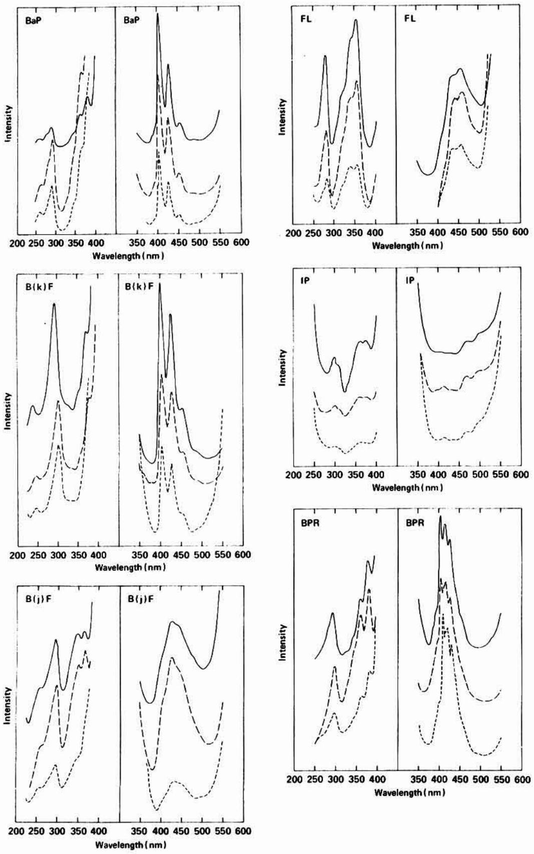

Figure 1. Fluorescence emission (right) and excitation (left) spectra of model PAH and those identified in Huntington water samples

In each case, three spectra represent these spots—top: model compound, middle: raw water, bottom: treated water

compounds and the dashed lines the spectra from the TLC spot of the unknown having the same R_B values (ratio of the distance traveled by a specific compound to that of BaP) as the model compound. The superimposed spectra for most samples were significantly similar. The fact that they were not obliterated, distorted, or even flattened out is suggestive of the excellent resolution obtained by the TLC procedure.

In addition to the six identified and quantitated spots, a number of unidentified luminescent spots appeared on TLC plates from various samples. A maximum of seven and a minimum of one such spots appeared from Huntington raw and Syracuse drinking water, respectively. Spectrofluorometric identification of these spots was not attempted because of nonavailability of matching spectra. A few of the recurring spectra are presented in Figure 2.

The data on the level of PAH in finished and raw waters show a considerable reduction in PAH concentration during water treatment. Whether the decrease of PAH concentrations is due to actual removal, deactivation, or transformation to other more carcinogenic products is not known. The removal/transformation efficiencies of PAH in three treatment plants are shown in Table III. It is evident that the treatment process at the Purification Plant at Pittsburgh has the highest PAH removal efficiency. This may be attributed to the fact that the treatment process at this plant employed two stages of activated carbon treatment (see Table I).

The concentrations of PAH detected in the drinking waters were well below the WHO recommended value of 200 ng/L (*16*). Of the six PAH quantified, three are carcinogenic and one of them, e.g., benzo(a)pyrene, is extremely potent. On the other hand, benzo(j)fluoranthene has moderate and indeno(1,2,3,-cd)-pyrene has weak carcinogenicity. Whether their presence in drinking water at the reported levels poses any health hazard by way of bioaccumulation or synergistic effects cannot be answered at the present time.

Conclusions

The sampling method developed for the collection of PAH from raw and finished waters provides an excellent routine method for field monitoring. The addition of radiolabeled

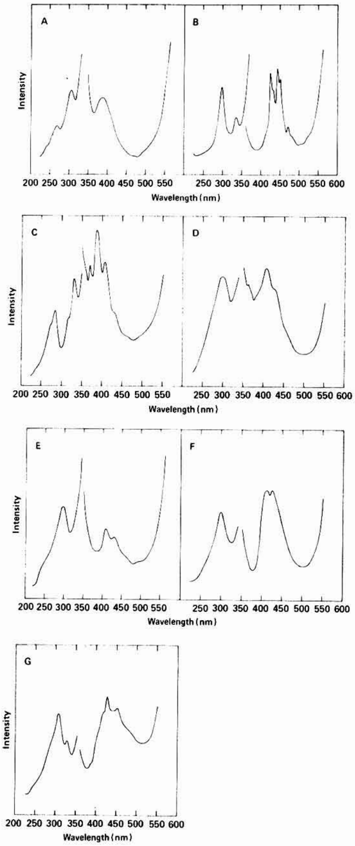

Figure 2. Fluorescence emission and excitation spectra of recurring unknown compounds

Table III. PAH Removal/Transformation Efficiency of Water Treatment Processes

PAH	% Removal/transformation Pittsburgh	Philadelphia	Huntington
FL	100.0	92.2	89.9
BaP	99.0	99.3	91.1
BkF	99.0	100.0	94.4
BjF	99.2	100.0	94.0
IP	98.0	97.7	87.4
BPR	98.0	91.7	76.6
Total	99.5	95.8	87.7

benzo(a)pyrene as an internal standard allows determination of the recovery factor for each analysis and thus accounts for any losses of PAH during elution, cleanup, and analysis. The TLC–spectrofluorometric method used for analysis is capable of detecting PAH at sub-ng/L levels and provides excellent resolution. With the application of the method, six representative PAH were quantified in the nanogram per liter range at all the water supplies sampled. In addition, the presence of several unidentified fluorescent compounds was also demonstrated. The PAH levels detected were well below the WHO recommended limit of 200 ng/L. Health hazards to man from the presence of such low levels of PAH in drinking water are not clearly understood. Water treatment processes were efficient in reducing the concentration of PAH. Further research to establish the mass balance of PAH during treatment is needed to elucidate whether reduction is due to removal, deactivation, or transformation to more carcinogenic products.

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Composite Hazard Index for Assessing Limiting Exposures to Environmental Pollutants: Formulation and Derivation

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■ A calculational hazard index methodology is developed for limiting human exposure to environmental pollutants. Hazard index is defined as Q/Q_L, where Q is a measure of exposure, such as an organ's burden of a pollutant from all environmental pathways, and Q_L is a corresponding limit that should not be exceeded because of health risk to human beings. Mathematical formulations relating hazard indices to environmental pollutant concentration are developed for each sampling medium corresponding to each effluent mode. These formulations are used to derive limiting pollutant concentrations such that the resultant measure of exposure will not exceed the health risk limit. Mathematical formulations for composite hazard indices for multiple pollutants are presented.

This report describes a hazard assessment methodology for limiting human exposures to environmental pollutants such that exposure or dose will not exceed some preselected value. An estimation of total pollutant intake by human beings and resulting health effects must include contributions from all possible routes of exposure. Models must be used for estimation of potential health impacts of pollutant releases that have not yet occurred. They are also useful when measurements can be made. Therefore, an assessment approach has been developed using environmental transport models to predict transport from point of pollutant release or measurement to eventual intake and absorption by human beings.

This assessment methodology is based on consideration of interrelationships between environmental compartments. A measurement in a particular sampling medium, for example, is sufficient to calculate total human intake via all routes of exposure from that sampling medium, within limits imposed by model input data. The assessment methodology in part extends an existing radiological assessment index (CUEX) to the nonradioactive area (*1, 2*). Although the assessment problems are similar, some features of radioactive releases have facilitated assessment of their environmental impact. Radioactive releases have been relatively small and subject to strict controls. Possible health hazards of radiation were recognized early in the development of nuclear technology; thus, research on biological effects and transport of radionuclides through the food chain has been underway for many years. The pharmacological action of radionuclides has not been considered. If only radiation effects are considered, a common unit, the rem, is used to sum effects of several different radionuclides. No comparable index of effect exists for nonradioactive pollutants. This latter point is particularly critical in nonradioactive pollution assessment because simultaneous exposure to several pollutants may result in synergistic or antagonistic effects rather than simple additive effects. Experimental data are essential to assess these effects and are not available for most combinations of pollutants. Therefore, at present, the methodology is strictly applicable to single pollutants only. The methodology provides a way to organize and use data obtained from experimental and theoretical studies. In its initial stages, the methodology is purposefully kept as simple as possible while still considering multiple pollutants and multiple environmental pathways.

Transport models estimate pollutant dispersion through air and water, deposition on soil and plant surfaces, uptake by plants, concentrations in air and water, intake by animals, and human exposure through inhalation and ingestion. Physiological models estimate pollutant uptake and subsequent distribution among organs. Models used at the Oak Ridge National Laboratory are described in the following paper (*3*).

The overall methodology ties together pollutant emission, environmental transport, exposure of man, and a human health effect endpoint (for example a statutory limit or standard, organ level, total-body burden, or specific disease state). The methodology provides a useful technique to assess compliance with existing standards; to suggest standards where none exists; to estimate health effects of a given pollutant release; or to estimate the amount of pollutant released based on concentrations found in a sampling medium.

A major feature of the methodology is that it relates the concentration of a pollutant in air or other sampling medium to a preselected endpoint such as an organ concentration by consideration of all pathways from point of measurement to endpoint. Derivation of the formulation required for this calculation is presented here.

The following paper (*3*) illustrates application of the methodology to cadmium release from the smelter complex in East Helena, Mont.

Formulation

Hazard Index. A hazard index (HI) is a quotient of some measure of exposure of man to a given environmental pollutant over a corresponding "accepted" or "selected" limit. Its application is implied in any case where actual or estimated exposure of total body or a critical organ or tissue to a particular agent is compared to a recommended limit. The President's Science Advisory Committee on Chemicals and Health (*4*) recommends that some index of probability of human exposure be used to rank chemicals in the environment. It is suggested that physical, chemical, and economic information along with information on biological effects might be combined into an aggregate index of hazard. Such an approach has been used to rank particulate pollutants (*5*). However, estimation of hazard index when a straightforward measurement or calculation does not apply is neither simple nor widely accomplished. When exposure of human beings to multiple environmental pollutants via multiple environmental pathways is of concern, complexities and lack of information often render determination of hazard indices crude at best. Still the concept is useful in a general way because it provides a meaningful comparison between exposure or dose levels on the one hand and limits based on biological effects on the other.

The hazard index may be defined as

$$HI = Q/Q_L \tag{1}$$

where Q is a measure of exposure of man to a pollutant, and Q_L is a selected or established limit that should not be exceeded because of health risk to man. The determination of Q is assumed to consider all applicable environmental pathways and may be based on exposure pathway models and metabolic or physiological models to relate environmental levels to total-body, organ, or tissue burden if Q_L is stated in these terms.

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In the following discussion, we restrict attention to the case where Q represents the burden (in μg, say) of the pollutant in an organ of the body. We assume that the rate of intake into the body from each environmental pathway is constant and make use of the convolution

$$Q(T) = \int_0^T I(T-t)\cdot f\cdot r(t)dt \quad (\mu\text{g}) \qquad (2)$$

where I is the total intake rate from all pathways (μg/day), f is the fraction deposited in the organ, and $r(t)$ is the fraction of the organ burden retained t days after initial deposition $[r(0) = 1]$. Since we treat I as being constant, Equation 1 reduces to

$$Q(T) = I\cdot f\cdot \tilde{r}(T) \qquad (3)$$

where

$$\tilde{r}(T) = \int_0^T r(t)dt \quad (\text{days}) \qquad (4)$$

As T becomes infinite, $Q(T)$ approaches the steady-state level, at which the rate of deposition of material in the organ is balanced by the organ's removal processes. For finite T (e.g., the life of the individual), $Q(T)$ represents the maximum burden attained by the organ in that time due to sustained uptake rate $I\cdot f$.

We express the organ burden Q as the sum

$$Q = Q_R + Q_D + Q_S \qquad (5)$$

where Q_R, Q_D, and Q_S represent components due to intakes through the respiratory system, digestive system, and transport through the skin, respectively. We may further express these quantities as follows:

$$Q_R = C_A V_A f_R \tilde{r} \quad (\mu\text{g}) \qquad (6)$$

where C_A = concentration of pollutant in air (μg/cm^3), V_A = breathing rate of reference individual (cm^3/day), f_R = fraction of inhaled pollutant deposited in the reference organ, and $\tilde{r}$ was defined in Equation 4.

$$Q_D = (C_F M_F + C_W V_W)\cdot f_D\cdot \tilde{r} \quad (\mu\text{g}) \qquad (7)$$

where C_F = average concentration of pollutant in food (μg/g), M_F = mass consumption rate of food (g/day), C_W = average concentration of pollutant in drinking water (μg/mL), V_W = volume consumption rate of drinking water (mL/day), and f_D = fraction of ingested pollutant deposited in reference organ.

$$Q_S = \left(C_A K_A + e_W C_W K_W + \sum_j e_{Pj} C_{Pj} K_{Pj}\right)\cdot f_S\cdot \tilde{r} \quad (\mu\text{g}) \qquad (8)$$

where C_A = concentration of pollutant in air (μg/cm^3), K_A = skin flux coefficient between air and blood (μg/day entering blood per μg/cm^3 in air), e_W = fractional exposure factor of skin to the contaminated water, C_W = average concentration of pollutant in water used for swimming, washing, and utility (μg/mL) (assumed to be from the same source as drinking water), K_W = skin flux coefficient between water and blood (μg/day entering blood per μg/mL in water), Σ_j = summation taken over various products containing the pollutant substance, with which the reference individual is assumed to have tactile contact, e_{Pj} = fractional exposure factor of skin to j-th product, C_{Pj} = concentration of pollutant in j-th product (μg/g), K_{Pj} = skin flux coefficient between j-th product and blood (μg/day entering blood per μg/g in the product), and f_S = fraction of skin-absorbed pollutant deposited in the reference organ.

Entry through a break in the skin or a wound, an intake pathway not considered above, is not generally quantifiable and must be analyzed for each specific instance. Fortunately, this intake pathway is not usually significant in comparison with the major pathways of inhalation, ingestion, and for some agents absorption through the intact skin.

Equations 6–8 are illustrative and might require revision for special cases. And a different formulation is obviously required when Q represents a measure of exposure other than organ burden. But for purposes of exposition we proceed from Equations 6–8 as they are written.

Single Pollutant, Multiple Effluent Modes, Multiple Pathways. Determination of the concentrations C_A, C_F, and C_W defined above requires an environmental human exposure assessment. If the relationships among the various environmental compartments are understood, then measurements in a particular sampling medium (air, water, food) can suffice, along with transport models, to assess human intake from that sampling medium. Measurements in at least two sampling media, along with transport models, will be necessary to assess total human intake if there is more than one effluent mode.

If only one sampling medium contributes to human intake, then the limiting air concentration is determined such that intake via all environmental pathways from that sampling medium is equal to some preselected value. Thus the limiting air concentration, $\hat{C}_A$, for an airborne effluent with air as the sampling medium is

$$\hat{C}_A = Q_L\cdot\{[V_A f_R + f_{AF} M_F f_D + f_{AW}(V_W f_D + e_W K_W f_S) + K_A f_S]\tilde{r}\}^{-1} \quad (\mu\text{g/cm}^3) \qquad (9)$$

where f_{AF} = transfer coefficient from air to food (μg/g in food per μg/cm^3 in air), and f_{AW} = transfer coefficient from air to water (μg/mL in water per μg/cm^3 in air). The transfer coefficients f_{AF} and f_{AW} satisfy the equations

$$C_F = f_{AF} C_A, \quad C_W = f_{AW} C_A$$

for steady-state concentrations C_A, C_F, and C_W, where C_F and C_W are attributable exclusively to the deposition of airborne material. The coefficients f_{AF} and f_{AW} may therefore be determined by environmental transport models restricted to an assumed atmospheric release and driven to steady state. Equation 9 is derived by substituting Equations 6–8 into Equation 5, deleting the contribution $\Sigma_j e_{Pj} C_{Pj} K_{Pj}$ from exposure to consumer products, setting $Q = Q_L$, and solving for $C_A = \hat{C}_A$.

For a liquid effluent with water as the sampling medium, the limiting water concentration is

$$\hat{C}_W = Q_L\cdot\{[f_{WF} M_F f_D + V_W f_D + e_W K_W f_S]\tilde{r}\}^{-1} \quad (\mu\text{g/mL}) \qquad (10)$$

where f_{WF} = transfer coefficient from water to food.

When both effluent types and consumer product exposure are present, we may proceed from the inequality $Q \le Q_L$ and Equations 5–8 to write

$$\left[(V_A f_R + f_{AF} M_F f_D + K_A f_S) C_A + (f_{WF} M_F f_D + V_W f_D + e_W K_W f_S) C_W + f_S \sum_j e_{Pj} K_{Pj} C_{Pj}\right]\tilde{r} \le Q_L \qquad (11)$$

in which we have made use of the relationship

$$C_F = C_A f_{AF} + C_W f_{WF}$$

The inequality (Equation 11) may be recast as

$$C_A/C_A^* + C_W/C_W^* + \sum_j C_{Pj}/C_{Pj}^* \le 1 \qquad (12)$$

where

$$C_A^* = Q_L\cdot[(V_A f_R + f_{AF} M_F f_D + K_A f_S)\tilde{r}]^{-1} \qquad (13)$$

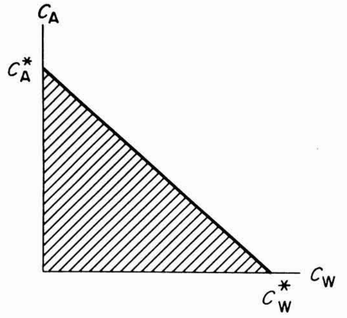

Figure 1. Geometric interpretation of concentrations of a pollutant in air and water for atmospheric and liquid effluent modes
Shaded region (inequality 12′ and Equations 13 and 14) corresponds to concentration pairs C_A, C_W for which limiting organ burden Q_L is not exceeded

$$C_W^* = Q_L \cdot [(f_{WF}M_Ff_D + V_Wf_D + e_WK_Wf_S)\tilde{r}]^{-1} \quad (14)$$

$$C_{Pj}^* = Q_L \cdot (e_{Pj}K_{Pj}f_S\tilde{r})^{-1} \quad (15)$$

We note that $\hat{C}_W = C_W^*$ and that $\hat{C}_A$ reduces to C_A^* when $f_{AW} = 0$. For nonzero f_{AW}, the difference of $\hat{C}_A$ and C_A^* expresses the contribution of the atmospheric pathway to the aquatic pathway.

When the consumer product exposure pathway is absent, the inequality 12 simplifies to

$$C_A/C_A^* + C_W/C_W^* \leq 1 \quad (12')$$

which is equivalent to $HI = Q/Q_L \leq 1$.

The inequalities 12′ and $C_A > 0$ and $C_W > 0$ correspond to the shaded region in Figure 1. The analysis can be extended to higher dimensions when other pathways must be considered, as we have already seen with the inclusion of the consumer products terms in inequality 12.

The above discussion illustrates the major features of the hazard index methodology for a single pollutant. As environmental transport models evolve for determination of f_{AF}, f_{AW}, f_{WF}, etc., so will the methodology concept. As more complicated kinetic processes are incorporated into the models, such as photochemical, chemical, or biological alterations of pollutants, application of the methodology will become more precise.

Formulation of Composite Hazard Index for Multiple Pollutants. We consider measures of exposure Q_1, Q_2 to two pollutants, such as burdens in an organ. Associated with the presence of either or both is assumed to be a discernible effect that can be used to quantify limits.

We conceive of a series of experiments in which various combinations of the two toxicants are introduced into the tissues at risk. For a given level of Q_1, we imagine an increase in Q_2 until the limiting effect is observed, and the process is repeated for other levels of Q_1. The results might be visualized as in Figure 2, where the plotted x's represent the attainment of the limiting effect. A model for the limiting curve on which the x's lie might be hypothesized as

$$F(Q_1, Q_2) = A_1Q_1 + A_2Q_2 + B_{12}Q_1Q_2 = 1 \quad (16)$$

which describes a conic section in the Q_1, Q_2 plane. Our problem may be viewed as that of estimating the parameters A_1, A_2 (both positive), and B_{12} in order that we might control the biological availability of the pollutants in such a way as to keep

$$F(Q_1, Q_2) < 1 \quad (17)$$

The coefficients in Equation 16 have the following interpretations: A_1^{-1} = limiting burden of Q_1 in the absence of Q_2, A_2^{-1} = limiting burden of Q_2 in the absence of Q_1, B_{12} = interaction term which characterizes the synergistic effect of both agents: $B_{12} > 0$ implies reinforcement, $B_{12} < 0$ implies interference, and $B_{12} = 0$ implies no interaction (the conic section degenerates to a straight line). These interpretations may be visualized as in Figure 3. The inequalities $F(Q_1, Q_2) < 1$, $Q_1 > 0$, and $Q_2 > 0$ correspond to the shaded region bounded by the conic section given by Equation 16 and the coordinate axes, as shown in Figure 2 for the case $B_{12} > 0$.

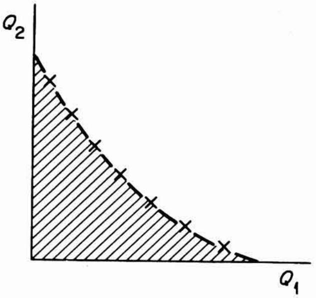

Figure 2. Conceptual experimental data points (x's) representing joint critical tissue concentrations of two pollutants for which an effect is observed
Curve represents a conic section (Equation 16) fitted to the data. Figure drawn to suggest case of interactive reinforcement ($B_{12} > 0$)

Generalization of the formulation to higher dimensions is straightforward:

$$F(Q_1, \ldots, Q_N) = \sum_{i=1}^{N} A_iQ_i + \sum_{j=1}^{N}\sum_{i=1}^{j-1} B_{ij}Q_iQ_j + \text{higher-order interaction terms} \quad (18)$$

In general, however, it is doubtful that sufficient experimental information could be generated for estimation of higher-order interaction coefficients.

To illustrate the application, consider environmental levels of pollutants 1 and 2, with air concentrations $C_{A,1}$, $C_{A,2}$. The equation for one pollutant is Equation 9. The limit for two pollutants is reached whenever

$$F(Q_1, Q_2) = A_1E_1C_{A,1} + A_2E_2C_{A,2} + B_{12}E_1E_2C_{A,1}C_{A,2} = 1 \quad (19)$$

where

$$E_k = [V_Af_{R,k} + f_{AF,k}M_Ff_{D,k} + K_{A,k}f_{S,k} + (f_{WF,k}M_Ff_{D,k} + V_Wf_{D,k} + e_WK_{W,k}f_{S,k})f_{AW,k}]\tilde{r}_k,\ k = 1, 2 \quad (20)$$

The notations are as before, except that the subscript k is

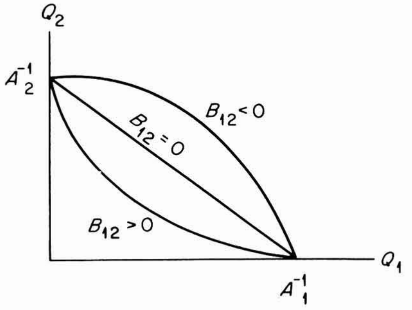

Figure 3. Curves representing conic section model (Equation 16) of burdens of two pollutants in an organ for positive, negative, and zero values of interaction coefficient B_{12}

appended to those parameters that are specific to the pollutant. The derivation of E_k proceeds from Equations 5–8 (with appropriate additions of subscript k and deletion of the consumer product sum) and the relations

$$C_{F,k} = C_{A,k}f_{AF,k} + C_{W,k}f_{WF,k}$$

$$C_{W,k} = f_{AW,k}C_{A,k}$$

and

$$Q_k = E_kC_{A,k}$$

with the last being substituted into Equation 16 to obtain Equation 19. It should be noted that the interaction characterized by B_{12} is biological rather than environmental. The derivation of E_k (Equation 20) assumes independent transport of the two chemical species through the environment, an assumption that may be false for some pairs of pollutants.

From the foregoing discussion, we see that each critical air concentration pair ($C_{A,1}$, $C_{A,2}$) lies on the curve defined by Equation 19. Moreover, when a concentration pair converts Equation 19 into a >1 inequality, the image burdens (Q_1, Q_2) in the reference organ lie outside the shaded region in Figure 2, which implies unacceptable composite levels.

The above analysis applies for multiple pollutants in one sampling medium which produce the same biological effect. The application may be extended to incorporate multiple effluent types and multiple sampling media in a manner similar to that given above for single pollutants.

Multiple Pollutants, Different Biological Effects. The discussion of multiple pollutant effects given above applies strictly only if the multiple pollutants affect the same target organ and influence the same biological effects. If the pollutants affect different organs or produce different biological effects in the same or different organs, then other considerations must be included in the model. For example, each pollutant may have to be weighted according to its influence on the total well being of the organism. Research along such lines should eventually lead to a comprehensive approach for determination of composite hazard indices.

Conclusions

It is conceptually feasible to determine multimedia, multipathway, and multipollutant composite hazard indices such that control of pollutant concentrations in one or two sampling media (corresponding to one or more effluent modes) will assure that total human intake will not exceed some preselected value. These composite hazard indices are site specific in terms of emission sources and sampling media, but there is no conceptual barrier to determination of indices for multiple sources as well as multiple pathways to the sampling medium.

Composite hazard indices conceptually provide an interface between human exposure assessments and human health risk assessment. Their practical determination, however, requires detailed knowledge of source emission characteristics, environmental transport processes, metabolism in man, and biological effects. Thus composite hazard indices provide a framework to assimilate such knowledge and to point out where more research is needed. Their application will be more definitive as information develops; however, it is certain that such concepts will have to be applied conservatively before all desired information is available.

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Composite Hazard Index for Assessing Limiting Exposures to Environmental Pollutants: Application Through a Case Study

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Application of the composite hazard index assessment methodology (*1*) requires implementation of atmospheric, terrestrial, and aquatic transport models and selection of an exposure or dose limit that should not be exceeded because of health risk to man. Models in present use at Oak Ridge National Laboratory for this purpose are: an atmospheric transport model (ATM), based on a Gaussian plume model (*2, 3*) capable of predicting wet and dry deposition and air concentration of gaseous and particulate pollutants at various receptor points located within 50 km of a source or sources; a terrestrial transport model, TERMOD (*4, 5*), which uses the output of ATM in μg/m^2/day of pollutant deposition on soil and plants as inputs and yields intakes of pollutants by man through consumption of milk, beef, and plant parts; and an aquatic transport model, AQUAMOD (*6*), which is being developed to simulate pollutant flow through aquatic food chains.

The human exposure or intake determination, based upon transport models, may be linked to the exposure concentration of dose limits for organs by physiological transport models. The physiological models used in each application will vary with the properties of the pollutant being studied. The model discussed by Friberg et al. and Kjellström (*7, 8*) was used for the assessment of cadmium release described in this paper.

Selection of an exposure, dose, or concentration limit de-

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[1] Health and Safety Research Division.

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[3] Computer Sciences Division.

[4] Environmental Mutagen Information Center.

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■ The composite hazard index assessment methodology described in the previous paper is applied to cadmium releases from a smelter complex in East Helena, Mont. Environmental transport models are used to estimate cadmium dispersion through air, concentrations in air, deposition on soil and plant surfaces, uptake by plants, intake by animals, and human intake through inhalation and ingestion. A physiological model is used to estimate cadmium uptake and distribution among human organs. A review of toxicological information on cadmium results in the selection of 200 μg Cd/g wet weight kidney cortex as a cadmium concentration that should not be exceeded due to health risk. A limiting cadmium air concentration is calculated as that air concentration that will limit the accumulation of cadmium within the human kidney cortex to below the 200-μg/g level over a 50-year exposure period.

Table I. Average Cadmium Concentrations

Sample medium	U.S. (*7*)	Helena Valley (*11*)	East Helena
Air (μg Cd/m)	0.02 Urban 0.003 Nonurban	0.03	0.06–0.29
Water (μg Cd/L)	<10	<10	<10

pends upon knowledge of biological effects of the particular environmental pollutants of concern. Selection of kidney cortex as the critical tissue for cadmium is based on a review of cadmium toxicity (*9*).

Selection of Case Study

Selection of Cadmium as Pollutant. Cadmium is a toxic heavy metal used widely in a variety of consumer products. It produces acute health effects when inhaled or ingested at high concentrations and chronic effects at lower concentrations. As a ubiquitous element in the environment, it is found in normal diet and in air in most urban areas. It is excreted from the body extremely slowly, accumulating to potentially toxic levels when intake is sufficient. As an environmental pollutant of increasing importance due to increasing commercial use and fossil fuel combustion and as a pollutant about which health effects data are available, cadmium is well suited for testing the methodology (*7, 9, 10*).

Selection of Limiting Physiological Concentration. The endpoint chosen for calculation of a limiting air concentration for cadmium release is 200 μg Cd/g wet weight of kidney cortex (i.e., $Q_L = 200$ μg Cd/g). From epidemiological and experimental studies, kidneys are the long-term target organ for low-level exposure to cadmium. A concentration of 200 μg Cd/g wet weight of kidney cortex is generally accepted as a level above which kidney damage occurs. At constant exposure levels the increase in cadmium concentration in kidney is almost linear through age 50 years. The calculations in this report are intended to prevent accumulation above 200 μg Cd/g wet weight kidney cortex in a 50-year period, assuming a total kidney weight (two kidneys) of 300 g and a fractional absorption into the blood of 0.05 for ingestion and 0.25 for inhalation. One-third of the cadmium in the blood is assumed to be taken up by the kidney. Excretion is assumed to be 0.005% of total body burden per day (*7–10*).

Selection of Helena Area. CUMEX is a site specific assessment methodology; therefore, a site of cadmium release was selected where source data and other input data for the transport models were available. A study of the U.S. Environmental Protection Agency (EPA), conducted between June 1969 and June 1970, provided the required data for an area around East Helena, Mont., site of a lead smelter and slag processing facility (*11*). Cadmium is one of the major pollutants released from this smelter complex.

Environmental Concentrations of Cadmium. Average cadmium concentrations in air and water for the United States as a whole and for the Helena Valley and East Helena are given in Table I. Average cadmium concentrations in foods are quite variable but usually less than 0.05 μg Cd/g wet weight (*10*).

Table II shows the cadmium concentration in items of selected food categories given on a wet weight (μg/g) basis. The cadmium concentration values have been taken from a number of different source documents (*7, 10, 12–17*) as listed in Table II. Table II also gives the daily intake of cadmium for each of the major food categories with the daily cadmium intake value for all categories given at the bottom of the table.

Because of differences in the amount of consumption of various foods within a category, an average of the range of concentrations of cadmium in foods cannot be used. This becomes obvious when food categories are further broken down into individual items and fresh vs. processed foods.

East Helena and Helena Valley figures are based on the assumption that only 12% of the garden vegetables consumed there are grown locally and that the other 88% of the diet is shipped in from other areas.

Daily intake values given in Table II are based on a daily food intake of 1.75 kg as compiled by the U.S. Department of Agriculture (*18*) rather than 0.2–2.5 kg per day as usually reported for the United States (*7, 10, 16*). Extrapolation from intake values in Table II to those arising from intake of 2.0–2.5 kg per day gives the following daily intake of cadmium: average U.S., 128–160 μg; Helena Valley, 170–113 μg; and East Helena, 222–278 μg.

Table II. Average Daily Intake of Cadmium as a Function of Diet for the U.S. and the Study Site in Helena, Mont.

Food category	Consumption g/day edible portions	Cadmium concn range (μg/g wet wt)	Av intake (μg/day)			Refs
			U.S.	Helena Valley	East Helena	
Meat, fish, poultry	245	0.03–0.054	11.9	12.3	15.5	*7, 12, 13*
Vegetables, potatoes	434	0.038–0.090	31.5	69.2	109.4	*7, 10, 12, 14, 15*
Fruits, juices	179	0.040–0.070	12.0	11.4	13.0	*10, 15*
Dairy products, eggs	486	0.021–0.028	13.3	13.3	13.3	*16, 17*
Grain products	177	0.026–0.211	21.8	21.8	21.8	*14*
Fats, oils (coffee, tea)	81	0.01–0.04	2.7	2.7	2.7	*7*
Sugars, sweeteners	149	0.04	6.0	6.0	6.0	*7*
Water and beverages	1270	0.01	12.7	12.7	12.7	
Total from food	1751		99.2	136.7	181.7	
Total including water and beverages			111.9	149.4	194.4	

Table III. Source Data for East Helena Smelter Area

	ASARCO	Anaconda
Stack height	122 m	36 m
Stack radius	2.44 m	1.38 m
Stack gas velocity	8.2 m/s	2.1 m/s
Stack gas temperature	127 °C	121 °C
Particulate emissions	56 g/s	112 g/s
Particle size	Unknown[a]	Unknown[a]
Particle density	Unknown[b]	Unknown[b]
Cd concn in particulate emissions	200–1000 ppm[c]	200–1000 ppm[c]
Plume rise parameters		
PKAPPA[d]	877	155
QKAPPA[d]	235	100

[a] Simulations made for several particle diameters (0.1, 1.0, 5.0, 10.0, 20.0 μ). [b] Assumed to be 7 g/cm^3. [c] 1000 ppm used in calculations. [d] Values determined from consideration of stack gas velocity, stack radius, stack gas temperature, wind speed and other factors and used to calculate increase in effective stack height (plume rise) due to buoyancy of the plume (*3*).

Cadmium Standards. There are no standards set for cadmium in food products or ambient air; however, a World Health Organization Report on food additives proposed an intake limit of 400–500 μg Cd per week (*19*). A threshold limit value (TLV) of 100 μg/m^3 of air is established for occupational exposure to cadmium (*20, 21*). The maximum permissible concentration of cadmium in drinking water is 0.01 ppm (10 μg/L) (*22*).

Application

Atmospheric Transport Model (ATM). *Input Data.* Input data necessary to apply the methodology to cadmium release from the smelter complex in East Helena, Mont., were obtained from the open literature. Source data were taken from ref. *11*. The two sources considered, the American Smelting and Refining Co. (ASARCO) lead smelter and the Anaconda slag processing facility, are located side-by-side in East Helena. Table III lists source data.

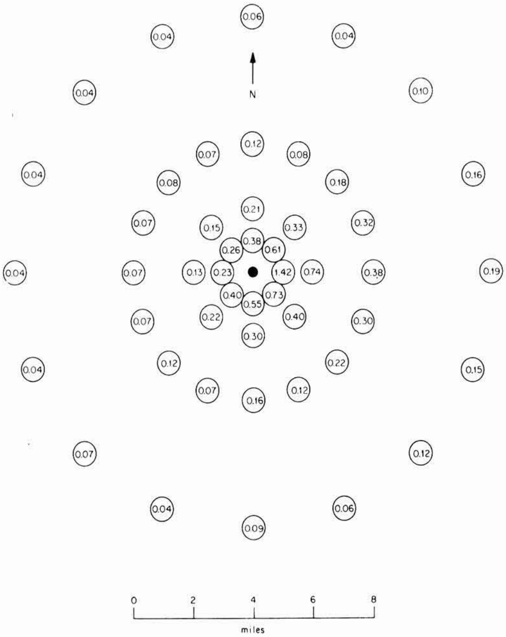

Figure 1. Average deposition of cadmium (5 μ) around East Helena smelter (mg/m^2/month)

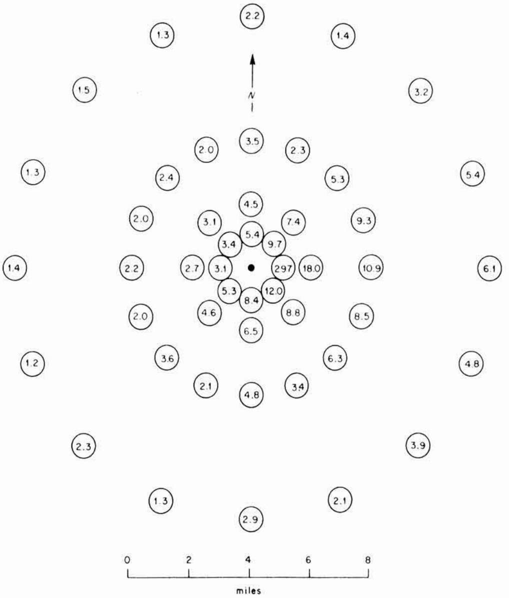

Figure 2. Average air concentration of cadmium (5 μ) around East Helena smelter (mg/m^3)

Meteorological data given in ref. *11* included monthly wind rise data for six velocity groups ranging from 0 to 12.5 m/s, percent occurrence of stability classes A–F, average monthly and yearly rainfall, and average yearly rainfall intensity.

Terrain surrounding the smelter complex was assumed to be grassland with a surface roughness factor of 0.15 m (*2*). Receptor points were uniformly spaced, eight each at distances of 1 and 2 miles, and 16 each at distances of 4 and 8 miles, for a total of 48.

