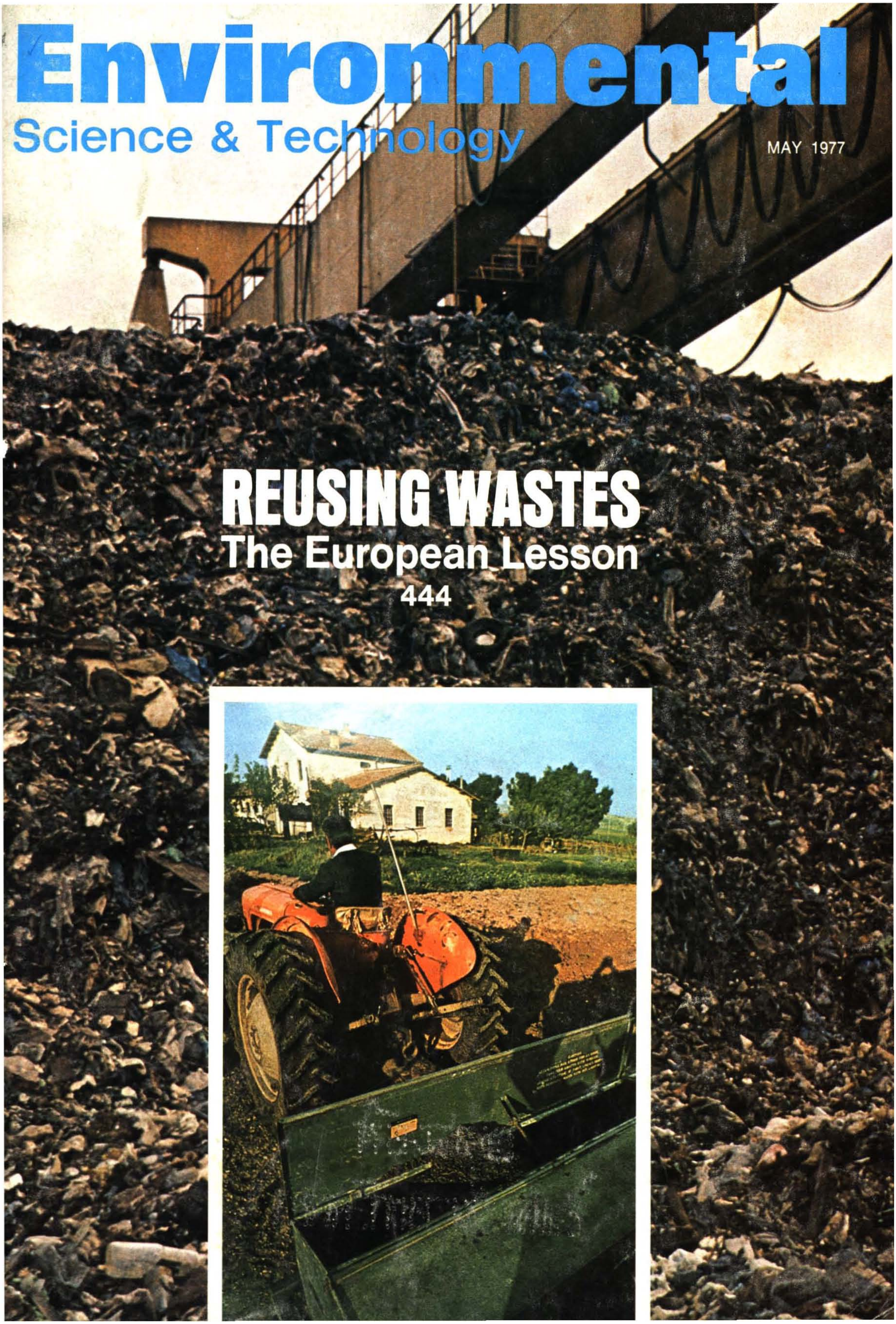
Environmental
Science & Technology

MAY 1977



REUSING WASTES
The European Lesson
444

Designed for maximum accuracy in SO_2 sampling

NEW RAC 3-Gas Sampler

Unique thermoelectric cooling-heating system* assures optimum stability for SO_2 samples at ambient temperatures from –25°C to 50°C

Recent studies performed by the EPA have revealed that the accuracy of wet-chemical sulfur dioxide (SO_2) sampling procedures are adversely affected by high ambient temperatures. At 50°C (122°F), for example, roughly 75% of the SO_2 in a collected or stored sample will be lost (because of thermal instability) within a 24-hour period. Sample degradation begins in the 20°C (68°F) range, with an initial loss factor of less than 1% in 24 hrs.

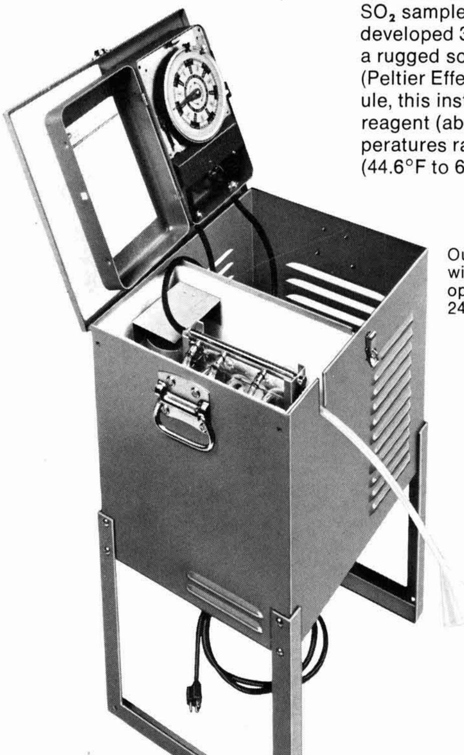
RAC has eliminated this problem in SO_2 sample collection with its newly developed 3-Gas Sampler. Featuring a rugged solid-state thermoelectric (Peltier Effect) cooling-heating module, this instrument maintains the SO_2 reagent (absorbing solution) at temperatures ranging from 7°C to 17°C (44.6°F to 62.6°F).

As a result, all the SO_2 collected during a sampling cycle is preserved for optimum accuracy of sample evaluation. **Another first from RAC!**

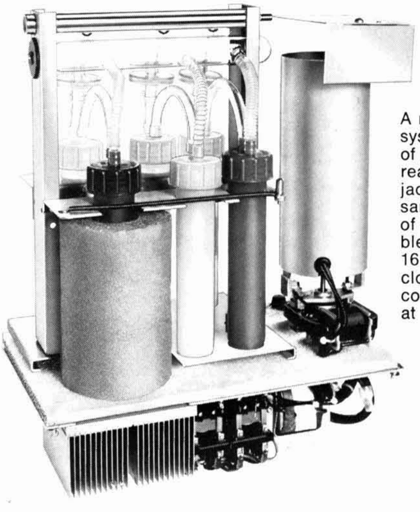
The RAC 3-Gas Sampler is designed to collect nitrogen dioxide (NO_2) and a third (optional) gas simultaneously with SO_2 samples. In fact, it will sample any gas for which there is a suitable reagent, including hydrogen sulfide (H_2S), ammonia (NH_3), and aliphatic aldehydes (CHO).

The latest RAC gas sampler design is available in a portable outdoor model and a smaller, lighter weight indoor model. The outdoor model can be equipped with optional 24-hour or 7-day (skip) timer mechanisms.

For details, send for BULLETIN 2441



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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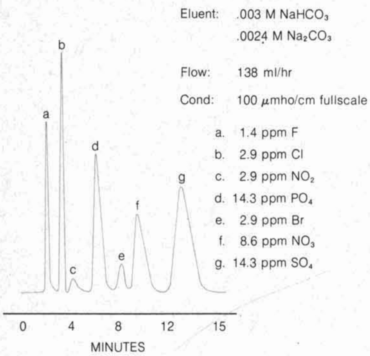
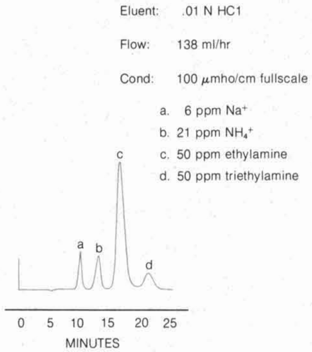
The technique of Ion Chromatography represents a major advance in analytical chemistry. **It permits direct analyses of large classes of compounds which were laborious or impossible to analyze previously.** For this reason the originators of the technique have received the 1977 Pittsburgh Applied Analytical Chemistry Award. A second award, the John C. Vaaler Award, was given for excellence in instrumentation useful in the chemical process industry.

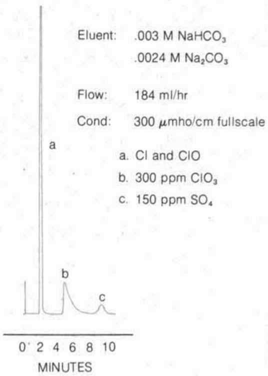
Analysis of typical anions in water



Analysis for cations in a waste stream



Analysis of anions in 50% caustic



APPLICATIONS

AIR POLLUTION

Analysis of ambient aerosol filter extracts for nitrate and sulfate, sulfuric acid (SO_3) in stack gas, sulfite and sulfate in FGD scrubber liquors and trace ions in rain water.

WATER POLLUTION

Ion characterization of waste effluents, routine ion analysis of ground waters, nitrate-N and phosphate-P in hatchery and bio-pond water, chloride, sulfate and oxalate in paper mill effluent.

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Trace level and interference free analysis of organic fluorine, chlorine, bromine, iodine, sulfur and phosphorus after Schöniger oxidation.

SOIL ANALYSIS

Direct anion analysis of KCl, ammonium acetate and ammonium fluoride, sulfuric acid or bicarbonate soil extracts.

BRINE ANALYSIS

Direct analysis of chlorate, sulfate, calcium and magnesium in 25% brine and 50% caustic solutions; phosphate, bromide, nitrate, sulfate, calcium and magnesium in 2% brine.

POWER PRODUCTION

Trace ion analysis in boiler, boiler feed and cooling tower waters.

QUALITY CONTROL

Fluoride, chloride, sulfate and chromate in plating bath process water, trace ions in electronic device process water, glycolate in surfactants, monomethyl amine in ethylenedichloride, thioacetic, thiolactic and thioglycolic acid in water, tetraethylammonium and tetra-N-butylammonium bromide in water, monomethylamine, dimethylamine and trimethylamine in water, mono and dibutyl phosphate in water and halides and sulfate in foods and food additives.