ATM Output Data. Output from ATM includes wet and dry deposition values and air concentrations of cadmium at each of the 48 receptor points for each quarter of the year. Wet and dry deposition values are nearly equal. Total depositions and air concentrations of cadmium (5 μ particle) are computed for each quarter, plus a yearly average, as a function of distance and direction from the smelter. In general, seasonal deviation is less than 10% of the average. Yearly averages are plotted in Figures 1 and 2 to show spatial distribution. Values are highest toward the east since the wind blows 45% of the time from the WNW to WSW sectors. At a distance of 8 miles, values to the east are five to eight times higher than values to the west. Figures 3 and 4 show how air concentrations and depositions of cadmium change as a function of particle size and distance on a straight line east from the smelter complex. The curves for 0.1-μ particles are not shown because they are close to the ones for 1-μ particles. There is a decrease of one to two orders of magnitude as the distance increases from 1 to 8 miles. It is apparent that the simulated values for cadmium deposition and air concentration are quite dependent on the assumed particle size. At a distance of 1 mile east, deposition of 20-μ particles is about 20 times as great as for 1-μ particles. At 8 miles, there is less than a factor of 4 difference since larger particles are depleted from the plume. At a distance of 1 mile east, there are more 20-μ particles per unit volume of air than smaller sizes, whereas at 8 miles 5-μ particles are most abundant.

Comparison of ATM Output with Measurements. Partial validation of ATM simulations for the smelter area is possible through comparison of the results with data in the EPA report

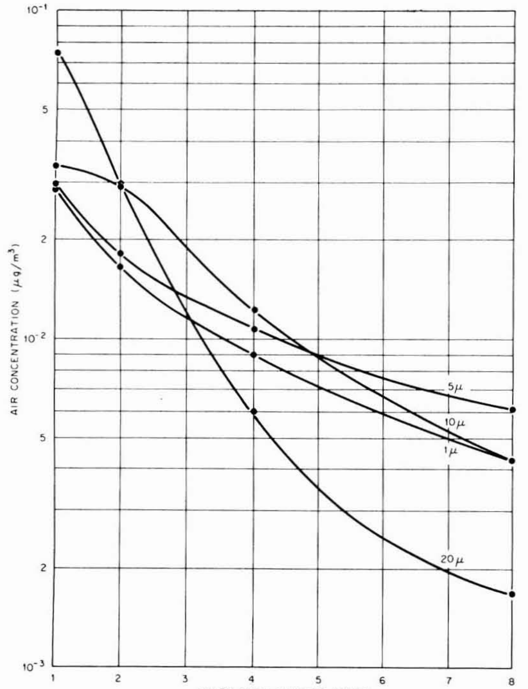

Figure 3. Air concentration of cadmium around East Helena smelter as a function of particle size and distance

(*11*) (see Table IV). Within a radius of 1 mile of the smelter measured cadmium depositions ranged from 1 to 4 mg/m²/month. Simulated results at 1 mile east of the smelter ranged from 0.7 mg/m²/month for a 1-μ particle to 15 mg/m²/month for a 20-μ particle. Thus, simulated results for 1–10-μ particles compare favorably with experimental data. Within 60 square miles around the smelter, levels of 0.1–1 mg/m²/month were measured. At a distance of 8 miles east, the simulated results were 0.1–0.3 mg/m²/month for 1–10-μ particles. Measured 24-h average air concentrations of cadmium at various locations within East Helena ranged from 6.0 to 29.0 μg/100 m³, whereas simulated results at a distance of 1 mile east ranged from 3.0 to 7.0 μg/100 m³ for 1–20-μ particles.

Thus the ATM appears to be giving reasonable results for cadmium concentrations in the area surrounding the East Helena smelter. These data may be used to estimate annual additions to the soil or depositions on crops at specified locations within an 8-mile radius.

Terrestrial Transport Model (TERMOD). Starting with given cadmium ground deposition rates, obtained from monitoring data for the U.S. and from the ATM output for East Helena, TERMOD simulated cadmium intake by the average U.S. adult and by an East Helena adult. Pathways considered were air inhalation, milk, beef, and solid-food consumption, and direct deposition on truck crops (uptake of truck crops is after washing and removal of inedible portions (*23*). The model applies only for soil concentrations of cadmium <10 ppm. Crop production is reduced for higher soil concentrations (*9*).

TERMOD Input Data. The input to the model is a constant ground deposition rate of 15 μg Cd/m²/day which corresponds to an average air concentration of 0.025 μg/m³ and a deposition velocity of 600 m/day. The air concentration is a typical value for areas near large cities in the U.S. (*7*). Therefore, model predictions are for current, equilibrium (background) concentrations in soil, grass, milk, and beef and current uptakes of cadmium via the pathways considered. A ground deposition of 86 μg Cd/m²/day at 1 mile east of the smelter was obtained from the ATM output for the East Helena simulation. This ground deposition corresponds to an air concentration of 0.14 μg/m³ for a deposition velocity of 600 m/day.

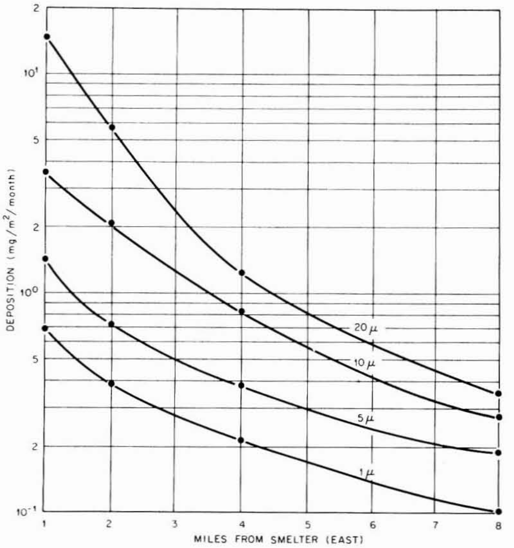

Figure 4. Deposition of cadmium around East Helena smelter as a function of particle size and distance

Table IV. Cadmium Concentrations in Area Around East Helena

	Cadmium concn	
	Measd	**Calcd**
Deposition (mg/m²/month)	1–4 (1 mile radius of smelter)	0.7–15 (1–20-μ particles 1 mile east of smelter)
	0.1–1 (within 60 sq miles around East Helena)	0.1–0.3 (1–10-μ particles 8 miles east of smelter)
Air concn (μg/100 m³)	6–29 (within East Helena)	3–7 (1–20-μ particles 1 mile east of smelter)

The model was run for two values (10 and 50 years) for the half-time of cadmium in subsurface soil pool and pasture soil (*9*).

A literature survey was made to find reasonable values for all TERMOD input parameters and to ensure that the calculated transfer coefficients were reasonable. The only parameter not specifically calculated for cadmium or verified to apply to cadmium was the coefficient associated with transfer from soil surface to subsurface soil pool. A value of 0.0693 day^{-1} was assigned to this coefficient. A sensitivity study was conducted to determine the importance of this parameter to model calculations. It was found that model calculations are relatively insensitive to this parameter.

The model simulation began with cadmium present only in the air. Buildup of cadmium in other compartments (from initial values of zero) was calculated as a function of time after this constant cadmium concentration appeared in air. Cadmium concentrations in these compartments were also calculated as a function of time after an impulse source of cadmium was in the air.

TERMOD Output Data. Equilibrium concentrations in

Table V. Equilibrium Cadmium Concentrations in Various Compartments

Compartment	Equilibrium concn (ppm) 10-yr half-time in soil 15[a]	86[a]	50-yr half-time in soil 15[a]	86[a]
Surface food	0.07	0.40	0.07	0.40
Subsurface soil pool	0.27	1.55	1.30	7.45
Grass	0.46	2.64	0.51	2.92
Pasture soil	0.24	1.38	1.16	6.65
Milk	0.002	0.011	0.003	0.017
Beef	0.06	0.34	0.07	0.40

[a] Deposition rates in μg/m^2/day.

Table VI. Equilibrium Intakes by Reference Man

Pathway or compartment	Intake (μg/day) 10-yr half-time in soil 15[a]	86[a]	50-yr half-time in soil 15[a]	86[a]
Subsurface soil pool	67	384	326	1870
Surface food	18	103.1	18	103
Beef	20	114.6	22	126
Milk	2.3	13.2	2.6	15
Air inhalation	0.5[b]	3[c]	0.5[b]	3[c]
Total	108	618	369	2115.0

[a] Deposition rates in μg/m^2/day. [b] Air concentration 0.025 μg/m^3. [c] Air concentration 0.14 μg/m^3.

various compartments resulting from ground deposition rates of 15 and 86 μg Cd/m^2/day are shown in Table V.

Equilibrium intakes by reference man (*24*) for an air concentration of 0.03 μgm/m^3 and constant ground deposition rates of 15 μg Cd/m^2/day and 86 μg Cd/m^2/day are shown in Table VI.

Comparison of TERMOD Output with Measurements. A ground deposition rate for cadmium of 1–4 mg/m^2/month or 30–133 μg/m^2/day occurred on a 1.5-sq-mile area around the East Helena industrial complex. Equilibrium uptake rates and plots given here apply for a deposition rate of 15 μg/m^2/day. Thus, TERMOD predicts an equilibrium uptake of cadmium by a "fencepost" reference man (*24*) in East Helena of $[(30\text{–}130)/15] \times 100 \sim 200\text{–}950$ μg/day for a 10-year half-time in soil and $[(30\text{–}130)/15] \times 370 \sim 740\text{–}3200$ for a 50-year half-time in soil. The range calculated from food concentrations was 197–811 μg/day for an average East Helena adult with 876 as the reasonable, maximum daily uptake. The corresponding equilibrium subsurface soil pool concentration would be $[(30\text{–}130)/15] \times 0.27 = 0.54\text{–}2.3$ ppm for a 10-year half-time in soil and $[(30\text{–}130)/15] \times 1.30 = 2.6\text{–}11$ ppm for a 50-year half-time in soil. Note that the model will not apply for cadmium concentrations in soil >10 ppm (*9*). The ground deposition rate of 86 μg Cd/m^2/day calculated by the ATM falls about midway in the range determined by actual measurements. Such a deposition rate corresponds to an air concentration of 0.14 μg Cd/m^3 for a deposition velocity of 600 m/day.

Calculation of Limiting Air Concentration

A limiting air concentration for the maximally exposed individual in the area surrounding the smelter complex in East Helena, Mont., is calculated based on the following data and assumptions (see previous discussion and refs *1*, *7–9*, *10*):

1. 100% of diet obtained locally
2. 2100 g Cd/day in diet from 0.14 μg Cd/m^3 in air = 15 000 μg Cd/day in diet from 1 μg Cd/m^3 in air (50-year cadmium half-time in soil, Table VI)
3. selected limit = 200 μg Cd/g wet weight of kidney cortex in 50 years
4. total weight of kidneys = 300 g
5. concentration in kidney cortex = 1.5 × concentration in total kidney
6. half-time of cadmium in body = 38 years
7. fraction of cadmium from air to blood = 0.25
8. fraction of cadmium ingested to blood = 0.05
9. fraction of cadmium from blood to kidney = 0.33.

Inhalation and ingestion of food are the routes of exposure considered since cadmium concentrations in water were low (Table I) for the Helena area (*9*, *11*). Therefore Equation 9 in ref. *1* was used with the transfer coefficient from air to water, f_{AW}, set equal to zero:

$$\hat{C}_A = \frac{Q_L}{(V_A f_R + f_{AF} M_F f_D)\tilde{r}}$$

where Q_L = 200 μg/g wet weight kidney cortex = 4×10^4 μg in total kidneys (from 3, 4, and 5 above), V_A = 20 m^3/day (*23*), f_R = 0.08 (from 7 and 9 above), f_D = 0.016 (from 8 and 9 above), $f_{AF}M_F$ = 15 000 μg/day m^3/μg (from 2 above), and $\tilde{r}$ = 1.2×10^4 days (based upon simple exponential retention with T = 50 years). Thus,

$$\hat{C}_A = 1.3 \times 10^{-2} \frac{\mu\text{g}}{\text{m}^3}$$

The limiting concentration calculated above represents a cadmium concentration in air believed by us to be low enough to prevent a cadmium related health effect to persons receiving continuous exposure at that level in the study area for a 50-year period. It is a conservative estimate when applied such that if the maximally exposed individual is protected, all others will also be protected. The maximally exposed individual as applied here to derive the limiting air concentration is assumed to breathe only air containing the maximum concentration of cadmium and to eat food produced only at the site of maximum cadmium deposition. The assumption regarding food is especially significant since according to the above calculations, more than 95% of the cadmium in kidneys is due to ingestion of food. Less conservative limiting concentrations can be calculated if justified by site characteristics. For example, the proportion of total diet produced at the point of maximum exposure (12%) can be considered as in Table II. In this case the limiting air concentration would become about 0.1 g Cd/m^3.

The calculated value of 0.013 μg Cd/m^3 is near the average urban concentration of 0.02 μg Cd/m^3 in air in the U.S. (Table I) and about 5–20% of levels actually measured in East Helena (0.06–0.29 μg Cd/m^3). Thus depending primarily on patterns of food consumption and in some cases water consumption, existing urban levels of cadmium could be too high. Even at the higher concentration of 0.1 μg Cd/m^3, which is corrected roughly for food grown outside the study area, the levels measured in East Helena at the time of the EPA study (*11*) appear to be too high. Thus the composite hazard index methodology as applied here predicts that appreciable long-term health effects may occur in the East Helena population if the higher levels of exposure (>0.1 μg Cd/m^3) continue for long time periods. If such a methodology were to be applied for standard setting in more general cases, we believe it would be preferable to apply the more conservative limit (i.e., 0.013 μg Cd/m^3) since changes in food consumption could be partially offset by significant cadmium concentrations in water.

The methodology could also be applied to an occupational setting. In most cases of occupational exposure, inhalation is the exposure route considered in deriving threshold limit values (TLV). In such a case we set $f_{AF} = 0$ and obtain $\hat{C}_A \sim$ 2 μg Cd/m^3. Cadmium intakes are likely to be much greater in some occupations because the TLV for industrial exposure in the United States is 100 μg/m^3 for cadmium fumes (*20, 21*). If we assume an inhalation rate of 10 m^3/8 h working day and that 25% of the inhaled cadmium is absorbed, we can arrive at a daily intake value of 250 μg. Based on our analysis, we could judge an occupational exposure of this magnitude to be of extreme significance and the TLV itself much too high. Assuming an excretion rate of 0.005%/day and 224 workdays/year along with the above assumptions, the necessary cadmium concentration in industrial air for exposed workers to accumulate a critical cadmium concentration in renal cortex of 200 μg/g wet weight through inhalation would be 6.5 μg/m^3 for a 30-year occupational exposure. For a 50% pulmonary absorption it would be 3.3 μg/m^3. Recently, the American Conference of Governmental and Industrial Hygienists (ACGIH) has recommended a reduction in the TLV for cadmium to 50 μg/m^3 (*21*). The ACGIH recommendation was set to avoid pulmonary effects and did not consider long-term cadmium damage to kidney tissue. An examination of daily intake values that will result in renal damage indicates that the 50-μg/m^3 occupational exposure level could produce critical levels of cadmium in kidney tissue even without consideration of other exogenous sources of cadmium.

Conclusions

Application of the composite hazard index assessment methodology to cadmium release from a smelter complex in East Helena, Mont., illustrated the usefulness of the approach. The methodology can be applied to other sites and other pollutants in a similar manner by developing site specific information for parameters of the transport models incorporated into the methodology. When sufficient information is not available, the structure of the methodology provides guidance on needed information such that expenses for a particular study can be minimized.

For application to single pollutants, further development of the methodology does not appear necessary and application is straightforward. Application of the formulation for multiple sources also appears practicable. However, application of the formulation for multiple pollutants must, in most cases, await better information on pollutant interactions and biological effects. It is important to identify examples of conjoint exposures where enough information is available to test the methodology for multiple pollutants.

The composite hazard assessment methodology described herein can be developed to provide a comprehensive approach for development of standards.

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Worldwide Deposition of ^{90}Sr Through 1976

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■ In 1976 the annual rate of deposition of ^{90}Sr from atmospheric tests of nuclear weapons reached its lowest value since the systematic measurement of radioactive fallout began in the 1950's. The late 1976 Chinese tests may have contributed about 9 kCi to the total of about 49 kCi deposited during 1976.

The past few years have seen a renewed public and scientific interest in the fallout of the radioactive debris produced by atmospheric tests of nuclear weapons. This interest has mainly concerned environmental levels of the fission product, ^{131}I, which has an 8.04-day half-life. This nuclide was studied less intensely during the early years of fallout measurements, however, than was the long-lived fission product, ^{90}Sr, which has a half-life of 28.6 years. Consequently, there is some merit in considering the more complete historical record of deposition of ^{90}Sr in evaluating the relative significance of the contribution by recent nuclear weapons tests to levels of environmental radioactivity.

The Environmental Measurements Laboratory (EML), which prior to October 1977 was named the Health and Safety Laboratory (HASL), has maintained a worldwide network of samplers since 1957 to collect fallout to be measured for ^{90}Sr. Based upon data from this network, an estimate has been made each year (*1*) since 1958 of the annual worldwide deposition and of the cumulative deposit of ^{90}Sr. The EML network of samplers of ^{90}Sr fallout grew during 1957–1964, and included 142 sites in 1964, 99 in the Northern and 43 in the Southern Hemisphere. During 1964–1975 the network gradually decreased in size, and in mid-1976 it was cut back to 72 sites, 47 in the Northern and 25 in the Southern Hemisphere. The samples are collected at these sites by exposing either a steep-walled, stainless steel pot or a plastic funnel which drains through a column containing Dowex-50 ion-exchange resin. At the end of each month, the total material collected in each pot and each exposed column of ion-exchange resin is analyzed radiochemically for ^{90}Sr. Starting with the July 1976 sample, analyses have been made on quarterly composites. The analyses are performed at contractor laboratories using procedures similar to those used at EML (*2*).

Results

All of the detailed monthly precipitation and radiochemical data accumulated since the inception of the EML pot and column network have recently been tabulated (*3*).

Various methods for calculating the total fallout of ^{90}Sr on the surface of the earth from limited data were discussed by Volchok (*4*). Some of these methods involve the analysis of soil samples, while others involve the analysis of precipitation samples. In some of these methods, the values of ^{90}Sr per unit area of the surface of the earth are averaged over each latitude band, while in others the concentrations of ^{90}Sr per unit volume of rainfall are averaged over each latitude band and this average is multiplied by an assumed value of average annual precipitation for the band. The differences between the results given by the different methods were found generally to be small. The approach used at EML assumes that our sampling sites are representative, on the average, of the fallout in the 10 degree latitude band within which they are located. The average quarterly ^{90}Sr deposition (in mCi/km^2) for each such latitude band is multiplied by the area of the band (in km^2) to give the total quarterly deposition in that band. Values are obtained for the unsampled polar areas north of 80°N and south of 70°S by extrapolating a smoothly decreasing ^{90}Sr deposition to zero at the poles. Summing the calculated totals for the 10 degree latitude bands gives the worldwide deposit for each quarter. No attempt is made to correct for any possible bias in the amount of precipitation at the sampling sites as compared to an assumed average amount of precipitation for the latitude band in which they are located. Neither is an attempt made to correct for any postulated oceanic effects on local rates of deposition.

In general, both the annual and cumulative values of ^{90}Sr fallout calculated by this method have been in reasonably good agreement with those determined by other measurement programs (*5, 6*). Moreover, the ^{90}Sr global cumulative deposit calculated by this method is consistent with that expected based on the estimated total production of ^{90}Sr by all atmospheric tests of nuclear weapons (*7*). Finally, the rates of ^{90}Sr deposition on the surface of the earth calculated by this method have generally shown good agreement with the rates of decrease of the stratospheric burden of ^{90}Sr calculated by programs in which stratospheric concentrations of radionuclides are measured (*1, 7*).

Table I contains the calculated annual ^{90}Sr deposition and the cumulative deposit of ^{90}Sr on the surface of the earth at the end of each year, both within each hemisphere and worldwide. The data presented cover the period from the beginning of the EML pot and column program in 1958 through 1976.

Discussion

The worldwide fallout of ^{90}Sr during 1976 was 49 kCi, with 27 kCi falling in the Northern, and 22 kCi falling in the Southern Hemisphere. This was the lowest annual rate of ^{90}Sr deposition observed since the EML sampling network was established in 1958, and was probably the lowest rate since the atmospheric testing of megaton-yield nuclear devices was first performed. As the data in Table I indicate, the annual rate of

Table I. Annual-Cumulative Worldwide ^{90}Sr Deposition, Megacuries

	Annual deposition			Cumulative deposit		
	Northern Hemisphere	Southern Hemisphere	Total	Northern Hemisphere	Southern Hemisphere	Total
Pre-1958				1.7	0.6	2.3
1958	0.63	0.26	0.88	2.3	0.8	3.1
1959	1.05	0.18	1.24	3.3	1.0	4.3
1960	0.26	0.17	0.43	3.4	1.1	4.6
1961	0.35	0.17	0.52	3.7	1.3	5.0
1962	1.44	0.26	1.71	5.0	1.5	6.6
1963	2.62	0.31	2.93	7.5	1.8	9.3
1964	1.66	0.42	2.08	9.0	2.2	11.1
1965	0.77	0.36	1.13	9.5	2.5	12.0
1966	0.33	0.21	0.54	9.6	2.6	12.2
1967	0.17	0.11	0.28	9.5	2.6	12.2
1968	0.20	0.10	0.30	9.5	2.7	12.2
1969	0.15	0.14	0.29	9.4	2.8	12.2
1970	0.21	0.13	0.33	9.4	2.8	12.2
1971	0.19	0.15	0.34	9.3	2.9	12.2
1972	0.086	0.096	0.18	9.2	2.9	12.1
1973	0.032	0.031	0.063	9.0	2.9	11.9
1974	0.121	0.039	0.160	8.9	2.8	11.7
1975	0.058	0.034	0.092	8.7	2.8	11.5
1976	0.027	0.022	0.049	8.5	2.8	11.3

Table II. Calculation of "Excess ^{90}Sr" Deposition During Fourth Quarter of 1976

	Northern Hemisphere			Southern Hemisphere		
	^{90}Sr deposition, kCi		% of deposition during same interval of 1975	^{90}Sr deposition, kCi		% of deposition during same interval of 1975
Quarters of year	1975	1976	1976	1975	1976	1976
1st	21.0	6.2	30	13.8	4.8	35
2nd	23.8	6.2	26	7.9	2.8	35
3rd	9.4	4.4	47	5.4	6.8	127
1st–3rd	54.2	16.8	31	27.1	14.5	53
4th—observed	4.1	10.2	248	7.1	7.1	99
4th—expected	...	1.3	31	...	3.8	53
"Excess ^{90}Sr" during 4th quarter of 1976		8.9			3.3	

deposition peaked in 1963, while the cumulative deposit of ^{90}Sr peaked during the period 1966–1972. Since about 1971, the ^{90}Sr deposit on the surface of the earth has decreased as its radioactive decay has exceeded the rate of deposition of new ^{90}Sr.

It is of interest to estimate the extent to which the three announced atmospheric detonations of nuclear devices by the People's Republic of China, during 1976 contributed to the fallout of ^{90}Sr during that year. No radioactivity was detected by the EML surface air sampling program (*8*), which could be attributed to the very low yield, 20 kilotons (kt) test of January 23, 1976. During October–December 1976, easily measurable concentrations of short-lived fission products were intercepted by the surface air sampling program. Based on nuclide ratios, as well as on the fact that the highest concentrations were intercepted during October 1976, all or most of these fission products were attributed to the September 26, 1976 test, which had a yield of 20–200 kt, and not to the November 17, 1976 test, which had a yield of 4 megatons (Mt). Presumably almost all of the radioactive debris from the November 17 test was injected into the stratosphere and did not enter the troposphere in substantial amounts until the spring of 1977. On the other hand, the debris from the September 26 test was probably mainly injected directly into the troposphere, and had largely been deposited on the surface of the earth by the end of 1976. If we assume that the September 26 test had a fission yield of 100%, and that the ^{90}Sr yield was 0.11 Ci/ton of fission yield (*9*), we would conclude that this nuclear detonation produced between 2.2 and 22 kCi of ^{90}Sr. If we assume that the fission yield was less than 100% or that some radioactivity fell out locally, we would expect the total worldwide fallout of ^{90}Sr from this test to be less.

In Table II we have summarized the data used in calculating the amount of the worldwide deposit of ^{90}Sr during the last quarter of 1976 which can be attributed to the September 26 test (plus the November 17 test). We have used 1975 as a basis for comparison because no atmospheric tests of nuclear weapons were performed during that year. In the Northern Hemisphere the deposition of ^{90}Sr during the first three quarters of 1976 amounted to 31% of that which had occurred during the first three quarters of 1975. We assume that in the absence of the September and November 1976 tests, the deposition of ^{90}Sr in that hemisphere during the last quarter of 1976 would also have been 31% of the deposition which occurred during the last quarter of 1975: 1.3 kCi. Instead, 10.2 kCi were deposited, giving an "excess ^{90}Sr" deposit of 9 kCi, which we attribute to the late-1976 tests.

If we apply this same approach to the ^{90}Sr data for the Southern Hemisphere, we estimate that instead of an expected 3.8 kCi, about 7.1 kCi were deposited in that hemisphere during the last quarter of 1976, giving an "excess" of 3 kCi. There are several reasons for not believing that this "excess ^{90}Sr" was produced by the late 1976 tests, however. During October, November, and December 1976, radioactive debris (and specifically ^{95}Zr) attributable to the late 1976 tests was intercepted by the EML surface air sampling program at all of its Northern Hemisphere sampling stations, from Barrow, Alaska to Balboa, Panama, but at none of its Southern Hemisphere sampling stations, from Guayaquil, Ecuador to the South Pole Station. Further, in the Southern Hemisphere, only the first two quarters of 1976 experienced deposition rates of ^{90}Sr that were low (35%) compared to those which prevailed during 1975. The third quarter as well as the fourth experienced rates of deposition that were rather high when compared to the 1975 rate. Thus, the processes that produced the "excess ^{90}Sr" in the Southern Hemisphere were already operating during the third quarter of 1976, prior to the late 1976 nuclear tests. Finally, excess ^{90}Sr in the Southern Hemisphere was deposited in about equal amounts north of 30°S and south of 30°S. Had its source been the troposphere of the Northern Hemisphere, we would expect it to be deposited preferentially north of 30°S. We believe, therefore, that the approximately 3 kCi of "excess ^{90}Sr" estimated for the Southern Hemisphere are indicative of the uncertainty in this type of calculation. We conclude that the total worldwide deposit of ^{90}Sr attributable to the late-1976 nuclear weapons tests was about 9 kCi, with an uncertainty of perhaps ±50%. This amount of ^{90}Sr is within the range expected for an event with a total yield of 20–200 kt.

The deposition rate of ^{90}Sr during 1977 was considerably higher than the 1976 rate as radioactive debris from the November 1976 test reentered the troposphere from the stratosphere and was deposited on the surface of the earth. Preliminary measurements suggest that the deposition rate during 1977 was slightly higher than during 1975. The year 1976, however, had the lowest deposition rate of ^{90}Sr since the systematic measurement of such deposition was begun, and perhaps a fifth of this was contributed by the late 1976 tests.

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Chemiluminescent Reactions of Oxygen Atoms with Reactive Hydrocarbons (HC)
II. Basis for Reactive HC Monitor at 3064 Å

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■ The chemical mechanism for the production of $OH(A^2\Sigma - X^2\Pi)$ emission observed in reactive hydrocarbon instruments is demonstrated for the prototype olefin, ethylene. The mechanism is studied in a discharge-flow tube reactor at 1 torr total pressure, and the data are consistent with the mechanism $CHO^* + O \rightarrow OH(A^2\Sigma) + CO$, where CHO^* is either electronically or vibrationally excited CHO. This mechanism will be operative in all reactive hydrocarbon–oxygen atom systems, and it produces a rotationally cold $OH(A^2\Sigma)$. A reactive hydrocarbon analyzer (RHA) is constructed to observe emission from paraffins, lower olefins, and benzene, and the emission correlates well with the group reactivity scale of Dimitriades and also with the rate constants for the rate-determining step in the proposed kinetic mechanism. Our RHA has an ultimate sensitivity of better than 6 ppb ethylene equivalent concentration at 4.5 torr total pressure and a linear response to at least 1000 ppm.

The suggestion was made in our earlier work (*1*) (Part I) that reactive hydrocarbons (HC) could be monitored using near ultraviolet or near infrared emission from OH $(A^2\Sigma)$, $OH(X^2\Pi)$ or $O_2(^1\Sigma)$ associated with oxygen atom attack on the reactive hydrocarbon. It was therein suggested that the observed chemiluminescence could be a direct measure of the classical reactivity and that conditions might be found under which a "reactivity" detector for hydrocarbons in atmospheric air masses as well as automotive exhaust gases could be developed. In this context, the word "reactivity" refers to the atmospheric group reactivity scales, such as those proposed by Heuss and Glasson (*2*), Glasson and Tuesday (*3*), Darnall et al. (*4*), Dimitriades (*5*), Altshuller (*6*), and Altshuller and Bufalini (*7*). A common feature of these scales involves the rate of HC reaction in the atmospheric photochemical cycle. These suggestions in Part I have now been verified (*8, 9*), and it is quite clear that a very sensitive device can indeed be constructed.

While it is not necessary to know the detailed reaction mechanism for operation of a reactive hydrocarbon analyzer (RHA), that knowledge is imperative to a correct interpretation of field data and to the design of operating conditions for RHA's required to meet the diverse needs of ambient air as well as automotive exhaust monitoring. Even for ambient air monitoring, measurements made in air masses characterized by early times in the photochemical oxidation mechanism must emphasize the highly reactive olefins, whereas measurements made in air masses late in the photochemical cycle must emphasize the less reactive hydrocarbons (*10, 11*). Hence, the design of RHA's must be based on specific chemical kinetic data if they are to be used for valid hydrocarbon control strategy decisions covering the diverse needs of the country. We shall show in this work that the observed intensity of $OH(A^2\Sigma - X^2\Pi)$ can be strongly correlated with the rate constant (and the HC concentration) for the rate-determining step in the O + HC reaction mechanism, or under other operating conditions, it can be a measure of the total reactive hydrocarbon concentration.

As can be seen in Figures 1 and 2, the RHA concept is based on the observed intense emission at 3064 Å (and 6128 Å in the second order) in the chemiluminescent spectrum of a variety of hydrocarbons resulting from oxygen atom attack at pressures of about 1 torr and contact times of a few milliseconds. The first order peak is at 3064 Å reproduced in higher resolution in Figure 3 from reactions of $O + C_2H_4$ and $O + C_2H_2$. It is well established (*12, 13*) that this emission is due to the transition $OH^*(A^2\Sigma) \rightarrow OH(X^2\Pi)$, with a lifetime of 6×10^{-7} s (*14*).

Experimental

The mechanism studies reported herein employed the same equipment as described in Part I (*1*), except that Canberra photon counting detection was employed using a thermoelectrically cooled RCA C31034A photomultiplier. A detailed description of this equipment and the results has been given in ref. *15*.

Relative reactivity studies were performed in the discharge flow system shown schematically in Figure 4. The concept and apparatus have been described in more detail elsewhere (*16–18*). Molecular oxygen was discharged in a Broida cavity at 2450 Hz using a Raytheon PGM 19 (100 W) series Microwave Power Generator. Tests with O_2 in either helium or argon in the discharged gas stream gave a background signal much higher than that for a pure O_2 discharge in our experimental configuration. As Fontijn and Ellison (*8*) suggested, we found that O_2 reduces the absolute signal. However, further work showed that we could improve our signal-to-noise ratio and therefore measure lower concentrations of hydrocarbons if a pure O_2 discharge system was employed. The discharged oxygen was passed into a cylindrical brass reactor through a Teflon tube with a multiperforated exit stream. This permitted excellent mixing with the test gas in such a way that the reaction took place near the quartz window observation port. The inside diameter of the reactor was 3.8 cm, and typical gas velocities were 5–7 m/s using a Welch Duo-Seal Vacuum Pump Model 1376. An RCA C31025C uncooled photomultiplier tube at 1000 V was used to measure the intensity of the signal as a current via a Kiethley 414S Picoammeter, and recorded on a Texas Instrument Servo/riter II chart recorder. A Baird Atomic UV-7 A optical filter with peak wavelength of 3059 Å and a bandwidth at half of peak transmittance of 250 Å ± 50 Å, was used to determine the $OH(A^2\Sigma)$ emission at 3064 Å. This filter permitted integration over the entire $A^2\Sigma - X^2\Pi$ OH transition, regardless of the rotational excitation of the emitting species.

The test gas consisted of a mixture of N_2 and low concentrations of hydrocarbons which were prepared in the laboratory with a ±1% accuracy. All gases were obtained from Linde division of Union Carbide. Hydrocarbons had a purity of 99%, or greater, except for methyl acetylene (96%) and ethyl acetylene (95%). Nitrogen was 99.9% pure, and oxygen and helium were 99.5% pure.

The optimum signal for ethylene occurred at a total pressure of 4.5 torr and 40% discharge power; the lowest background signal occurred at a molecular oxygen pressure of between 1.5–2.0 torr. Under these conditions the introduction

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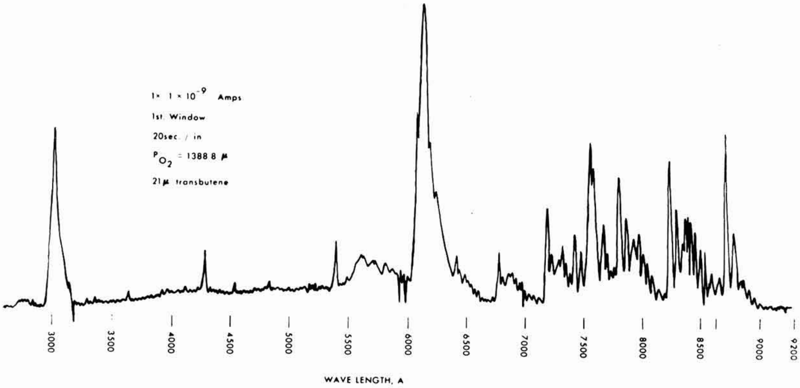

Figure 1. Intensity vs. wavelength spectrum for O atoms reacting with *trans*-butene

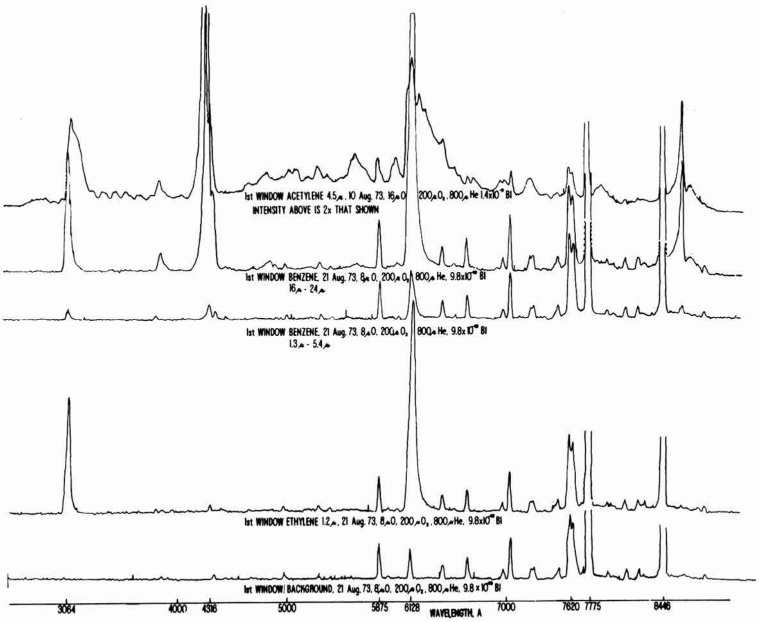

Figure 2. Intensity vs. wavelength spectrum for O atoms reacting with acetylene, benzene, and ethylene

of our gas in N_2 rather than air should have little effect. These operating conditions were employed for all of the relative reactivity measurements.

Linearity tests were conducted for N_2–C_2H_4 and N_2–C_4H_8 mixtures. Relative intensity studies were conducted for a series of HC all at concentrations of 1000 ppm. The latter concentration is not meant to be representative of actual monitoring conditions, but rather ensured that all HC could be detected while also remaining in a linear region even for the most reactive HC.

Formation of Electronically Excited OH($A^2\Sigma$)*

Evaluation of Potential Mechanisms. A number of mechanisms have been suggested to explain OH($A^2\Sigma$) emission in a variety of systems. We have examined each of these mechanisms using the energetics as displayed in Figure 5, the kinetics as obtained from the literature and interpreted via a computer simulation of our experimental apparatus, and a variety of experiments performed to evaluate the potential mechanisms for producing the OH($A^2\Sigma$) state, 93 kcal/gmol above the OH($X^2\Pi$) state.

$$CH + O_2 \rightarrow CO + OH \;\Delta H^\circ = -158 \text{ kcal/gmol} \qquad (1)$$

Becker et al. (*13*) have compared the spectra generated by O + C_2H_2 and O + C_2H_4. They support Reaction 1 in the O + C_2H_2 system, but they note that a different mechanism must be operative in the C_2H_4 system because, as illustrated in Figure 3, the rotational spectrum of OH($A^2\Sigma$) produced by O + C_2H_2 is "hot", while the rotational spectrum produced by O + C_2H_4 is "cool".

In the present work, there were also several factors that suggested that this is *not* the production mechanism for rotationally cold OH* in O + ethylene. First, the 3064 Å emission appears with almost equal intensity in a molecular oxygen discharge or an N_2 discharge with NO added, so that O_2 does not play an important part in the production of OH* in olefin systems. Molecular oxygen was added to the N_2 discharge system and did not decrease or increase the 3064 Å intensity significantly until concentrations (about 200 μ) were sufficiently large to cause electronic quenching of OH*, as is con-

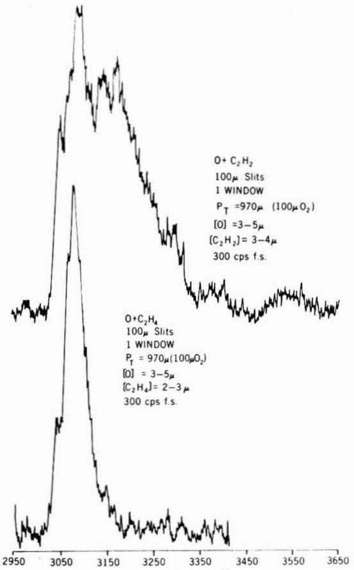

Figure 3. Comparison spectra of OH(0, 0) band observed in this work from O + C_2H_4 and O + C_2H_2 reactions

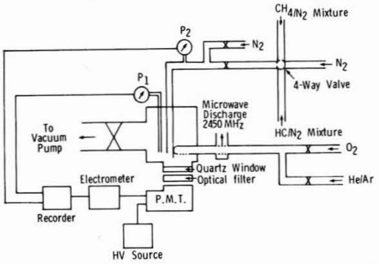

Figure 4. Schematic of chemiluminescence reactor and detection systems for relative reactivity studies

sistent with ref. *12*. Secondly, the olefin + O atom reaction is known to yield far less CH than the acetylene system. The work of Kanofsky et al. (*22*) indicated a yield of less than 5% of CH_2 in the ethylene–O atom system, which suggests the yield of CH would be even smaller.

$$H + O(+M) \rightarrow OH(+M) \; -102 \text{ kcal/gmol} \qquad (2)$$

In O + HC systems, a large concentration of H is produced; hence, reactions of H must be considered. From Figure 5 it can be seen that the only other ground state reaction besides Reaction 1 with sufficient energy to populate this state is Reaction 2.

The rate constant for this two-body reaction to produce OH(A) has been determined by Ticktin et al. (*23*) to be 3 ± 1×10^{-21} cc/s at 1 torr total pressure, which is much too small to make this reaction important in O + HC systems. In addition, we have reacted H + O in our experimental system under conditions in which both [H] and [O] exceed their respective values in the O + HC system. From the very low resulting intensity of the 3064 Å emission in the H + O (+M) experiment, shown in Figure 6, Reaction 2 can be ruled out as the source of electronically excited hydroxyl emission in this system.

$$H + O_3 \rightarrow OH + O_2 \; -77 \text{ kcal/gmol} \qquad (3)$$

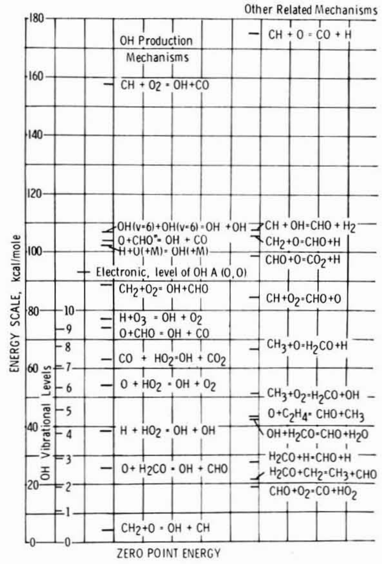

Figure 5. Energetics of O + C_2H_4 system reactions

Vibrational spacings taken from Chu et al. (*19*). Standard heats of reaction taken from refs. *20* and *21*

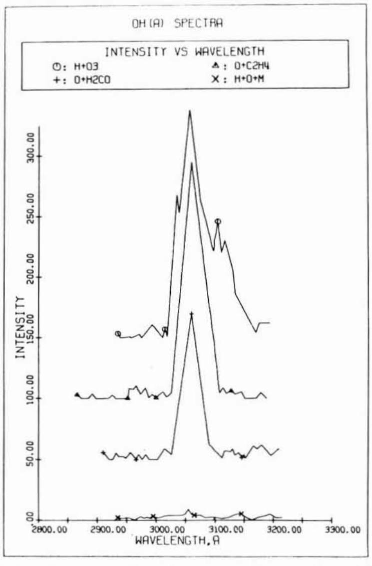

Figure 6. Intensity vs. wavelength spectrum for reaction of O + H_2CO and O + C_2H_4 to produce OH* in N_2 discharge system; reaction of H + O_3 to produce OH*; reaction of H + O + M to produce OH*

Base for each successive plot offset by 50 intensity units

In any system containing O_2 and O, the reaction O + O_2 + M produces O_3. Hence, reactions of H and O_3 should be considered. However, the reaction of H + O_3 is not sufficiently exothermic to directly produce OH in the $A^2\Sigma$ state. Therefore, this reaction can only participate indirectly via Reaction 4 through the production of OH($X^2\Sigma$, $\upsilon < 0$). Furthermore, the addition of O_2 to this system reduces rather than enhances the observed emission intensity, as this mechanism would suggest.

$$OH(\upsilon = 6) + OH(\upsilon = 6) \rightarrow OH + OH(A) \qquad (4)$$

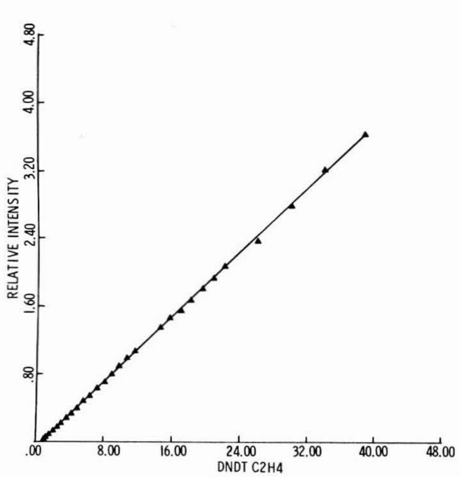

Figure 7. Intensity vs. ethylene flow rate (*dn/dt*) in μmol/min for reaction of $O + C_2H_4$ to produce OH*

8 μmol/min = 100 ppm for conditions of this experiment. Contact time, approx. 1 ms; O_2 partial pressure, 930 μ; oxygen atom partial pressure, 27 μ

Broida (*24*) suggests that

$$OH^{\dagger}(v \geq 6) + OH^{\dagger}(v \geq 6) = OH^{*}(A^2\Sigma) + OH^{\ddagger}$$

is the method by which OH* is created in his $H + O_3$ system. For the same conditions as in the O + HC measurements, the emission from $OH^*(A^2\Sigma)$ at 3064 Å was observed from the reaction of $H + O_3$, and its spectrum is compared with those from O + HC and H + O in Figure 6. The 3064 Å emission generated by $H + O_3$ is characterized by an elevated rotational temperature, similar to that observed by Broida (*24*), but different from the rotationally cold peak observed in the O + HC system. We have also monitored the $OH(X^2\Pi, v = 4 \rightarrow 9)$ concentration in the O + HC systems (*15*). The predicted rate of $OH^{\dagger}$ $(v \geq 6) + OH^{\dagger}$ $(v \geq 6)$ at our experimental concentrations of 10^{10} molecules/cc can be ruled out as producing the observed $OH^*(A^2\Sigma)$ concentration (*15*).

$$O_3 + C_2H_4 \tag{5}$$

OH chemiluminescence in the near infrared has been observed in O_3 + olefin systems (*25*). Experiments performed under Reaction 1 preclude this mechanism from being a substantial contributor here.

Proposed Mechanism. In first trying to postulate another mechanism for the production of OH* in the $O + C_2H_4$ system, there are several experimental results that must be correctly accounted for. One is the high intensity OH* emission from the $H_2CO + O$ reaction system. The two 3064 Å peaks with their respective experimental conditions are also shown in Figure 6. Since the OH* emission spectrum is similar in both reaction systems, the precursor in the chemiexcitation reaction step appears to be common to both $C_2H_4 + O$ and $H_2CO + O$ mechanisms. Secondly, the quantum yield of the emission step is only 10^{-5} by comparison of absolute emission levels with the initial reaction rate of $O + C_2H_4$ and about the same in the formaldehyde system (*15*). This suggests that either the production step of OH* or its precursor has a low probability of occurring, or that the precursor has a high probability of loss due to a competitive path. Third, the intensity of the emission is linear in hydrocarbon concentration as illustrated in Figure 7. Fourth, O_2 quenches, rather than enhances, the intensity.

A mechanism for the production of rotationally cold OH* that agrees with the experimental findings and energetic considerations in the reaction of either vibrationally excited $CHO^{\dagger}$ or electronically excited $CHO^*(\tilde{A}^2A'')$ with O atoms, i.e.,

$$\begin{Bmatrix} CHO^* \\ CHO^{\dagger} \end{Bmatrix} + O \rightarrow OH^* + CO, \Delta H > 93 \text{ kcal/mol} \tag{6}$$

The Ã state of CHO* is described by Herzberg (*26*) as a bent configuration of the formyl radical as opposed to the linear configuration of the ground state. This explains the rather low energy of an electronic state, 9294 cm^{-1} (~26 kcal). There is some experimental evidence for the existence of this state of CHO* in $O + C_2H_4$ systems as indicated by the infrared spectra of the $O + C_2H_4$ and $O + H_2CO$ reactions done by Kadaj (*27*) and in the $O_3 + C_2H_2$ work of Hansen and Pitts (*28*). The emission at 1.07 μ (9294 cm^{-1}) is observed by Kadaj (*27*) for $O + C_2H_4$ and $O + H_2CO$, but not in $H + H_2CO$ systems. The excited $CHO^{\dagger}$ (or CHO*) could be formed from the reactions appearing below. If the reaction energies based on ground state heats of formation are summed, we obtain the necessary 93 kcal/mol for the OH* production in each case:

	kcal/mol
$O + C_2H_4 \rightarrow CHO + CH_3$ (7)	−42
$O + CHO \rightarrow OH + CO$ (6)	−73
	Net −115
$O + H_2CO \rightarrow CHO + OH$ (8)	−28
$O + CHO \rightarrow OH + CO$ (6)	−73
	Net −101

The energies of the above reactions are sufficient to cause the OH*(1, 0) transition observed by Becker et al. (*13*) in the ethylene system. Hence, even though the CHO fragment will not carry all of the exothermicity of Reactions 7 or 8, a high probability of excitation of OH* should exist nonetheless. This was well below the −158 kcal/mol occurring in the $CH + O_2$ reaction which is postulated to produce rotationally "hot" OH*. The $OH(A^2\Sigma, v = 1)$ state requires −103.2 kcal/mol to populate it. As previously noted, the intensity of the cold OH(0, 0) band decreases with addition of O_2 (*12*). This is consistent with the destruction of CHO by O_2, which is a relatively fast reaction ($k = 5.7\,E - 12$ cc/molecule s (*29*)], even when CHO is in the ground state. Our finding, that small concentrations of O_2 have little effect, is also consistent with the competition of O + CHO with O_2 + CHO which occurs in this system (*29*). Large concentrations of O_2 do have the important effect of depleting CHO, as previously discussed.

The above mechanisms for the production of $OH^*(A^2\Sigma)$ were *all* included in a computer model (*15*) of the reacting system. The relative rates of Reactions 1, 2, and 4 discussed above are compared with and without O_2 in results of the computer model, illustrated in Table I. As discussed by Krieger (*15*), it can be readily shown that each mechanism is a minor contributor to the population of the $OH^*(A^2\Sigma)$ state in HC systems compared to Reaction 6. The predicted intensity due to the O + CHO* reaction is linear in the initial HC concentration, as observed, and the system can be initiated by either C_2H_4 or H_2CO, according to the Niki mechanism (*33–36*) as experimentally observed in Figure 6.

Our conclusion is that a likely candidate for production of $OH^*(A^2\Sigma)$ is the reaction of $CHO^* + O \rightarrow OH + CO$, ($\Delta H$ = −103 kcal/gmol for OH in the ground state). This mechanism would fit the experimental evidence and is sufficiently energetic to produce rotationally "cold" OH* $(v \leq 1)$, as found in the $O + C_2H_4$ reaction system.

Table I. OH* Production Mechanism (Time = 2 ms)

Initial concentrations:
$[C_2H_4]_0 = 3.3E + 13$ molecules/cc
$[M] = 3.1E + 16$ molecules/cc (total pressure)
$[O_2] = 3.3E + 15$ molecules/cc (100 μ O_2)

Reaction	k, molecular units	With 100 μ O_2 rate $(cc\ s)^{-1}$	Without O_2 rate $(cc\ s)^{-1}$	Ref.
$H + O + M \rightarrow OH^* + M$	1.6E − 37[a]	3.0E + 06	3.6E + 06	(23)
$H + O_3 \rightarrow OH^* + O_2$	2.6E − 17	1.1E + 06	1.2E + 03	(30)[b]
$CH + O_2 \rightarrow OH^* + CO$	1.0E − 15	5.1E + 07	2.3E + 04	(31)
$OH^\dagger + OH^\dagger \rightarrow OH^* + OH$	1.0E − 13	5.2E + 07	1.2E + 08	(32)
$\left\{\begin{matrix} CHO^\dagger \\ CHO^* \end{matrix}\right\} + O \rightarrow OH^* + CO$	1.0E − 12	7.7E + 10	9.0E + 10	This work
$OH^* \rightarrow OH + h\nu$	1.7E + 06	7.7E + 10	9.0E + 10	(14)

[a] 1.6E − 37 = 1.6 × 10^{-37}. [b] 0.001% of the rate constant for the overall reaction (30). † Vibrational excitation. * Electronic excitation.

Table II. Chemiluminescent Response of Hydrocarbons

Hydrocarbon	k, cc/s	Ref.	I_{3064}	I_{3089}[a]
Class V, reactivity[b] = 14.3				
Ethylene	8.1 × 10^{-13}	37	100.	100.
Propylene	3.7 × 10^{-12}	37	102.	104.
Butene-1	3.8 × 10^{-12}	37	56.	91.
cis-2-Butene	1.7 × 10^{-11}	37	82.	
trans-2-Butene	2.3 × 10^{-11}	37	74.	
Butene-2 (isomer unknown)	2.0 × 10^{-11}	8		94.
Isobutene	2.0 × 10^{-11}	37		78.
1,3-Butadiene	2.0 × 10^{-11}	37	142.	113.
Propadiene	Unavailable			48.
Class IV, reactivity = 9.7				
Toluene	6.1 × 10^{-14}	38		29.
Class III, reactivity = 6.5				
n-Butane	2.7 × 10^{-14}	37		6.
n-Heptane	1.3 × 10^{-13}	37		10.
Isooctane	9.1 × 10^{-14}	8		10.
Class I, reactivity = 1.0				
Ethane	9.1 × 10^{-16}	37	1.0	3.0
Propane	1.5 × 10^{-14}	37	2.3	7.0
Benzene	1.6 × 10^{-14}	38	8.1	3.0
Methane	1.7 × 10^{-17}	37	0.04	<0.01
Acetylene	1.6 × 10^{-13}	37	195.	
Methyl acetylene	2.1 × 10^{-12}	39	149.	
Ethyl acetylene[c]	2.1 × 10^{-12}	39	180.	

[a] Fontijn and Ellison (8), Table I (relative to ethylene = 100). [b] Reactivity of classes and numbers as suggested by Dimitriades (5). [c] Rate constant unavailable, estimated to be same as that for methyl acetylene.

Relative Reactivity Measurements

In all HC + O systems, CHO* (* refers hereinafter to either vibrational or electronic excitation) is produced to some extent via

$$O + HC \rightarrow R_1\cdot + R_2\cdot$$

followed by the extremely rapid radical reactions summarized by

$$O + \left\{\begin{matrix} R_1\cdot \\ R_2\cdot \end{matrix}\right. \rightarrow \cdots \rightarrow n\mathrm{CHO}^*$$

Thus, the intensity of the emission at zero reaction time in the system should be proportional to the rate constant for the rate limiting step, which is always O + HC, to the initial hydrocarbon concentration and to n, the number of CHO* radicals produced per molecule of HC.

Therefore, we would first expect that a plot of intensity vs. k for HC with the same value of n at constant HC concentration would be linear with a slope (on log-log paper) of unity. Sample data are tabulated in Table II and are plotted in Figure 8. Rate constants for O atom attack on HC have the dimensions of cc/molecule s and are taken from Herron and Huie (37) except as noted. As illustrated there, the paraffins and simple olefins do indeed fall on a straight line with a slope of 1.1 verifying the concept. However, the variation in intensity for different olefins is much smaller compared to the wide range of their rate constants with oxygen atoms. As shown by Kanofsky et al. (22), not all of the products of the O + HC reaction lead to radical formation. In fact, some of the adduct formed in the initial attack of oxygen atoms on hydrocarbon leads to stabilized products while the rest give radicals which, in turn, lead to CHO* formation. Thus, the effective rate constant for CHO* formation is kn. For higher olefins, more steps are required to produce nCHO* and if part of the product in each step is stabilized, the final production of CHO* would be smaller, thereby reducing n. Thus, the effective rate constant is much lower than the elementary rate

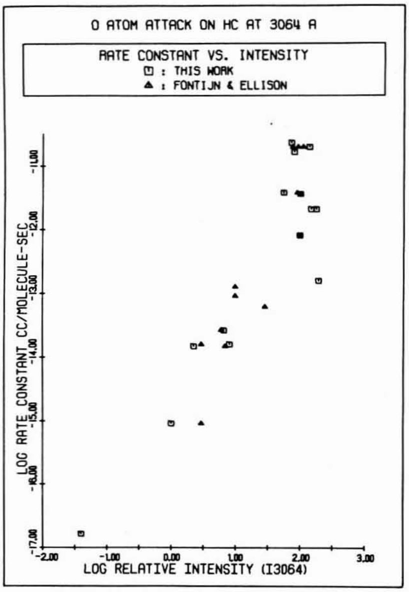

Figure 8. Rate constant vs. intensity of chemiluminescence at 3064 Å for O atom attack on HC, corresponding to Table II

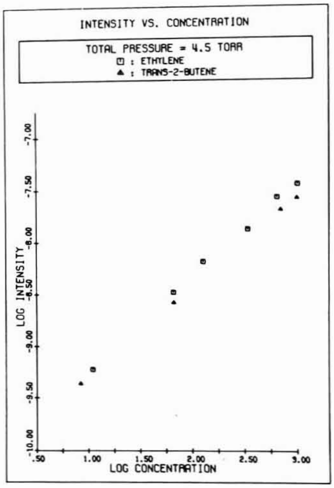

Figure 9. Intensity vs. concentration for ethylene and *trans*-2-butene at 3064 Å

constant for higher olefins than it is for the lower olefins, thereby reducing the difference in their potential to produce CHO*. Also, olefins react sufficiently rapidly in both the experimental apparatus and the atmosphere such that their effect is essentially independent of the rate of reaction. As suggested by Fontijn and Ellison (*8*), this effect can be used to selectively deplete the more reactive HC before detection, which would reduce their apparent signal. Our system behaves more like a stirred tank reactor; therefore, we integrate over the entire reaction time domain. When that domain is sufficiently long, the entire HC is consumed. Hence, for those hydrocarbons above a certain reactivity level on the reactivity scale, the only difference in intensity would be due to the different values of *n*.

Secondly, we have examined the intensity-concentration relationship for individual hydrocarbons. We expect and find a linear relationship as illustrated for ethylene and *trans*-2-butene in Figure 9. We do not see evidence for oxygen depletion over the range of the present experiments. Therefore, the relative reactivity scale proposed at the concentration of 1000 ppm should be concentration independent.

Acetylene gives a large signal, but it is well established that C_2H_2 does not produce significant quantities of CHO. Hence, to obtain correlation with phenomenological photochemical reactivity scales, a simple subtraction mechanism such as that suggested by Fontijn and Ellison (*8*) must be employed to obviate the C_2H_2 signal. If good spectral resolution is obtained in this subtraction process, other hydrocarbon signals should be unaffected by the subtraction of acetylene. However, instrument noise could somewhat degrade the sensitivity we report here.

In our instrumental configuration, we could detect methane which, of course, is normally considered to be photochemically unreactive. Nonetheless, CH_4 has a definite reaction rate with O atoms producing CH_3 and OH. Hence, it should appear on a sensitive reactivity scale despite the fact that i will have negligible reactivity. At a concentration of 1000 ppm, methane gives a signal 2500 times less than that for ethylene.

By using ppb mixtures of hydrocarbons in nitrogen, an estimate of the ultimate sensitivity of the instrument was made. A 557 ppb ethylene in N_2 mixture gave a signal-to-noise ratio of better than 100. From these data the sensitivity of the instrument was projected to be better than 6 ppb ethylene. Thus, the projected sensitivity of the instrument in the lower ranges, suitable for ambient air monitoring, and the experimental data in the higher ranges suitable for auto exhaust monitoring, makes such an instrument very useful for various needs of reactive hydrocarbon measurements.

In unpublished work (*40, 41*), we have examined the spectral region around 3000 Å and find no competing emission from common compounds such as NH_3, CO, NO, NO_2, and N_2H_2. Substituted hydrazine compounds do exhibit emission at 3064.

Discussion

The important role of the CHO radical in O + ethylene chemiluminescence has a considerable impact upon the proposed detection devices for reactive hydrocarbons (*1, 2*). There are two generally accepted mechanisms described in Figures 10 and 11 for low-pressure oxygen atom attack on olefins. The thrust of both mechanisms suggests that CHO is formed in all O + HC (including CH_4 + O) as well as O + RCHO reaction systems. An analysis (*15*) of the kinetics of such systems in reactive hydrocarbon detectors shows that the first step in the reaction sequence is rate limiting. All loss reactions of the radicals are very fast, causing steady state concentrations to occur. Thus, the steady state value of the intensity of the chemiluminescence should be proportional to the rate constant for O + HC as well as the HC concentration. Both

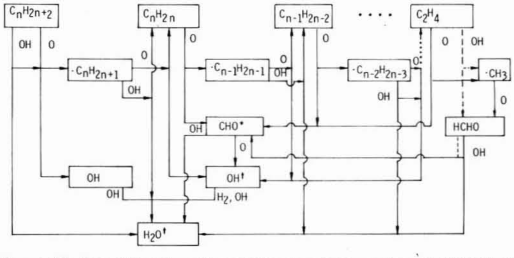

Figure 10. Simplified flow diagram for low-temperature straight chain hydrocarbon oxidation

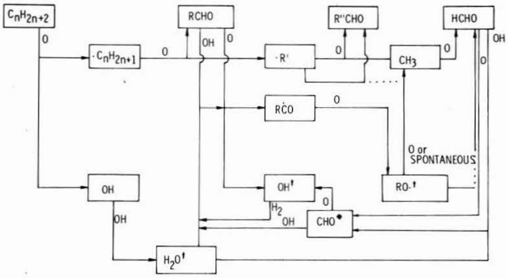

Figure 11. Alternative model for HC oxidation through aldehyde intermediate mechanism

functional relationships for our RHA configuration have been demonstrated in this work. Thus, we conclude that the common feature in O atom oxidation of HC will be the eventual production of CHO*, which at short times is linearly related to the effective rate constant for the rate-determining step as well as linearly related to the concentration, as suggested in Part I.

The data and the analysis also suggest that the choice of residence time in the RHA can be guided by kinetic considerations to measure either hydrocarbon reactivity suited for urban atmospheres at short times or total hydrocarbon concentrations applicable to downwind rural areas at long residence times. The calibration of the instrument to achieve either of these objectives must be done at a specific total pressure and O_2 concentration to yield meaningful data.

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Biological Growth on Activated Carbon: An Investigation by Scanning Electron Microscopy

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■ The physical and structural characteristics of biological growth on activated carbon in water and wastewater treatment applications are examined by scanning electron microscopy. An effective technique for fixing, dehydration, drying, and examining bio-coated granular materials is detailed. Micrographs illustrating a variety of bioforms are presented. These micrographs clearly demonstrate an ecosystem including bacteria and bacteriovorous protozoans. The micrographs also demonstrate that the biofilm is not uniform, but is comprised of a loosely knit matrix.

Biological growth on activated carbon in water and wastewater treatment applications is an expected consequence of the favorable environment provided by this material. The surfaces of activated carbon are excellent for colonization by microorganisms. Its adsorptive properties serve to enrich substrate and oxygen concentrations (*1*), the craggy surface provides recesses that are sheltered from fluid shear forces (*2*), and the variety of functional groups on the surface can enhance attachment of microorganisms (*3*).

The effects of such growth have been variously reported as advantageous (*1, 4–7*) and disadvantageous (*8, 9*) to the primary adsorptive function of the carbon. It has been demonstrated clearly, however, that under proper conditions of design and operation, biological activity in activated carbon systems can improve removal of certain types of water and waste components and can prolong periods between required regenerations of the carbon (*1*).

Despite extensive observations of such growth, its nature and extent of coverage of pore openings have been matters of speculation. The objective of this paper is to demonstrate that scanning electron microscopy can be used to observe the physical relationships between the carbon and its attached growth, as well as the types and structural characteristics of organisms that colonize carbon particles.

Materials and Methods

Granular activated carbon particles (Filtrasorb 400, Calgon Corp.) from two different sets of experiments involving biological growth were examined by means of a scanning electron microscope. The first set of experiments employed a completely mixed batch (CMB) reactor to contact the carbon with chemically coagulated and settled raw sewage from the Ann Arbor Sewage Treatment Plant. After 17 days, the carbon particles were removed and fixed according to methods described below. In the second set of experiments, an expanded-bed continuous flow reactor, operated at 2 gpm/ft^2 (0.08 m^3/min-m^2), was used to contact carbon with a 5-ppm solution of humic acid (Aldrich Chemicals, Inc.) in glass-distilled water buffered with potassium phosphate. After 10 days, abundant growth was evident, and particles were removed and fixed for observation.

Preparations were fixed by the method of Karnovsky (*10*). The carbon particles were immersed for 2 h in 2% paraformaldehyde–2.5% glutaraldehyde solution in 0.1 M sodium phosphate buffer at pH 7.3. A 3-h postfixation followed, using 1% OsO_4 in 0.1 M sodium phosphate buffer at pH 7.3 (*11*). Subsequently, dehydration was accomplished by rinsing the particles in graded ethanol (50, 70, 80, 90, and 100%). Samples were prepared for critical point drying in a 1:1 100% ethanol–amylacetate solution, and stored overnight in amylacetate.

A DCP-1 critical point dryer was used for drying the fixed particles (*12*). The particles were then mounted on aluminum stubs and coated with 100 Å gold in a glow-discharge coater to minimize charging and increase the conductivity of the biological material. The final two steps were carried out as precisely as possible after critical point drying to avoid rehydration and consequent damage to the fixed biological growth. For controls (activated carbon particles without attached growth) the fixation, dehydration, and drying steps were unnecessary; these unprocessed particles were glued to the stubs and gold coated prior to observation. A JOEL JSM-U3 scanning electron microscope operated at an accelerating voltage of 15–25 keV was used for observing the specimens.

Results and Discussion

The scanning electron microscope has several advantages over the conventional light microscope, including greater magnification, increased depth of field, and higher resolution. The most striking feature of a scanning electron micrograph is the resulting three-dimensional image, which is invaluable for studying topographic and structural features.

For effective observation of microorganisms by electron microscopy, it is necessary to first kill the organism rapidly to reduce swelling or shrinking. Paraformaldehyde, a low molecular weight compound, accomplishes quick kill because of rapid cellular penetration. Glutaraldehyde forms crosslinks with proteins in the cell membrane, forming a rigid network that preserves fine structures. The liquid portion of the membrane is fixed by the OsO_4 (*13*). Dehydration and replacement of ethanol by a nonpolar solvent such as amylacetate further preserve the fine cell structure since nonpolar solvents freeze more like an amorphous glass than a rigid ice crystal (*14*). In the critical point drying process, the sample is first rapidly frozen by replacing the amylacetate with liquid

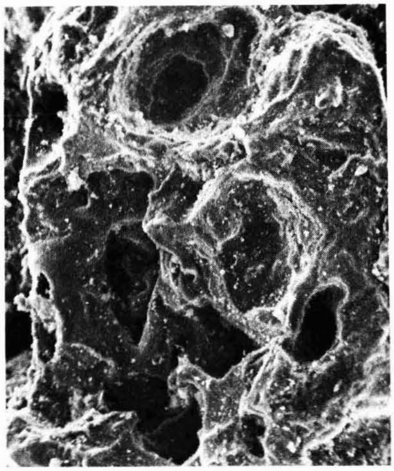

Figure 1. Scanning electron micrograph of surface of activated carbon (Filtrasorb 400) without biological growth. X440

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CO_2. Then, under pressure, the temperature is gradually increased to the critical pressure, at which point the densities of the vapor and liquid phases of the CO_2 are equal. Problems associated with air drying, such as disruption of cellular structures caused by surface tension, are thus circumvented, and the stability of the fixed structure is ensured (*12*). It is essential that great care be exercised in handling, fixing, dehydration, drying, and coating the samples, since fragile biological materials are easily damaged, and artifacts or unrecognizable features may result.

The surface of a particle of activated carbon free of biological growth is shown in Figure 1. The obvious holes ($\simeq$50–100 μ), crevasses, and ridges are sites where organisms would be shielded from shear forces, providing a favorable environment for growth.

Figures 2–4 show carbon samples that had been exposed to the coagulated-settled raw sewage in CMB reactors. The predominant organisms in these micrographs are probably stalked protozoans, more specifically, in Figures 3 and 4, ciliates. The size of the organism in Figure 2 is 23 × 3.6 μ, compared to an average of about 1.2 μ for the bacteria scattered on the surface. The attachment site for the stalk of the protozoan can be seen and appears to be a sturdy, gelatinous structure. The spherical ciliate in Figure 3 has a diameter of about 16 μ. A bacterial colony with an average cell size of about 1.6 μ is clearly visible below the sphere. Figure 4 shows a similar ciliate (16 μ diameter). The most striking feature of this micrograph is the floating nature of the organism tethered to the carbon surface by a thin (0.8 μ) stalk. The survival of these stalked protozoans in the turbulent CMB reactor demonstrates how firmly the organisms attach to the carbon surface, despite the known effects of fluid shear forces (*2*) and high flow rates (*15*) on the thickness and density of a biological slime mass.

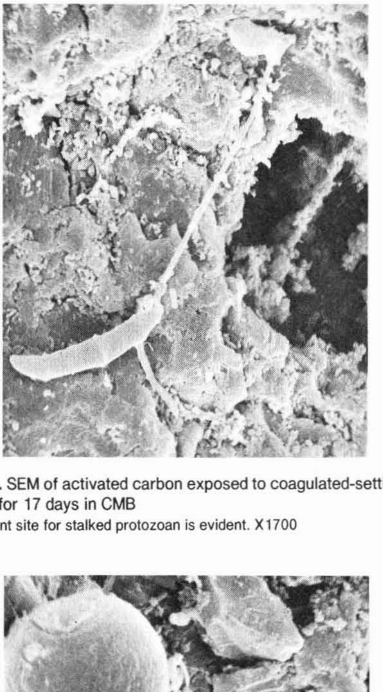

Figure 2. SEM of activated carbon exposed to coagulated-settled raw sewage for 17 days in CMB

Attachment site for stalked protozoan is evident. X1700

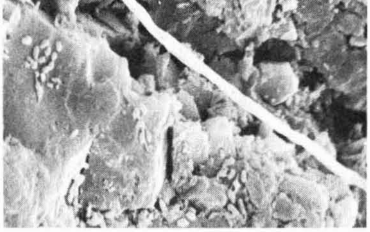

Figure 3. SEM of activated carbon exposed to coagulated-settled raw sewage for 17 days in CMB reactor

Size of the bacteria ($\simeq$ 1 μ in length, located directly below spherical protozoan) can be compared to stalked protozoan ($\simeq$ 16 μ in diameter). X2500

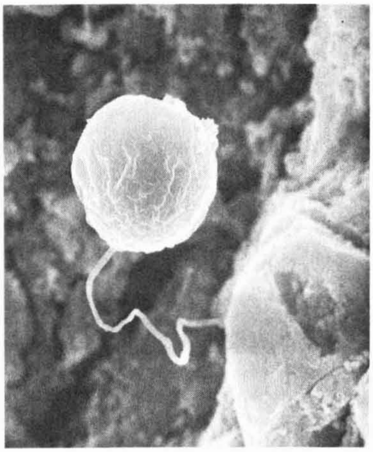

Figure 4. SEM of activated carbon exposed to coagulated-settled sewage for 17 days in CMB reactor

Stalked protozoan is anchored to carbon surface, but is not itself in contact with carbon. X1800

Figures 5–7 are micrographs of carbon particles taken from the expanded-bed reactor experiments. One feature of Figures 5 and 6 is the excellent resolution, which emphasizes the rough and porous texture of the activated carbon particle surface. Micropores of less than 0.05 μ diameter can be seen. The

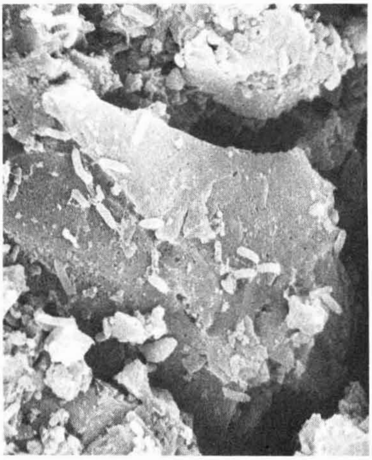

Figure 5. SEM of activated carbon exposed to 5-ppm solution of humic acid for 10 days in expanded bed reactor

Notice spongy, porous texture of carbon surface and rod-like bacteria ($\simeq$ 1–2 μ in length). X4000

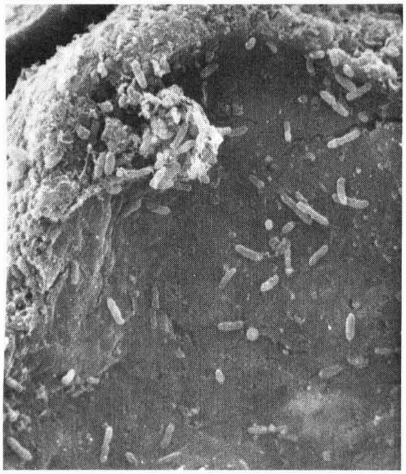

Figure 6. SEM of activated carbon exposed to 5-ppm solution of humic acid for 10 days in expanded bed reactor
Again, very porous texture of carbon surface is evident. Clump of bacteria in foreground shows beginnings of slime matrix. X6820

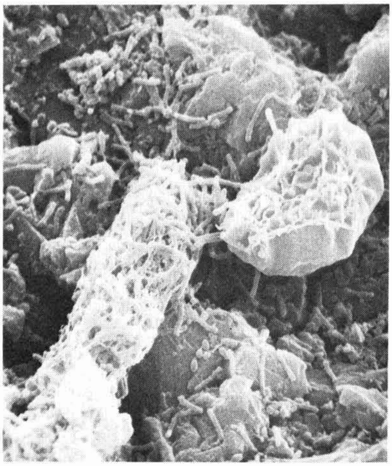

Figure 7. SEM of activated carbon exposed to 5-ppm solution of humic acid for 10 days in expanded bed reactor
Nonhomogeneous coverage of carbon surface and porous tangled nature of slime matrix are clearly evident. X2800

rod-like bacteria are about 1.3 μ in length. Organisms of this size could grow in the larger macropore openings at the external surface of the carbon, thereby limiting access of adsorbates to the internal micropore surface area.

The bacteria colonizing the surface produce slime, as seen in Figures 6 and 7. That many aquatic bacteria secrete capsules is well known, the most notable species being *Sphraetilus natans,* but also certain Myxobacteria. The polysaccharide slime matrix allows attachment to the substrate as well as other cells. The nonhomogeneous nature of this coverage is evident.