For information regarding applications of IC, circle the appropriate number on the information card or call the Dionex applications laboratory to discuss your particular application.

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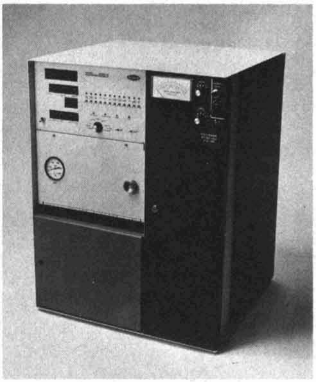
Available with automatic sampling and data handling accessories.



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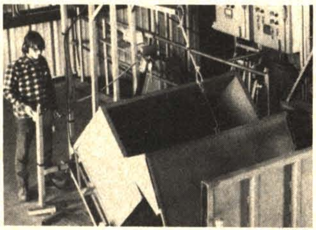
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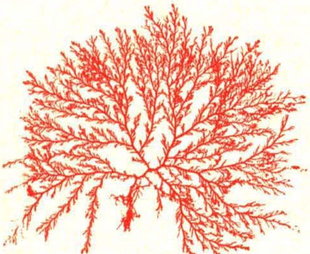
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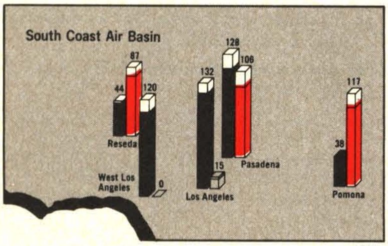

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CURRENT RESEARCH

Analysis for beryllium in ambient air particulates by gas chromatography 467

William D. Ross*, James L. Pyle, and Robert E. Sievers

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James E. Jones, Jr., and Richard I. Kermode*

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Cary T. Chiou*, Virgil H. Freed, David W. Schmedding, and Rodger L. Kohnert

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Johannes J. Rook

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Leo Zafonte*, Paul L. Rieger, and John R. Holmes

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Phillip R. Westmoreland, James B. Gibson, and Douglas P. Harrison*

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Steven J. Eisenreich* and David E. Armstrong

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Yehuda Shekel and Rosa Ravid*

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Anatomy of two ozone transport episodes in the Washington, D.C., to Boston, Mass., corridor 506

George T. Wolff*, Paul J. Lioy, Ronald E. Meyers, Richard T. Cederwall, Gregory D. Wight, Ralph E. Pasceri, and Richard S. Taylor

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Joseph L. Thompson* and David A. Olehy

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Daniel L. Flamm* and Theodore J. Wydeven

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Credits: 433, *C&EN*'s R. Seltzer; 441, Ankers Capitol Photographers (Washington, D.C.); 442, *ES&T*'s J. Jcsephson; 444, NCRR's Harvey Alter; 446, Crown (British Official photo); 452 (large), KLM Aerocarto n.v.; 456, 457, Los Angeles County Air Pollution Control District; 461, *ES&T*'s J. Josephson; 463 (two photos), 465 (three photos), U.S. Army Photograph

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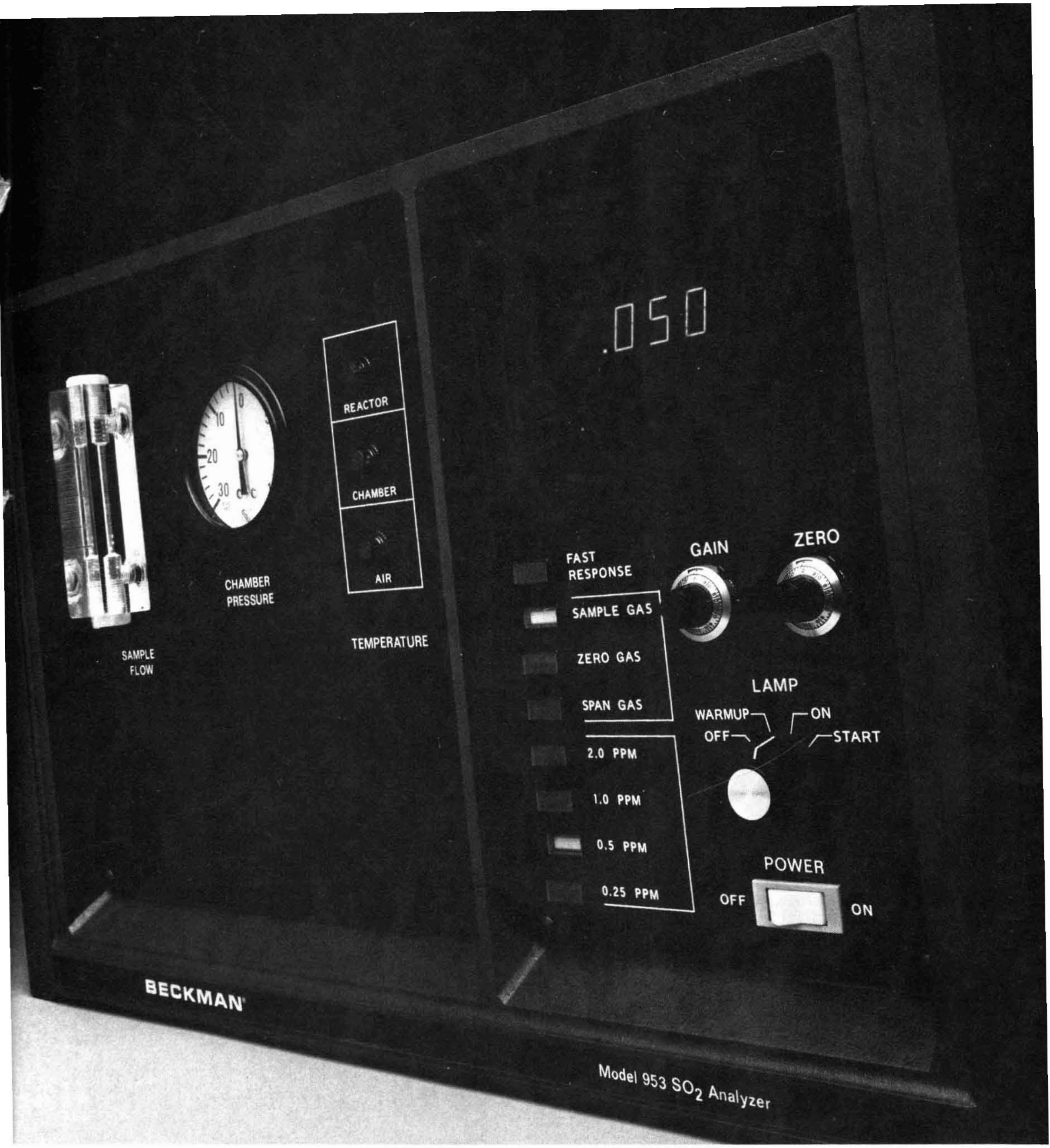
* To whom correspondence should be addressed.

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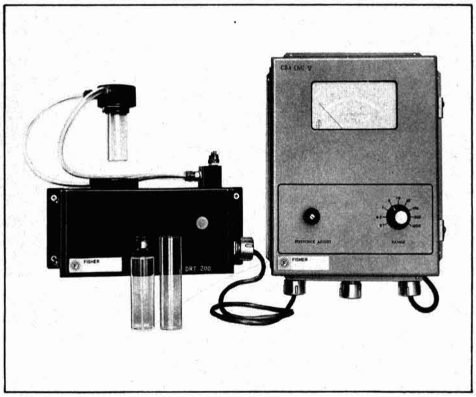

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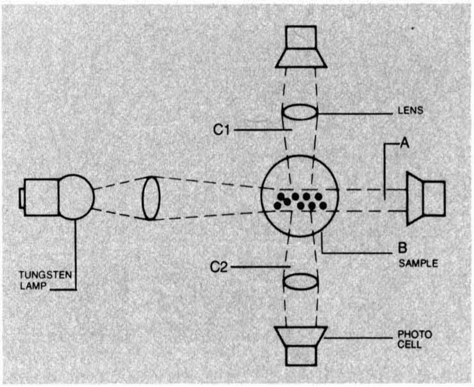

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The technological imperative

Each culture has its ideals and principles, its goals and gods. Advanced western society, and to an increasing extent the rest of the communicative world, has placed its sacrifices on the altar of technological advancement. The "can do" credo, so much a part of the American engineering ethic, has rooted itself so deeply in our national sense of purpose that it has become equated with "should do." What Herman Daly has magnificently labeled as growthmania is really just a symptom of our moral commitment to a deeper technological imperative.

The question is why? Surely we are not inherently inclined to be "gadgeteers"; we have no genetic bent toward materialism. The reason, of course, is fundamentally humanitarian. In our culture we provide social advancement through a commitment to steady increases in material productivity that has depended on technology. The distribution of the fruits of productivity, however, in terms of income and wealth is nonuniform, and were it not for a guarantee that through increasing GNP each person will be better off than last year, social instability would result. We have never really addressed the problem of income/wealth distribution head on; only in remedial ways through welfare programs designed primarily to stimulate total production. Thus, an increasingly well-known but poorly understood cycle develops; each year more growth is required than the year before, and in a finite world the concept becomes unacceptable somewhat before it becomes impossible through resource or ecological limitation.

The palliative that no other society has found a better way is intellectually and morally unsatisfying. If we are committed to the technological imperative for humanitarian reasons, then it's time to change the neocapitalistic system, as it cannot provide equity. In fact, it could be argued that the evolution of our national sense of social equity over the last 50 years has had an increasingly paralytic effect on the institutions of our system.

The issue of reliance on technology and the equitable distribution of welfare is the most profound issue of our time. The concepts involved have been the exclusive domain of economists, philosophers, and politicians. As chemists and engineers, we have a responsibility to be more in our society than part of the technology delivery system. Technology is what we do, not what we are. Although we are not trained researchers on social questions, we cannot afford a complacent attitude toward their importance.