The appearance of stalked protozoa indicates a more advanced microbial colonization of the carbon surface. The establishment of an ecosystem including bacteria and bacteriovorous protozoans is evidence of improved mineralization of organics, as well as nutrient regeneration. These types of processes, which are basic to trickling filter wastewater systems, could be quite advantageous to the performance of activated carbon systems, providing an additional means for removal of biodegradable organic substances in both wastewater and water treatment applications.

Summary and Conclusions

Bioactivity on carbon is ubiquitous in water and wastewater treatment systems. The surface of carbon offers an attractive environment for colonization. It is clear from previous work that such bioactivity can significantly affect the performance of adsorption systems, and it is thus necessary that it be quantified and properly accounted for in the design and operation of adsorption units.

The present work, while not elaborating the full range of character and quantity of growth to be expected for the wide variety of organic substrates encountered in such applications, does describe and illustrate an effective method for studying bioactivity on carbon utilizing scanning electron microscopy. Micrographs such as those presented herein can provide much needed insight. It is clearly possible with the technique that has been described to observe both the complex nature of carbon surfaces and the character of biogrowth developed thereon.

The nonhomogeneous nature of the surface coverage indicated by the results of the present work suggests that precise quantification of the interplay between attached biological growth and the diffusional transport processes associated with adsorption may not be straightforward.

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Statistical Models for Ambient Concentrations of Carbon Monoxide, Lead, and Sulfate Based on the LACS Data

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■ An analysis of pollutant data gathered in the Los Angeles Catalyst Study is presented. The ultimate purpose is to use the data to determine any increase or decrease in the observed emissions since the introduction of the catalytic converter. An empirical model describes the observed pollutant concentrations as a function of wind speed, wind direction, traffic counts, and the speed of traffic. Therefore, the analysis takes into account varying traffic patterns and meteorological effects upon the observed pollutant concentrations. The empirical model helps determine any trends in the data after adjusting for changes in the traffic and meteorological conditions.

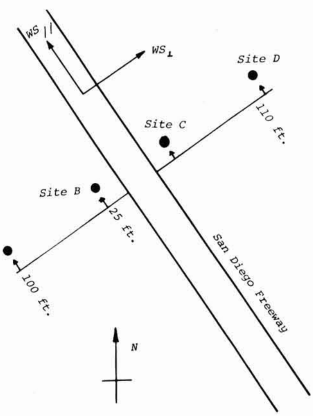


Figure 1. Simplified map of air monitoring sites

This paper presents a statistical analysis of the Los Angeles Catalyst Study (LACS) data covering the period June 1974 through November 1976. Our main objective is to assess the effects on the atmospheric concentration of various pollutants due to the introduction of the catalytic converter.

The catalytic converter was adopted by American automobile manufacturers on new cars since the fall of 1974. It was designed to reduce the emission of carbon monoxide (CO) and hydrocarbons (HC). Also, new cars equipped with the converter must run on unleaded gasoline so that its use should lead to reduction in the lead (Pb) emissions. However, tests have shown (*1*) that the converter increases the emissions of sulfuric acid which reacts in the atmosphere to form sulfate (SO_4). To study the environmental impact of the catalyst, four air monitoring sites (A, B, C, and D), two on each side of the San Diego Freeway (see Figure 1), were established by the Environmental Monitoring Support Laboratory of the Environmental Protection Agency. Data on a number of pollutants including SO_4, CO, and Pb and meteorological variables such as wind speed and wind direction have been collected since June 1974 (*2*). Also, traffic counts and speeds have been measured since September 1976.

This paper reports our preliminary findings on the daily 4-h afternoon (3–7 p.m.) SO_4 readings (from two different sampling equipment, the hi-volume and the membrane samplers), the 24-h hi-volume SO_4 readings, hourly CO readings, and the 4-h afternoon hi-volume Pb readings. Hourly wind speed and wind direction data for the entire period and the available hourly traffic counts and traffic speed for the period September 1976 through November 1976 will be used in our analysis.

We first present an empirical-mechanistic model relating the CO readings at site C to wind speed, wind direction, traffic counts, and speeds. The model is used to assess the trend in CO emissions since June 1974. We then analyze the 4-h hi-volume Pb data. In particular, the model developed for CO is extended to the Pb data for assessing the trend. Finally, a preliminary analysis of the 4-h hi-volume, 4-h membrane, and the 24-h hi-volume SO_4 data will be given.

Principal Findings. Our principal findings are as follows:

CO. There appears to have been a decrease in CO emissions from 1975 to 1976.

Pb. There was a steady decrease in Pb emissions from 1974 to 1976. At site C the average 3–7 p.m. concentration level is about 60% higher on the weekends than that for the weekdays.

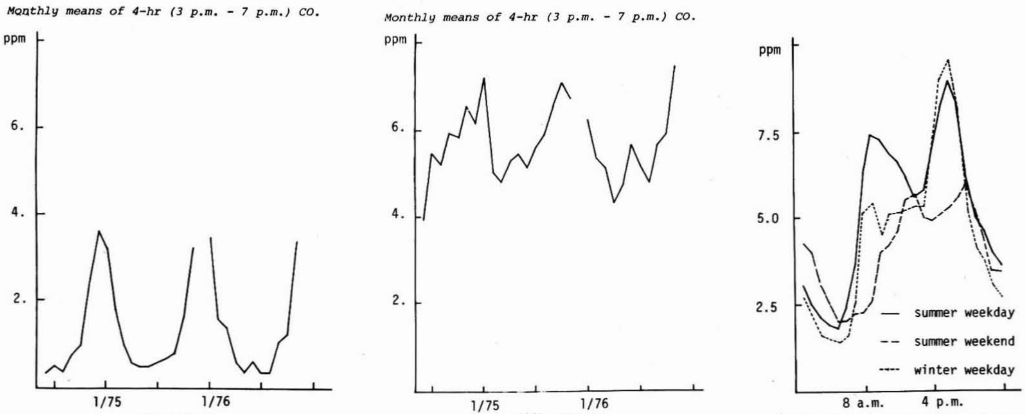
SO_4. The background level (from sources other than the freeway) of SO_4 decreased from 1974 to 1976. The across the freeway difference of the 4-h hi-volume readings decreased from 1975 to 1976. The across the freeway differences for both the 4-h membrane and the 24-h hi-volume readings increased from 1975 to 1976. The 4-h hi-volume data appear to be measuring something different from the 4-h membrane data. Further research seems necessary to determine the cause of this discrepancy.

Analysis of CO Data

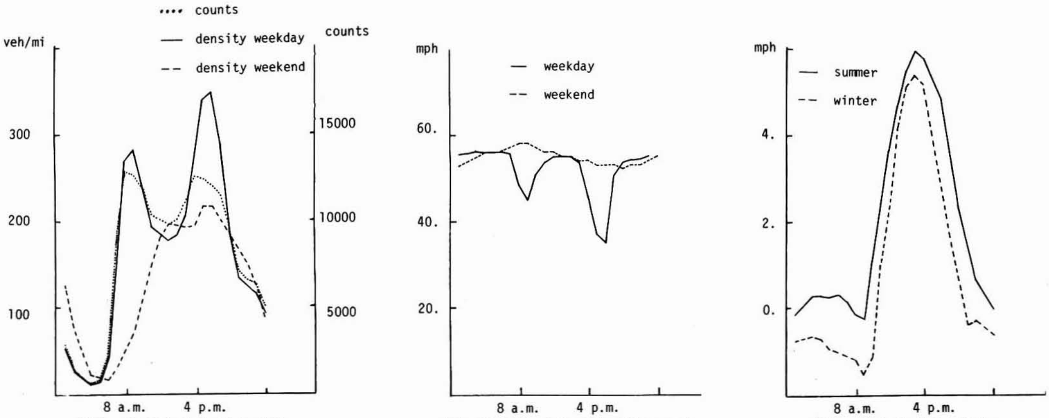
As an initial step in the analysis of the various pollutant data, we have employed the available readings to calculate monthly averages for different hours at various sites. In computing monthly averages, extreme observations were eliminated according to the following procedure. For a particular month, let Y be an observation, $\overline{Y}$ be the average, and s the estimated standard deviation of Y. If $|Y_i - \overline{Y}| > 3s, Y_i$ will be excluded and then $\overline{Y}$ and s recalculated. The process will be repeated until all observations fall within $\overline{Y} \pm 3s$.

CO data consist of hourly readings at sites A and C. As a preliminary step in our analysis, monthly means of the daily 4-h (3–7 p.m.) averages were determined. They are shown in Figure 2(i), (ii) for sites A and C, respectively. The 4-h readings are of particular interest since, during the afternoon hours, the wind is usually blowing in a direction roughly perpendicular to the freeway (*2, 3*) so that the difference in readings between sites across the freeway should reflect contributions from the freeway traffic.

From Figure 2(i), (ii) we can make the following observations. The behavior of CO is markedly seasonal, being higher in the winter months than in the summer months. Thus, any trend analysis must make proper allowance for the seasonal effect. The level at site C is considerably higher than that at site A. At site A the level is particularly low in the summer months, about 0.5 ppm. Since we are mainly interested in the freeway contribution of CO, in what follows we will concentrate our analysis on the downwind site, C.



(i) Site A. (ii) Site C. (iii) Diurnal plot of CO, site C.



(iv) Diurnal plot of traffic. (v) Diurnal plot of traffic speed. (vi) Diurnal plot of $WS_{\perp}$

Figure 2.

Various models describing the ambient concentrations of CO have been proposed (*3–7*). These studies show that two major factors influencing the behavior of CO are traffic and the wind. They must be appropriately taken into account in studying the effect of the catalytic converter. We have available hourly readings of wind speed and wind direction for the entire period, and traffic counts and traffic speeds for the period September through November 1976. In what follows we built an empirical-mechanistic model (*8*) that relates the diurnal behavior of the CO concentrations at site C to the wind and traffic. The model will then be used to assess the trends in CO emissions.

Motivation for Model. Figure 2(iii) gives the average diurnal curves of CO at site C computed from the following three data periods: summer weekday: Mondays–Thursdays, June–October 1975; summer weekend: Sundays, June–October 1975; and winter weekday: Mondays–Thursdays, December 1974–April 1975. The Friday figures are excluded in our definition of "weekday" because the diurnal pattern is somewhat different from those of Mondays–Thursdays, essentially due to changes in traffic pattern. For the same reason, we only use the Sunday figures for the "weekend". The model developed later in this section could equally well be used for the Friday and Saturday CO data. These three diurnal curves illustrate that the behavior of CO changes from weekday to weekend and from summer to winter. The summer weekday curve has two peaks that roughly correspond to the morning and afternoon rush hours. In contrast, the summer weekend plot fails to have these peaks. The diurnal behavior of CO also changes from summer weekday to winter weekday, the most notable change being the absence of a peak corresponding to the morning rush hours in the winter.

In Figure 2(iv) the dotted line gives the diurnal pattern of the average counts of vehicles passing the monitoring sites on weekdays. The figures shown are average counts for each hour of weekdays (Monday–Thursday) obtained during the period September 1976 through November 1976. Since this is the only period for which traffic data are available and the traffic patterns in Los Angeles are not expected to vary much over time, we will for the moment assume that the figures shown are applicable to the entire period (June 1974–November 1976) under study.

Comparing the diurnal pattern of the weekday counts with that of the summer weekday CO, we observe that the counts do not seem to reflect the magnitude of CO during the evening rush hours. A possible reason for this is the increase in traffic congestion during that time. The solid curve in Figure 2(v) shows the diurnal pattern of the traffic speed for weekdays. Notice the two dips during the morning and the evening rush hours and the difference in magnitude between them. Thus, there is a large volume of traffic moving very slowly during the evening rush hours, and the vehicle counts do not accurately reflect the density of the traffic.

Traffic Density. To more appropriately reflect the situation, we consider the traffic density (TD) defined as

$$TD = \frac{\text{number of vehicles passing sites per hour}}{\text{average speed per hour}}$$

which is a measure of the intensity of traffic around the sites (in units of vehicles per mile). The solid line in Figure 2(iv) shows that the diurnal pattern of *TD* for weekdays seems to match the CO pattern much better than the vehicle counts. In addition, for the weekends, the diurnal pattern of *TD* shown by the dashed line in Figure 2(iv) also correlates with that of CO given in Figure 2(iii). From the above discussion it appears that the observed concentrations of CO are approximately proportional to *TD*.

Wind Vector. Another major factor influencing the pollutant readings is the speed and direction of the wind. Data on wind speed and wind direction are available on an hourly basis. Following ref. *3*, we have decomposed the observed hourly wind vector at site A into two components: one that is perpendicular to the freeway ($WS_\perp$) and the other parallel to it ($WS_\parallel$). The positive directions for the two components are shown in Figure 1. Specifically, let *WS* be the wind speed and *WD* the wind direction. ($WD = 0$ when the direction is due north). Then, since the freeway is situated at approximately 145° from the north, we have

$$WS_\perp = WS \cdot \cos(WD - 235^\circ)$$

$$WS_\parallel = WS \cdot \sin(WD - 235^\circ)$$

The diurnal patterns of $WS_\perp$ for the summer months (June–October 1975) and the winter months (December 1974–April 1975) are plotted in Figure 2(vi). We observe that the $WS_\perp$ in the winter is lower than that in the summer. In particular, for the winter, from midnight to 9 a.m. the $WS_\perp$ is negative so that the wind is blowing away from site C. The $WS_\perp$ for the same hours in the summer months is nearly zero. This change in the $WS_\perp$ from the summer to the winter could explain the absence of a peak in CO during the morning rush hours in the winter [see Figure 2(iii)]. Therefore, it appears that seasonal changes in $WS_\perp$ may account for the observed changes in the diurnal behavior of CO from the summer to the winter.

To determine more precisely the effect of $WS_\perp$ on CO, we have divided all the available hourly $WS_\perp$ readings into intervals of 0.5 mile per hour. For each interval we have calculated the average of the corresponding CO readings. These averages are plotted in Figure 3(i). Observe that a convenient way to characterize the dependency of CO on $WS_\perp$ is to take CO proportional to the dispersion factor $e^{-b(WS_\perp - W_o)^2}$, where b and W_o are two appropriate constants.

CO Model. The above considerations have led us to consider the following tentative model for the diurnal behavior of CO at site C:

$$\mathrm{CO}_t = \alpha + K \cdot TD_t \cdot e^{-b(WS_{\perp t} - W_o)^2} + a_t \qquad (1)$$

where CO_t = the observed CO for site C at hour t, TD_t = the traffic density at hour t, $WS_{\perp t}$ = the perpendicular component of the wind vector at hour t, a_t = an added error term for hour t= α = a parameter measuring the background CO, K = a parameter proportional to emissions, and $e^{-b(WS_{\perp t} - W_o)^2}$ = a diffusion factor involving the perpendicular wind component and two parameters b and W_o.

Given a set of data on CO, $WS_\perp$, and *TD*, the parameters can be estimated by employing standard nonlinear procedures. Specifically, on the assumption that the errors a_t's are independently and normally distributed with mean zero and variance σ^2, (α, K, b, and W_o) are estimated by minimizing the sum of squares of the a_t's with respect to these parameters simultaneously.

Testing the Model. The model (Equation 1) is useful for our purposes because of the following reasons. It is a relatively simple model with only four parameters to be estimated from the data. It takes into account the effects of the traffic and the wind. The parameter K has an important interpretation. It is proportional to emissions and hence will play a crucial role in determining if there have been significant changes in emissions over time.

Table I. CO Model Test Fits

Parameter	Estimate	Std error
	June 1975–Oct. 1975 weekdays (M-R)	
α	1.90	0.14
b	0.035	0.005
W_o	3.27	0.13
K	0.0241	0.00096
	June 1975–Oct. 1975 Sunday	
α	1.79	0.23
b	0.013	0.011
W_o	2.54	1.11
K	0.0190	0.0016
	Dec. 1974–Apr. 1975 weekdays	
α	1.42	0.17
b	0.029	0.006
W_o	2.89	0.26
K	0.0228	0.0010

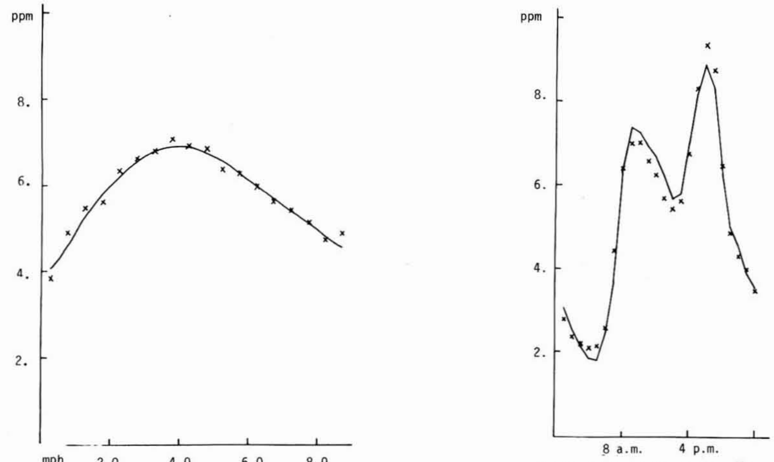
However, before we use the model (Equation 1) for trend assessment, it is important to verify that it can in fact account for the changes in the observed behavior of CO from weekday to weekend and from summer to winter. For this purpose, we have employed the three sets of CO average readings shown earlier in Figure 2(iii), the corresponding $WS_\perp$ averages, and the *TD* values given in Figure 2(iv).

The parameter estimates are shown in Table I. The actual CO readings and the predicted values are plotted in Figure 3(ii)–(iv). It seems that the model (Equation 1) produces very close agreement between the actual and the predicted in all three cases. Notice from Table I that for the weekend the estimated emission constant K is considerably lower than those for the weekdays. This is perhaps due to the fact that CO emissions may also depend on the driving mode (in particular, accelerations and decelerations), which is very different between weekdays and weekends.

Evaluation of Trend. Our main objective is to assess the effect of the catalytic converter on ambient CO concentrations. This can be done in terms of the model (Equation 1) ideally by allowing the parameter K to depend on the fraction of vehicles equipped with catalytic converters. Since precise estimates of the fractions of catalyst cars are not available, we

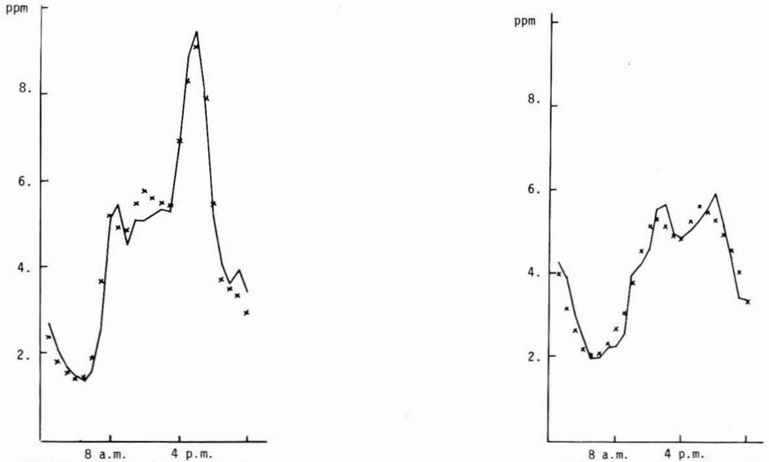
Table II. Assessment of CO Trend

Period	Parameters	Estimate	Std error
	α (ppm)	1.71	0.076
	b	0.026	0.002
	W_o (mph)	2.93	0.098
Summer 74	K_1 (μg/m^2)	0.0195	0.0006
Winter 74–75	K_2 (μg/m^2)	0.0235	0.0008
Summer 75	K_3 (μg/m^2)	0.0245	0.0007
Winter 75–76	K_4 (μg/m^2)	0.0196	0.0008
Summer 76	K_5 (μg/m^2)	0.0209	0.0006
	σ_1	0.68	
	σ_2	0.88	
	σ_3	0.66	
	σ_4	0.90	
	σ_5	0.63	



(i) Plot of CO vs. $WS_\perp$

(ii) CO model summer weekday fit (x predicted - observed).



(iii) CO model winter weekday fit (x predicted - observed).

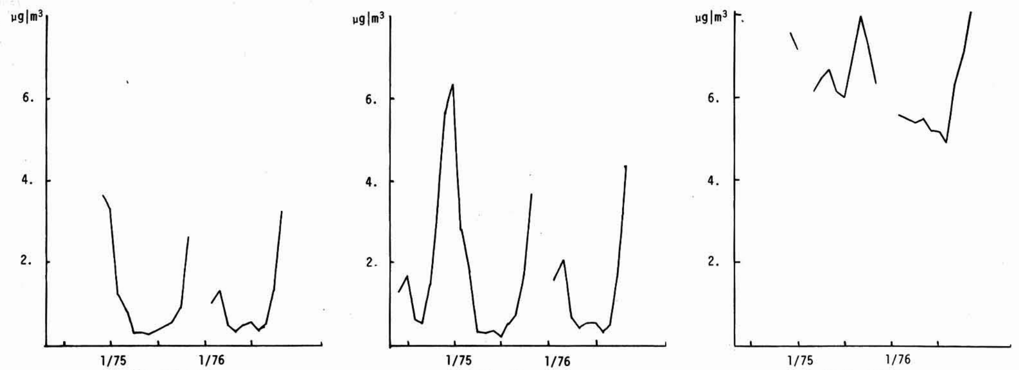
(iv) CO model summer weekend fit (x predicted - observed).

Figure 3.

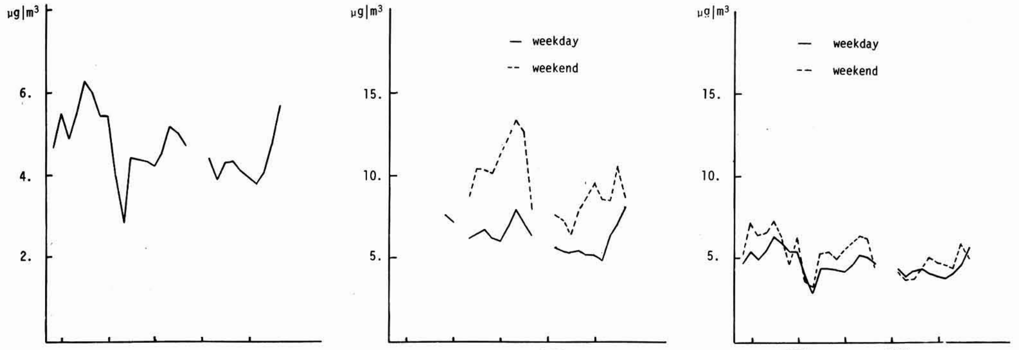
shall proceed with a trend analysis by investigating possible changes in the value of K over different time periods.

As a first attempt, the model (Equation 1) has been used for evaluation of trends as follows. We divided the entire time span of the data into the following five periods: June 1974 through October 1974, November 1974 through April 1975, May 1975 through October 1975, November 1975 through April 1976, and May 1976 through October 1976. This division roughly corresponds to the "summer" and the "winter", and each period is of sufficient length to allow for an appreciable increase of catalyst equipped cars. The emission parameter K was allowed to vary from period to period, but the other parameters, α, b, and W_o, were constrained to be the same for all five periods. The weekday data were employed in estimating the parameters. Within each period we calculated the 24 hourly averages of CO and $WS_\perp$ for each of three consecutive two-month segments. (For the first period, we took averages for June, then July and August, and finally September and October.) The CO and $WS_\perp$ averages for all five periods together with the averages of the available weekday TD were then employed to estimate the parameters α, b, W_o, $K_1, \ldots, K_5$ where K_j is the emissions parameter in period j for $j = 1, \ldots, 5$. In addition, we used a weighted least-squares estimation procedure to allow for possible changes in the variance from period to period. The parameter estimates are given in Table II.

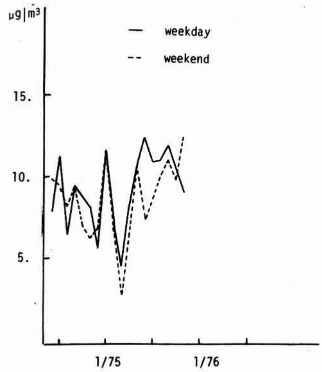
Consider the changes in the emission parameter K over these five periods. We see from Table II that the estimated K decreased between the first and the second winters, and also between the second (1975) and the third (1976) summers. This can be associated with the increase in the number of catalyst cars. On the other hand, the increase in K between the first and the second summers, from 0.0195 to 0.0245, is somewhat surprising. This anomaly may very well be due to the fact that the *same* TD data were used for all five periods. While the traffic pattern is not expected to vary much over time in Los Angeles, because of the energy crisis, the (estimated) total traffic volume did show a slight dip in 1974, from 182 500 in 1973 to 180 000 in 1974 and to 182 500 in 1975. These are estimated daily traffic totals near the sampling sites obtained from the State of California Department of Transportation publications "Traffic Volume on California State Highways" for 1973, 1974, and 1975. Thus, there was an increase of about 1% from 1974 to 1975. In the meantime, a major change in the speed limit occurred around January 1975, from 70 to 55 mph, representing roughly a 20% decrease. Since TD is the ratio of



(i) *Site A.* (ii) *Site B.* (iii) *Site C.*



(iv) *Site D.* (v) Monthly means of afternoon Pb. at site C. (vi) Monthly means of afternoon Pb. at site D.



(vii) Monthly means of morning Pb. at site D.

Figure 4. (i)–(iv): Monthly means of 4-h hi-vol afternoon readings of Pb for various sites. (v)–(vii): Comparisons of weekday and weekend Pb

traffic counts over average speed, the density figures used in the estimation contain a considerable upward bias for the first period and could account for most, if not all, of the increase in *K* from 1974 to 1975.

Conclusions. We have developed a model that relates the observed behavior of CO at site C to traffic density and the perpendicular wind component. The most important conclusion to be drawn from this model is that CO emissions dropped by about 15% from the summer of 1975 to the summer of 1976 and for the winter of 1974–75 to the winter of 1975–76.

Analysis of Pb Data

We now give a preliminary analysis of the lead readings. The Pb data consist mainly of the 4-h afternoon hi-volume readings from June 1974–October 1976. Hi-volume readings for four morning hours were also collected during the period June 1974–January 1976. (Samplers operated 6–10 a.m. from June 1974 to January 1975 and 8–12 a.m. from January 1975 through January 1976.) To begin with, we consider the monthly means of the weekdays (Monday through Thursday) afternoon readings. These monthly averages for sites A through D are plotted in Figure 4(i)–(iv), respectively. It is clear that the levels at sites C and D are much higher than those at A and B. Also, in the summer months there is very little Pb at these latter sites. As in the case of CO, we shall concentrate our analysis on the downwind sites, C and D.

For both site C and site D, the level of Pb in the summer

Table III. Simple *t*-Tests to Compare Summer Means of Pb, 1974–1976

Year	Mean	SD	No. of observations
	May–October, Site D		
1974	5.30	1.20	68
1975	4.49	0.79	84
1976	4.11	0.92	76
Years		***t*-Statistic**	**Sig level**
1974–1975		4.75	0.000
1975–1976		2.79	0.006
1974–1976		6.59	0.000
Year	**Mean**	**SD**	**No. of observations**
	May–October, Site C		
1975	6.76	1.40	84
1976	5.80	1.44	76
Years		***t*-Statistic**	**Sig level**
1975–1976		4.28	0.000

Table IV. Assessment of Pb Trend

Period	Parameters	Estimate	Std error
	Site C		
	b	0.013	0.002
	W_o (mph)	2.28	0.40
Summer 75	K_3 (μg/m^2)	0.00640	0.00023
Winter 75–76	K_4 (μg/m^2)	0.00514	0.00025
Summer 76	K_5 (μg/m^2)	0.00514	0.00025
	σ_3	1.25	
	σ_4	1.19	
	σ_5	1.44	
	Site D		
	b	0.020	0.002
	W_o (mph)	2.45	0.19
Summer 74	K_1 (μg/m^2)	0.00507	0.00013
Winter 74–75	K_2 (μg/m^2)	0.00428	0.00021
Summer 75	K_3 (μg/m^2)	0.00454	0.00013
Winter 75–76	K_4 (μg/m^2)	0.00416	0.00016
Summer 76	K_5 (μg/m^2)	0.00378	0.00016
	σ_1	1.00	
	σ_2	1.53	
	σ_3	0.50	
	σ_4	0.76	
	σ_5	0.99	

months appears to have steadily decreased from 1974 to 1976. Table III shows that these decreases are statistically significant.

Extension of CO Model to Pb Data. The model (Equation 1) developed for the hourly CO data can be readily extended to the 4-h Pb readings. This is achieved by summing the righthand side of Equation 1 over the four afternoon hours to obtain

$$\mathrm{Pb}_{t'} = \alpha' + K' \sum_{t=16}^{19} (TD)_t^{t'} e^{-b(WS_{\perp t}^{t'} - W_o)^2} + a_{t'} \qquad (2)$$

where t' stands for a particular day, $(TD)_t^{t'}$ is traffic density at hour t on day t', $WS_{\perp t}^{t'}$ is perpendicular wind speed at hour t on day t', $a_{t'}$ is the error term for day t', α' is a parameter measuring the background, K' is a parameter proportional to Pb emissions, and b and W_o are, as before, parameters measuring effect of the wind.

Evaluation of Trend in Pb Emissions. Model 2 has been used to assess the trend in Pb emissions in a manner similar to that for the CO data. Specifically, we divided the time span of the data into the same five periods as was done in the case of CO. The daily 4-h (3–7 p.m.) afternoon Pb readings from June 1974 through October 1976, the corresponding hourly $WS_\perp$ for the four afternoon hours, together with the (same) average TD figures for these 4 h were then employed to estimate the parameters α', b, W_o, K_1', . . . , K_5'. Here, K_j' measures the Pb emissions for period j, $j = 1, \ldots, 5$. In an initial fitting α' was found to be insignificant and hence ignored in our final estimation. The parameter estimates of b, W_o, K_1, . . . , K_5 for sites C and D are given in Table IV.

We observe that for both sites there was a decrease in Pb emissions. This is probably due to an increased use of unleaded gasoline. Also, the estimated values of the emission constant at site D are lower than those at site C. This seems reasonable because site D is situated farther from the freeway and a part of the lead particles will settle on the ground before reaching D.

Comparison of Weekday and Weekends. As reported earlier in ref. *3*, we have found that the afternoon Pb readings are substantially higher in the weekends than during the weekdays. The monthly means of both the weekday and weekend afternoon Pb readings for sites C and D are plotted in Figure 4(v), (vi), respectively. It is clear from these figures that there is a considerable difference; for site C the weekend values are about 60% higher than the weekday values. This increase on the weekend is somewhat puzzling since there is a *decrease* in traffic density from weekday to weekend [see Figure 2(iv)].

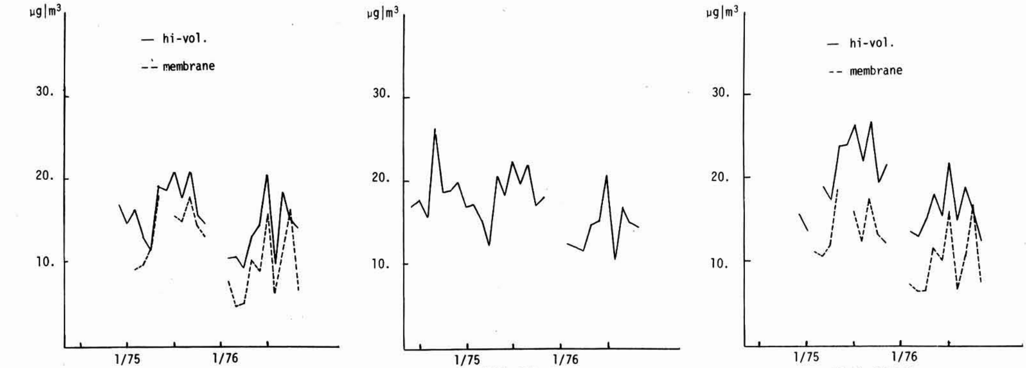
Now, recall from Figure 2(v) that the speed of the traffic decreases drastically during the weekday afternoon rush hours. However, we see from the dotted line in the same figure that such a decrease does not occur on the weekend. This would explain the observed weekday to weekend difference if emissions of Pb varied proportionally with the speed of traffic. This theory is partially supported by a comparison of the weekday vs. weekend monthly means of the morning Pb readings shown in Figure 4(vii). Specifically, we observe from Figure 2(v) that, in the morning, the difference between weekday and weekend speed is smaller than that in the afternoon. At the same time Figure 4(vii) indicates that there is no real difference between the weekday and weekend morning Pb readings. In fact, it has been reported in ref. *9* that Pb emissions do tend to vary proportionally with the traffic speed.

Analysis of SO_4 Data

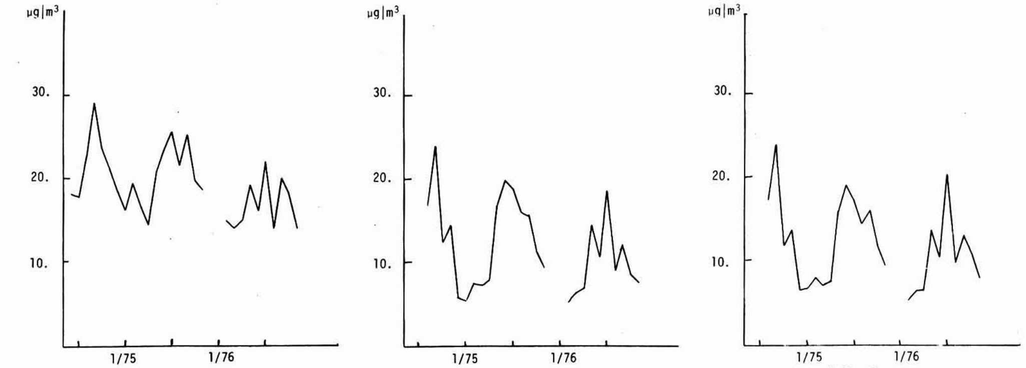
Data on SO_4 consist mainly of daily 4-h afternoon (3–7 p.m.) readings from the hi-volume sampler and the membrane sampler, and the daily 24-h hi-volume readings.

Analysis of Monthly Means. The monthly averages of the 4-h hi-volume readings at sites A–D are shown by the solid lines in Figure 5(i)–(iv), respectively. From these plots we make the following observations. At each location there appears to have been a decrease in the SO_4 readings from 1974 to 1976. The monthly means at the sites C and D downwind from the freeway are higher than those for the upwind sites A and B, indicating a contribution of SO_4 from the freeway traffic. The freeway contribution is, however, very small when compared to the average level of SO_4 across these four sites.

Next, the monthly means of the 4-h membrane data for sites A and C are given by the dotted lines in Figure 5(i), (iii).



(i) Site A. (ii) Site B. (iii) Site C.



(iv) Site D. (v) Site A. (vi) Site C.

Figure 5. (i)–(iv): Monthly means of 4-h hi-vol and membrane afternoon readings for SO_4 for various sites. (v), (vi): Monthly means of 24-h hi-vol readings of SO_4

Similar to the 4-h hi-volume data, at both sites the level decreased from 1975 to 1976. Finally, the monthly means of the 24-h hi-volume readings at sites A and C are shown in Figure 5(v), (vi). Again the level of SO_4 at both sites decreased during the data period.

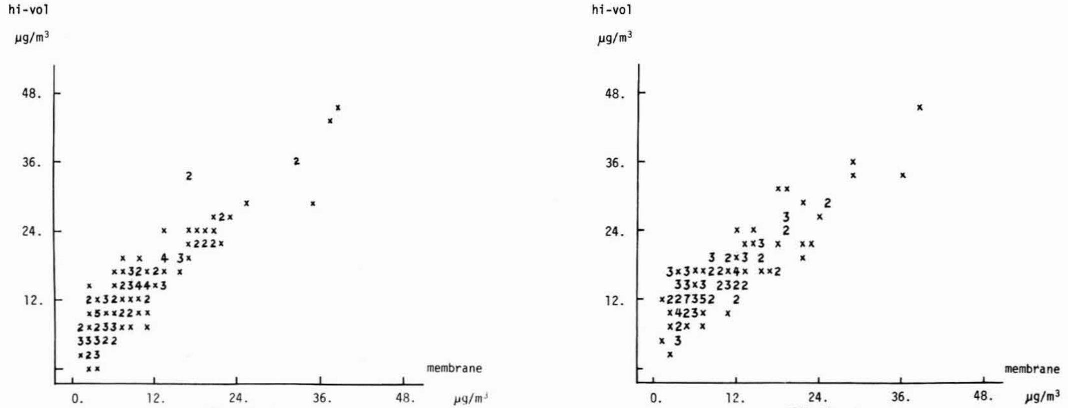
Comparison of Hi-Volume and Membrane Readings. It is of interest to compare the 4-h hi-volume and membrane readings. Figure 5(i), (iii) shows that while the seasonal patterns of these two readings are similar, the hi-volume means are consistently higher than the membrane means. For further comparison, Figure 6(i), (ii) shows, respectively, for sites A and C, the scatter plots of the daily 4-h membrane vs. hi-volume readings. We observe that for site A the points fall close to a line with a slope approximately equal to 1 and an intercept of about 4 $\mu g/m^3$. On the other hand, for site C the points are again close to a line but having a slope of about 0.8 and an intercept of 7.7 $\mu g/m^3$. These figures strongly suggest that the membrane and the hi-volume readings are systematically biased and that the nature of the bias is different at different sites.