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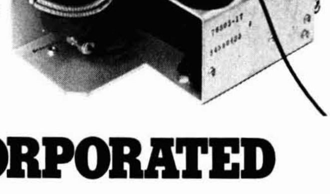

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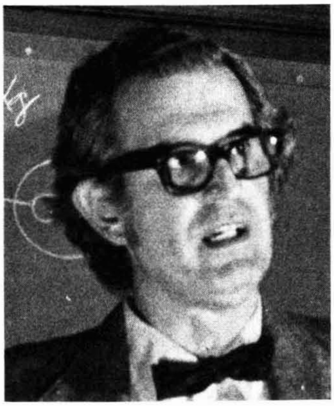
In the first of a series of reports, the National Research Council finds that environmental protection is hampered by haphazard and sometimes conflicting legislative mandates. This overview report, "Perspectives on Technical Information for Environmental Protection," also finds that the EPA has a "dearth of technically trained people with experience in pollution control employed at the decision-making levels." On EPA's monitoring program, the study finds "a proliferation of programs that are inefficient, inflexible, and productive of data of poor or unknown quality." The study also finds that EPA does not systematically or comprehensively consider all feasible alternatives in its decision-making processes. Ten other reports in this 2.5-y, multimillion dollar effort will be released shortly.

The use of tall stacks without SO_2 emission controls will decrease visibility according to a recent EPA report. The report, prepared for the EPA by Battelle Pacific Northwest Labs, states that "Widespread tall-stack utilization combined with projected increases in fuel consumption without control of sulfur compound emissions will aggravate existing ground-level sulfate concentration levels throughout the U.S." In the meanwhile, the Tennessee Valley Authority is turning to burning low-sulfur coal as a method of controlling SO_2 emissions at four of its older power plants, which TVA claims are too old to justify the use of scrubbers, and at another six coal-burning plants. EPA says this "very clearly does not meet" the requirements of the Clean Air Act and the agency will issue a compliance order to TVA.

Oxidation ditches provide the highest degree of treatment of municipal wastewater, according to an EPA Region VII study. Of all possible secondary municipal wastewater treatment processes, the oxidation ditch is the only one to consistently meet the standards for secondary treatment. Complicated process control and insufficient operator skill or attention were cited as reasons for the violation of discharge permits by plants using lagoon, activated sludge and trickling filter processes. In this study, 226 municipal treatment plants were studied for over 3 years. In a report prepared by the EPA for Congress, the agency found that groundwater is contaminated "on a local basis in all parts of the U.S. and on a regional basis in some heavily populated and industrialized areas."

EPA's 1976 "Needs Survey" estimates that control of water pollution from municipalities will cost $96 billion, $55 billion less than that estimated in the agency's 1974 survey. The $96 billion is that amount estimated to be needed to construct sewage treatment plants to meet the 1983 municipal effluent requirements mandated by P.L. 92-500; it excludes pollution from storm sewers, however. Former acting administrator John Quarles has stated that the 1983 deadline for advanced treatment of municipal sewage is unrealistic and that this goal will probably not be achieved in the U.S. until 1990. This third needs survey used essentially the same categories as those listed in the earlier survey, but changes in technique were undertaken, some at the suggestion of the now-defunct National Commission on Water Quality.

NIEHS scientists have found evidence that dioxin contamination may be greater than previously realized (*ES&T,* December 1976, p 1190). Chlorinated dioxins are present at high concentrations in pentachlorophenol (PCP), a widely used wood preservative in the U.S. In an National Institute of Environmental Health Sciences study, livestock housed in a Michigan barn constructed with PCP-treated wood have been found to be heavily contaminated with dioxin, and these animals have become ill. An association between the dioxin and illness is likely. In a letter discussing the problem, David Rall, director of NIESH says, "If, as the NIEHS data strongly suggest, the dioxins . . . move into the domestic animals . . . the possibility for extensive human exposure must be considered."



NIEHS director Rall

While the recombinant DNA research debate continues, the EPA and other agencies are reviewing federal policies for conducting this research. EPA has the authority to regulate hazardous air pollutants under Section 112 of the Clean Air Act and toxic effluents under Section 307 of P.L. 92-500; yet the agency would need more information on the hazards from recombinant DNA before it could promulgate standards under these sections of the laws. Under Section 6 of the Toxic Substances Control Act, the EPA has some regulatory options open to it; yet this law needs to be tightened up for effective regulation of this new research. One deficiency in TSCA is the lack of EPA's authority to compile a registry of laboratories and persons doing recombinant DNA research. New legislation is in the works that may possibly mandate that NIH set the standards and the Center for Disease Control enforce them.

STATES

Oregon is the first state to ban the sale of aerosols containing chlorofuorocarbons (CFC). Under the law, which became effective in March, merchants are banned from selling aerosols containing CFCs and violators can be fined $1000 and/or receive a 1-year prison sentence. These sales are considered a criminal misdemeanor. However, exempted from the ban are medicines propelled by CFCs. When the ban became effective, sales of CFC sprays in Oregon were estimated at $40 million yearly. Twenty other states and the Federal government are also considering the curtailment of the use of these products. N.Y.'s labeling law for these products goes into effect in July, and the law provides for a ban decision by 1978.

El Paso and Teller Counties, Colo., now have the first completed 208 Plan to control water pollution. The Pikes Peak regional plan, called Project Aquarius, was certified by Gov. Richard D. Lamm and will be implemented by the Pikes Peak Area Council of Governments. Regionalization of waste treatment service will center around the Colorado Springs area, and about 80% of the total municipal wastes for the two-county area will be treated at the Colorado Springs plant. The total cost for the 20-y plan is estimated at $82 million (in 1976 dollars), with $32 million of the total needed through 1981.

Colorado governor Lamm

Are fish in Lake Ontario contaminated with the pesticide Mirex? The Hooker Chemical and Plastics Corp., which once manufactured Mirex at Niagara Falls, N.Y., claims that tests of lake fish conducted by the U. of New Orleans show no Mirex present in some fish. The N.Y. State Dept. of Environmental Conservation (DEC) states that while these tests do not confirm the identity of Mirex, they do not rule out the possibility that Mirex is not one of the hydrocarbons detected by mass spectroscopy. The DEC has relaxed restrictions on fishing for some fish, banned others and warned pregnant and nursing women, infants and young children not to eat any fish taken from the lake. DEC has also warned that fish permitted to be taken from the lake should be ingested not more than once a week.

For 10 years the Metropolitan Council has guided growth in the Minneapolis–St. Paul, Minn. area, a 3000 mi^2, seven-county region. Recently, the state passed the "Metropolitan Land Planning Act" that will permit the Council to impose the concept of regional planning on such matters as pollution control, waste disposal practices, water supply, transportation and health care. Under the new act, the Council will provide localities with detailed plans for sewers, highways, mass transit and parks as well as population projections until 1990. But by 1980, each town must prepare a comprehensive land-use plan that conforms with the Metropolitan Council's regional plan.

The Calif. Water Resources Control Board feels that water reclamation and reuse could help the state meet nearly 60% of its anticipated water needs in the year 2000. The Board has adopted an action plan for water reclamation that calls for basinwide studies to identify potential projects, and an R&D program to assess health and environmental effects and to determine the market potential for reclaimed water. Calif. now has 200 water reclamation and reuse (including groundwater recharge) projects under way; another 37 projects are in the planning or construction stage. Arsenic waste disposal near Charles City, Iowa, has contaminated the Cedar Valley aquifer and has prompted the state's water commission to request that no large groundwater withdrawals be allowed with a 15-mi radius of the city.

MONITORING

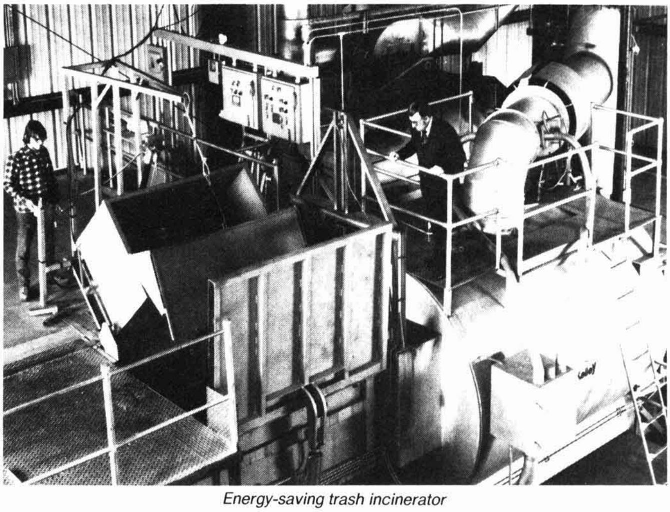
NO_2 and SO_2 concentrations can be measured with a solar radiometer developed at NASA's Langley Research Center (Hampton, Va.). Measurements are easily performed; the radiometer is aimed directly at the sun, then at a plume. The ratio of these measurements of solar intensity is the transmittance of the plume, from which NO_2 and SO_2 can be deduced. The radiometer is inexpensive, portable, and easily operated, and it eliminates the need for troublesome in-stack measurements. It uses wavelengths of 310 nm (ultraviolet), 400 and 600 nm (visible), and 800 nm (infrared), and also measures aerosol opacity. NO_2, SO_2, and opacity measurements were found to agree with those taken in-stack.

A method to continuously determine acid sulfate aerosols has been developed by scientists at the Institut National de Recherche Chimique Appliquée (France). By using a permeation tube containing a filter of glass fiber impregnated with $FeSO_4$, sulfuric acid can be selectively retained while SO_2 passes through the filter. In the presence of 30–600 $\mu g\ SO_2/m^3$, the standard deviation is 0.9 $\mu g\ H_2SO_4/m^3$.

TECHNOLOGY

A new gas scrubbing system saves energy while it removes particulate matter from industrial gases. The system, patented by Daniel Murray, an engineer at Hammermill Paper Co. (Erie, Pa.), feeds contaminated gases into the bottom of a large cylinder with a central core that spins at high speeds. The spinning core sprays out water that washes down heavier particulates that are held in the cylinder by centrifugal force. The captured particles go to a holding tank for disposal. Scrubbed gases go to another control chamber for removal of excess moisture; emissions are particulate-free. The core spin speed can be varied as the density of gases to be treated requires; this feature results in "dramatic" energy savings over conventional systems, according to Murray.

A fluidized-bed incineration system for sludge has started up in the United Kingdom, and can serve a population of 70 000. It replaced drying beds for sludge disposal, and enables sewage to be reduced to a fine, inert ash. Only



Energy-saving trash incinerator

steam is emitted to the air. The system was developed by Dorr-Oliver Co. Ltd. (Croyden, England), and is installed at the Thames Water Authority in Surrey. Sludge is conditioned with lime and copperas, and filtered. It is then introduced into the Dorr-Oliver FluoSolids incinerator—a reactor with a bed of sand fluidized by oil-heated air. Sludge is fully mixed in the sand and gas suspension, and thermally oxidized. Organics are burned and water is quickly evaporated, leaving the inert ash. Scrubber wash water is recycled.