Across the Freeway Differences. We next consider the monthly means of the across the freeway difference (C-A) of SO_4 for the 4-h hi-volume, the 4-h membrane, and the 24-h hi-volume readings. There are plotted in Figure 6(iii)–(v). We observe that the 4-h hi-volume readings indicate a decrease in the across the freeway differences from 1975 to 1976; on the other hand, the 4-h membrane readings indicate that there was an increase in the across the freeway difference from 1975 to 1976; and the 24-h hi-volume readings also show an increase from 1975 to 1976. These observations are partially confirmed by the t-values given in Table V for comparing the overall means of the across the freeway differences (C-A) for the months June through October between 1975 and 1976. Specifically, the t-values indicate that the increase in the 4-h hi-volume readings and the decreases in the other two measurements are real.

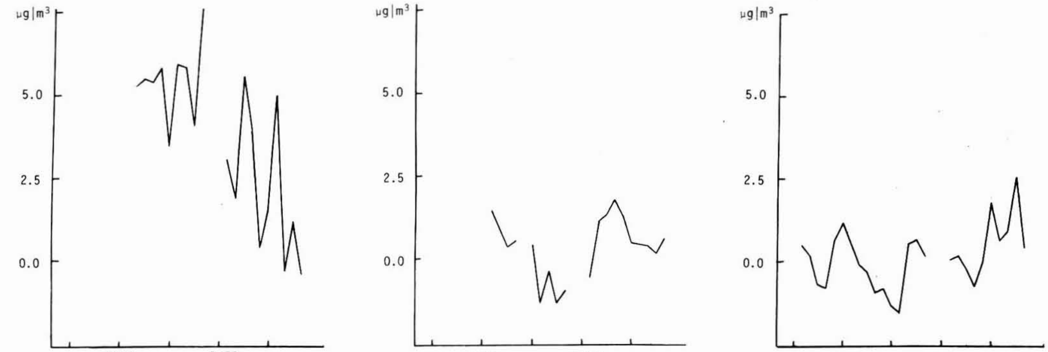
The sample means and standard deviations given in the table also show that for each year, the across the freeway differences in the 4-h hi-volume readings are considerably larger than those for the other two. Thus, both in terms of the level and the trend, the 4-h membrane measurements and the 24-h hi-volume measurements are in close agreement, but they are incompatible with the 4-h hi-volume readings.

A Conjecture. The preceding analysis raises a number of perplexing questions. First, how can we account for the discrepancies between the different methods of measuring SO_4? Second, which, if any, of the methods are giving correct pollutant readings? These questions must be answered before any conclusions about trends in the across the freeway difference can be made.

According to ref. *10*, SO_2 can react on filters used in the hi-volume sampler to form SO_4, and this may be a reason for the observed discrepancies. One possible theory that could explain what we have observed runs as follows: the 4-h hi-volume difference (C-A) is mostly SO_4 formed by SO_2 reacting on the filter. This artifact formation progresses more quickly at site C in the afternoon because of exposure to additional chemicals from the freeway. The artifact formulation does not occur on the membrane filter. After a sufficiently long time the artifact formation of SO_4 will be about equal at sites A and C so that the 24-h hi-volume difference represents largely contributions from the freeway. Although this theory could



(i) Site A. (ii) Site C.



(iii) Monthly means of 4-hr. hi-vol. SO_4 (C-A). (iv) Monthly means of 4-hr. membrane SO_4 (C-A). (v) Monthly means of 24-hr. hi-vol. SO_4 (C-A).

Figure 6. (i), (ii): Scatter plots of hi-vol vs. membrane SO_4. (iii)–(v): Differences of SO_4 at sites A and C

explain to a certain extent the observed discrepancies, further research seems needed to determine the precise nature of these two sampling methods.

Conclusions. We can tentatively conclude from our analysis that there is a substantial difference between the 4-h hi-volume and membrane SO_4 readings; and from the available data, there is a small amount of SO_4 being contributed from the freeway traffic.

Summary

We have illustrated for the CO data that a simple model involving the wind speed and traffic density can, to a good approximation, describe the behavior of the pollutant near the freeway. This model has been used in assessing changes in CO and Pb emissions since the introduction of the catalytic converter. A decrease was found in both CO and Pb emissions, which can probably be attributed to the increased number of catalyst equipped cars on the freeway. There is an increase in Pb emissions from the weekday to weekend. This increase is probably due to the increased speed of the traffic on the weekend. In our analysis of the SO_4 data, there is a discrepancy between the 4-h hi-volume readings and the 4-h membrane readings. A plausible explanation seems to be that there is an artifact formation on the hi-volume filter causing the discrepancy, but much further research is needed to determine the precise nature of these two sampling techniques.

Nomenclature

α = a parameter reflecting background pollution
a_t = normally distributed error
b = diffusion parameter
K = emissions parameter
TD = traffic density, vehicles per mile
W_o = diffusion parameter
WD = wind direction, degrees from north
WS = wind speed, mph
$WS_\perp$ = component of wind vector perpendicular to the freeway, mph
$WS_\parallel$ = component of wind vector parallel to the freeway, mph

Table V. Comparing Means of Across the Freeway Differences Between 1975 and 1976

	June–Oct. 1975			June–Oct. 1976			Difference 1975–1976	
	Mean	SD	No. of obs	Mean	SD	No. of obs	*t*-Value	Sig level
4-h hi-volume	5.11	4.45	143	2.22	3.74	133	5.86	0.0000
4-h membrane	−0.40	1.82	36	1.00	1.56	119	−4.15	0.0001
24-h hi-volume	−1.32	1.54	123	0.45	1.80	125	−8.28	0.0000

Acknowledgment

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Effects of Sulfur Dioxide in Air on the Fruit Fly, *Drosophila melanogaster*

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■ Four isofemale lines of *Drosophila melanogaster* were examined in long-term low-level sulfur dioxide fumigation studies. Continuous fumigations of developing larvae (0.7 ppm/11 days; 0.4 ppm/10 days) resulted in large significant increases in developmental time and decreases in survival. Fumigation of adults (0.7 ppm/4 days) demonstrated no consistent effect on subsequent fecundity. Fumigation of prepupae and pupae (0.4 ppm/4 days) resulted in decreased survival. All of the above experiments showed differential effects in the experimental lines. The magnitude of these effects, together with the pervasive evidence of genetically controlled differential response, suggests that sulfur dioxide in air may have important effects on insect populations.

This investigation concerns chronic sulfur dioxide fumigation of various life stages of the fruit fly, *Drosophila melanogaster*. Its purpose is to provide a preliminary evaluation of the potential impact of sulfur dioxide in air on insect populations.

Though this problem has received little attention in the past, the small amount of available data suggests that insects may be adversely affected by ambient sulfur dioxide levels and that these effects may have ecologically and economically important consequences.

In the only previous experimental study that has attempted to assess the effects of chronic exposure, honey bee (*Apis mellifera*) colonies were fumigated for a 14-week period at sulfur dioxide concentrations ranging from 0.5 to 3 ppm (*1*). Reductions in total colony weight gain, which might be taken as a measure of overall colony success, were approximately 35% at each of the sulfur dioxide treatment levels. Further, measurements made within the hive bodies indicated that sulfur dioxide levels were uniformly lower, by as much as 90% than the nominal treatment concentration, which suggests that honey bees may be affected by rather low sulfur dioxide levels.

Field observations further indicate the sensitivity of insects to sulfur dioxide air pollution. Several studies have linked the phenomenon of industrial melanism, the spread of dark or black forms of normally light colored cryptic moths in areas subject to industrial pollution, to elevated sulfur dioxide levels (*2–5*). Though best known as an example of on-going evolution, the shift to melanic forms has been so rapid in many species as to suggest radical alteration of the environment, and may imply less spectacular but more ecologically important effects on other insect species. This view is supported by several observers who have noted elevated populations of herbiverous insects, coupled with reduced parasitism levels, in areas subject to sulfur dioxide stress (*1, 6, 7*). It is well known that insecticide stress may, through destruction of a key insect parasite or predator, cause population explosions of herbiverous insects (*8*), and it would appear that sulfur dioxide may act in a similar manner.

Experimental

Given the absence of any significant body of existing data, the orientation of the present study was extensive rather than intensive. Four isofemale lines (lines initiated from single wild caught females) (*9*) of *D. melanogaster* which had earlier been shown to be genetically different with respect to body weight and adult high-level sulfur dioxide (500 ppm/2.5 h) tolerance as reflected by percentage mortality (*10*) were included to assess the importance of genetic variability in low-level fumigation responses. The four lines were designated 1, 5, 10, and 14. Lines 1 and 5 consisted of relatively heavy flies that showed high adult sulfur dioxide tolerance, whereas lines 10 and 14 comprised relatively light flies that showed low adult sulfur dioxide tolerance. Further, the experiments encompassed different combinations of the four life stages (eggs, larvae, pupae, and adults) to assess effects over the entire life cycle. All fumigations took place in a Conviron plant growth chamber (Model E8H; Controlled Environments Inc., Pembina, N.D.) modified for air pollution studies, and were performed under conditions of 25 °C temperature, 70% relative humidity, and 18-h photoperiod. Controls were maintained under the same conditions in a Jamesway incubator (Model 252B; Butler Mfg. Co., Jamesway Division, Fort Atkinson,

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Wis.). Temperature and relative humidity conditions in the two chambers were continuously recorded by built-in hygrothermographs. Equivalence of temperature and relative humidity was further verified prior to the initiation of each experiment, through the use of a Yellow Springs Instrument Co. telethermometer (Model 44TD) and an Abbeon hygrometer (Model AB167).

Because the flow rate of air through the fumigation chamber was relatively high (approximately 350 cfm), the desired sulfur dioxide concentrations were obtained by introducing pure anhydrous sulfur dioxide at low flow rates (3–7 cc/min). This gas was injected on the negative side of the fan which moved air through chamber, through a Teflon tube built into the chamber for this purpose. This approach is similar to that described by Setterstrom and Zimmerman (*11*).

Sulfur dioxide concentrations were continuously monitored by a Meloy Laboratories flame photometic sulfur hydrocarbon analyzer (Model SH202) and recorded by a Leeds and Northrup Speedomax W recorder. The sample air was drawn from the chamber through a 4-ft length of ¼-in. Teflon tube inserted through an instrument port in the side of the fumigation chamber.

Prior to the initiation of experiments, the fumigation chamber was set up to maintain a concentration of 0.7 ppm sulfur dioxide. After an initial 72-h period of equilibration, measurements of sulfur dioxide concentration were made with the gas delivery tube in five locations, corresponding to the four corners and center of the 61 × 122 cm floor area of the exposure chamber. All measurements were taken at a height of 15 cm above the floor. Concentration varied less than 0.05 ppm over the floor of the chamber. As a further check for lateral concentration gradients, all exposures were carried out using three blocks of four bottles (one per strain), which were placed in three corners of the fumigation chamber. This procedure likewise showed no evidence of lateral concentration gradients.

The standard rearing container consisted of a ½-pint milk bottle containing 30 mL of a dead yeast medium (*12*). The medium was selected because it provides adequate nutrition for *D. melanogaster* in the absence of yeast growth, which might well be inhibited by sulfur dioxide. Since it was felt that sulfur dioxide might influence the pH of the medium and thus indirectly affect *Drosophila* development, six bottles containing medium, but no flies, were fumigated for a period of 8 days at a concentration of 0.4 ppm sulfur dioxide. Surface pH values as well as pH values of homogenates of the medium were measured at the end of fumigation. All six bottles showed pH values of 4.5, the same as that of unfumigated medium. All bottles were fitted with loose cotton stoppers which prevented the escape of flies but allowed rapid gaseous diffusion. Diffusion calculations indicate that these stoppers would allow equilibration of sulfur dioxide concentration between the bottles and the chamber within a few minutes (*13*).

The first experiment was designed to assess the effects of fumigation over the entire life cycle. Each replicate consisted of 25 pairs of 1–3-day-old flies placed in a ½-pint bottle. Control and experimental replicates were put in their respective chambers for a period of 4 days, after which the adults were removed. Experimental bottles were fumigated for an additional 7 days (11 days total). Throughout this 11-day period a concentration of 0.7 ppm sulfur dioxide was maintained in the experimental chamber.

The number of progeny of each sex were counted every 24 h for a period of 7 days following onset of emergence in a given bottle. These counts were used to calculate productivity (total number of flies of a given sex produced) and mean developmental time. The day the experiment was initiated was taken as day 0 in the calculation of developmental time.

These two variables were then analyzed in separate three-way analyses of variance. The independent variables of both analyses were line, sex and treatment. In the analyses involving productivity the data were logarithmically transformed because the experimental stocks were known to differ in productivity. Therefore, equal effects take the form of equal percentage reductions in productivity, which are rendered additive by a log transformation (*14*).

Replicates in the second experiment consisted of the parental flies used in experiment 1, which had been transferred to fresh media. Thus, this experiment assessed the effects of fumigation of adults on subsequent adult fecundity. All replicates, therefore, consisted of 25 pairs of 5–7-day-old flies. Adults were allowed to lay eggs for 2 days, then discarded.

Productivity and developmental time were determined and analyzed as in experiment 1, with the exception that a 5-day counting period was used.

The third experiment concerned mainly the effects of fumigation on larvae. Replicates were set up as in experiment 1, but both experimental and control replicates were kept in the control chamber for a period of 2 days to minimize effects on adults and eggs. Following this, the experimental flies were put in the fumigated chamber. Two days later (day 4) all parental flies were discarded. Experimental replicates were then fumigated on additional 8 days (10 days total). Based on the results of experiment 1, this and the subsequent fumigation were carried out at a sulfur dioxide concentration of 0.4 ppm. Productivity and mean emergence time were determined and analyzed as in experiment 1.

The fourth and final experiment examined effects on prepupae and pupae. Each replicate consisted of 40 pairs of 7–10-day-old adult flies. (This age difference from experiments 1 and 3 is due to an equipment failure which forced a 7-day postponement of this experiment). Adults were allowed to lay eggs for a period of 36 h, then discarded. Larvae were allowed to develop an additional 5½ days (at which time almost all larvae had reached the prepupal or pupal stage) before the experimental replicates were placed in the experimental chamber and fumigated for a period of 4 days, in the same way as in experiment 3.

Productivity and developmental time were determined and analyzed as above with the exception that counting was done for 4 days at 12-h intervals.

Results

In experiment 1, fumigation greatly increased developmental time and decreased productivity (Figure 1). This extreme increase in developmental time was responsible for fumigation being terminated after 11 days.

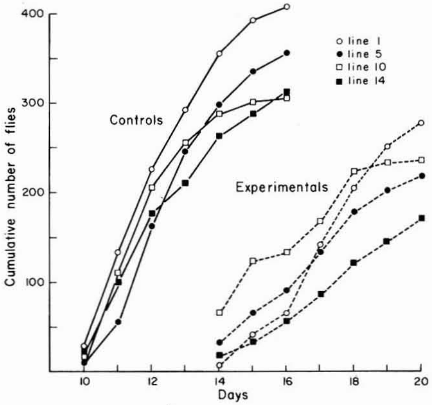

Figure 1. Total cumulative emergence curves of experiment 1 (adults + eggs + larvae, 0.7 ppm/11 days). Each curve represents mean of three replicates

Table I. Results of Three-Way Analyses of Variance of Productivity [a]

Source of variation	df	Experiment 1		Experiment 2		Experiment 3		Experiment 4	
		MS	F	MS	F	MS	F	MS	F
Main effects									
Lines	3	30.333	13.83[b]	14.479	11.83[b]	44.012	7.33[b]	46.853	37.17[b]
Sex	1	3.731	1.70	2.822	2.31	1.320	0.22	1.649	1.31
Treatment	1	226.926	103.47[b]	0.218	0.18	278.449	46.35[b]	40.724	32.31[b]
2-Way interactions									
Lines × sex	3	0.421	0.19	0.286	0.23	0.756	0.13	0.100	0.08
Lines × treatment	3	6.231	2.84	10.624	8.68[b]	46.656	7.77[b]	13.711	10.88[b]
Sex × treatment	1	6.300	2.87	0.006	0.01	5.498	0.92	1.026	0.81
3-Way interactions									
Lines × sex × treatment	3	0.451	0.21	0.449	0.37	2.561	0.43	0.639	0.51
Residual	32	2.193		1.224		6.008		1.260	

[a] Experiment 1 (adults + eggs + larvae, 0.7 ppm/11 days), experiment 2 (adults, 0.7 ppm/4 days), experiment 3 (larvae, 0.4 ppm/10 days), and experiment 4 (prepupae + pupae, 0.4 ppm/4 days). Since the same basic experimental design was used in all experiments, the sources of variation and degrees of freedom (df) are the same in all cases. [b] $p < 0.001$.

Table II. Results of Three-Way Analyses of Variance of Developmental Time [a]

Source of variation	df	Experiment 1		Experiment 3	
		MS	F	MS	F
Main effects					
Lines	3	2.752	16.38[b]	5.286	30.16[b]
Sex	1	0.102	0.61	0.014	0.08
Treatment	1	221.124	1315.79[b]	390.091	2225.88[b]
2-Way interactions					
Lines × sex	3	0.052	0.31	0.053	0.53
Lines × treatment	3	1.456	8.66[b]	1.882	10.74[b]
Sex × treatment	1	0.226	1.35	0.022	0.12
3-Way interactions					
Lines × sex × treatment	3	0.020	0.12	0.021	0.12
Residual	32	0.168		0.175	

[a] Experiment 1 (adults + eggs + larvae, 0.7 ppm/11 days) and experiment 3 (larvae, 0.4 ppm/10 days). Since the same basic experimental design was used in both cases, the sources of variation and degrees of freedom are the same for both analyses. [b] $p < 0.001$.

Table III. Mean Productivity Values and Their Standard Errors [a]

	Experiment 2				Experiment 4			
	Control		Experimental		Control		Experimental	
Line	x	SE	x	SE	x	SE	x	SE
1	263.0	4.4	233.3	7.7	174.0	3.0	179.3	10.0
5	241.3	24.8	246.0	7.5	259.0	7.4	229.0	4.0
10	216.3	5.6	285.7	10.2	314.3	8.9	196.7	9.5
14	212.7	18.4	185.3	8.3	304.3	10.7	265.0	13.2

[a] Experiment 2 (adults, 0.7 ppm/4 days) and experiment 4 (prepupae + pupae, 0.4 ppm/4 days). Each value is based on three replicates.

The analyses of productivity and developmental time presented in Tables I and II demonstrate that the effects of fumigation on both developmental time and productivity are highly significant and that developmental time in the experimental lines was differentially affected by fumigation.

Behavioral observations made during the course of fumigation indicated that the activity levels of the developing larvae were very low. Drosophila larvae, under normal conditions, are very active and feed constantly. In the case of the fumigated replicates the larvae appeared torpid and were observed to feed only sporadically. This was assumed to be the proximate cause of delayed development. It is also of interest to note that activity and feeding rate increased to apparently normal levels within 24 h after the experimental replicates were transferred to the control chamber.

The results of the second experiment are summarized in Tables II and III. The effect of fumigation on adults, as evidenced by subsequent productivity, is at best equivocal. The ordering of the lines with respect to productivity was different (Table III), but no overall reduction in productivity, which might be indicative of some sublethal damage to adult females, was observed. As might be expected, fumigation of adults had no effect on development time of larvae, and these data are therefore not presented.

Figure 2 displays the cumulative emergence curves resulting from experiment 3. As in the first experiment, fumigation both increased developmental time and decreased productivity. These results are shown to be highly significant in the analyses of variance shown in Tables I and II. In addition both developmental time and productivity in the experimental lines were differentially effected by fumigation.

It may be noted that the emergence curves for the experimentals (Figure 2) in this experiment extends over a 9- rather than a 7-day period. This is because large numbers of apparently viable pupae were present in the experimental replicates of lines 1 and 14. Emerging flies were therefore counted for an additional two days to better determine total emergence. The analyses of variance presented in Tables II and III are based on a 7-day counting period. However, it is apparent that the reduced 7-day productivity of lines 1 and 14 is largely an illusion created by an extreme increase in developmental time. Behavioral observations indicated that, as in the first experiment, delayed development was caused by drastically reduced larval activity levels.

The results of Experiment 4 are summarized in Tables II and III. With the exception of line 1, fumigation significantly decreased pupal survival and differentially affected the experimental lines. Fumigation had no effect on developmental time, and these data are therefore not presented.

Discussion

The suflur dioxide/exposure time combinations considered in these experiments are severe in that though similar conditions have been observed in ambient air (*15*), they are extremely uncommon (*16*). However, the responses observed here indicate ways in which sulfur dioxide could affect insect populations, and the magnitude of the responses suggests that effects on natural populations might be expected at more

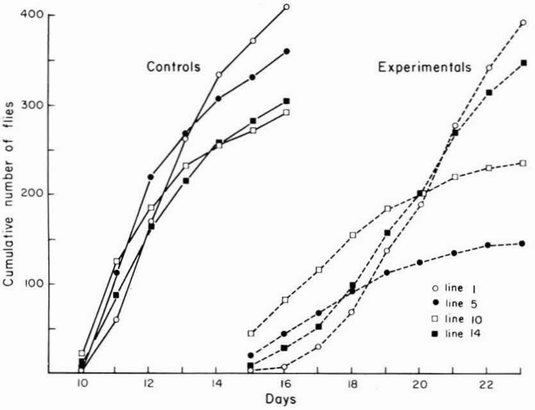

Figure 2. Total cumulative emergence curves of experiment 3 (larvae, 0.4 ppm/10 days). Each curve represents mean of three replicates

commonly occurring sulfur dioxide concentrations and exposure times.

In the fumigations involving developing larvae (experiments 1 and 3), the same general effects of increased development time and decreased survival were observed. Further, the same general behavioral pattern of reduced activity in the presence of sulfur dioxide followed by greatly increased activity and growth upon cessation of fumigation was present in both cases. The larvae of some insect species might be able to simply reduce their activity level during periods of high sulfur dioxide concentration and thus avoid any ill effects (as was apparently the case in lines 1 and 14 in experiment 3). Many insect species, however, exploit ephemeral resources (rotting fruit in the case of *Drosophila*) which place a premium on rapid development, and any increase in developmental time would expose most insects to increased risk of mortality due to such factors as parasitism or predation (*8, 17*).

Likewise experiment 4, which involved a 4-day exposure of pupae, decreased survival by an average of 17%. Mortality factors that cause on the order of 5–10% mortality late in the life cycle (i.e., the pupal stage) have been shown to have significant effects on the dynamics of insect populations (*17*) and 4-day periods during which sulfur dioxide concentrations may average 0.1–0.2 ppm are by no means unknown.

The results reported here also indicate that genetic constitution is an important determinant of response to sulfur dioxide. This is suggested by the presence of a significant lines × treatment interaction in all but one analysis. The reactions of a given line are not consistent from experiment to experiment. This is reasonable because the experiments considered different treatments both in terms of life stages exposed and, in experiment 1, sulfur dioxide concentration. Further, such variability in the responses of different life stages is in agreement with other studies of stress reactions in Drosophila (*9*).

The presence of genetic variability suggests that one might expect sulfur dioxide resistance to evolve in insect populations exposed to this gas. Such evolutionary responses could be of ecological importance. Undesirable species such as houseflies (*Musca domestica*) are routinely found in urban situations and may have already evolved resistance. Thus, these species might be at a competitive advantage in the presence of this gas and could displace other less objectionable species in areas newly subjected to sulfur dioxide stress (*8*).

On a more positive note, *Drosophila melanogaster* responds readily to selection in the laboratory. One might therefore be able to select strains sensitive to sulfur dioxide (or other pollutants) which could find use as bioindicators.

Though this study has identified potential effects of sulfur dioxide on insect populations, the broader question of what response one might expect in an insect population exposed to a given level of sulfur dioxide remains unanswered. In a natural population one finds a mixture of individuals at different life stages. Sulfur dioxide concentrations vary both spatially and temporally and are, in general, lower than those considered here. Other factors such as varying temperature and humidity and possible interaction of sulfur dioxide with other pollutants further complicate the situation. None the less, the magnitude of the responses observed here strongly suggests that sulfur dioxide may have ecologically significant effects on natural insect populations.

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Fate of Polycyclic Aromatic Hydrocarbons in Controlled Ecosystem Enclosures

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■ Prudhoe crude oil enriched with a number of polycyclic aromatic hydrocarbons was added as a dispersion to a controlled ecosystem enclosure suspended in Saanich Inlet, Canada. Concentrations of various aromatics were determined in water, zooplankton, oysters, and bottom sediments. Initial water concentrations of the lower weight aromatics, naphthalenes and anthracene, were 10–20 μg/L, whereas the initial concentrations of benzo(a)pyrene, benz(a)anthracene, and fluoranthene ranged from 1 to 6 μg/L. These concentrations decreased at an exponential rate due to evaporation, photochemical oxidation, microbial degradation, and sedimentation. Only naphthalenes were significantly degraded by microbes with removal by this process of up to 5% per day from the water. Sedimentation and photochemical oxidation were responsible for the decrease in concentrations of the higher weight aromatics.

This paper summarizes an experimental study of the fate of a number of polycyclic aromatic hydrocarbons of increasing molecular weight in a controlled ecosystem enclosure. The hydrocarbons included naphthalene, methylnaphthalenes, dimethylnaphthalenes, anthracene, fluoranthene, benz(a)-anthracene, and benzo(a)pyrene. Prudhoe crude oil was enriched with these aromatics and added as a dispersion to a quarter-scale enclosure (ca. 2 m diameter and 15 m deep—60 000 L). After oil addition, water, sediment, zooplankton, and oysters in the enclosures were analyzed for the various hydrocarbons. A second experiment involved adding radiolabeled benzo(a)pyrene to an enclosure to allow quantification of hydrocarbon products.

The changes in the concentration of the different hydrocarbons in water are a reflection of the action of evaporation, biological degradation, photochemical oxidation, and adsorption to living or dead particles with subsequent sedimentation. Using the results of our experiments we have attempted to evaluate the importance of these processes as it affects different types of aromatic hydrocarbons.

Experimental

Polyethylene enclosures (ca. 2 m diameter and 15 m deep) were filled with 60 000 L of water from Saanich Inlet which is located in western Canada. Naphthalene (1 g), 1-methylnaphthalene (1 g), 2,3-dimethylnaphthalene (1 g), anthracene (1 g), fluoranthene (0.5 g), benz(a)anthracene (0.5 g), and benzo(a)pyrene (0.2 g), all from Aldrich Chemical Co., were dissolved in 100 g of Prudhoe crude oil (kindly donated by W. Cretney from Environment Canada, British Columbia). Prudhoe crude oil appears similar to other crudes, e.g., Kuwait and South Louisiana; therefore, the amounts of naphthalene, 1-methylnaphthalene, 2,3-dimethylnaphthalene, fluoranthene, benz(a)anthracene and benzo(a)pyrene contributed by the 100 g of crude oil would be 80, 300, 10, 0.2, and 0.1 mg, respectively (*1–3*). A dispersion of this oil with its spiked compounds was formed by mixing the oil with 1 L of acetone, 0.5 L of ethanol, and 40 L of seawater. This dispersion was stirred for 24 h and then pumped through a diffusion ring throughout the top 10 m of the water column. One liter of acetone and 0.5 L of ethanol were pumped into a control enclosure. In a third enclosure 10 mCi of (G,^{3}H) benzo(a)pyrene (20 mCi/mM-Amersham) and 72 mg of benzo(a)pyrene (Aldrich Chemical Co.) were dissolved in 6 L of acetone, then mixed with 20 L of seawater, and the dispersion pumped through the diffusion ring into the top 10 m of the enclosure.

Water samples were collected by a pump from three depths with a peristaltic pump through a flexible tube. Some water samples were also collected with a Niskin water sampler. Hydrocarbon concentrations were the same with both collecting methods, suggesting that the tubing was not adsorbing significant amounts of the hydrocarbons. Samples of bottom sediment were collected by pumping through flexible plastic pipes permanently connected to the bottom of the enclosure. Zooplankton samples were collected with a 50-cm-diameter, 200-μm mesh net.

For bioaccumulation studies a cage with oysters (*Crassostrea virginica*) was suspended at 7 m in the oil-treated enclosure. At various time intervals, oysters were removed for analysis or depuration work. For depuration studies oysters were removed from the polluted enclosures and placed in a second cage suspended in outside "clean" water.

For microbial degradation studies, water was collected from 3 and 7 m in the oil treated and control enclosures. Radiolabeled hydrocarbons (^{14}C) dissolved in 2 μL of acetone were added to 100-mL water samples in 250-mL flasks capped with silicone stoppers. After incubation for various time intervals at the in situ temperature (12 °C) in the dark, the respired $^{14}CO_2$ released after the addition of acid was collected on filters soaked with phenethylamine and counted. A more detailed description of the method is given by Hodson et al. (*4*). To determine if any chemical degradation to CO_2 occurred, 5 mg of mercuric chloride was added to some samples. Four samples were run for each time interval. The radioactive hydrocarbons used with 2-methylnaphthalene-8-^{14}C (7.98 mCi/mN–California Bionuclear Corp.), ^{14}C-1-naphthalene (3.67 mCi/mM—Amersham), anthracene-9,10-^{14}C (33 mCi/mM—California Bionuclear Corp.), ^{14}C-12-benz(a)anthracene (48 mCi/mM—Amersham), benzo(a)pyrene-3,6-^{14}C (21 mCi/mM—Amersham).

For adsorption studies the radiolabeled hydrocarbons were added to 100-mL water samples. Concentrations of naphthalenes, anthracene, benz(a)anthracene, and benzo(a)pyrene were 25, 25, 10, and 3 μg/L, respectively. After incubation for 3 h at the in situ temperature, the water was filtered onto a 0.4-μ filter (Nucleopore Co.). The particles were washed off with a stream of filtered seawater and then filtered again. The second filtration was necessary because hydrocarbons not associated with particles collected on the first filter. Hydrocarbons not associated with particles were not removed by the washing procedure. Most detrital particles and phytoplankton cells washed off the first filter, but up to 20% of the free bacterial cells could not be removed.

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For radioautographic studies (G, ^{3}H) benzo(a)pyrene (25 Ci/mM—Amersham) was added to water samples. A two-step filtration was carried out as described above, and filters from the second filtration were stained with a general bacteriological stain (3% Erythrosin B in 5% phenol solution). After several washes, slides were dipped in Kodak NTB-2 emulsion as described by Paerl and Goldman (*5*). After exposure and development, filters were examined with phase optics at 1200× to determine which particles contained radioactivity.

Analysis. Water samples were extracted with hexane (J. T. Baker—spectral grade), and an ultraviolet spectrophotometric method (*6*) was used to quantitate naphthalene, methylnaphthalenes, and dimethylnaphthalenes. Earlier experiments in these enclosures showed that determination of naphthalenes by gas-liquid chromatography agreed with results obtained by the ultraviolet method (*3*). The sensitivity of the ultraviolet method was 0.5 μg/L for each of the various naphthalenes. To determine polycyclic aromatic hydrocarbons, other than naphthalenes, hexane extracts were concentrated to dryness under nitrogen and dissolved in 10 μL of methanol. Anthracene, fluoranthene, benz(a)anthracene, and benzo(a)pyrene were measured by passing 5 μL of the methanol solution through an assembled liquid chromatograph equipped with a fluorometric detector (Fluoromonitor—American Instrument Co.). The sensitivity of the method was 0.01 μg/L for anthracene, fluoranthene, and benzo(a)-pyrene and 0.02 μg/L for benz(a)anthrane. A standard curve was prepared for each compound. The chromatograph was equipped with a LiChrosorb RP-2 (Merck) column (25 cm long and 2.0 mm i.d.). The sample was eluted with three solvent mixtures added sequentially (solvent 1—methanol:water, 1:1; solvent 2—methanol:water, 2:3, solvent 3—methanol: water, 3:2).

The concentration of total hydrocarbons in the water 1 day after the addition of oil was obtained using an infrared absorption procedure (*8*). One-liter samples were acidified with 1 mL of sulfuric acid (50%) and extracted with 20 mL of carbon tetrachloride (Burdick and Jackson, analytical grade). Absorbance at 2930 cm^{-1} was compared to a calibration curve constructed for solutions of the Prudhoe crude oil in carbon tetrachloride.

The procedure used to analyze volatile aromatic hydrocarbons in seawater using helium partitioning gas chromatography has been described (*9*). Data obtained from the gas chromatograms were treated according to the method of McAuliffe (*10*) to calculate aromatic concentrations.

Animal tissues were homogenized in a blender for 2 min. Sediment samples were mixed with an equal volume of water. One milliliter of tissue or sediment slurry was saponified with 0.5 mL of 4 N NaOH by heating at 95 °C for 2 h. The sample was mixed with 5 mL of hexane. The hexane extracts were analyzed by either the ultraviolet spectrophotometric method (for naphthalenes) or liquid chromatography (anthracene, fluoranthene, benz(a)anthracene, and benzo(a)pyrene). Between 90 and 95% of the selected aromatics was recovered when sediment and animal tissues were spiked with these compounds.

For the radiolabeled benzo(a)pyrene experiment, water was collected from the following depth intervals: 0–5, 5–10, and 10–13 m. Four liters of water were passed through a glass fiber filter. The filter was added to a liquid scintillation cocktail (Aquasol—New England Nuclear) and counted (Beckman Model LS 100C liquid scintillation counter). The values obtained were assumed to be total counts in the water. Separate extractions of the water with benzene indicated that glass fiber filters removed 70–90% of the radioactivity in the water. Benzene extracted benzo(a)pyrene, hydroxy derivatives, and quinones when these were added to water samples. In addition to determining total radioactivity, filters were also extracted with methanol:benzene (1:2 v/v). This extract was concentrated to a small volume under nitrogen in the dark, added to a silica gel thin-layer plate (Merck Co.), and run in a solvent system (ethanol:benzene, 1:9 v/v) to separate degradation products from the benzo(a)pyrene. Benzo(a)pyrene and 3-hydroxybenzo(a)pyrene and benzo(a)pyrene-1,6-dione were used as standards. The hydroxy benzopyrene and quinone were provided by A. R. Patel through the National Cancer Institute Carcinogenesis Research Program.