Many hazardous inorganic wastes are destroyed by chemical means. These wastes include complex mixtures, strong acids, oleum, hydrofluorics, hexavalent chromium (Cr^{+6}), copper, and the like. Also, with the system developed by Rollins Environmental Services (RES, Wilmington, Del.), cyanide is removed by oxidation. Cr^{+6} is reduced to trivalent chromium (Cr^{+3}), which is much less toxic; copper is rendered elemental. After heavy metals are removed, and cyanides oxidized, the waste stream goes to the main reactor where acids are neutralized. The next step is a decant system where precipitates settle out, and liquors are separated for further biological treatment, leaving a sludge to be disposed of by means of cementation.

During the coldest winter this century, at least two plants needed no gas or oil to keep open; their trash bins were their energy sources. Through a pyrolysis-type incinerator developed by the Kelley Co. (Milwaukee, Wis.), the K. W. Muth Co. (Sheboygan, Wis.) kept open all winter, and generated no smoke. In fact, 60% of the heat available from the trash was enough for Muth's needs. The pyrolyzer at Muth generates a net 5.5 million Btu/h, and saved about $53 000 in the first year, based on present fuel and waste haulage costs. And Xerox Education Publications (Columbus, Ohio) produced over 30% of its comfort heat needs with the same technology. A net 2.7 million Btu/h—equivalent to heat from 25 gal/h of oil—was yielded to save Xerox oil costs of $25 000/y.

Timber-like products can be made from very contaminated scrap plastics, such as old fertilizer bags, wire and cable waste, domestic trash, and films. Mitsubishi Petrochemical Co. (Japan) has improved the process, which can use very impure plastic wastes, to the point at which the product material can be used as fence posts, cable drums, beams for housing improvements, or other applications, and is, in fact, in use. The material is made by the "REVERZER" process, which involves a highly specialized extrusion system. This system homogenizes the melt very fast, and under extremely high shear. The material is rugged, and seems to hold up even under low temperatures.

A new submerged aeration system is twice as energy-efficient as present diffused air systems, and 1.5 times as efficient as mechanical surface aerators, according to Clevepak Corp. (Fall River, Mass.), its developer. The system, called AEROCLEVE, uses a unique votex action that disperses air into small bubbles that are distributed throughout an aeration basin or lagoon. Unlike venturi-type aerators or diffused-air media systems, the AEROCLEVE system has no small orifices or restrictive passages to clog. According to Clevepak, the system can reduce operating costs by about 50%, as compared to diffused-air systems, and 25%, as compared to surface aerators. Several systems have been sold in the U.S. Clevepak is a manufacturer of recycled paperboard and packaging products.

INDUSTRY

The Clean Air Act can delay, impair, or kill industrial growth and energy projects unless Congress changes a May 31 deadline for nationwide compliance of six regulated pollutants. Review of the present amendments bill, H.R. 4151 was advocated, especially in such a way as not necessarily to interpret the bill's aim of "adequate margin of safety as "zero risk." Also, a careful look should be given at non-attainment alternatives, especially since certain pollution in these areas may stem from natural sources and be uncontrollable. In many areas, in fact, extensions are needed, because standards cannot be economically attained. These and other views were presented at a House subcommittee by the Manufacturing Chemists Association, the American Petroleum Institute, and the Business Roundtable.

Industry cannot relax efforts in dealing with environmental problems, even though energy problems may have taken the spotlight. That is the view of James Wright, general manager, environmental systems department of Westinghouse Electric Corp. (WEC). Some examples of environmental issues Wright listed included national surface mining legislation, Clean Air Act revisions, and possible laws to come on nonreturnable containers. Wright's group at WEC has built an international reputation for handling tough environmental problems for the company, its electric utility customers, and, more recently, clients from other industries. He observed that most executives of polluting industries are as concerned about pollution as government officials, but may have different ideas as to the best solutions.

Determination of the adequacy of tests to ascertain safety of chemicals should be the subject of more basic research, Leon Golberg, president of the Chemical Industry Institute of Toxicology (CIIT, Research Triangle Park, N.C.), said. He explained that, for example, there are no valid short-term tests to indicate the carcinogenicity of a substance. Also, long-term animal tests do not take into account the difference between a large dose of a chemical given to an animal, and very low, very long-term doses taken by humans, Golberg noted. He also said that toxicology often generates "problems that defy solution by ready-made rule of thumb," and that scientists have not tried long or hard enough to answer questions about acceptable levels people may take in without observable effect.

DOW USA president Oreffice

Regulations cost Dow Chemical Co. (Midland, Mich.) $147 million/y, and about $60 million were the result of excessive or questionable regulations, according to Dow U.S.A. president Paul Oreffice. The company indicated that the largest percentage of excessive regulation occurs in health and safety—$9 million of $22 million/y. As for environmental control, Dow had to put up $63 million, of which it said that $19 million represented excessive cost, and $2 million, "questionable" cost. Moreover, the firm noted that 71 federal agencies are concerned with it. However, Dow's study also says that not all regulations are wrong or unnecessary, and concluded that about 59% of its regulatory costs were properly spent to protect health and safety workers, customers, and the public at large.

Stabilizing waste materials for landfills

IU Conversion Systems reviews the test procedures used to evaluate the suitability of landfilled materials and to determine the leachate from such materials

When one is faced with landfilling operations of 500 000–1 million tons annually, stabilized, well-engineered, and well-managed landfills are usually much more environmentally acceptable than sluicing untreated sludges down water courses or holding operations in unlined, or, for that matter, lined ponds. In fact, under the new solid waste law, P.L. 94-580, wastes, residues, and hazardous materials cannot be disposed of in other than approved sanitary landfills.

How does one predict the effect of hazardous materials placed in landfills? Mass transport of polluting salts to the water system is the real concern. The magnitude of that problem cannot be determined by the initial leachate or by any test of a single property without regard for the physical properties of the material, the manner of placement, and the pertinent water movement mechanisms at the landfill site.

Some ongoing programs on leachate testing will not be completed for several (1–4) years. But IU Conversion Systems has come up with fast and effective methods of evaluating residues to be landfilled. These test procedures enable one to design environmentally effective landfills.

Of the 60 million tons of fly ash produced annually in the U.S. from electric utility operations, only about 8% is utilized. The other 55 million tons are discarded, 80% of this material being sluiced. Add to that the SO_2 scrubber sludge that is being, and is expected to be, generated, and one is confronted with one of man's biggest residual disposal problems.

For illustration, compare an unstablized, sluiced SO_2 sludge with the IU Conversion System stabilized material, Poz-O-Tec. These materials are considered to be at opposite ends of the stabilization spectrum. Most materials are somewhere between these extremes, but the stability concept is generally applicable to all such materials and should be used to evaluate all landfilled materials.

As suppliers of waste management systems, IU Conversion Systems finds part of the job simple and another part complex and difficult. The easy part is where there are long-established and accepted test methods to demonstrate specific properties. The difficult part is convincing regulatory authorities to use applicable test methods to predict field properties. The latter is the case with wastes that are to be landfilled.

Physical properties

The first requisite of the IU concept is investigation of the material's physical properties relevant to landfill disposal. There are well-established test methods to determine such parameters as unconfined compressive strength, California bearing ratio, triaxial shear strength, consolidation, shear strength, and slope stability. Standardized methods for these properties are readily available and are completely acceptable for use with landfill materials.

The method of placement, a second requisite, is of extreme importance. Placement establishes some of the critical properties and conditions of the material and the completed landfill.

A sluiced material, because of its nature, must be ponded. Since it is saturated, all of the internal surfaces are exposed and all of the soluble salts are available for leaching. The leachate will, therefore, always be at the solubility limit or maximum concentration after the transient period.

Although untreated sludge will leach indefinitely, the duration of leaching from treated material will depend on the type of treatment. For example, the use of an impermeable liner in the pond creates a perched water table that one day could overflow; it also presents an exposure to the hazard of a ruptured liner. Although the use of a liner material may solve an immediate problem, it is a permanent potential for pollution at a later time.

Water movement

The third requisite is determination of the mechanisms of water movement. Six categories of water movement could theoretically occur. These are hygrometric, capillary, thermal, freeze/thaw pumping, osmotic flow, gravitational flow (permeation), and surface runoff.

Hygrometric flow releases water vapor to the atmosphere as the result of differences in relative humidity. Since only distilled water is produced, there is no transport of pollutants out of the mass.

Capillary action could cause the flow of water from Poz-O-Tec to the ground, or vice-versa, if the ground is unsaturated and contains pores smaller than those of the landfilled material. That generally means that the permeability of the soil must be less than 1×10^{-7}. If so, the soil is impermeable and groundwater pollution is unlikely.

Thermal flow is dependent on a temperature gradient with flow from the higher to lower temperature area; a condition that is unlikely to have any significant effect on a landfill.

Freeze/thaw pumping occurs when water in the material expands as it freezes, forcing it deeper into the material. When thawing occurs, the surface area is recharged, setting the stage for a repetition of the cycle. This condition is easily controlled by proper cover on the completed fill area and it should have little or no effect on the transport of salts from the fill.

Osmotic flow occurs when solutions of different concentrations come into contact with each other, resulting in the flow of ions from the higher to lower concentration by diffusion. If groundwater contacts the bottom of the fill material, such flow will occur.

What if groundwater does contact the material? For a material of low permeability, such as Poz-O-Tec, the only water movement mechanism that can transport pollutants from the bottom surface to the groundwater is diffusion. Groundwater moves very slowly and the flow is laminar, not turbulent. Any mixing effect the flow might have has been discounted in determining the diffusion characteristics.

Extensive testing has shown Poz-O-Tec material to have an average TDS diffusion coefficient of 2×10^{-5} cm^2/sec. Water must, therefore, be in contact with Poz-O-Tec for extremely long periods before enough salts are transported to the groundwater to be of concern. A properly designed landfill will prevent such prolonged contact.

Gravitational flow or movement of water caused by its own weight is considered to obey Darcy's law. As applied to soils, it quantifies flow and establishes permeability coefficients. Whether it can be applied directly, at hydraulic gradients close to one, is a matter of contention. Work done by the Russians indicates that at a permeability of 1×10^{-7}, a gradient of 20 is required to initiate flow.