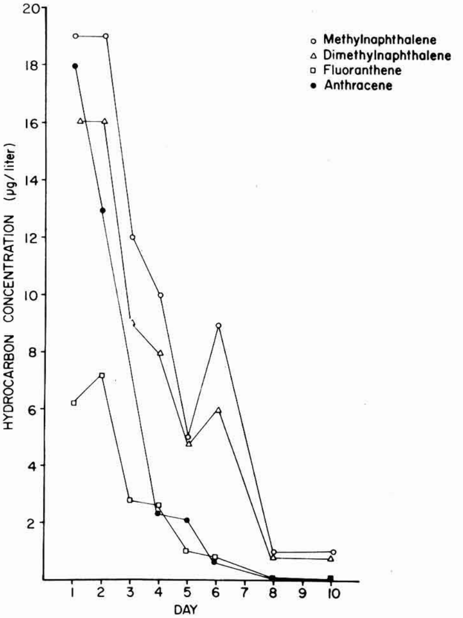

Figure 1. Polycyclic aromatic hydrocarbons from 3-m water

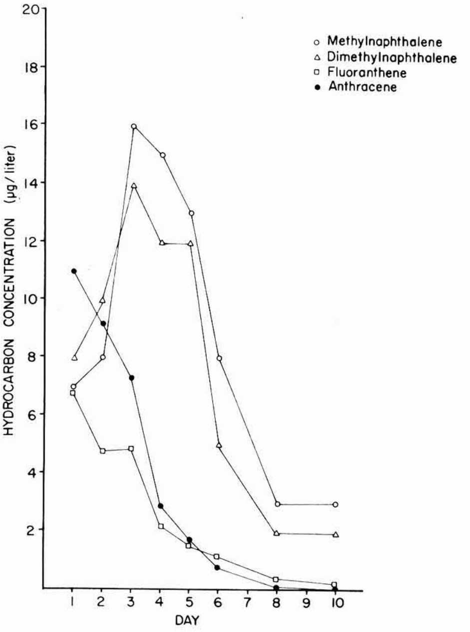

Figure 2. Polycyclic aromatic hydrocarbons from 7-m water

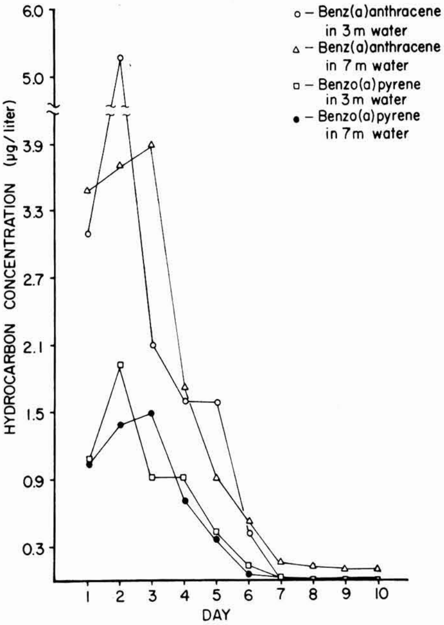

Figure 3. Benz(a)anthracene and benzo(a)pyrene from 3- and 7-m water

Results

The addition of a dispersion of 100 g of Prudhoe crude oil to the top 10 m of the water column resulted in small oil slicks on the surface which gradually disappeared over 10 days. After 1 day the nonvolatile hydrocarbon concentration at 7 m by the infrared method was 280 µg/L. The concentrations of volatile aromatic hydrocarbons, namely, benzene, toluene, ethylbenzene, xylene, and trimethybenzenes, were 1700, 1500, 300, 540, and 1500 µg/L, respectively. No other measurements were made of total nonvolatile or volatile hydrocarbon concentrations. In similar experiments with fuel oil, volatile hydrocarbons were not detected after 3 days (*11*).

The concentrations of naphthalene, methylnaphthalenes, dimethylnaphthalenes, anthracene, fluoranthene, benz(a)anthracene, and benzo(a)pyrene on day 1 were 11, 19, 16, 18, 6.2, 3.1, and 1.1 µg/L, respectively. The concentration of each hydrocarbon decreased at an exponential rate during the following 17 days of the experiment (Figures 1–4, Table I). Naphthalenes increased slightly in surface waters on day 6 (Figure 1), which may be due to more of these components dissolving in the water from the surface slick. A liquid chromatogram of a day 3 water sample from 7 m is shown in Figure 5 where the concentrations of anthracene, fluoranthene, benz(a)anthracene, and benzo(a)pyrene were 7.3, 4.9, 3.9, and 1.5 µg/L, respectively. Use of the high-pressure liquid chromatograph with a fluorescence detector allowed separation and detection of these polycyclic aromatic hydrocarbons in water, sediment, zooplankton, and oysters during the course of the experiment. The time for the hydrocarbons to decrease to 50% of their original values, i.e., half-life, was 3–4 days in water from 3 m and 4–6 days in water from 7 m. By day 17 all of the spiked hydrocarbons were below the level of detection in water from 3 m.

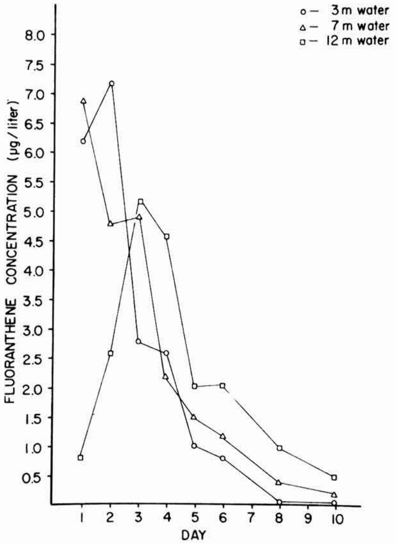

Figure 4. Changes in fluoranthene concentration with depth and time

Table I. Addition of ^{3}H-Benzo(a)pyrene to an Enclosure—Concentration Changes of Hydrocarbon and Degradation Products

Day	Sample depth (m)	Total benzo(a)pyrene and degradation products (µg/L)	Benzo(a)pyrene (µg/L)	Hydroxylated derivatives and quinones (µg/L)
1	0–5	1.4	1.2	0.08
1	5–10	1.3	1.1	0.05
1	10–13	0.1	0.1	0
2	0–5	1.1	0.7	0.01
2	5–10	0.9	0.6	0.01
2	10–13	0.2	0.2	0
3	0–5	0.9	0.5	0.1
3	5–10	0.9	0.6	0.1
3	10–13	0.4	0.2	0.02
4	0–5	0.9	0.3	0.2
4	5–10	0.7	0.5	0.1
4	10–13	0.6	0.4	0.01
6	0–5	0.4	0.2	0.1
6	5–10	0.3	0.2	0.1
6	10–13	0.3	0.2	0.02
8	0–5	0.2	0	0.07
8	5–10	0.6	0.4	0.05
8	10–13	0.4	0.3	0.04
10	0–5	0.1	0	0.02
10	5–10	0.2	0.1	0
10	10–13	0.2	0.2	0

A phytoplankton bloom, predominantly centric diatom species, with an initial chlorophyll-a concentration of 19 µg-atoms/L, and a phytoplankton carbon concentration of 3 mg/L was captured in the enclosure. This bloom rapidly depleted nutrients, and the phytoplankton sank to the bottom of the enclosures, which resulted in a large decrease in chlorophyll-a in the water of both control and treated enclosures. Similar cycles of centric diatom blooms, depletion of nutrients, and subsequent sinking of the phytoplankton are a normal summer feature of Saanich Inlet (*12*). Hydrocarbons associated with the phytoplankton are carried to the bottom sediments by this sinking process. Analysis of fluoranthene in water from 3, 7, and 12 m showed the path of fluoranthene through the water column. On day 1 fluoranthene was 6.2 µg/L at 3 m but decreased to 2.8 µg/L by day 3 with subsequent increase in the water from 7 and 12 m and eventual incorporation into the sediment (Figure 4 and Table II).

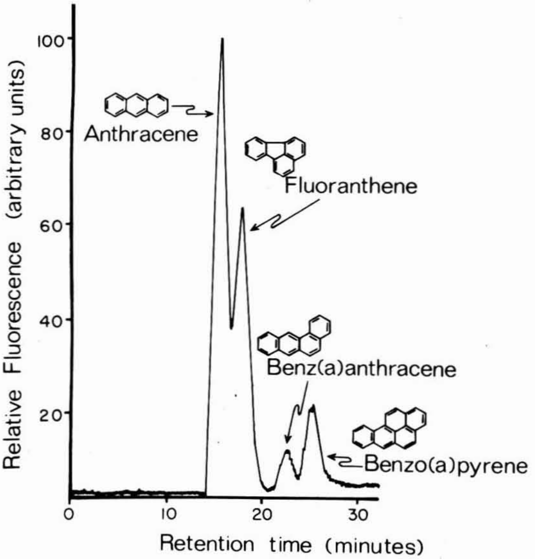

Figure 5. Liquid chromatogram of 7-m water on day 3

Photochemical Oxidation. The importance of photochemical oxidation can only be inferred from our results. The higher weight polycyclic aromatic hydrocarbons, in particular benzo(a)pyrene and benz(a)anthracene, are susceptible to photooxidation (*13*). The short wavelengths required for photooxidation of these compounds penetrate only a few meters in the ocean, and should be even more attenuated in the presence of a phytoplankton bloom. The experiment with tritiated benzo(a)pyrene suggests that photooxidation of this compound was important in the top 5 m (Table I). On day 4, 30% of the radioactivity collected in the upper 5 m of the enclosure was due to benzo(a)pyrene. On thin-layer plates the remaining radioactivity was collected in the area of quinones and more polar compounds. Benzo(a)pyrene accounted for the majority of the radioactivity in bottom waters and sediments. Approximately 40% of the benzo(a)pyrene in the waters of the oil-treated enclosures was recovered in the sediment, suggesting that no more than 50% of the benzo(a)pyrene could have been photooxidized (Table III).

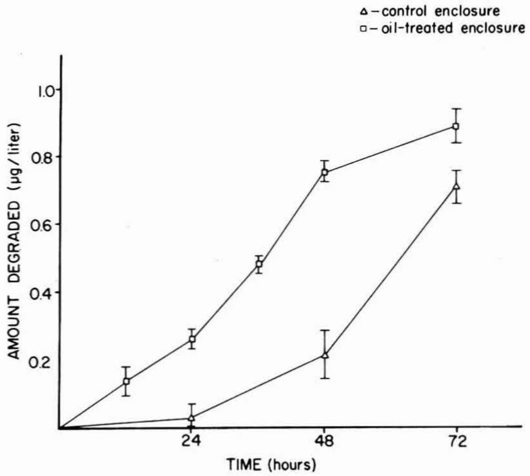

Figure 6. Microbial degradation of ^{14}C-1-methylnaphthalene (25 µg/L) in oil-treated and control enclosures

Microbial Degradation. The rate of microbial degradation was evaluated by the addition of ^{14}C-labeled hydrocarbons to water samples from the enclosures and later measurement of $^{14}CO_2$ produced. Radiolabeled benz(a)anthracene and benzo(a)pyrene were not degraded in water in the dark from either the treated or control enclosures. Anthracene was not degraded in the control water but slowly degraded (0.02 µg/L/day) in water from the treated enclosure. No degradation was observed in mercury treated controls. As a result of adding oil to an enclosure, radiolabeled naphthalene and methylnaphthalene were degraded on day 3 at a rate of approximately 0.4 µg/L/day (Figure 6; only the degradation of methylnaphthalene is shown, but very similar curves were obtained for naphthalene). If the amount of unlabeled methylnaphthalene in the water (12 µg/L) is taken into account, the calculated degradation rate is 0.5 µg/L/day. Assuming a uniform rate throughout the enclosure, then 30 mg of methylnaphthalene would be degraded to CO_2 in one day. On day 3 there was approximately 600 mg of methylnaphthalene in the water of the oil-treated enclosure. Thus up to 5% of the naphthalenes in the water could be degraded daily. Water in the control enclosure showed an initial lag in the degradation of naphthalene

Table II. Aromatic Hydrocarbons in Bottom Sediments from Oil-Treated Enclosure

	Naphthalene		Methylnaphthalenes		Dimethylnaphthalenes	
Time after oil addition (days)	Concn (µg/g)	Amt in sediment (mg)	Concn (µg/g)	Amt in sediment (mg)	Concn (µg/g)	Amt in sediment (mg)
2	70	28	71	28	169	68
4	15	9	22	13	66	40
7	5	3	5	3	22	12
10	7	6	10	9	30	26
14	2	2	3	3	6	7
17	<0.5	<1	<0.5	<1	<0.5	<1

	Anthracene		Fluoranthene		Benz(a)anthracene		Benzo(a)pyrene	
	Concn (µg/g)	Amt in sediment (mg)	Concn (µg/g)	Amt in sediment (mg)	Concn (µg/g)	Amt in sediment (mg)	Concn (µg/g)	Amt in sediment (mg)
2	<0.2	<0.1	<0.2	<0.1	<0.4	<0.2	<0.2	<0.1
4	1.8	1.1	2.4	1.4	2.2	1.3	0.8	0.5
7	5.3	2.9	4.4	2.4	5.4	3.0	2.1	1.2
10	3.5	3.1	2.8	2.5	3.8	3.3	1.3	1.1
14	5.1	5.6	6.2	6.8	10.0	11.0	4.9	5.4
17	8.4	11.8	10.0	14.0	24.0	33.6	6.0	8.4

Table III. Total Amount of Aromatic Hydrocarbons in Bottom Sediments and Water

Hydrocarbon	Estimated amt in water on day 1 (mg)	Total in sediment (mg)	% recovered in sediment
Naphthalene	440	48	11
Methylnaphthalenes	760	56	7
Dimethylnaphthalenes	480	153	32
Anthracene	600	25	4
Fluoranthene	276	27	10
Benz(a)anthracene	132	52	39
Benzo(a)pyrene	44	17	39

and methylnaphthalene, but after incubation with the labeled hydrocarbons for 72 h the amount degraded was nearly the same as in the oil-treated enclosure (Figure 6).

Sedimentation and Adsorption Studies. Determination of the concentration and amount of the hydrocarbons in the bottom sediments at various times after addition of oil allowed us to evaluate the importance of sedimentation processes in removing hydrocarbons from the water. Most of the naphthalenes, with a predominance of dimethylnaphthalenes, appeared in early sediment samples, i.e., during the first 7 days, whereas the less soluble higher weight aromatics appeared in later samples. A comparison between the amount of hydrocarbon in the water column on day 1 (estimated by assuming all of the hydrocarbon was in the top ten meters) and the total collected in the sediment is shown in Table III. The percent recovered in the sediment varied from 4% for anthracene to 39% for benzo(a)pyrene.

The hydrocarbons in the bottom sediments were presumably carried there by particles originally in the water column. Particles that could take up hydrocarbon included phytoplankton, detritus, and zooplankton. Zooplankton were sampled on days 4 and 7. On day 4 the concentrations of anthracene, fluoranthene, benzo(a)pyrene, and benz(a)anthracene in a zooplankton sample, predominantly the copepod *Pseudocalanus minutus*, were 3.3, 1.4, 0.3, and 1.2 μg/g, respectively. These concentrations were less than those in the bottom sediment after day 4 (Table II). After 9 days the concentration of these compounds in zooplankton was below detectable levels, i.e., less than 0.1 μg/g. The ability of copepods and other zooplankton to degrade and discharge hydrocarbons may account for this decrease (*14–16*).

On day 5 a water sample from 12 m was analyzed before and after filtering through a glass fiber filter. Less than 10% of the benz(a)anthracene and benzo(a)pyrene and 50% of the anthracene and fluoranthene passed through the filter. For laboratory adsorption studies, radiolabeled hydrocarbons were added to water samples collected from the control enclosure. After a 3-h incubation period, 2% of the radiolabeled naphthalene and methylnaphthalene at a concentration of 25 μg/L were taken up by suspended particles. The relative adsorptions of anthracene (15 μg/L), benz(a)anthracene (3 μg/L), and benzo(a)pyrene (2 μg/L) to suspended particles were 11, 59, and 75%, respectively. Radioautographs with tritiated benzo(a)pyrene added to water samples indicated that this hydrocarbon was associated with detrital particles rather than with living phytoplankton cells. Under the microscope these detrital particles appeared to be aggregates of dead phytoplankton cells and bacteria.

Hydrocarbon Uptake by Oysters. Oysters suspended in the oil-treated enclosure rapidly took up all hydrocarbons with very high accumulation of naphthalenes (Table IV). For depuration experiments, oysters were transferred to water outside the enclosure. Naphthalenes were rapidly released and were not detectable after 23 days. There was a much slower release of accumulated anthracene, fluoranthene, benz(a)anthracene, and benzo(a)pyrene. They were still present at the end of the 23 days. Based on these depuration experiments, calculated half-lives of the naphthalenes, assuming exponential discharge, were 2 days; whereas for anthracene, fluoranthene, benz(a)anthracene, and benzo(a)pyrene, the half-lives were 3, 5, 9, and 18 days, respectively. Thus the higher weight aromatics appear to persist for longer periods than the lower weight naphthalenes. Other depuration studies with mussels collected from oil-contaminated waters have indicated the persistence of higher weight aromatics (*17, 18*).

Discussion

We propose that the primary processes effecting the concentration of the hydrocarbons in the waters of the enclosures were evaporation, microbial degradation, sedimentation, and photochemical oxidation. Based on the data presented here and from other reported studies, we have attempted to evaluate the relative importance of these processes as they effect the concentration of the different aromatics.

Most studies on evaporation have been concerned with hydrocarbon losses from an oil slick. Hydrocarbons below C_{15} (BP—270 °C) volatilize in a few days from an oil slick (*19–21*). In our experiments loss of naphthalenes from the upper waters, particularly naphthalene (BP—210 °C) would be pre-

Table IV. Uptake and Depuration of Aromatic Hydrocarbons by Oysters from Oil-Treated Enclosure

Time of exposure (days)	Depuration time (days)	Naphthalene		Methylnaphthalenes		Dimethylnaphthalenes	
		Oyster (μg/g)	Water (μg/L)	Oyster (μg/g)	Water (μg/L)	Oyster (μg/g)	Water (μg/L)
2		30	5	56	8	84	10
8		12	3	36	3	72	2
2	7	1	...	1	...	8	...
8	7	2	...	2	...	4	...
8	23	nd[a]	...	nd	...	nd	...

Time of exposure (days)	Depuration time (days)	Anthracene		Fluoranthene		Benz(a)anthracene		Benzo(a)pyrene	
		Oyster (μg/g)	Water (μg/L)	Oyster (μg/g)	Water (μg/L)	Oyster (μg/g)	Water (μg/L)	Oyster (μg/g)	Water (μg/L)
2		5.6	13	5.0	7.2	2.8	5.3	0.36	1.9
8		2.5	1	4.0	0.4	1.8	0.1	0.30	0.1
2	7	1.2	...	1.7	...	1.9	...	0.40	...
8	7	0.4	...	1.4	...	1.0	...	0.20	...
8	23	0.1	...	0.4	...	0.3	...	0.12	...

[a] nd, not detectable, less than 0.5 μg/g.

dicted. Hydrocarbons in the C_{15}–C_{25} range (BP—250–400 °C), anthracene and fluoranthene in our experiments, are volatilized from an oil slick only to a limited extent.

Microbial degradation was measurable only for naphthalenes and anthracene in the oil-treated enclosure. Water from the control enclosure required incubation with ^{14}C-naphthalenes for 48 h before appreciable degradation occurred, whereas in water from the oil-treated enclosure, measurable degradation of ^{14}C-naphthalenes took place within 4 h after addition. An earlier hydrocarbon experiment showed marked increases in microbial degradation rates of naphthalenes 3 days after hydrocarbon addition (*7*). Several studies have shown higher numbers of oil degrading microbes in oil-polluted areas relative to nearby "clean" areas (*22, 23*).

Photochemical oxidation, involving free radical addition catalyzed by light or metal ions, appears to be an important process in the destruction of oil slicks (*21*). Based on laboratory studies it appears that anthracene, fluoranthene, benz(a)anthracene, and benzo(a)pyrene of the aromatics studied in our experiments are subject to photochemical oxidation in slicks or near surface waters (*13, 24, 25*). Benzo(a)pyrene is the most susceptible of these compounds to photooxidation, and the results of the experiment involving addition of tritiated benzo(a)pyrene to an enclosure suggested that photochemical oxidation was important in the surface waters. Approximately 40% of the benzo(a)pyrene in the water was recovered in the bottom sediments. Since microbial degradation and evaporation were not important, it is suggested that as much as 50% of the benzo(a)pyrene was photooxidized during the 17 days of the experiment. It is probable that there were losses to the side of the plastic enclosure and incomplete recovery of hydrocarbon in the sediment so that photooxidation was less than 50%.

Sedimentation is important in carrying hydrocarbons from both oil slicks and from the water to the bottom (*21*). Particles such as fine-grained clays and detritus can adsorb dissolved, dispersed, or particulate hydrocarbons (*26–28*). Experimental oil spills have shown rapid hydrocarbon decreases in the water after disappearance of the oil slick with increases of the aromatics in the sediments (*29, 30*).

In our experiments, naphthalenes, particularly dimethylnaphthalenes, were found in the bottom sediments during the first 7 days, whereas the heavier weight aromatics were slower to sediment. This suggests that the mechanisms for carrying naphthalenes to the bottom were different than those of the other aromatics. Soto et al. (*31*) showed active uptake of naphthalene by phytoplankton. We suggest that naphthalenes, but not the larger aromatic hydrocarbons, were actively taken up by living phytoplankton cells which subsequently sank to the bottom. Radioautographs with tritiated benzo(a)pyrene indicated that this hydrocarbon, and presumably other higher weight aromatics, were associated with detritus, composed of clumps of dead phytoplankton cells and associated bacteria. These particles probably sank at a slower rate than living phytoplankton cells. Figure 3 shows a large increase in naphthalenes in 7-m water on days 3 and 4, which was not observed with the other aromatics. Presumably this increase was due to naphthalenes in surface water phytoplankton being carried to deeper waters. The lower concentration of naphthalenes in later sediment samples (after 7 days) could be due to increases in the microbial degradation rates of these compounds in sediment or bottom waters. Since it appears that phytoplankton take up but cannot metabolize naphthalenes (*31*), autolysis of the phytoplankton cells may release naphthalenes that are degraded.

It is difficult to explain the loss of anthracene from the enclosure. The rate of decrease in the water was very rapid (Figures 1 and 2) with only small increases seen in the 7- and 12-m water samples between days 2 and 4. Other aromatics increased on these days as particles with associated hydrocarbons were carried to the bottom. Only 4% of the anthracene in the water was recovered in the bottom sediments. The microbial degradation rate was very low for anthracene. With a boiling point of 340 °C, evaporation was not expected to be important, although laboratory studies have shown up to 15% loss of anthracene from solution (*32*). Possibly, photochemical oxidation was extremely rapid for this compound.

Conclusions

Changes in the concentration of various fluorescent aromatics in water, sediment, zooplankton, and oysters from an oil-treated enclosure were easily determined by using crude oil enriched with the compounds of interest and a liquid chromatograph with a fluorescence detector. The sensitivity of the method allowed detection of 0.01 μg/L of the individual hydrocarbons.

Our results indicated that aromatic hydrocarbons have short residence times, i.e., on the order of a few days, in marine waters. For lower molecular weight aromatics, such as benzenes, naphthalenes, anthracenes, and phenanthrenes, microbial degradation and evaporation are the primary removal processes. The concentrations of higher weight aromatics, such as chrysenes, benzanthracenes, and benzpyrenes, are primarily effected by sedimentation and photochemical oxidation. Because of their low solubility in water, the higher weight aromatics are associated with particles in the water. After sedimentation of higher weight aromatics, biological degradation by interactions between macrofauna, meiofauna, and microfauna of the sediment becomes an important factor in their removal (*23, 33*). In studies now being conducted we are adding bottom material collected from an oil-treated enclosure to trays of marine sediments to determine rates of hydrocarbon degradation in the sediment. When oil from a spill is incorporated into fine sediments, it may persist for many years with storms and tides sometimes causing resuspension of these sediments with their associated hydrocarbons (*34*).

In open ocean areas with low concentrations of suspended particles, rates of hydrocarbon sedimentation would be low, but because of the clear waters, photochemical degradation rates should be high. In the case of an oil spill, hydrocarbons should continue to be found in the water as long as a slick persists followed by rapid decreases in their concentration as a result of the various natural removal processes.

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Rapid Weathering Processes of Fuel Oil in Natural Waters: Analyses and Interpretations

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■ The fate-determining steps of weathering petroleum in the aquatic environment were studied in model experiments. Capillary column gas chromatography and infrared absorption measurements showed different weathering processes for No. 2 fuel oil, depending on the turbulence and the level of suspended solids (kaolinite) in water during experiments. Partial dissolution, adsorption, dispersion, and agglomeration of No. 2 fuel oil initially occurred and resulted in the fractionation of the original oil mixture. Alkylated benzenes and naphthalenes were enriched in the water phase (up to 5 mg/L), certain aliphatic hydrocarbons above mol wt 250 were adsorbed onto kaolinite (200 mg/kg), and oil droplets were agglomerated with suspended minerals (20 g/kg) after increased turbulence. The same fractionation pattern was observed for a ground water oil spill, although the oil was already biochemically altered.

One would like to be able to characterize the processes that influence the fate of oil in the aquatic environment. A number of authors (*1*) have described various physical and biological processes that contribute to the distribution and degradation of petroleum products in the aquatic environment. Difficulties have arisen in determining the relative magnitude of the various processes. Reliable information on the distribution of oil components in aquatic environments is important because the more water soluble aromatic hydrocarbons, even in minute concentrations, may have toxic effects on aquatic organisms (*2*).

This work presents an analysis of the initial short-term processes affecting the distribution of fuel oil in surface water containing a suspended clay mineral. Processes studied include dissolution, suspension, agglomeration, and adsorption. Evaporation was not studied, since surface oil spills generally contribute less to oil pollution than continuous inputs from diffuse sources (*3*).

Model experiments were done with No. 2 fuel oil and water containing suspended particulates. Then a comparison was made of these model experiments and an actual case involving polluted ground water.

Experimental

Model Experiments. A 250-mL erlenmeyer flask was filled with distilled water containing sodium chloride (10^{-3} M) and sodium bicarbonate to stabilize the pH at 7.5. To withdraw samples, a U-tube was placed in the flask, with one end near the bottom and the other end outside. Ten milliliters of No. 2 fuel oil were carefully placed on top of the water body with a pipet, avoiding single oil droplets. The flasks were then stirred with a magnetic stirrer at a constant speed (3 cycles/s). Different flow conditions were achieved by changing the length of the magnetic stirrer: 2 cm for low intensity and 3 cm for high intensity (oil/water interface disrupted). Ten grams per liter of kaolinite (0.2–2 μm) with a relatively high specific surface (10 m^2/g) were used as the particulate material. Experiments were performed for a period of 24 h at 20 °C as follows: I: oil/water without suspended solids, low stirring intensity; II: oil/water with suspended solids, low stirring intensity; III: oil/water with suspended solids, high stirring intensity; IV: gasoline/water without suspended solids, low stirring intensity.

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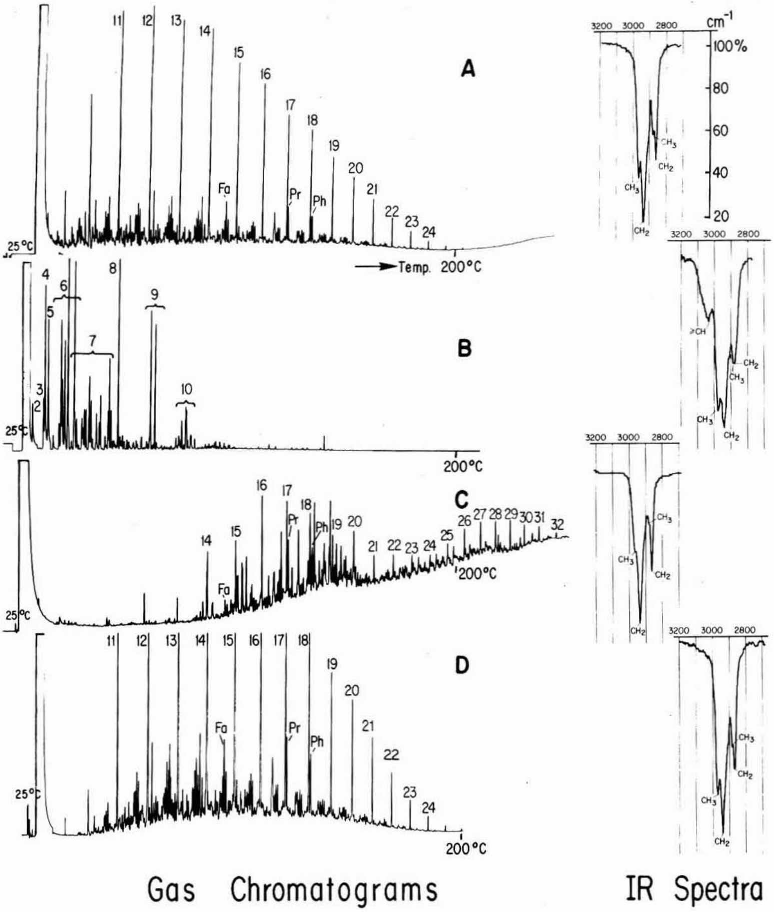

Figure 1. No. 2 fuel oil fractions from model experiments

Gas chromatogram and partial IR spectra (C—H stretch region) of: (A) original composition; (B) water-soluble fraction; (C) adsorbed fraction; (D) agglomerate fraction. For identification of GC peaks, refer to Table I. Column: SE 52 coated glass capillary (20 m × 0.30 mm i.d.). Conditions: 1.5 μL, splitless, carrier gas pressure H_2, 5.9 psig, 3 °C/min, 25–250 °C

Samples of 50 mL were withdrawn through the U-tube and ultracentrifuged (30 000-g centrifugal force) for 30 min to separate settlable, dissolved, and floating oil fractions. The carefully separated sediment was allowed to dry at room temperature and was then completely powdered by mixing with the same amount of dry sodium sulfate. This powder was transferred to a small chromatographic column (6 mm id., 80 mm height), and eluted with a minimal volume (2.5 mL) of carbon tetrachloride for the quantification of hydrocarbons by IR spectrometry. Recovery was between 80 and 90% when compared to soxhlet extraction. For gas chromatographic analyses, the sediments were eluted from the columns with pentane.

The water phase was extracted in a separatory funnel with carbon tetrachloride for IR analyses or with pentane for GC analyses. The floating oil fraction was prepared by diluting with carbon tetrachloride for IR analyses or with pentane for GC analyses.

Samples from a ground water contaminated by an oil spill were taken in the following manner: Before the excavator reached the ground water table (4 m below surface), a soil-sand sample was collected directly into an aluminum box. About 20 cm deeper the water sample was taken with an all glass bottle. At the same level a sample of the oil film was collected. For control, another water sample was taken from a digging 50 m downstream, with respect to the ground water flow. No oil film could be observed.

The workup of these samples was the same as for the model experiment except that the water/oil phases were separated by settling instead of centrifuging.

Analytical

Infrared Measurements (IR). The hydrocarbon content of the samples was determined by IR according to the API method (*4*). The sum of the absorptions from wavenumbers 2850, 2925, 2870, and 2960 cm^{-1} was compared with the corresponding sum from No. 2 fuel oil used as a calibration standard. The detection limit was 0.5 mg fuel oil type hydrocarbons per liter of water sample and 20 mg/kg dry sediment.

In addition to the IR, a Total Organic Carbon Analyzer was used to quantify the soluble fraction from No. 2 fuel oil. For determination of alkylated benzenes the TOC values were corrected by a factor of 1.1 for their carbon content.

Gas Chromatography (GC). Gas chromatography was performed on a Carlo Erba gas chromatograph, equipped with glass capillary columns (*5*), which had been purchased from H & G Jaeggi, CH-9043 Trogen, Switzerland (50 m OV-101 and 56 m Ucon HB) or provided by K. Grob (20 m SE-52). The Grob splitless injection technique was used (*6*). The column temperature was programmed at 3°/min from 30 to 250 °C (180° for Ucon HB). Peak identifications were based on retention times and coinjection with standards.

Reagents. Reagents used were: practical grade pentane and redistilled hexane; carbon tetrachloride, nanograde (Mallinckrodt, Inc., St. Louis, Mo.); anhydrous sodium sulfate, dried, AR grade; and kaolinite (M. Müller-Vonmoos, Institute for Petrography, ETH-Zürich).

Results

Model Experiments. The results of the model experiments are shown in Figure 1. On the left, the separation of the hydrocarbon mixture by capillary GC is shown. The key components that were followed in this study are listed in Table I. The right side gives the corresponding IR spectra in the C—H stretch region for the unseparated mixtures. The absorptions are indicative of CH_3, CH_2, and aromatic CH bands. The original mixture of No. 2 fuel oil, which has a broad boiling range of 170–350 °C, is shown in chromatogram A. The mixture is dominated by *n*-paraffins, isoparaffins, and naphthalenes. This pattern was also found for the oil phase separated in model experiments I and II (low intensity stirring with and without suspended solids). As expected the IR spectrum for No. 2 fuel oil has only weak aromatic CH absorption since the aromatic content of No. 2 fuel oil is less than 10% and the C—H stretch in aromatic compounds is normally weak.

In contrast, the water phase of model experiments I–III gave patterns dominated by alkylated benzenes (peaks 1–7) and naphthalenes (peaks 8–10). The aromatic character was demonstrated by the IR spectrum. Absorption between 3100 and 3000 cm^{-1} can be attributed to hydrogen attached to aromatic rings, and the shoulder at 2930 cm^{-1} (on CH_2 band) to methyl groups bound to aromatic rings (*7*). It appears that the amount and distribution of dissolved aromatic hydrocarbons in water ranging from benzene to about C_2-naphthalenes depend on their concentration in the original mixture (distillate fraction).

Figure 2 compares the water soluble aromatics originating in gasoline and No. 2 fuel oil. For this comparison we used a GC column (Ucon HB) suitable for separation of alkylated benzenes. Since the gasoline has a high aromatic content (~30%), the GC chromatograms of gasoline (Figure 2a) and of that portion of the gasoline dissolved in water (Figure 2b) are similar (see Peaks 1–6). In contrast to water soluble parts of No. 2 fuel oil, benzene and toluene dominated in water soluble fractions of gasoline, whereas C_4-benzenes and naphthalenes were found only in minute concentrations. Qualitatively, the water soluble components of these two petroleum products are similar. To quantitate the partial dissolution of No. 2 fuel oil in distilled water, the saturation level reached after 1 h at 20 °C during experiment I was determined by TOC: 5 mg/L (±0.5). The saturation concentration of gasoline determined by TOC and also found by gas chromatography was: 200 mg/L distilled water, 20 °C, after 1 h (experiment IV).

Table I. List of Hydrocarbons Indicated in Chromatograms

	Peak no.
Benzene	1
Toluene	2
Ethylbenzene	3
m-/*p*-Xylene	4
o-Xylene	5
C_3-benzenes	6
C_4-benzenes	7
Naphthalene	8
Methylnaphthalenes	9
C_2-naphthalenes	10
n-Alkanes C_{11}–C_{27}	11–27
Farnesane	Fa
Pristane	Pr
Phytane	Ph

In experiment II, we were able to measure the maximum adsorption capacity of kaolinite because of the large oil reservoir that allowed each substance to have a maximum partial pressure in water during the experiment. The saturation level for aliphatic hydrocarbons in water fell below the detection limit (10 $\mu g/L$) (chromatogram B, Figure 1). The distribution and characterization of hydrocarbons on the solid surface are shown in chromatogram C (Figure 1) and the corresponding IR spectrum. In contrast to A, a drift to higher boiling hydrocarbons can be observed and is demonstrated by the increase of *n*-alkane traces (No. 22–27). This agrees with the Traube rule (*8*) that homologous series of organic substances adsorb more rapidly from water with increasing molecular weight. The IR measurement (C) shows further that straight-chain structures dominate the adsorbed hydrocarbon mixture because of the higher CH_2/CH_3 ratio compared to the IR spectrum A. The clay mineral contained about 200 mg hydrocarbons per kg dry material after 10 h exposure in experiment II. This hydrocarbon loading did not change even after 100 h exposure time.

In experiment III the water/oil interface was disrupted by the high stirring intensity (turbulence). Oil droplets were dispersed and came into contact with the suspended kaolinite. The resulting oil/particle agglomerates were still settlable. Chromatogram D (Figure 1) of the agglomerated oil, separated by centrifugation, is similar to that of the original No. 2 fuel oil mixture. Loss of highly volatile hydrocarbons at the beginning of the chromatogram is mainly due to evaporation during sample preparation (see experimental). The IR spectrum D does not differ from that of the original fuel oil A. Quantitative IR measurements showed an oil load on kaolinite of 20 g fuel oil per kg dry material after 20 h exposure time in experiment III. This value is a hundred times higher than the amount of hydrocarbons adsorbed out of solution.

Case Study. The analyses of the oil spill-contaminated ground water showed a fractionation pattern (Figure 3) similar to model experiment II. Because of the unknown history of the spill, we were not able to identify a distinct type of petroleum distillate that had been lost from tanks. We would assume a mixture of No. 2 fuel oil and gasoline type fractions. Their boiling ranges overlap and give indications for the type of oil only at the lower and upper end of the distribution. The more volatile components, dominated by isoparaffins and probably naphthenes (Figure 3a: gas chromatogram and IR spectrum), could have originated from gasoline-type distillates. The isoprenoids pristane (Pr) and phytane (Ph) are common constitutents in fuel oil. The absence of the corresponding *n*-alkanes (peaks 17 and 18) indicate a possible biological degradation of parts of the hydrocarbons (*9*).

The soluble aromatics (peaks 1–9) detected in the ground water (Figure 3b) are the same as those demonstrated by model experiment II. Biological degradation seems to be less probable for dissolved aromatics than for *n*-alkanes. The alkylated benzenes and naphthalenes are mobile in the ground water and therefore show a large spreading tendency. Analyses of the ground water in other nearby locations again showed these aromatic hydrocarbons, whereas no oil phase could be detected.