For a sluiced sludge of relatively high permeability and constant recharge, the overriding mechanism is gravitational flow; assuming, of course, that there is no runoff or discharge and the supernatant is returned for transport of fresh material. The permeate will be at, or close to, saturation limits, and the maximum concentrations and amounts of pollutants will be carried to the ground.

The stabilized material

For a stabilized material such as Poz-O-Tec, three conditions—permeation, surface runoff, and groundwater contact—must be considered. These conditions could result in pollution of water systems.

By definition, permeability can only be measured when there is flow. To have flow, the material must be saturated in some areas. For example, some of the channels through the pores of the material must be completely filled with water. In this way, the pressure exerted at the top by recharge will result in flow from the bottom.

In the laboratory, the sample is force saturated and the falling head permeability test is run at a hydraulic gradient of about 10. This condition bears no resemblance to what takes place in a commercial landfill. For example, a hydraulic gradient of 10 on a 10-ft deep landfill requires 90 feet of standing water, which is a wholly unlikely situation in the field.

IU landfills are designed for rapid runoff and immediate dissipation of surface water. Recharge, therefore, only occurs during a rain.

Surface runoff water can be contaminated by dissolution of the surface salts and diffusion of the subsurface salts to the bulk solution—runoff—if there is sufficient contact time. For a properly designed landfill, contact will be extremely short, and diffusion is of minor consequence.

IU Conversion Systems uses three tests to determine the effects of Poz-O-Tec on the environment. These procedures are designed to test the water movement mechanism that could result in the transfer of pollutants from a low permeability, structurally stable material such as Poz-O-Tec. The procedures are the 48 Hour Shake test, Runoff test, and Falling Permeability test. Materials with different physical and environmental properties will require different tests.

Testing for groundwater contact

PROCEDURE: ***Specimens are immersed in deionized water, and total dissolved solids (TDS) are measured as function of time and distance. For a material of low permeability such as the stabilized Poz-O-Tec material the only water movement mechanism that can transport pollutants from the bottom surface to the groundwater is diffusion.***

CALCULATION: ***Assuming a maximum TDS of 5000 ppm, the solubility limit, as determined from the shake tests, the diffusion coefficient was calculated to be 2×10^{-5} cm^3/sec.***

CONCLUSION: ***Water must be in contact with the Poz-O-Tec material for extremely long periods of time before enough salts are transported to the groundwater to be of concern.***

Some facts: stabilized materials

THE PROCESS: ***The Poz-O-Tec process is a method of stabilizing SO_2 sludge, fly ash, and bottom ash with lime and other additives (ES&T, October 1972, p 874).***

THE USERS: **Various industries and electric utilities are using the process to stabilize their wastes today. These include General Battery (Reading, Pa.); Duquesne Light (Phillips and Elrama) and Indianapolis Power & Light Co. (Petersburg); and Columbus and Southern Ohio Electric, Conesville.**

THE PRODUCT: ***The product is environmentally acceptable; its properties can be engineered and controlled. the stabilized product is highly suitable for landfill, road embankments, mine reclamation, impermeable liners, and other similar uses.***

THE RESULTS: ***The physical and environmental properties of the Poz-O-Tec material improve with time as the pozzolanic reaction proceeds. The cementitious nature of the reactions produces a landfill that is monolithic in nature, or low permeability and is subject to leaching from the external surface only.***

IU Conversion System's test procedures

TESTING FOR SURFACE CONTACT. ***Two procedures are utilized—the 48 Hour Shake test for rapid determination of total soluble surface salts and the runoff test to stimulate actual field conditions.***

PROCEDURE. 48 HOUR SHAKE TEST. ***A sample of known weight and superficial surface area is placed in a container of distilled water at a ratio of 1 g of material to 4 ml of water (typically 500 g to 2000 ml). The container is oscillated (60–70 1-in. strokes/h) for 48 hours. The water is filtered and analyzed. Test is repeated five times with fresh water.***

CALCULATION. ***After 3–4 washings, the TDS reaches an equilibrium TDS of 200 ppm. The equilibrium represents the diffusion-controlled leaching process of soluble salts encapsulated below the immediate surface.***

CONCLUSION: ***Diffusion is significant only when the water is in contact with the material for long times.***

PROCEDURE. RUNOFF TEST. ***The apparatus consists of a box 1 ft long × 1 ft deep × ½ ft wide.***

TESTING FOR RUNOFF. ***This test is flexible enough to simulate any amount of rainfall over any period of time and any length of flow. Clean inert material of high permeability is placed in the bottom and the material to be tested is placed on top and compacted as in the field.***

Water is sprayed on top of the material to simulate any desired rainfall, usually a 1-in. rain, once a week. The box can be tilted to any angle to conform with the expected slope of the landfill. The runoff is collected for analysis and there are drains in the bottom to remove any permeate for testing.

EXPLANATION. ***IU Conversion Systems' studies show that an average surface loading of 0.05 g/in.^{2} is available for leaching with Poz-O-Tec material. Applying this to a 1-acre site, 698 lbs of leachate material are available for the first washing. For the 1-in. rain, approximately 208 000 lbs of water will contact the 1-acre site. Assuming a 48-h contact, a maximum loading of 3000 ppm TDS will be produced in the runoff. Subsequent rainfalls will produce lower TDS, with the third approaching 100 ppm for stabilized high sulfite and 500 ppm or less for stabilized high sulfate sludges.***

OUTLOOK

Stratospheric ozone: an agenda for tomorrow

UNEP held a meeting in the U.S. to discuss the consequences of man's activities on Earth's protective shield

For seven days in March, the United Nations Environment Program held a meeting at the State Department in Washington, D.C. Representatives from 31 countries and 10 international organizations came. The topic under discussion: the effects of man's technological and agricultural activities on modifications of the stratospheric ozone layer.

This was the first major UNEP meeting held in the U.S., according to Mostafa Tolba, UNEP's executive director. The topic, stratospheric ozone, falls within the province of UNEP's Earthwatch program (*ES&T,* March 1976, p 230).

No controversy raged at this meeting. All participants recognized the problem, and conceded its global nature, though there was disagreement over the urgency of the scientific issues. Furthermore, the delegates were aware that the more difficult socioeconomic questions did not have to be answered here, although they were to some degree addressed. This March meeting was convened specifically to ferret out the gaps in research, make recommendations for further studies and devise a mechanism for coordinating a multilateral research and monitoring effort.

So in deliberate diplomatic language, the delegates hammered out their report—a world plan of action on the ozone layer. This scientific overview contains an assessment of some possible biological and climatological effects resulting from a depletion of the ozone layer; a recognition of where more research efforts are needed; and a general agreement that knowledge of the ozone layer, as it exists today, is imperfect.

A limited success

Indeed, the meeting was successful in that it accomplished the rather limited goals set for it. It did bring together an array of countries—from the least to the most industrialized—to evaluate the state of knowledge on the ozone layer. It did identify relevant ongoing research and monitoring activities. It did define the types of activities required in the future. And it did define the activities that need to be undertaken at the international level.

West Germany's Ulrici
urges caution

What was not forthcoming was a more rigorous statement of priorities and specific courses of action by international agencies. While the meeting recognized that the formation of a Coordinating Committee on Stratospheric Ozone under the UNEP umbrella—one of the recommendations actually made—was absolutely necessary to the success of the action plan, in the words of one delegate, it was a rather "bland and unexciting" recommendation.

Physical and photochemical processes occurring in the stratospheric ozone layer have been under investigation—mostly at the national level—for five decades. But it is only recently that it has become obvious that human activities in aviation, in high-yield farming (with the obligatory use of nitrogenous fertilizers) and in the development of halocarbons as aerosol propellants and refrigerants, could modify Earth's protective shield.

In an opening address, Tolba stated that "There is little doubt that the problem is an urgent one," and of global dimensions. Since international cooperation is a necessity, the UNEP has stepped in, in the words of Tolba, to play "its customary catalytic and coordinating role."

It was Robert White, NOAA's administrator, who, in another address, colorfully called the ozone layer "Earth's Achilles' heel." White stated that of all the myriad global environmental threats, those to the ozone layer are among the most complex and insidious.

But while the problems were perceived as important, there was no consensus on the degree of urgency. Despite the fact that a discussion of control measures, including regulation, was not on the agenda, a statement to the effect that the state of knowledge made it imperative that some kind of regulation at some specific time is necessary might have been forthcoming. It was not. The recommendations that were made were couched in neutral language, possibly because as many politicians as scientists sat as delegates.

An urgency exists

Nevertheless, the urgency exists. Studies on the ozone layer performed under the auspices of U.N. agencies such as WHO, WMO and FAO, as well as some individual countries, have indicated that a decrease in this fluid envelope, with a resultant increase in UV radiation, could result in accelerated skin aging and an increased incidence of skin cancer, including the dreaded melanoma. There would probably be effects on global climate, but the state of this science is too rudimentary for the effects to be fully perceived.

Increased UV radiation in the B band (290–320 nm) would depress photosynthetic reactions, cause cellular damage and decrease crop production rates. Also, growth in ocean surface-level phyloplankton, the basic food source for higher marine life, would be adversely affected. These terrestrial and aquatic biological effects present a specter of food scarcity that is unthinkable.

While naturally occurring events such as volcanic eruptions and solar activities

NOAA administrator White
"Earth's Achilles' heel"

can disturb the ozone layer, many of man's activities—supersonic flights, nitrogenous fertilizers and the production of chlorofluromethanes (CMF)—may have greater and more immediate effects on the Earth's upper atmosphere.

It was the consensus of the meeting that the threat to the ozone layer from nitrogen oxide emissions from the current fleet of high-flying sub- and supersonic aircraft is probably negligible. But an expanded fleet flying at supersonic speeds at higher altitudes would present a problem. Long-term impacts from the use of nitrogen fertilizers are to be expected, especially if usage continues to rise, but these cannot be assessed now and more research and monitoring is needed.

The largest threat

There was general agreement that the gravest threat to Earth's protective shield comes from the production and release of CFMs. In 1973, worldwide production of Freon 11 was 368 000 metric tpy, of which 45% was produced by the U.S.; for Freon 12, 441 000 metric tpy, of which the U.S. produced 55%. More than 80% of these CMFs are released to the atmosphere.

Should worldwide CFM emissions continue at the 1973 level, the U.S. National Academy of Sciences estimated in its 1976 report that ozone depletion over a period of 50–200 years would be near 8% with an uncertainty range of 2–20%. The UNEP meeting generally concurred with these figures. However, the West German delegation expressed some reservation, emphasizing the possibility of factors that are still unrecognized or unaccounted for.

West Germany's concern is not unwarranted. Originally, the NAS predicted a maximum ozone reduction of 14%. But when it was learned that a critical factor, chlorine nitrate ($ClONO_2$), was more stable than had previously been thought, the NAS reduced its prediction to 7.5%. The stability of this chemical species came as a surprise to the scientists, and it is certainly possible that other photochemical surprises are in store.

One possible surprise may be a tropospheric (lower atmosphere) sink for the CFMs. Recently, two chemists at the National Bureau of Standards demonstrated a possible sink in laboratory experiments. P. J. Ausloos and R. E. Rebbert reported at the March meeting of the ACS that the wavelengths of solar radiation reaching the Earth's troposphere can destroy the halocarbons CCl_4, Freon-11 and Freon-12, if these chemicals are first absorbed onto sand or quartz particles. These chemists caution that the extent to which this breakdown actually occurs is presently unknown.

Edward Epstein, head of the U.S. delegation to the UNEP meeting, told *ES&T* that the proposed NBS mechanism is physically and photochemically feasible. However, he felt that sand particles would probably be an insignificant sink.

> ***"For my part, I do not propose to raise an alarm now, but I have my finger on the button, and I want to be ready to push it if the evidence suggests I should."***
>
> Mostafa Tolba

The existence of tropospheric sinks pales in significance in light of the fact that CFMs have been produced and released to the atmosphere since the late fifties. Rising slowly to the stratosphere, the CFMs can now be acted upon by UV radiation. Not discounting this legacy, countries must nevertheless consider regulating further release of these compounds.

To ban or not

Twenty major companies produce CFMs throughout the world. In the U.S. alone, 10 industrial sectors would be affected by regulations that attempted to limit the production and release of these compounds. A complete ban would have an immediate and severe impact in the short-term; in the long run, the effects would depend on the degree to which substitutes for CFMs can be found, developed and marketed.

The U.N. Dept. of Economic and Social Affairs (UNESA) in a study of the economic and social implications of banning CFMs concluded that, in general, a complete ban on CFM production and release would not be an efficient way of dealing with the problem. Rather, if regulation is considered necessary, then the problem would be better handled by controlling emissions at the source; in this way, social and industrial dislocation would be lessened.

In the long run, unilateral or multilateral regulation of CFMs will be ineffectual, according to the UNESA. What is needed is an international regulatory body that will monitor and control CFMs and other of man's activities of consequence to the stratosphere. However, UNESA cautions that historical precedence for effective control by an international agency is not encouraging.

The action plan

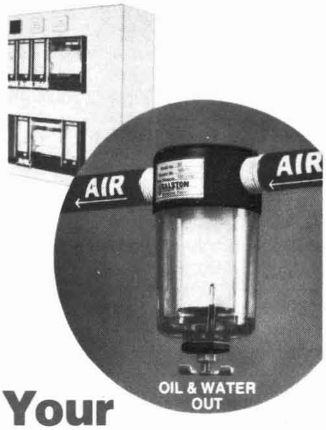
While it is expected that most of the work outlined in the plan of action will be done (and financed) at the national level, coordination will be through the specialized international agencies such as WMO and WHO. Overall coordination will be through the UNEP Coordinating Committee on Stratospheric Ozone composed of representatives from the specialized agencies, individual countries and others.

Because the substances that need to be measured are found in low concentrations in the stratosphere—as low as a fraction of a ppb—improved systems to monitor ozone, solar radiation, and selected chemical species need to be developed and implemented. The plan of action calls for the WMO to coordinate these activities.

Among the many other activities recommended under the category "The Natural Ozone Layer and its Modification by Man's Activities," is the development of models to better depict the interrelationships of chemical, radiative, hydrodynamic and thermodynamic processes controlling the troposphere and stratosphere in their natural and disturbed states. This is also to be coordinated by WMO.

Under the category "The Impact of Changes in the Ozone Layer on Man, the Biosphere and Climate," the action plan calls for monitoring the spectral distribution of UV-B radiation at the Earth's surface for at least one complete solar cycle, and for improved instrumentation for measuring UV-B radiation. These activities are to be coordinated by WMO, WHO and FAO. WHO is also to coordinate efforts to develop improved epidemiological studies on skin cancer; research into the cellular and molecular mechanisms of UV-B irradiation that induce skin cancer, skin aging and eye damage; and research into potential beneficial effects of increased UV-B, including Vitamin D production.

The FAO will coordinate studies on other biological effects of increased UV-B on aquatic and terrestrial plant and animal communities. WMO will coordinate efforts to document climatic changes resulting



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from changes in the ozone layer.

The plan of action recommends that UNESA and OECD develop improved methods including, at the request of the Swedish delegate, multidisciplinary systems analysis, to assess the costs and benefits associated with levels of control of CFM use, aircraft emissions and nitrogenous fertilizer use. Another recommendation is the attainment of more detailed data on present and projected human activities at or near the stratosphere, and on current and projected production, emission and use of substances that may affect stratospheric ozone. UNEP, OECD and other international organizations will spearhead these activities.

The UNEP meeting served to catalyze international cooperation on future research and monitoring activities; it was an essential source of information for a second meeting on ozone held last month. This April conference, sponsored by the EPA, FDA and the Consumer Product Safety Commission, was held to receive views on approaches to regulating the nonessential uses of CFMs. These views were sought from those industrialized countries who are major producers or users of CFMs.

The U.S. pushed for the April meeting because it recognized that unilateral regulation on its part would be ineffectual in the absence of international agreement to regulate nonessential uses of these compounds.

Those countries with a sizable investment in CFM production, such as Britain, France, Italy and West Germany, want to proceed very cautiously toward regulation. From their comments at the UNEP meeting, it is obvious that they are not totally convinced that there is a problem of the magnitude expressed by the U.S.

Their attitude is understandable. The U.S. was the first to recognize the menace from CFMs, and it has been studying the problem longer and more intensely than any other nation. The U.S. is now eager to forge ahead to international agreement on regulation. The other countries have had less time to digest and accommodate themselves to the probable consequences of decreased stratospheric ozone. They are therefore less willing to proceed as expeditiously as the U.S. would like.

The problem of regulation is compounded by the fact that cause—CFM emissions—and probable effects of ozone depletion are widely separated in time. If countries take action now—that is, curtail some profit-making activity—they would in the words of White "never know—except through scientific argument—that the effect would indeed follow the cause." And White continues, "If we ignore the advice, and those scientific arguments are correct, we will have ushered in human discomforts that we will be powerless to stop." LRE

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P.L. 92–500: changes downstream

For the last few years, much talk was heard about "mid-course corrections." But the time for talk has passed, and the time for action has arrived

Accompanying the famous Japanese cherry blossoms and first balmy days of spring in Washington, D.C., was the 11th annual government affairs seminar of the Water Pollution Control Federation (WPCF), headquartered in the same city. For a few years, now, these seminars have heard detailed discussions of needs for "mid-course corrections" for P.L. 92-500, as *ES&T* readers will recall. However, as WPCF president Horace Smith told the March seminar, with more than 400 people in attendance, concrete mid-course corrections could not be initiated until the National Commission on Water Quality (NCWQ) had concluded its work. Since the NCWQ's mission is now accomplished, and it is out of business, Smith said, "The need for change is clear, the time is now, so let's get on with the job of cleansing the nation's waters."

Complex, but effective

"P.L. 92-500 has been a most complex but most effective tool," and has so far led to improvement in the quality of about 35% of U.S. waters tested, EPA's new deputy administrator, Barbara Blum, told the seminar. She did say, however, that EPA could support some changes. For instance, the flow of grant funds could be improved, especially to smaller, financially less well-off municipalities. Also, second and third stages of the grant process could be consolidated and made more flexible for meeting operation/maintenance (O/M) costs. Blum cited the lack of resources that smaller communities often suffer, and called for a smoothing out of the present boom-and-bust funding pattern that may be a major factor of the municipal compliance lags.

Blum also called for considerably more state and regional involvement, as well as for "streamlining" in administration of the laws, as long as standards are not compromised, and the integrity of P.L. 92-500 is maintained. She advocated allowing states to use part of their allotments for meeting implementation costs and delegating to them more regulatory functions, as long as there is water pollution reduction for each dollar spent on it.

Time extensions were also discussed. Andrew Breidenbach, EPA's assistant administrator, Office of Water and Hazardous Materials, expressed support for extensions for municipalities and industries on a case-by-case basis. He said, however, that it would be more efficient for extensions to be granted up to July 1, 1983, or "best available" (BATEA) deadline. But he also said that just because of a delay occasioned by the unavailability of an interceptor, for example, a municipality gets a compliance extension, an industry under contract to use that municipality's sewer system should not automatically be granted a deferral.

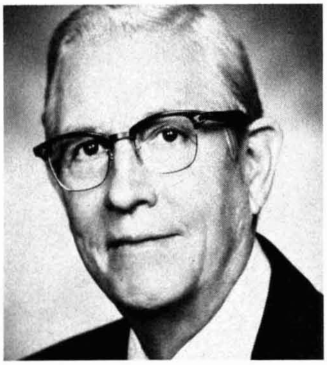
Amendments of 1977

Addressing the seminar luncheon, Rep. Ray Roberts (D-Tex.) cited some mid-course changes proposed in H.R. 3199, the "Federal Water Pollution Control Act Amendments of 1977." One provision would allow a grantee to use excess funds, if any, for a collection system already under construction. Another would allow ad valorem taxes as a means of defraying O/M costs. Also, each industrial user would pay a fee directly related to strength, volume, and other characteristics of its discharge into a treatment works.

Yet another provision would offer industries an extension to July 1, 1979, in cases in which the EPA administrator finds that "best practicable" (BPCTCA) cannot be completed or applied by July 1 of this year. Moreover, industries might get a July 1, 1978, or construction completion date deadline if they received research grants to develop innovative technology, but have not accomplished their research goals by this July 1. For an idea of the direction mid-course corrections could take, H.R. 3199 and the parallel S. 57 make worthwhile reading.

Voice from industry

Matthew Gould, corporate director, energy and environment at Georgia-Pacific Corp., said that most of industry will be in BPCTCA compliance by this July. However, he asked for a Congressional dispensation for those plants that made good-faith efforts to comply, but fell short because of paperwork delays, equipment failures, or force majeure. He also expressed support for the NCWQ proposal that 1983 BATEA be delayed until the extent to which this year's goals have satisfied 1983 requirements for fishing and swimming have been evaluated. As for the 1985 goal of "zero pollution discharge" (ZPD), Gould observed that some types of industry, but not all, will succeed in complying, just as "municipal sewage and garbage cannot be made to vanish without a trace."