The adsorption of aliphatic hydrocarbons on soil in the zone with residual ground water saturation is shown in chromatogram 3c. High boiling hydrocarbons such as farnesane, pristane, phytane, and series of *n*-alkanes above C_{20} have been found. These results agree with those of model experiment II where oil was allowed to stay in contact with slowly moving

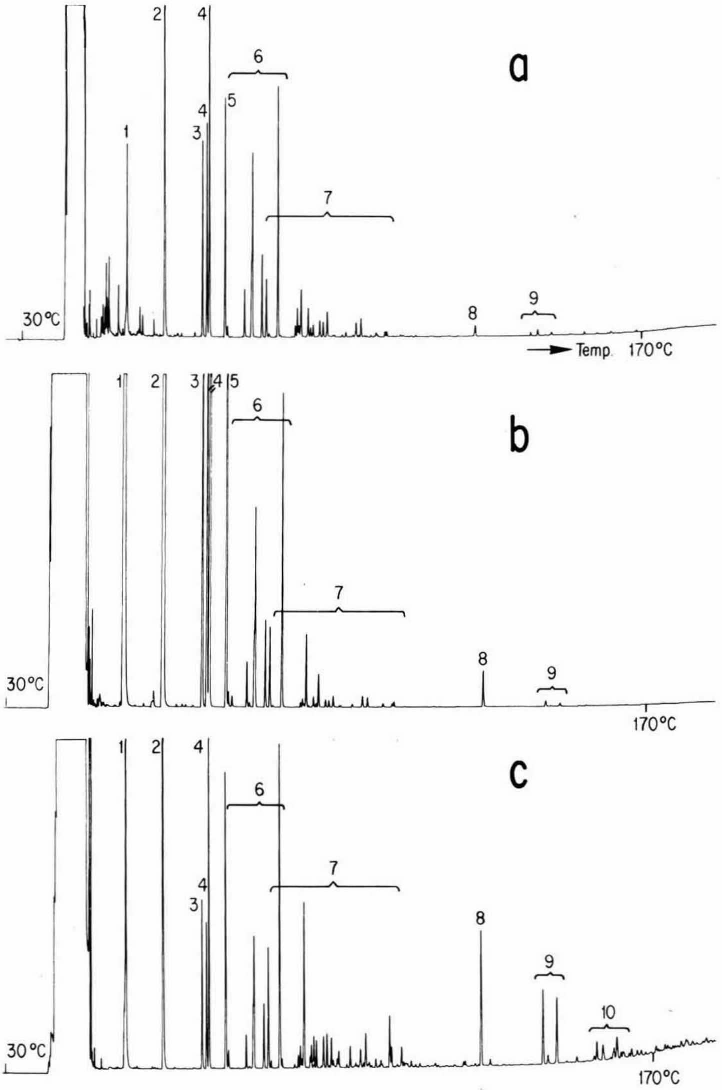

Figure 2. Low molecular aromatic hydrocarbons dissolved in water from petroleum products

Gas chromatographic analyses of (a) gasoline; (b) water, saturated with gasoline, hexane extract; (c) water, saturated with No. 2 fuel oil, hexane extract. For identification of GC peaks, refer to Table I. Column: Ucon HB coated glass capillary (56 m × 0.32 mm i.d.). Conditions: 1.5 μL, splitless, carrier gas pressure H_2, 8.8 psig, 3 °C/min, 25–180 °C

water containing mineral particulates. As approximated by the model, we found about 80 mg hydrocarbons per kg dry soil. The high pristane/n-heptadecane ratio indicates substantial biological degradation (*9*).

Discussion

The analyses of model experiments and the ground water pollution case have shown that mineral-oil products (No. 2 fuel oil) do physically fractionate after contact with water. The liquid phase and the solid phase control the distribution of oil in the water column by dissolution, suspension, adsorption, and agglomeration. These processes start from the beginning of oil–water contact and are easily detectable within the first hours. Under model conditions the saturation level for No. 2 fuel oil in water was reached after 15 min of contact. The amount of hydrocarbons adsorbed on kaolinite reached a constant value within the first 10 h. Suspended oil in water existed only during the intensive stirring period and acted as a transition state for agglomerates. Within the first 5 h the amount of oil (droplets) on settlable kaolinite particles in experiment III exceeded threefold the values of adsorptive loading. We therefore conclude that the fate of oil in the water column is strongly directed by fast dissolution, adsorption, dispersion, and agglomeration. These primary weathering processes are followed by sedimentation, biochemical alteration, etc.

The water-soluble aromatic hydrocarbons are ideal tracers for the study of pollution because of their mobility and relatively slow biological degradation (*10*). Therefore, it appears that one- and two-ring aromatic hydrocarbons are found in water samples due to dissolution of soluble petroleum fractions. Our observations are in good agreement with results from Boylan and Tripp (*11*); they found principally the same water-soluble fractions from two different crude oils (Kuwait

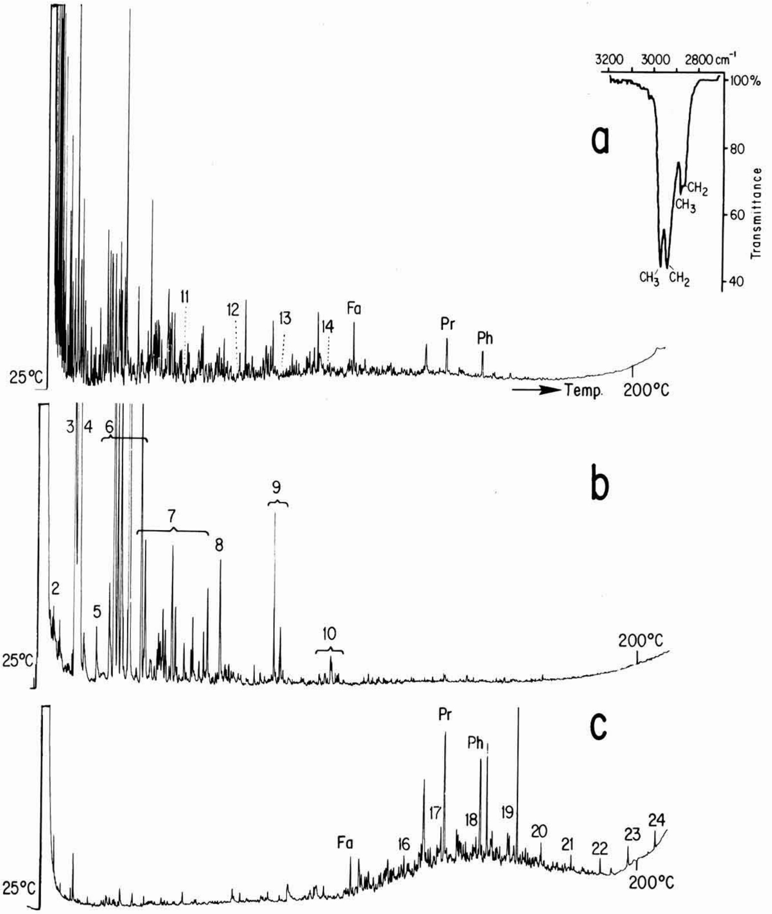

Figure 3. Gas chromatograms of hexane extracts from a ground water

(a) Oil film found at ground water level, 4 m below ground (1 g/L in hexane); (b) ground water, hexane extract; (c) soil, hexane extract. For identification of GC peaks, refer to Table I. Partial IR spectrum of oil film, see (a). Column: OV 101 coated glass capillary (50 m × 0.34 mm i.d.). Conditions: 1.5 μL, splitless, carrier gas pressure H_2, 7.3 psig, 3 °C/min

and Louisiana). Jeltes and Tonkelaar (*12*) have measured saturation levels of seven different oil products in water by gas chromatography. They found predominantly aromatic hydrocarbons in water extracts from No. 2 "diesoline" fuel oil (8 mg/L) and "super" gasoline (173 mg/L), which supports our observations. Brown and Huffman (*13*) have also found one- and two-ring aromatic hydrocarbons in subsurface seawaters of tanker routes, but in contrast to the observations of Boylan and Tripp (*11*) and our model experiments I and II, they concluded that their source could not be shipped petroleum with its one- to four-ring aromatic content. Harrison et al. (*14*) have determined evaporation rates for isopropylbenzene (cumene) and nonane by measuring the decreasing content of these substances in spilled crude oil. They attributed the faster loss rates of cumene to a higher solubility of nonane in the oil phase. Since evaporation from an oil slick is in competition with dissolution, our results would suggest that the rapid loss of cumene, compared to nonane, is mainly due to dissolution.

Kaolinite clay was used as a suspended solid for model experiments II and III. Meyers and Quinn (*15*) have compared the association of No. 2 fuel oil with different minerals in saline solutions at 25 °C and found that minerals derived from natural sediments behaved as the laboratory clay experiment predicted. Their value for kaolinite fuel oil associates (162 mg/kg dry kaolinite) is in good agreement with our value. Corresponding to this and the ground water pollution case study, a similar hydrocarbon distribution was also found in sediments from regions with known mineral oil discharge (*16*, *17*). Sutton and Calder (*18*) found a solubility decrease of *n*-paraffins in unfiltered seawater compared to distilled water. Since the seawater had been spiked with alkanes and afterward filtered through a 0.45-μm membrane before analyses, we suggest that their observation was due to adsorption of hydrocarbons on natural suspended solids rather than to salting effects. Such adsorptions would also explain the increasing discrepancy between measured and predicted salting out parameters (*18*) with increased chain length of *n*-paraffins.

From model experiment III and the discussion of Thüer and Stumm (*19*), we would predict that oil layers from spills are rapidly removed from flowing water (river, rough sea) by dispersion followed by agglomeration with particulates. These processes would promote the distribution of oil products in the water column by subsequent dissolution, adsorption, suspension, and sedimentation.

Since weathering processes do change the original oil mixture, we would not support the interpretation of oil pollution cases by simple comparison of waterborne oil with common oil products as suggested by Dell'Acqua et al. (*20*). Exclusively in the case of dispersion and agglomeration, we found almost the original paraffinic and naphthenic oil hydrocarbons in "water samples" as in oil.

Conclusions

The fractionation of the original hydrocarbon mixture in water into residual oil, dissolved, and solid surface-bound fractions has been demonstrated in the model experiments as well as in the ground water spill study.

From our observations we can conclude that dissolution, adsorption, and agglomeration play an important role as initial processes in weathering of oil in natural aquatic systems. These processes seem to be rapid and instrumental in the elimination of an oil phase because the fractionation pattern of oil components is not changed by biological activity in the examined ground water area. Dissolution of one- and two-ring aromatic hydrocarbons in water always occurs independent of the type of oil (fuel oil, gasoline, crude oil) and reaches a saturation level depending largely on the one- and two-ring aromatic content. These experiments permit distinction between two types of oil/solid associations. The *adsorption* of higher boiling hydrocarbons (mol wt > 250) is dependent on the character of the solid surface. In a water containing 20 mg/L suspended kaolinite, 4 μg hydrocarbons/liter could be adsorbed. From analysis of sediments (*3, 16, 17*), it would seem that the adsorbable amount of hydrocarbons in natural systems would be even higher. The *agglomeration* depends on the formation of dispersed oil droplets through water turbulence and interfacial tension of the oil, and plays a substantial role in oil sedimentation (*19*). The amount of oil agglomerates in a water containing 20-mg/L suspended kaolinite could reach 0.4 mg/L.

These experiments have shown that the understanding of the fate of oil in natural aquatic systems will depend largely on the use of proper sample preparation and on the subsequent analytical interpretation. For identification of petroleum products in case of water pollution, we no longer analyze water samples without prior separation of particulates. Finally the differentiation between dissolved, adsorbed, and colloidally dispersed oil is of great ecological importance, as suggested by Blumer et al. (*21*): The water-soluble fraction is responsible for acute toxicity, but the interruption of biological communication (chemotaxis) could possibly be caused by fractions adsorbed on particulates and accumulated in the sediments.

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CORRESPONDENCE

SIR: Calvert (*1*) has shown that $[O_3][NO]/[NO_2]$ from atmospheric measurements were generally higher than his estimates of k_1/k_3 in his analysis of LARPP operation 33 data. k_1 and k_3 are rate constants of the reactions that are primarily responsible for the establishment of a photostationary state ozone concentration in photochemical smog.

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

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

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

Calvert suggested this disagreement was the result of inhomogeneity of the air with respect to those species. Seinfeld (*2*) expanded this concept by defining a fictitious mixing fraction, η, which is defined at any point and may be characterized by a probability density function. Assuming that η was normally distributed, he then showed the effects of changing both the standard deviation of η and polluted parcel concentration on the photostationary state relationship. The approach taken by Seinfeld illustrates quite well the effects of inhomogeneity, but its usefulness for characterizing the atmosphere is somewhat limited since there is no single set of concentrations that represents background air (parcel 1), and no single set that represents recently polluted air (parcel 2). This letter is intended to set forth an alternate means of parameterizing the inhomogeneous character of ambient air and to show some of the properties of this parameterization.

When measurements are taken on board a helicopter, they are spatial composites, not pollutant concentrations at a single point. They are weighted averages over some finite distance. The average rates of reactions of order greater than one are not necessarily equal to the rates calculated from measured (averaged) concentrations. The main reason for the apparent deviations from photostationary state is believed to be that the reaction of O_3 and NO is slower than $k_3 \langle [O_3] \rangle \langle [NO] \rangle$, where $\langle \ \rangle$ represents a spatially averaged quantity.

At any point, the rate of change of ozone due to Reaction 3 is

$$\frac{-d[O_3]}{dt} = k_3[O_3][NO] \tag{1}$$

and the rate of change of the ozone averaged over some path is

$$\frac{-d\langle [O_3] \rangle}{dt} = k_3 \langle [O_3][NO] \rangle \tag{2}$$

We are not able to know $\langle [O_3][NO] \rangle$ directly from the LARPP data since we do not know point concentrations, $[O_3]$ and $[NO]$.

The point concentrations may be related to measured concentrations by

$$[O_3] = \langle [O_3] \rangle + [O_3]' \tag{3}$$

$$[NO] = \langle [NO] \rangle + [NO]' \tag{4}$$

where $[O_3]'$ and $[NO]'$ are the deviations of point concentrations from the measured values at any point along the path of the measurement such that $\langle [O_3]' \rangle$, 0 and $\langle [NO]' \rangle = 0$.

Substituting Equations 3 and 4 into 2 yields:

$$\begin{aligned} \frac{-d \langle [O_3] \rangle}{dt} &= k_3 \langle (\langle [O_3] \rangle + [O_3]')(\langle [NO] \rangle + [NO]') \rangle \\ &= \langle \langle [O_3] \rangle \langle [NO] \rangle \rangle + \langle \langle [O_3] \rangle [NO]' \rangle \\ &\quad + \langle \langle [NO] \rangle [O_3]' \rangle + \langle [O_3]' [NO]' \rangle \end{aligned} \tag{5}$$

Equation 5 may be simplified since

$$\langle \langle [O_3] \rangle \langle [NO] \rangle \rangle = \langle [O_3] \rangle \langle [NO] \rangle$$

$$\langle \langle [O_3] \rangle [NO]' \rangle = \langle [O_3] \rangle \langle [NO]' \rangle = 0$$

$$\langle \langle [NO] \rangle [O_3]' \rangle = \langle [NO] \rangle \langle [O_3]' \rangle = 0$$

Thus,

$$\frac{-d\langle [O_3] \rangle}{dt} = k_3 (\langle [O_3] \rangle \langle [NO] \rangle + \langle [O_3]'[NO]' \rangle) \tag{6}$$

The term $\langle [O_3]'[NO]' \rangle$ is the covariance of O_3 and NO along the path of measurement, as pointed out by Martinez (*3*). Equating the average rate of ozone consumption to the rate of ozone formation by Reactions 1 and 2 (and letting $\langle [O_3]'[NO]' \rangle = \text{cov}(O_3, NO)$) gives the photostationary state expression corrected for inhomogeneity:

$$\frac{k_1}{k_3} = \frac{\langle [O_3] \rangle \langle [NO] \rangle + \text{cov}(O_3, NO)}{\langle [NO_2] \rangle} \tag{7}$$

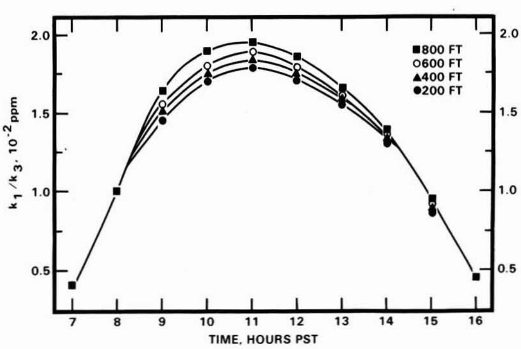

Figure 1. Theoretical estimates of k_1/k_3, the ratio of NO_2 photolysis rate constant to rate constant of NO–O_3 reaction at four altitudes for LARPP operation 33 trajectory

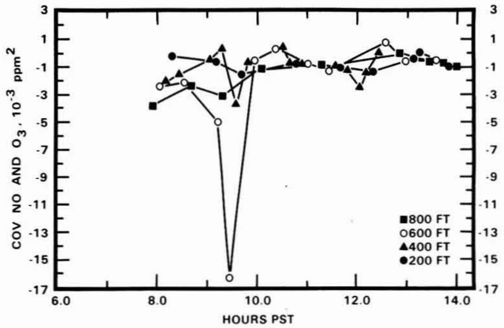

Figure 2. Estimated helicopter pattern average covariances of NO and O_3 for LARPP operation 33

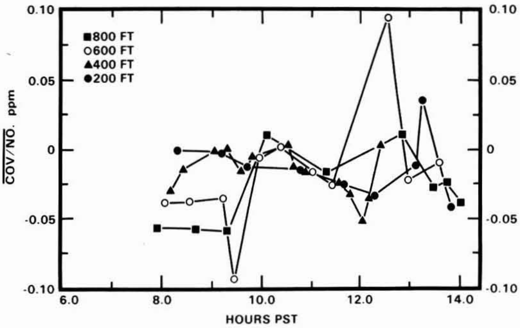

Figure 3. Estimated helicopter pattern average ratios of cov (NO, O_3) to measured NO concentrations for LARPP operation 33

For LARPP operation 33, k_1/k_3 was calculated at four altitude levels from 0700 to 1600 PST. The calculations were similar to Calvert's (*1*) with the following exceptions. (a) The estimated mixing depths and measured NO_2 concentrations along the LARPP trajectory were employed to correct irradiances for NO_2 absorption (b) Calvert performed computations at three arbitrary choices of albedo (0, 0.25, and 0.5); here, an albedo of 0.05 was used as suggested by Peterson (*4*). (c) Calculation of k_1 was carried through for the case of attenuation in the boundary layer and reflection at the ground, rather than Calvert's correction of k_1 through multiplication by the ratio of irradiances with and without attenuation and reflection. (d) Temperatures along the trajectory at appropriate altitude and times were used to calculate k_3. The resulting k_1/k_3 values are shown in Figure 1.

Based on the estimated k_1/k_3, the average cov (O_3, NO) were calculated for nearly all helicopter patterns, as shown in Figure 2. The most negative values occur in the morning in the inversion or just below the inversion. Also, the average ratios of the covariance to the NO concentration were calculated, as shown in Figure 3. The ratio is particularly interesting since it represents the contribution of inhomogeneity to the average (measured) ozone concentration as may be seen from Equation 7. Since the covariance term is negative for most measurements, the atmosphere is capable of maintaining a greater mean photostationary state ozone concentration than a homogeneous system with the same mean NO_2 to NO ratio and the same k_1/k_3.

Several other items should be noted here. (a) If the atmosphere were to be mixed to homogeneity, the average ozone would not be reduced by cov (O_3, NO)/$\langle [NO] \rangle$ since the average NO_2/NO would increase to partially compensate for the loss due to the mixing of O_3-rich parcels with NO-rich parcels.

(b) Since the boundary layer was being mixed throughout the day, which tended to reduce the absolute value of cov (O_3, NO), and the covariance within the boundary layer of the atmosphere was reasonably stationary (no time trend), it must be assumed that processes such as emission balanced the effects of mixing. Thus, it seems that cov (O_3, NO) was in stationary-state below the inversion base. (c) The estimates of covariance are accurate to the extent that the measurements equally weight the concentrations at all points along the measurement path. This may not present a great problem since the helicopters were moving at an air speed of about 31 m s^{-1}.

Through this approach it is possible to characterize the effects of inhomogeneity on photostationary-state through a single, estimable parameter. Inhomogeneity was shown to account for about 2 pphm of the ozone below the inversion base and somewhat more in the inversion. A more detailed discussion of the effects of inhomogeneity on measured photostationary-state ozone is presented by Feigley (*5*); the effects of mixing, oxidation of NO, and emission of NO_2 on the covariance of NO and O_3 were also considered.

Literature Cited

(1) Calvert, J. G., *Environ. Sci. Technol.* **10,** 248 (1976).
(2) Seinfeld, J. H., *ibid.,* **11,** 1218 (1977).
(3) Martinez, J. R., "Comments on Dynamics and Kinetics in Environmental Problems—Are They Separable?" Proc. of the Symp. on Chemical Aspects of Air Quality Modeling, L. D. Kornreich, Ed., University of North Carolina, Chapel Hill, N.C., Apr. 17–19, 1974.
(4) Peterson, J. T., "Calculated Actinic Fluxes (290–700 nm) for Air Pollution Photochemistry Applications", EPA–600/4-76-025, U.S. EPA, Research Triangle Park, N.C., 1976.
(5) Feigley, C. E., PhD dissertation, University of North Carolina, Chapel Hill, N.C., 1978.

Charles E. Feigley

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University of South Carolina
Columbia, S.C. 29208

ES&T INDUSTRY TRENDS

The Du Pont Co.'s Applied Technology section has formed a new management consultant service to provide in-depth compliance review of hazardous materials handling and shipping.

Sierra-Misco, Inc. (Berkeley, CA) resulted from a combination of Sierra Weather Instrument Corp., and Microchemical Specialties Co. It offers environmental products, including meteorological and air pollution instrumentation.

The Maxima Corp. has been established in Silver Spring, MD, as an information systems company specializing in marketing and training. Among its fields of endeavor are environment and energy resources. Design/operation of computer-based information is also offered.

The American Public Power Association (Washington, DC) has reaffirmed its support of the Clinch River (TN) liquid metal fast breeder, and called for provision of adequate funds for its continuation.

Autotrol Corp. (Milwaukee, WI) will provide Rotating Biological Contractors in support of municipal wastewater treatment (wwt) in Japan. Nippon Autotrol (Tokyo) will do the actual work.

Avco Corp. (Greenwich, CT) has established a Fossil Energy Technology Office at Everett, MA, to concentrate on developing new coal-using processes.

The Electric Power Research Institute (Palo Alto, CA) announced that 150 U.S. utilities are sponsoring 468 research projects in solar energy. Last year, there were 245 such projects.

Stanley Consultants, Inc. will prepare an environmental assessment study on proposed water/sewer improvements for Amman, capital of the Hashemite Kingdom of Jordan.

The Texas Utilities Company System has won the Edison Electric Institute's Edison Award for innovative development of lignite fuel resources for electricity generation.

Bahco Systems, Inc. (Atlanta, GA) has an order for two Compact Cell Fabric Filter units for coal-fired boiler emission control from Westpoint-Pepperell, Inc. (Opelika, AL).

Zimpro Inc. has a one-year renewable contract to supervise operations at the Wausau (WI) Sewage Treatment plant (9-mgd activated sludge).

Texas Instruments Inc. (Dallas) will make a detailed analysis of the impact of a proposed coal-fired electric generating complex near Colstrip, MT, under a $471 657 contract with the Bonneville Power Administration.

AB Svenska Fläktfabriken announced that its resource recovery system concept will be used in the first commercial resource recovery plant for Sweden. Startup, at Stockholm, is scheduled for 1980.

Deluxe Laboratories (Hollywood, CA) is marketing a patented ion-exchange technique for removing impurities from photographic washwaters. Up to 65% of water and gas-heating resources can be saved, Deluxe says.

Varian Associates (Palo Alto, CA) has two Dept. of Energy (DOE) contracts to improve direct solar-to-electricity conversion, and to design/build an experimental solar power unit for utility use.

Mitsubishi Heavy Industries, Ltd. (Tokyo, Japan) has completed advanced wwt facilities for a large foundry west of Kobe. It will use Dow Chemical's reverse osmosis permeator module to treat 300 m^3/d. Recycling for nonpotable use is possible.

Progressive Equipment Co. (Bloomfield, CT) will provide a Thermal Reductor System to United Technologies to dispose of plant waste and furnish supplementary steam from waste heat.

Lurgi (W. Germany) processing concepts will be used to treat sludge for the City of Frankfurt-am-Main. About 130 m^3/h will be processed. The Lurgi concept "won a competition," according to the company.

Natural Energy Corp. (Washington, DC) has received Dept. of Housing and Urban Development (HUD) approval for its most economical line of collectors for solar hot water heating for 10 northeastern states.

FMC Corp. will spend more than $7 million to reduce dust emissions "significantly" from its elemental phosphorus plant at Pocatello, ID.

Midland-Ross Corp. (Cleveland, OH) has completed installation of two furnace systems for deactivating explosives and detoxifying chemical munitions in an environmentally safe manner, for the U.S. Army at Tooele, UT.

Royco Instruments Inc. (Menlo Park, CA) has announced new, advanced concepts and hardware for particle monitoring and gas analysis. The key is sophisticated new uses of existing computer facilities.

The American Envirodyne Division of Pettibone Corp. (Chicago) is installing an odor and gaseous contaminant abatement system at the U.S. Pipe & Foundry Co. (Chattanooga, TN).

Wheelabrator-Frye, Inc. will provide two electrostatic precipitators, worth $6 million, to Toledo Edison Co., at Oregon, OH. They are designed to clean 460 000 acfm at 320 °F, with a 99.5% efficiency.

Research-Cottrell, Inc. will design/construct an electrostatic precipitator to remove fly ash from 248 000 acfm of gas at the paper mill of Chesapeake Corp. of Virginia, at West Point, VA. Efficiency 99.2%; 350 °F.

C-E Bauer (Springfield, OH) has delivered 60 "Hydrasieve" screens to the Western Regional Waste Treatment Facility under construction at Dayton, OH. C-E Bauer is an operating unit of Combustion Engineering, Inc.

Andersen Samplers Inc. (Atlanta, GA) was formed through the sale of the sampler division of Andersen 2000 Inc. to the former president of Andersen 2000. Among the products are environmental samplers.

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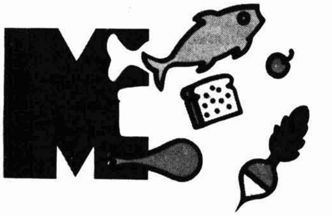

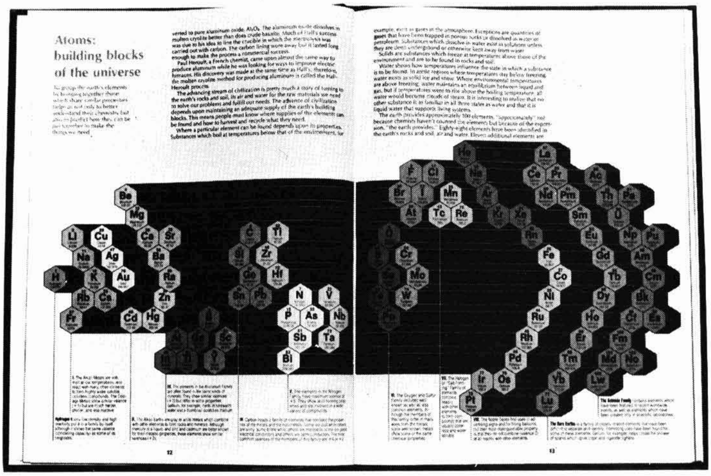

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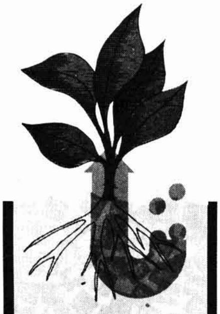

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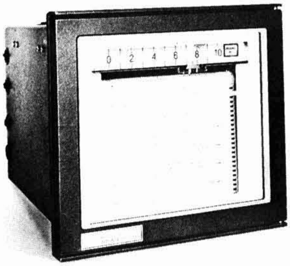
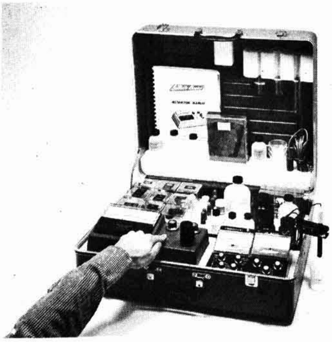


Strip-chart recorders
Recorders can be supplied with one or two pens and with disposable ink cartridges or thermal marking systems. Chart widths are 165 mm calibrated or 250 mm calibrated, depending on model. Leeds & Northrup **101**

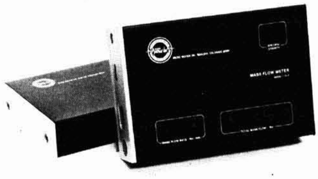
Rotary prefilter
This self-cleaning prefilter was designed as a "roughing filter" in air pollution control systems controlling the release of large particles. Oil for cleaning the filter is recirculated; the cleaning cycle is timed and can be started manually or automatically. United Air Specialists **103**



Soil colorimeter
This battery-operated system for analyzing soil nutrition factors includes reagent systems for measuring nitrate, phosphate and sulfate; an analog pH meter; and a conductivity meter for measuring dissolved salts. LaMotte Chemical **102**

Flocculant
This new liquid flocculant is designed to replace lime and metal salts formerly used for flocculation and dewatering of solids in industrial and municipal wastes. Applications include pulp and paper mill primary and secondary clarification and filter press dewatering. Nalco Chemical **105**

Remote wind sensor
The sensor determines wind velocity by detecting the doppler shift in a scattered acoustic signal. The sensor is a portable and ground-level system. Depending on the model, a continuous record of the vector wind profile up to 200 or 500 m is possible. Xonics **106**



Flow meter
Directly measures the mass flow rate of any liquid, multiple-phase systems, pulsating flows and slurries by measuring weight rather than volume of flowing liquids; temperature, viscosity and density need not be measured. The unit has no moving parts. Micro Motion **104**

Head-space sampler for gc
Analyzes, semiautomatically, those volatile components present in the gas phase above the sample; the nonvolatile residue never reaches the gas chromatograph injection system. Samples can be either solid or liquids. The sampler is thermostatically controlled to better than 0.1 °C over the temperature range 40–190 °C. Injection time is automatically controlled to 5 s. Perkin-Elmer **116**

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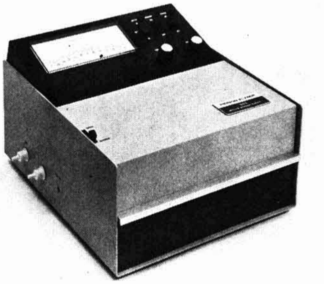
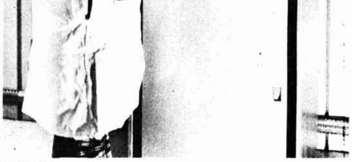


Mercury analyzer
Mercury is measured by atomic absorption. Flow of the pump is regulated by a screwdriver adjust on the side of the instrument; calibration is purported to be simple and stable; the recorder output is standard. Sensitivity is 0.01 μg on a scale of 0–0.28 μg full scale. Perkin-Elmer **108**

Portable pH meter
This model, Type 400, permits normal and expanded scale operation for pH and ion-specific measurements. Expanded pH range is 0–1.4. Sensitivity is 0.05 pH normal and 0.005 expanded. Accuracy is 0.005 pH expanded. Chemtrix **120**



TOC analyzer
Continuously records total organic carbon or total carbon in process or wastewater streams. The system features a high temperature, noncatalytic, fixed-bed reactor that eliminates catalytic poisoning. A sparge system removes inorganic carbon when TOC analysis is being performed. Seiscor **112**

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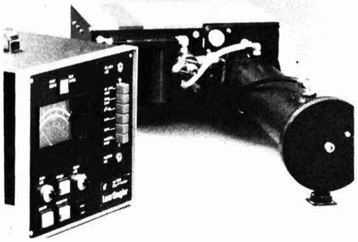


SO_2 monitor
By using the technique of gas measurement—second-derivative absorption spectroscopy—trace concentrations (down to 0.005 ppm) of sulfur dioxide in air can be measured. The monitor measures SO_2 directly, in real time, without the need for sampling systems. Lear Siegler **133**

Turbidimeter
The model provides rapid nephelometric tests of water, sewage and industrial process fluids. The instrument's sensitivity is 0.05 NTU (nephelometric turbidity units) in the 0–1 range. Hellige **123**

Boiler blowdown controller
The boiler system control maintains optimum boiler water conductivity and chemical treatment levels in steam-generating systems; the controller minimizes loss of water and energy—concomitants of excessive blowdown. Dexter Corp./Mogul Division **124**

Digital thermometer
This portable thermometer is designed for use under severe environmental conditions; precision is ±0.1 °C. Readout is in either degrees F or C. Temperature range of the unit is −100 to +200 °C (−150 to +400 °F). Doric Scientific **125**

Membrane filter bags
The filter matrix of these bags permits particulate filtration on the surface of the membrane, not through the cake buildup that usually occurs on filter felts and fabrics. Particulate release and emission control characteristics of these bags permit maximum air flow with minimum pressure drop; bag life is extended. W. L. Gore & Associates **126**

Hazardous wastes detoxifier
The apparatus detoxifies persistent organic wastes by treating them in a microwave plasma chamber. The unit will handle materials at a rate of about 10–30 lb/h. On-site decomposition studies by a portable unit will be conducted. Lockheed Missiles & Space **127**

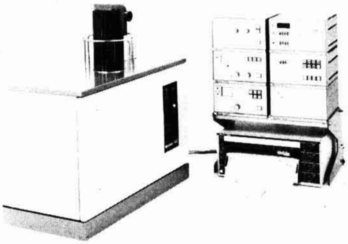
Air pollution "outfit"
The system consists of a battery-operated air sampling pump and colorimetric tests for 14 air quality parameters, including ammonia, cadmium, carbon monoxide, hydrogen sulfide, nitrogen dioxide, ozone, and sulfur dioxide. LaMotte Chemicals Products **128**

Programmable multipoint sequencer
The unit can perform rapid analysis of gas samples from 2–20 sources by switching sequentially the sample source into a single analyzer. In combination with the continuous gas analyzer, the system can analyze a sample point every 15 s. HNU Systems **129**

Solar heat-transfer fluid
Characteristics of this fluid include low-freeze point, superior heat-transfer capability and corrosion inhibition. The fluid permits the use of dissimilar metals in the construction of solar systems. It is available in 6-gal pails and 55-gal drums. Drew Chemical **130**

Personal sampler
This lightweight, battery-operated unit is designed to collect samples of airborne dusts, organic vapors, toxic metals, asbestos, and a variety of gases found in the workplace. Interchangeable sampling heads (options) permit one vaccum pump to sample a range of respirable air pollutants. Research Applicance Co. **131**

Digital data collector
The collector has its own built-in clock and formatting logic. Data are broken down by the printer into numbered blocks of numerical records that can be searched for rapidly. Precision Digital **132**



Thermal analyzer
This microprocessor-controlled instrument can conduct heat-flow differential scanning calorimetry in combination with thermogravimetry. The unit can be connected to a variety of electronic data processing equipment. Mettler Instrument **138**

Digital data recorder
It has a storage capacity of up to 64 × 10^{10} bits, and presents a histogram analysis of stored data for CRT display or a hard-copy listing, in seconds. Sun Systems **114**

Organic vapor dosimeter
The dosimeter meets the monitoring requirements of the OSHA emergency temporary standard for acrylonitrile. It provides, according to the manufacturer, accurate monitoring at concentrations of less than 1 ppm. Abcor **115**

Subminiature recorder
This portable, four-channel recorder, gathers information, unattended, for periods of up to 1 week. The recorder weighs less than 1 lb and measures 4 in. × 3⅛ in. × 1.5 in. The unit is useful in both industrial and environmental applications. Ambulatory Monitoring **122**

FT-GC/IR
These Fourier transform spectrometers are equipped with a gas chromatography/infrared accessory for the specific analysis of complex mixtures. The FT spectrometer with GC/IR will interface to a GC to achieve functional group identification. Sensitivity is better than 10 ng in the trapped mode. Digilab **119**

Compactor
This electrically operated unit can be used for the disposal of hazardous, low-level radioactive wastes. S&G Enterprises **121**

Plastic-barrel electrode
Performs reliably in general applications such as checking wastewater and water treatment processes or, in field applications, in checking streams and rivers. The electrode exhibits low drift and fast response over a temperature range of 10–80 °C. Corning Glass Works **117**

Chlorine residual analyzer
The unit, an amperometric instrument, is designed to analyze continuously free or total chlorine residual in water; the wall-mounted recorder provides a permanent record of the residual. Capital Controls **118**