Congressman Roberts
Explained H.R. 3199 provisions

Addressing the nonpoint source problem, Gould pointed out that such sources will be chief pollution culprits after point sources have all come into compliance. That situation "underlines the futility of pursuing ZPD when the minor increment of water quality gained by costly treatment will be largely obscured by non-point contaminants." By contrast, Khristine Hall of the Natural Resources Defense Council called for no more than very "minor" changes in P.L. 92-500, and said that granting extensions to some industries not in compliance would be unfair to those that invested large sums to meet deadlines, and succeeded in doing so.

The bottom line

What might be borne in mind is that much of the P.L. 92-500 discussion and debate entails end-of-pipe cleanup strategy. But source control is also well worth considering and pursuing, as Joseph Ling of 3M Corp. showed (*ES&T*, March 1977, p 234) when he listed recognized projects that bear him out.

Indeed, the bottom line for pollution abatement may be source control as the only viable means, Sidney Galler, deputy assistant secretary of Commerce for environmental affairs, bluntly told the seminar. Replacement of major processes will have to be effected, he predicted. Galler advised that the way to go is not to let successes in end-of-pipe treatment go to people's heads, but to look ahead to a concerted program of "ecological engineering" that addresses all available options. He observed that each environmental law covering a given aspect of needed corrections is as a pillar, but the engineering approach will be the ultimate bridge for which each pillar by itself is an unconnected support. JJ

Man is not the only polluter

Nature can do its share, too. Marine halocarbons are one salient example, as a Scripps Institution of Oceanography scientist discovered

Around the end of January, the National Oceanic and Atmospheric Administration (NOAA) announced the establishment of a national facility to detect and help define extremely small chemical changes in sea water or sediments. The facility, located at Seattle, Wash., has ultra-sensitive instruments that can detect contaminants to levels of less than one part per billion (ppb), in some cases. Among the different contaminants that NOAA's new equipment might find, there could be halogenated organic compounds, for example.

Now suppose that monitoring teams using this highly sophisticated equipment find halogenated organics in certain coastal waters. Suppose, further, that there is industrial activity in the vicinity. A scenario could develop in which some groups of people living near these coastal waters, or even a local government, might bring suit against the nearby industry for polluting the marine environment with halocarbons. But the plaintiffs might not necessarily win their case.

Go sue Mother Nature!

Contrary to what was believed until earlier this decade, halogenated organics do, in fact, occur naturally, and in considerable variety. The great majority of life forms that produce them are found in the marine environment, William Fenical of the Institute of Marine Resources, Scripps Institution of Oceanography (SIO, La Jolla, Calif.), told *ES&T.*

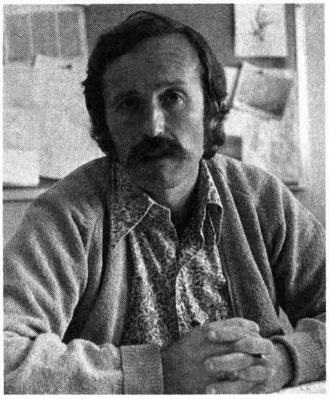
To be sure, some halogenated organics occur in the terrestrial biosphere. For example, certain iodine-containing amino acids are vital to mammalian and human metabolism. Some chlorine-containing compounds exist in a number of fungi and higher plants, and traces of a brominated substance are found in human cerebrospinal fluid. Also, as Fenical pointed out, a type of ratsbane plant from Asia has fluorocitric acid, and even common tea contains infinitesimal quantities of fluoroacetic acid.

However, in the sea, many species of brown seaweed, molluscs, sponges, and bacteria metabolize halogens. But the red algae, or Rhodophyta, are of the greatest interest, because while they use mostly bromine, they also synthesize an impressive diversity of organic substances, some containing chlorine and iodine. These substances range from low-molecular-weight compounds, such as halomethanes and certain ketones and aromatics, to higher-molecular-weight terpenes and fatty-acid-like products. As halogenating Rhodophyta, 5 orders, 9 families, and 17 genera are listed by Fenical in one of his papers.

The medical connection

In recent years, scientists have been looking to the sea and its biota as possible sources of pharmaceuticals, and precursors for pharmaceuticals. Fenical is one of those scientists, and it was in his search for medicines that he and his colleagues began to discover the wide variety of halogenated organics synthesized by many marine organisms. He told *ES&T* that the number of carbon atoms in the structures of these materials can range from 1–30.

Do any of these organisms produce substances similar to DDT, PCB's, or the like? According to the Scripps scientist, the biosynthetic pathways to produce these specific compounds do not exist. In fact, in some cases, materials such as PCB's and DDT can kill phytoplankton, even when these chemicals are in the parts-per-billion range. He did say, however, that the microorganisms that could metabolize, or even thrive on, say, DDT, could conceivably be developed, although no estimate could presently be made as to the rate of DDT consumption, or of reproduction of such a life form. Nevertheless, the possible acquired ability of certain marine biota in the food chain to metabolize man-made halogenated organics has been a matter of some concern in Japan (*ES&T,* February 1974, p 113).



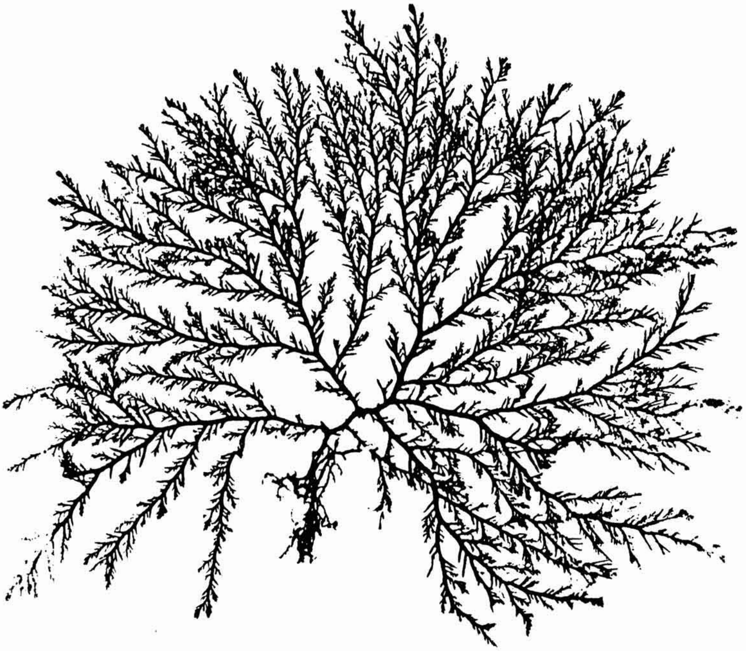
SIO's William Fenical
"Careful evaluation a 'must' "

Still, even if those busy little sea creatures are not producing DDT or PCB's, have no fear—there are other "pollutants" for anybody who wants them. For instance, one red seaweed of the genus *Asparagopsis,* which occurs worldwide, produces small, but measurable amounts of carbon tetrachloride. It also makes bromoform; in fact, on a dry-weight basis, bromoform has been found to the extent of 1%—that's 10 000 ppm—in this marine plant. Other compounds found in that same seaweed include small amounts of halogenated acetones; one such compound, monobromoacetone, is a principal component of tear gas.

Incidentally, the original effort that led to the discovery and cataloguing of biosynthesized halogenated organics (in 1975, Fenical enumerated 83 in a *Journal of Phycology* paper, and that is not a complete list)—that is, the search for pharmaceutical materials—might not go unrewarded. A number of the substances produced are bacteria- and invertebrate-toxic; for example, one compound related to bromophenol, called laurinterol, and produced by the red alga *Laurencia intermedia,* shows very strong activity against *Staphylococcus aureus,* a notorious human pathogen.

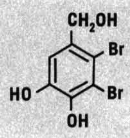
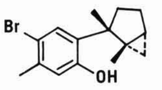
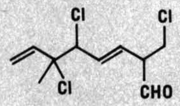
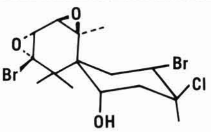
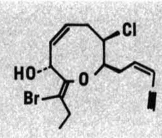
Detection

How does one go about detecting and determining biosynthesized halogenated organics? It is not easy, when one considers that there can be more biomass in



"Polluter." *This marine plant makes 5 halocarbons*

Some natural marine halocarbons

Compound	Structure	Origin
Lanosol		Polysiphonia lanosa, and other species
Laurinterol		Laurencia intermedia
Cartilagineal		Plocamium cartilagineum
Prepacifenol epoxide		Laurencia johnstonii
Chondriol		Laurencia (various species)

an acre of phytoplankton than in an acre of corn, as Fenical told *ES&T*. Also, many different types of marine algae could comprise that biomass.

Thus, it takes a scientist or technician "in the know," and with a practiced eye to select the proper sample, Once the sample or samples have been collected, painstaking methods must be used to pretreat them, extract chemical substances from them, and separate and isolate the materials believed to be in the extract. When all of the correct procedures have been followed, the actual determination is done, normally by combined spectro-chemical methods involving gas chromatography–mass spectrometry.

In the case of naturally occurring halogenated organics, the correct procedures for sampling, pretreatment, separation, isolation, and analysis must be most meticulously followed. For instance, some areas of the ocean, particularly coastal waters, may also be polluted by man-made organic compounds. In certain cases, the molecular structures of these compounds could look very similar to those of the naturally occurring "pollutant." Unless the halogenated organic-producing species are properly recognized, and analysis procedures correctly done, spurious results will be obtained, and the differentiation between natural and man-made products would be difficult or impossible to define. And it must be remembered that some of these products' concentrations may be in the parts-per-billion range.

Moreover, when news of halogenated organics in nearby coastal waters "hits the street," one could hear not only from activists; trained scientists with much cooler heads also become concerned, and rightly so. For this reason, it is most essential to pinpoint the sources of these compounds. If a source is human activity, for example, then some corrective action is certainly in order. But in fairness to the industrial community, the sources of any halogenated organics, especially toxic ones, must be ascertained properly and according to meticulous procedure before any accusations are made. JJ

FEATURE

European materials recovery systems

Several European countries are forging ahead in their efforts to retrieve materials and energy from growing mounds of solid waste; unlike the U.S., their main objective is paper recovery

Harvey Alter
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Washington, D.C. 20036

This feature is based on an article that appeared in the Fall 1976 NCRR Bulletin.