Cascade impactor
The instrument is a 10-stage piezoelectric particle cascade unit for the measurement and analysis of aerosol particles over a size range of 0.05–25 µm. The instrument can be used in the laboratory or in the field. California Measurements **111**

ES&T LITERATURE

Pyrolysis. "Reactor" No. 39 explains how pyrolysis—"Pyro-Processing"—originally used to roast iron ore can be used to solve sludge disposal problems. Case histories are given. Zimpro **151**

Humidity monitoring. Bulletin 3-120 fully explains the Model 220 Dew Point and Temperature Monitoring System. Accuracy is within 0.4 °C. Self-standardizing; has alarm built in. EG&G **152**

Sewer improvement. Case history tells how drastic sewer flow reduction could be effected to a town's treatment plant by grouting the entire sewer system. National Power Rodding Corp. **153**

Water quality. Bulletin 5500 describes three water-quality monitoring instruments that can handle more than 20 parameters. Wet chemistry provision for handling complex samples. Gam Rad, Inc. **154**

Air cleanup. Catalog No. 097710 lists a broad line of standardized component parts for air pollution control systems. Users can build own dust control and other systems. The Kirk & Blum Manufacturing Co. **155**

Clean air pumps. Catalog provides information on DIA-PUMP clean air pumps for industry. Chemical/petrochemical applications; environmental and laboratory sampling. Air Control, Inc. **156**

Temperature controller. Data bulletin describes Model 919 high-resolution digital-setpoint temperature controller. Eurotherm Corp. **157**

Stack gas analysis. Application brochure describes "Spherocarb," a spherical, non-friable carbon molecular sieve that can separate permanent, stack, and light hydrocarbon gases for pollution analysis, and other purposes. The Foxboro Co. **158**

Absorbers and scrubbers. Data sheets tell about SO_2 scrubbing with ammonia, with subsequent fertilizer production, and absorbing SO_2 with soda ash. As much as 304 000 acfm. Swemco Inc. **159**

Desalination. Brochure describes company's approach to desalination of water, and capabilities in that field. Ebasco Services, Inc. **160**

Phenol removal. Form H-6001 explains how potassium permanganate in a waste stream converts phenol into non-toxic compounds permissible in effluent water. Cost advantages are listed. Carus Chemical Co. **161**

Power transmission. Leaflet, "Transmission Systems", describes the company's experience in their planning/design, including environmental studies and reports. Harza Engineering Co. **162**

Spray booth controls. Bulletin PC-4 reviews ways to reduce paint-spray booth emissions with increased efficiency and decreased cost. Improving waste treatment plant efficiencies is also covered. Nalco Chemical Co. **163**

Chloropesticides. Application Note AN 176-22 tells how best to analyze chloropesticides and PCB's in food, particularly cheese. Hewlett-Packard **164**

Lagoon sizing. Bulletin 320 tells how to size lagoons for aeration for super-primary domestic wastewater treatment for population of 750–500 000. Data for 10, 15, and 20-ft depths. Hinde Engineering Co. **165**

Plume surveying. Company journal, "Environmental Measurements," gives methodology for complete quantification of emissions from stacks, and describes air monitoring at power plants in Maryland. Environmental Measurements, Inc. **166**

Fluoride removal. Brochure tells how a control system (patent pending) will reduce drinking water/wastewater fluoride levels to EPA standard of 1 mg/L, and even much less. Andco Environmental Processes, Inc. **167**

Seepage control. Brochure tells how bentonite can seal ponds, lakes, irrigation ditches, canals, dams, and the like. There is 100% sealing action, according to the company. Federal Bentonite **168**

Remote sensing. Catalog lists largest (in U.S.) collection of instructional aids for teaching earth sciences and remote sensing. Wide use. Pilot Rock, Inc. **169**

Membrane filters. Bulletin helps to select the exact membrane needed for a given application and effective filtration. A chemical compatibility chart is provided. Schleicher & Schuell, Inc. **170**

Slurry control. Bulletin 4000 tells how to monitor and control industrial slurry densities for a wide range of suspended solids in liquids. National Sonics Division, Envirotech Corp. **171**

Employee protection. Bulletin 5000-01 lists numerous products for personal protection, environmental surveillance, hazard control, and emergency care in the workplace. Mine Safety Appliances Co. **172**

Aeration. Brochure, "Dome Diffuser Aeration System," describes an activated sludge process. Norton Co. **173**

Analysis preparation. Literature review gives over 100 references for 50 application areas for "Uniseal" liquid pressure equipment for preparation of inorganic and organic materials for analysis. Columbia Organic Chemicals Co., Inc. **174**

Steel industry apc. Brochure discusses specific installation and results of air pollution control (apc) equipment at three steel mills. "Bahco Air Treatment—Solving Environmental Problems for the Steel Industry" is the title. Bahco Systems, Inc. **175**

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Evaporative gas cooling. Brochure describes gas cooling for municipal waste incinerators, cement plants, lime kilns, copper smelters, and many other facilities. Sonic Development Corp. **176**

Filter precoat. Bulletin WC-151 describes high-quality filter precoat materials as important aids for suspended solids removal and, in some cases, ion exchange. Ecodyne Corp. **177**

Spectrophotometers. Series of brochures and reports describes the "57-Series" of high-performance spectrophotometers for precise quantitative analysis. One offers turbid sampling ability. Perkin-Elmer Corp. **178**

Radioactive mineral finding. Brochure describes geophysical survey capability for reliable detection/location of radioactive minerals. Mapping software is also available. Texas Instruments Inc. **179**

Oily wastewater. Bulletin PC-5 will increase understanding of how problems of oily wastewater arise, and how it is treated. Oil reuse possibilities are discussed. Nalco Chemical Co. **180**

Pumps. Catalog describes 20 plunger and piston pumps for petroleum and industrial use. Another catalog offers pumps for the well servicing industry. Gaso Pumps, Inc. **181**

Technical books. Company offers price list and titles for technical books featuring chemical analysis, organic/inorganic chemistry, and related subjects. Sadtler Research Laboratories, Inc. **182**

Water disinfection. Brochure, "Disinfect with ESCOZONE" discusses advantages of ozone over chlorine for making water safe, especially for bottled water, beverage water, fish hatcheries, and food processing. TII Industries, Inc. **183**

Corrosion prevention. Paper explains how organic amines can neutralize acidity, thus preventing corrosion in boiler systems. Title is, "Selection of Neutralizing Amines for Condensate Systems." Wright Chemical Corp. **184**

Analysis. Catalog announces the availability of equipment and supplies for chromatographic analysis—gas and liquid. Data handling is also included. Varian **185**

Filter presses. Publication 315-181 describes fully automated diaphragm filter presses for dewatering sludge. Filtration cycle times is 15–30 min. Envirex **186**

Sludge dewatering. Brochure tells about unique dewatering system with low head layout and no need for a vertical section. Cake can be discharged to incinerators. Solids sometimes as high as 44%. Ashbrook-Simon-Hartley **188**

Pollution control bacteria. Case studies show how mutant bacteria can speed recovery of lagoons after aerator breakdowns, and after spillages of toxic chemicals. Polybac Corp. **189**

FGD cost cutting. Article, "Minimizing Operating Costs of Lime/Limestone FGD Systems explains importance of design and operating conditions to successful flue gas desulfurization (FGD). Cost factors are identified. Peabody Process Systems **190**

Gas cleaning. Brochure JV-1 describes new dry SO_2 and particulate removal system for cleaning boiler flue gas. Low capital costs and simple operation; flow diagram is included. Wheelabrator-Frye **191**

Particle-size analysis. Information is available concerning particle-size analysis systems, including MICROTRAC Monitor for dry-powder processes. Leeds & Northrup **192**

Water analysis. Brochure discusses services offered by the company's water analysis laboratories, which serve individuals, government, and industry. The Resource Sciences Corp. **193**

Oil in ground water. Brochure tells about the "first and only" method devised to remove infiltrated hydrocarbon wastes from the water table and surrounding soil. The key is bioreclamation. Suntech **194**

Sludge treatment. "Info-Pak" describes versatility and cost-effectiveness of the PURIFAX sludge treatment processes of rapid chemical oxidation. Advantages and applications are listed in detail. B I F **195**

2,4-D herbicide assay. "Columns", Vol. 3, No. 3, explains how problems in assaying 2,4-D herbicide products are solved. Chromatography is the key. Whatman, Inc. **196**

Cement industry apc. Bulletin ES-1-261 describes capabilities in air pollution control (apc) for the cement industry in all aspects. American Air Filter Co., Inc. **197**

Effluent toxicity. "Methods for Measuring the Acute Toxicity of Effluents to Aquatic Organisms". EPA-600/4-78-012. Environmental Monitoring and Support Laboratory, U.S. EPA, Cincinnati, OH 45268 (write direct).

Oil-polluted groundwater. Best ways to collect oil-polluted groundwater. CONCAWE Report 13/77, December 1977. CONCAWE, Van Hogenhoucklaan 60, The Hague 2018, The Netherlands (write direct).

Oil toxicity. Booklet sets forth properties of fuel oils that might harm the marine environment. "Chemical and Physical Properties of Refined Petroleum Products". Office of Public Affairs, NOAA, Boulder, CO 80302 (write direct).

Power plant sludges. Report FP-671, "State of the Art of FGD Sludge Fixation" (RP-786-1). Research Reports Center, EPRI, P.O. Box 10090, Palo Alto, CA 94303 (write direct).

"The Testing World." Environmental articles include soil testing, mobile laboratories, and the like. Issue No. 27. Soiltest, Inc., 2205 Lee Street, Evanston, IL 60202 (write direct).

Land disposal and the law. "Land Application of Wastewater and State Water Law: An Overview," Vol. I. Limited number of copies available. Robert S. Kerr Environmental Research Laboratory, U.S. EPA, Ada, OK 74820 (write direct).

Pollution monitoring. "Quality Control for Environmental Measurements Using Gamma-Ray Spectrometry." Environmental Monitoring and Support Laboratory, U.S. EPA, Las Vegas, NV 89114 (write direct).

The USGS. "A Guide to Obtaining Information from the USGS 1978." Geological Survey Circular 777. U.S. Geological Survey, Branch of Distribution, 1200 South Eads St., Arlington, VA 22202 (write direct).

Oil shale. "Oil Shale and the Environment." EPA-600/9-77-033. Research and Development Technical Information Staff, U.S. EPA, Cincinnati, OH 45268 (write direct).

ES&T BOOKS

Chemicals from Pulp and Wood Waste: Production and Applications. G. T. Maloney. xi + 289 pages. Noyes Data Corp., Mill Rd., at Grand Ave., Park Ridge, NJ 07656. 1978. $42, hard cover.

Pulp and wood wastes are potentially rich chemical sources. For instance, one can make methanol, ethanol, activated carbon, and many other products. Here, the latest patents, company and government research, and commercial utilization is explained in detail.

Topics and Terms in Environmental Problems. John R. Holum. x + 729 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1978. $24, hard cover.

What is acid mine drainage? A breeder reactor? NO_x? This book exhaustively defines 239 main terms from acaricide to weathering, and, where appropriate, presents technical discussions of these subjects.

Electrotechnology. Volume 1, Wastewater Treatment and Separation Methods. Robert P. Ouellette et al., Eds. xiii + 609 pages. Ann Arbor Sciences Publishers Inc., P.O. Box 1425, Ann Arbor, MI 48106. 1978. $39.95, hard cover.

Electrotechnology is widely used in wastewater treatment and separation, and this book presents a state-of-the-art survey of these uses. Major techniques discussed include reverse osmosis, ultrafiltration, electrodialysis, and similar advanced techniques. Materials recovery, ozone, gamma ray treatment, and many other pertinent topics are also covered.

National Coal Utilization Assessment. Compiled by John B. Burnham. vii + 275 pages. National Technical Information Center, 5285 Port Royal Road, Springfield, VA 22151. 1978. $10.25, paper.

This assessment was made by Battelle Memorial Institute for the U.S. Department of Energy. Among other considerations, it looks closely at air quality, ecosystem impact, land use, health effects, and many related problems.

Water: The Universal Solvent. Frank N. Kemmer. 155 pages. The Universal Solvent, Nalco Chemical Co., 2901 Butterfield Road, Oak Brook, IL 60521. 1978. $5, paper.

This timely book examines many aspects of water. Among topics covered are water chemistry, analysis, contaminants and their treatment, sampling, and types of water use. Much "how to" information is presented.

Environmental Mediation: An Effective Alternative? 55 pages. RESOLVE, 360 Bryant St., Palo Alto, CA 94301. 1978. $3, paper.

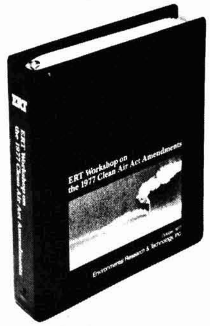
Much environmental activity in the U.S. has been of an adversary nature, involving court cases. Could this situation not be mitigated through mediation? Could better communications between industry be established? Perhaps so, but it will take much effort. A start in that direction has been made through a conference on this subject, presented in this book, and held at Reston, Va., in January. The foreword is by Russell Train and John Busterud. Proposed approaches to mediation are presented.

Energy Technology V—Challenges to Technology. 1000 pages. Government Institutes, Inc., 4733 Bethesda Ave., Washington, DC 20014. 1978. $38.

This work covers the 5th Energy Technology Conference, held in February at Washington, DC. It contains papers concerning coal, solar, nuclear, conservation, environmental controls, new technologies, and numerous other pertinent topics.

Toxic Substances Control Sourcebook. The Center for Compliance Information, Aspen Systems Corp., 20010 Century Blvd., Germantown, MD 20767. 1978. $59.50, hard cover.

This large work offers complete coverage of toxic substances, and what requirements concerning them are, and are expected. Examples of topics include vinyl chloride, all applicable laws (federal), management, testing, asbestos, impacts on industry, and other such considerations. Reporting and registration requirements are also discussed.



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Comprising 32 articles reprinted from Volumes 5–8, *Accounts of Chemical Research*

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This new collection of selected survey articles continues the coverage of the field started by Volume I. It will be extremely valuable for seminar and reference use by students, research chemists, and those seeking an introduction to the state of the art.

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To provide the fullest, most up-to-date information on the subject, most of the authors have contributed a short addendum to their papers.

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Energy: A Guide to Organizations and Information Resources in the United States. 221 pages. Public Affairs Clearinghouse, P.O. Box 30, Claremont, CA 91711. 1978. $20.

This is an update of "Energy: A Guide", published in 1974. It is organized by subject, such as coal, water power, environmental impacts, and so on. Detailed coverage of government energy agencies is given, and many programs are described. Energy agencies of state and local governments, and trade, professional and citizen's groups are also enumerated and described.

A Dictionary of the Environment. Michael Allaby, Ed. 532 pages. Van Nostrand Reinhold, 135 W. 50th St., New York, NY 10020. 1978. $17.95.

This book defines and explains some 6000 words and phrases used in all environment-related sciences. It was researched and compiled by an interdisciplinary panel of distinguished specialists.

The Synthetic Fuels Data Handbook. Cameron Engineers, Inc., 1315 South Clarkson St., Denver, CO 80210. 1978. $85.

Oil shale. Liquids from coal. Oil from tar sands. *In situ* recovery methods. These and many other related subjects are dealt with in this book, which is published by a firm with years of experience in these fields.

Cancer and the Worker. 77 pages. New York Academy of Sciences, 2 East 63rd St., New York, NY 10021. 1978. $2.

This book was written to provide information to workers and plant managers about what is known—and not known—about cancer risks in the workplace.

Part C: Environmental Health Sciences (Journal of Environmental Science and Health), Volume C13, Number 1. Robert J. Rubin, Ed. 4 issues per volume. Marcel Dekker, Inc., 270 Madison Ave., New York, NY 10016. 1978. $44/volume; add $5.40 for postage outside U.S.

This journal deals with biological effects of natural and synthetic chemicals being added to the human environment daily. The focus is generally on toxicology, and more specifically on carcinogenesis, mutagenesis, and teratogenesis. Guides for regulatory decisions needed to protect public health are also discussed.

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Dr. Maynard is an authority on patents, having been Chairman of the American Chemical Society Committee on Patent Matters and Division Head of Patents and Technical Information for E.I. duPont de Nemours and Co. He has drawn on over 20 year's experience in the field of patents to produce this clearly written, informative guide for the inventor.

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MEETINGS

July 23–28 Henniker, N.H.
Economic Impact of Energy Conservation Measures. The Engineering Foundation

Write: The Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

July 23–28 Cambridge, Mass.
International User's Conference on Computer Mapping Software and Data Bases. Harvard University's Laboratory for Computer Graphics and Spatial Analysis

Computer mapping in environmental and energy applications will be discussed. *Write:* Peggy Kilburn, Center for Management Research, 850 Boylston St., Chestnut Hill, Mass. 02167

July 24–28 Chicago, Ill.
Hydrogen Production and Utilization for Energy Distribution. Institute of Gas Technology (IGT)

Write: Ms. Kathy Fisher, IGT, 3424 S. State St., Chicago, Ill. 60616

July 24–28 Denver, Colo.
1st International Symposium on the Transfer and Utilization of Particulate Control Technology. EPA

Write: Fred P. Venditti, program chairman, Denver Research Institute, University of Denver, P.O. Box 10127, Denver, Colo. 80208

July 31–August 4 Ann Arbor, Mich.
Resource Recovery from Municipal Solid Waste. University of Michigan

Write: Continuing Engineering Education, University of Michigan/College of Engineering, 300 Chrysler Center, North Campus, Ann Arbor, Mich. 48109

August 1–4 Denver, Colo.
27th Annual Denver Conference on Applications of X-Ray Analysis. University of Denver and others

Write: Denver Research Institute, University of Denver, Denver, Colo. 80208

August 7–9 Washington, D.C.
1978 NIH Annual Symposium/Washington-National Instrumentation Exposition. National Institutes of Health, American Chemical Society and others

Write: Richard L. Greene, Trade Associates, Inc., 5454 Wisconsin Ave., N.W., Suite 1025, Washington, D.C. 20015

August 13–18 Henniker, N.H.
Waste Heat Utilization. The Engineering Foundation

Write: The Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

August 14–16 Gaithersburg, Md.
5th International Symposium on Controlled Release of Bioactive Materials. National Bureau of Standards

Among the topics to be discussed will be those on aquatic and terrestrial pesticides. *Write:* Ronald B. Johnson, Materials Building, Room B-348, National Bureau of Standards, Washington, D.C. 20234

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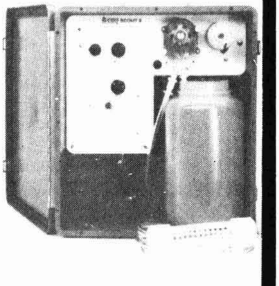

Fourth Joint Conference on Sensing of Environmental Pollutants

Conference Proceedings 1977

General Chairman:
Herbert G. Stewart, Jr., Special Assistant, Office of the Director, U.S. Geological Survey, Reston, Virginia

An intersociety conference hosted by the American Chemical Society.

Because of the importance of communication among those involved in the scientific, engineering, governmental and public aspects of environmental problems, the technical sessions for the conference featured information exchange on the interrelationship of sensing methodologies and the definition and evaluation of the consequences of man's interaction with his environment. The objective was to create dialogues among those who set standards, those who perform measurements, and the scientists and engineers who develop measurement and design instruments.

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August 14–16 Rockville, Md.
Coastal Mapping Symposium. American Society of Photogrammetry

Write: Peter N. Gibson, chairman, publicity committee, 11624 Bedford Court, Germantown, Md. 20767

August 14–17 Washington, D.C.
Energy from Biomass and Wastes. Institute of Gas Technology

Write: Ms. Kathy Fisher, Institute of Gas Technology, 3424 S. State St., Chicago, Ill. 60616

August 20–25 Geneva, N.Y.
Symposium for Innovation in Measurement Science. Instrument Society of America

There will be a session on environmental monitoring. *Write:* Peter Vestal, Instrument Society of America, 400 Stanwix St., Pittsburgh, Pa. 15222

August 20–25 San Diego, Calif.
Intersociety Energy Conversion Conference. American Society for Testing and Materials and the Society for Automotive Engineering

Write: Peter Fromme, manager, power department, ASME, 345 E. 47th St., New York, N.Y. 10017

August 21–25 Colorado Springs, Colo.
Energy Modeling and Net Energy Analysis. Institute of Gas Technology (IGT)

Write: Ms. Kathy Fisher, IGT, 3424 S. State St., Chicago, Ill. 60616

August 22–24 Minneapolis, Minn.
National Conference on Lake Restoration. U.S. EPA

Write: Susan Armstrong, Battelle's Columbus Laboratories, 505 King Ave., Columbus, Ohio 43201

September 9–13 Corpus Christi, Tex.
1978 Uranium Mining Seminar. American Institute of Mining, Metallurgical and Petroleum Engineers

Write: Glen R. Davis, South Texas Minerals Section, AIME, 1400 Bank and Trust Tower, B & T Box 175, Corpus Christi, Tex. 78477

September 10–13 Washington, D.C.
4th International Symposium on Contamination Control. International Committee of Contamination Control Societies

Write: Mrs. Betty Peterson, executive director, Institute of Environmental Sciences, 940 E. Northwest Highway, Mt. Prospect, Ill. 60056

September 10–12 Madison, Wis.
First Annual Conference of Applied Research and Practice on Municipal and Industrial Waste. Saint Croix Research

Write: Conference Committee, Box 5571, Madison, Wis. 53705

Courses

July 24–28 Nashville, Tenn.
Pollution Evaluation: Meeting EPA and OSHA Standards through IR and GC Techniques. Fisk Institute/Fisk University

Fee: $250. *Write:* Director, Fisk Institute, Box 8, Fisk University, Nashville, Tenn. 37203

July 24–28 Athens, Ga.
Estuary Studies, Course No. 161.3. EPA

Fee: $110. *Write:* Instructional Resources Center, National Training and Operational Technology Center, U.S. EPA, Cincinnati, Ohio 45268

July 24–28 Indianapolis, Ind.
Combustion Evaluation, Course No. 427. Air Pollution Training Institute

Fee: $110. *Write:* Air Pollution Training Institute, MD-20, Environmental Research Center, Research Triangle Park, N.C. 27711

August 7–8 Cincinnati, Ohio
Atomic Absorption: Applications Technology in Environmental Control, Course No. 107.5. EPA

Fee: $44. *Write:* Instructional Resources Center, National Training and Operational Technology Center, U.S. EPA, Cincinnati, Ohio 45268

August 7–11 Fort Collins, Colo.
Recognition of Occupational Health Hazards, Course No. 510. NIOSH/AIHA

Fee: $250. *Write:* American Industrial Hygiene Association, 66 S. Miller Rd., Akron, Ohio 44313

August 7–11 Research Triangle Park, N.C.
Principles and Practice of Air Polution Control. Air Pollution Training Institute

Fee: $99. *Write:* Air Pollution Training Institute, MD-20, Environmental Research Center, Research Triangle Park, N.C. 27711

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MEETINGS *(continued)*

August 7–11 Cambridge, Mass.
Interpretation of Gas Chromatographic Mass Spectrometric Data: Environmental Applications. Massachusetts Institute of Technology

Fee: $580. *Write:* Director of the Summer Session, Massachusetts Institute of Technology, Room E19-356, Cambridge, Mass. 02139

August 7–11 Ann Arbor, Mich.
Solar Energy Measurements and Instrumentation, Course No. 7835. University of Michigan

Fee: $375. *Write:* Continuing Engineering Education, University of Michigan, 300 Chrysler Center, North Campus, Ann Arbor, Mich. 48109

August 9–10 Cincinnati, Ohio
Gas Chromatography: Applications Technology in Environmental Control, Course No. 107.6. EPA

Fee: $44. *Write:* Instructional Resources Center, National Training and Operational Technology Center, U.S. EPA, Cincinnati, Ohio 45268

August 10–11 Chicago, Ill.
Industrial Noise Control and Its Management. New York University

Fee: $465. *Write:* Registrar, 14th Fl., New York University Conference Center, 360 Lexington Ave., New York, N.Y. 10017

August 14–18 Cambridge, Mass.
Concepts and Techniques in Experimental Pathology and Toxicology of Natural and Man-Made Agents. Massachusetts Institute of Technology

Fee: $600. *Write:* Director of Summer Session, Room E19-365, Massachusetts Institute of Technology, Cambridge, Mass. 02139

August 15–18 Golden, Colo.
Sewage and Industrial Wastes: Conversion and Treatment. Colorado School of Mines

Fee: $400. *Write:* W. E. Leckie, Director of Continuing Education, Colorado School of Mines, Golden, Colo. 80401

August 21–25 Nashville, Tenn.
Upgrading of Wastewater Treatment Plants. Vanderbilt University

Fee: $400. *Write:* Prof. W. W. Eckenfelder, Jr., Vanderbilt University, Box 6222, Station B, Nashville, Tenn. 37235

August 21–25 Cambridge, Mass.
Ecodynamic Analysis of Environmental Systems. Massachusetts Institute of Technology

Fee: $650. *Write:* Director of the Summer Session, Room E19-356, Massachusetts Institute of Technology, Cambridge, Mass. 02139

CLASSIFIED SECTION ■ POSITIONS OPEN

Air Quality Policy Analyst

Work with interdisciplinary team in programs to develop and evaluate alternative air quality management policies. Develop and apply analysis methodologies to provide decision-makers with data and evaluate tools. Outputs include policy recommendations, new data bases, and planning procedures. Experience should include emissions inventory development; air quality data analysis; control strategy development; familiarity with dispersion modeling, and air pollution management techniques and concepts. Applicants must have an M.S. or Ph.D. in physics; chemistry; mechanical, chemical, civil, or environmental engineering; or equivalent experience.

To apply for this position, send resume to: Mr. Walter D. McFall.

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North Texas State University invites applications for the following positions, which are authorized or expected to be authorized. Complete resume with 3 references should accompany application. Send to: **Search Committee, IAS/North Texas State University, N.T. Box 5057, Denton, TX 76203.**

ENVIRONMENTAL HEALTH—a program director level position in Environmental Health and Toxicology requiring terminal degree in biochemistry, toxicology, or related area. Experience in research development of toxicological methods; ability to develop a strong research program essential.

ENVIRONMENTAL CHEMISTRY—Research Scientist in Environmental Chemistry Program requiring a Ph.D. in chemistry or chemical engineering with expertise in analytical methods applied to organic pollutants.

ENVIRONMENTAL ENGINEER (Ph.D.)—Responsibilities require understanding of biological and chemical processes of potable and wastewater treatment. Bench scale or pilot plant experience and/or scholarly achievement essential. Teach halftime, develop research and graduate program in sanitary biology or microbiological processes associated with water treatment. Expertise in dynamic flow modeling and systems analysis highly desirable. Salary and rank open.

ENVIRONMENTAL CHEMIST

Tenure-track Assistant or Associate Professorship. Beginning January or September, 1979 in an A.C.S. accredited Department with 10 Chemists. Duties include teaching undergraduate environmental chemistry, quantitative analysis and participating in lower division environmental science and chemistry courses. Ph.D. required. Post-doctoral experience desired. Strong commitment to teaching and ability to develop a research program expected. Send application, 3 letters of recommendation and transcripts to: **Faculty Search Secretary, College of Arts, Sciences and Letters, The University of Michigan–Dearborn, Dearborn, MI 48128.** A nondiscriminatory, affirmative action, Title IX employer.

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International firm specializing exclusively in environmental consulting services has an immediate opening in its Detroit, Michigan office for a Project Manager experienced in the area of environmental assessment and air quality.

The Project Manager will be in charge of activities for the firm's Environmental Planning Division in the midwestern United States reporting directly to the Division President.

Minimum position requirements include:

Four years of technical experience in planning, design, and construction of air quality controls, diffusion modelling and predictive analyses, and three years of technical experience preparing environmental assessments.

Knowledge and familiarity with sludge, refuse and wastewater environmental engineering projects.

Professional engineering registration (preferred).

B.S. degree in Engineering or an Engineering Science.

M.S. degree in either Engineering, Environmental Science, Planning or a Natural Science.

Proven project management and new business development ability.

Proven writing skills.

For immediate consideration, qualified applicants are requested to send a detailed resume specifying salary history and requirements to:

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CHICAGO DEPARTMENT OF PUBLIC WORKS
Research/Planning Analyst $13–17,000

Our Project Development Section seeks candidates for staff positions in its environmental impact analysis group. Responsibilities will include the review, identification, prediction and measurement of impacts resulting from proposed public works capital improvements, especially relating to transportation projects. Studies are done under general supervision in an interdisciplinary atmosphere. Independent judgment and initiative are essential. Qualifying candidates will possess a Master's degree or equivalent in transportation, environmental, or civil engineering, public health, or other related field. Experience in air quality, noise or transportation system analysis desirable. Knowledge of impact prediction techniques a must. Selected candidates must reside within corporate limits of the City of Chicago at the time of employment. Send resume and salary requirements to: **S. P. Tokarz, Department of Public Works, Personnel Section, Room 600, 320 North Clark Street, Chicago, Illinois 60610.**

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CLASSIFIED SECTION

POSITIONS OPEN

PROFESSORS WITH ENERGY AND ENVIRONMENTAL INTERESTS

●

Like to work on challenging "real world" problems involving energy and the environment? Interested in learning about and contributing to government research in these areas? If so, you're the person we're looking for. EPA-Cincinnati needs a well-qualified scientist or engineer to accept an Intergovernmental Personnel Act assignment for up to two years in length.

We have a broad program on environmental aspects, both pro and con, of energy technologies in all sectors of the economy. Applicants should have a strong background and research interests in engineering science fundamentals related to energy and the environment, and desire to serve in a broad overview capacity related to: program priorities; program report and paper review; social, economic, legal and institutional problems; and the tie between EPA research and its implementation through environmental regulation.

We are an equal opportunity employer. Interested parties should send a recent resumé and any further questions to: **Dr. Harry E. Bostian, Chief, Power Technology and Conservation Branch, U. S. Environmental Protection Agency, Cincinnati, Ohio 45268.**

Energy and Environmental Analysis (EEA) has several positions available for highly qualified air pollution engineers. Applicants must have an M.S. in mechanical, chemical, or environmental engineering and 2–4 years of industrial or governmental experience. Negotiable salaries. EEA offers challenge within a rapidly growing consulting company located in the Washington, D.C. area. Send resume, salary requirement to: **M. Heisel, EEA, Inc., 1111 North 19th Street, Arlington, Virginia 22209.** An Equal Opportunity Employer.

FACULTY POSITION—Environmental Health with specialization in Environmental Epidemiology coupled with a strong background in the toxicology of chemical pollutants and environmental chemistry. Rank: Assistant Professor, 12 month's appointment with $2/3$ teaching and $1/3$ research effort beginning Sept. 1978. Salary competitive. For additional information, contact **Dr. Samuel D. Faust, Chairman, Search Committee, Rutgers University, P.O. Box 231, Department of Environmental Sciences, New Brunswick, N.J. 08903.** Rutgers University is an equal opportunity, an affirmative action employer, and will consider all qualified applicants without regard to sex, race, creed or religion, color, national origin, age, ancestry, handicaps, veteran's or marital status.

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Kemron laboratories are located in Baton Rouge, Louisiana; Chicago, Illinois; Farmington Hills, Michigan; and Port Neches, Texas.

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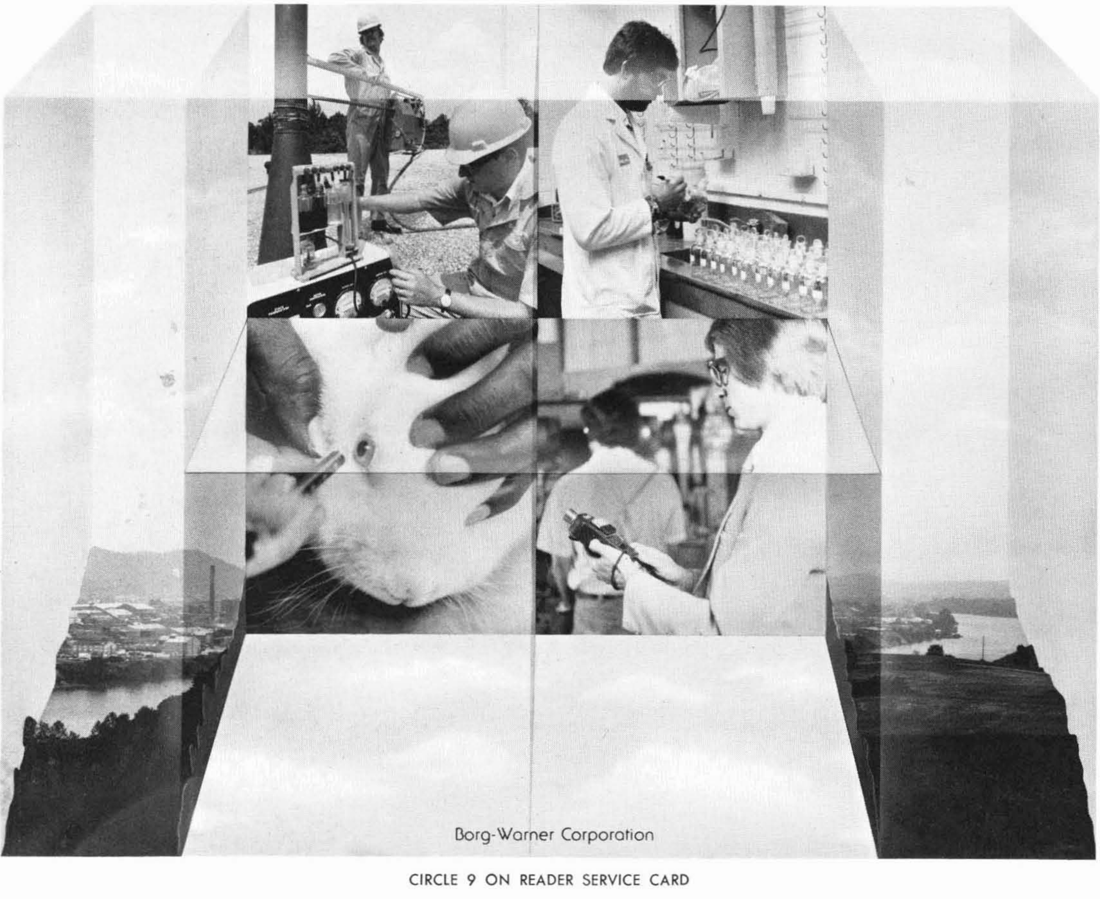


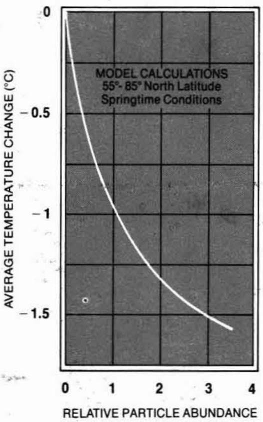
Borg-Warner Corporation

CIRCLE 9 ON READER SERVICE CARD

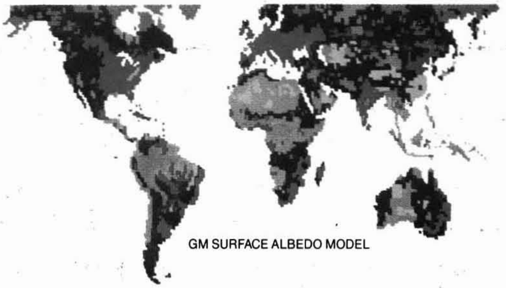
Churning throughout the earth's atmosphere are substances that could change the climate of tomorrow. One way in which scientists the world over try to anticipate the possible effects of these substances is via mathematical modeling. That's the approach we've been taking here at the General Motors Research Laboratories.

Our scientists started with one of the most complex atmospheric representations in existence: the radiative-convective model developed at Princeton University. They then reformulated it to include airborne particles.

Among the early uses of this new tool was an attempt to correlate an ice buildup in the Far North in 1971 with a reported jump in particle abundance. Just prior to the jump, four volcanoes had erupted in this region. Calculations with the model indicated that the particle increase could indeed have lowered temperature, thus delaying the spring melt and hastening the fall freeze (see graph).



In other experiments, we studied over 30 parameters . . . gas concentrations, albedos (reflectivities of the earth's surfaces), cloud and particle abundances, Rayleigh scattering coefficients. The goal has been to understand global temperature response to changes in O_3, CO_2, particles, and the chlorofluoromethanes.


GM SURFACE ALBEDO MODEL

So far, our findings lead to these main conclusions:

- Surface albedo exerts the most influence on global temperature change. Next in importance are Rayleigh scattering, humidity of the lower troposphere, and CO_2.
- Atmospheric particles work against the temperature increase attributed to CO_2 (the greenhouse effect).

Global temperature modeling: One of the many ways we're helping to explain, and maintain, this planet Earth.

Global temperature... looking toward 2001.

GM

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