With the great interest in resource recovery in the U.S., comparatively little attention has been given to parallel developments in Europe beyond incineration with heat recovery. Still, European countries (including Scandinavia and Great Britain) share U.S. concerns of increasing amounts of solid wastes, diminished land areas for disposal and needs for environmental, materials and energy conservation. As a result, there are a number of noteworthy resource recovery research and development activities under way in Europe.

This is a review of those activities in Europe directed to the mechanical processing of municipal solid waste for the recovery of materials and, in a few instances, refuse-derived fuel. The review is not all inclusive. Parallel developments in source separation, industrial waste utilization, processing for steel-can recovery, processing for compost and developments in incineration and pyrolysis are not included. Also, there have been extensive investigations of materials recovery and reuse of incinerator residues. These are not reviewed here; no large commercial plants for processing incinerator residue have yet been built.

European materials recovery objectives and, hence, practices, stress paper recovery. This differs from current U.S. practice, which stresses some type of fuel recovery. Many European countries anticipate fiber shortages, even short term; in addition their waste composition differs from U.S. waste. Municipal solid waste in many countries contains less metal than in the U.S. and there is, at present, less interest in glass recovery in Europe than in the U.S. As a result, in Europe gross revenues from sale of recovered products would be low, if not for the potential of selling some form of recovered paper.

Differences in waste composition among countries also determines, to some extent, the type of technology under development. As a starting point for later comparisons, Table 1 lists the solid waste composition reported for a number of cities and countries. Important differences are in the contents of metals, glass, paper and food wastes. It is interesting to speculate how the differences in composition may be related to standard of living and life style, particularly as related to centralized food processing and extent of household refrigeration.

Overview

There are major pilot-scale research efforts in mechanical sorting processes under way in England, Germany, Holland, Italy and Sweden. The research pilot plant in France, operated by the Bureau de Recherches Geologiques et Minieres, broadly parallels the one in England; U.S. technology from the Bureau of Mines is being adopted in Spain.

In Berlin, a private contractor is designing the machinery to recover magnetic metals and is investigating machinery to shred and air classify wastes. Household and office wastepaper (from separate collections) is used as 100% of the "furnish" to manufacture kraft-like paper in the city. A plant was built in Berlin to make aggregate for concrete ("sinter pumice") from incinerator residue. The performance of this aggregate was less than expected and the plant operates intermittently. Resource recovery research is actively being conducted at the Technical University in Berlin. All of these activities are being pursued to lessen the need for disposal sites in land-short West Berlin.

The mechanical separation of household waste is being investigated at the Technische Hochschule Aachen, including unit operations such as rising current and heavy-media separation. Air classification is being researched at the Technical University at Eindhoven and at the Universities in Karlsruhe and Erlangen-Nueremberg.

Resource recovery is an active field of research at Aston University (Birmingham), and at the Universities in Nottingham and Leeds. Research on the conversion of cellulosic wastes is actively pursued at Manchester.

In several European countries, there is great interest in the use of waste materials in the making of concrete. Among the various efforts toward the recycling of plastics is research at the University of Hamburg directed to the pyrolysis of waste plastics in molten salt and fluidized-bed reactors.

In France, PVC plastic recycling is facilitated by the separate collection of the popularly used 1.5-L mineral water bottles. Also in France, in the Paris suburb of Enghien, a refuse processing plant recovers steel and prepares a waste fraction for a special grade of compost by sieving and air classifying the shredded material. A unique air classifier is used to remove stone and glass smaller than about 1 cm from the shredded fraction.

In Holland, there is a joint effort by the recycling firm of Esmil, the can company Thomassen and Drijver, and the Dutch government-owned waste disposal and compost corporation VAM, to recover steel cans directly from raw waste. A mobile crane feeds the waste into a unique mobile processing plant that tears open plastic bags of household waste, magnetically removes the steel, which is then shredded to prepare the cans for detinning, a second magnetic belt separator conveys the cans to an adjacent trailer for shipment, and unrecovered material is discharged. The units move slowly, past the tipped waste, recovering steel prior to the waste being landfilled or composted.

Refuse-shredding plants are more common in Europe than in the U.S. Often, the shredded refuse is used to make compost. The engineering know-how and operating experience gained

TABLE 1.

Comparison of household solid wastes [a]

Wt %, as received

	LOCATION								
COMPONENT	**Holland**	**Sweden**	**Stockholm**	**Stevenage UK**	**Rome**	**Vienna**	**Prague**	**Sofia**	**Federal German Republic**
Paper	22.6	40–50	45	33	18	35.3	13.4	10.0	28
Iron and steel	3.1	4–8	6	7	3	9.7	6.2	1.7	7
Mixed nonferrous metals	0.1		0.5	<1	—				
Glass	13.0	8–10	7	10	4	9.1	6.6	1.6	9
Plastics	5.3	4–8	9	4	4	5.5	4.2	1.7	3
Textiles and rubber	2.6	2–6	—	4	—	5.6	8.1	7.0	3[b]
Food wastes (garbage)	49.6	8–20	17	14	50	24.1	41.8	54.0	15
Other organic materials			8.5	—		—	—	—	28
Sand, stones, other inorganic materials	1.4	—	7	28	—	9.9	19.7	24.0	7

[a] The columns may not total 100%, not every component of the waste was always classified. [b] Textiles only.

from these plants will be an incalculable assistance in establishing full-scale resource recovery plants later on.

The several operating pilot plants and one commercial sorting plant in Europe each approach the problem of resource recovery differently. The processes offer interesting comparisons.

England, Warren Spring

The Warren Spring Laboratory of the Department of Industry operates a research pilot plant for the physical sorting of household refuse to recover paper, magnetic metals, glass and refuse-derived fuel. The small amount of nonferrous metals in the waste can be recovered, as can a mixture rich in plastic film and sheeting. The pilot plant operates at 3–4 t/h.

Household refuse is conveyed to a device intended to open the plastic and paper bags and liberate the refuse. The device is adapted from a type of screw compactor used on collection trucks. The liberated refuse is screened through a rotary screen (trommel). Fine material (<13 mm) is discarded. Middling material (50 × 13 mm) is magnetically separated; putrescible material in the nonmagnetic portion is separated ballistically from denser glass and stones by bouncing the material off a rapidly rotating drum and by "sink/float" in brine. Glass can be recovered from the sink fraction by froth flotation.

The other middling fraction (200 × 50 mm) is similarly processed except, in this case, the organic materials from the ballistic thrower are air classified to a refuse-derived fuel. The air classifier used at Warren Spring is a rotating drum (not much different from some in the U.S.) with a screen section to remove fines. The light fraction is a refuse-derived fuel that has been densified for burning in stoker boilers.

The trommel oversize (>200 mm) is shredded and air classified for paper recovery. This product yield is about 20% of the input waste and contains from 6–8% "contraries," mostly plastics. The content of sand, glass and food waste in the recovered paper is reduced by the trommel screening; the content of plastic film and textiles can be reduced by two other efforts.

"Flexibles" are removed in the trommel. This is done by a constantly moving trolley wire through the trommel, near its top. Rags and plastic film drop over this wire, which carries these materials out. This not only removes rags and plastic film from the final paper product, but also reduces blinding of the trommel holes.

A second, experimental effort at removing plastics and textiles was in progress July 1976. Plastic film was distinguished and removed from the paper in the >200 mm trommel discharge product by using the specular reflectance of a laser to trigger a blower.

Plans are under way to build two full-scale (200 tpd) resource recovery plants in England patterned after the Warren Spring plant. The processing in one will combine some of the fractions to produce refuse-derived fuel (probably densified for stoker burning) and the other will produce paper for reuse. The plants, in the planning stage, are cooperative ventures among the Departments of Industry and Environment and the local authorities.

Germany, Krauss-Maffei

In Munich, Imperial-Krauss-Maffei Industrianlagen operates a 5-tph pilot plant, called System R-80, for paper and metal recovery. One fraction produced is suitable for compost and, potentially, for glass recovery. Work is under way to produce a usable plastics fraction. As with Warren Spring, there is no primary shredding.

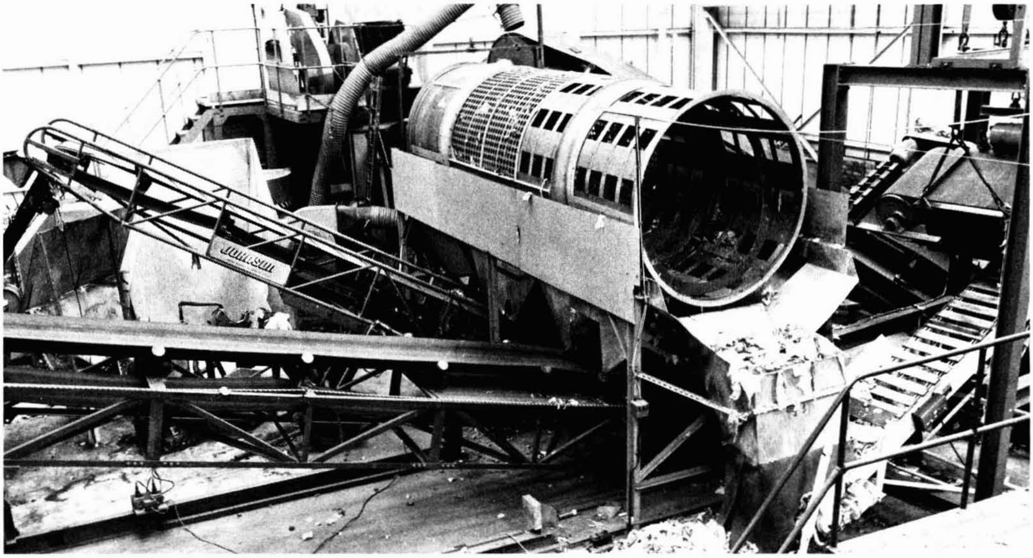
Magnetic metals are recovered from the raw waste. Such scrap must be washed, or otherwise cleaned, prior to detinning.

The nonmagnetic fraction is screened to remove organic material (principally food waste) that can be composted, glass and sand. The oversize is air classified to a light fraction of paper and plastics; the fraction is screened to remove a mixture of plastic film and large paper sheets as the oversize product. The undersize product is air classified to remove inorganic materials as a heavy fraction (to waste) and a light fraction consisting of newspaper, magazine stock and textiles. The paper fractions are combined. The recovered paper contains 5% plastics and other contraries.

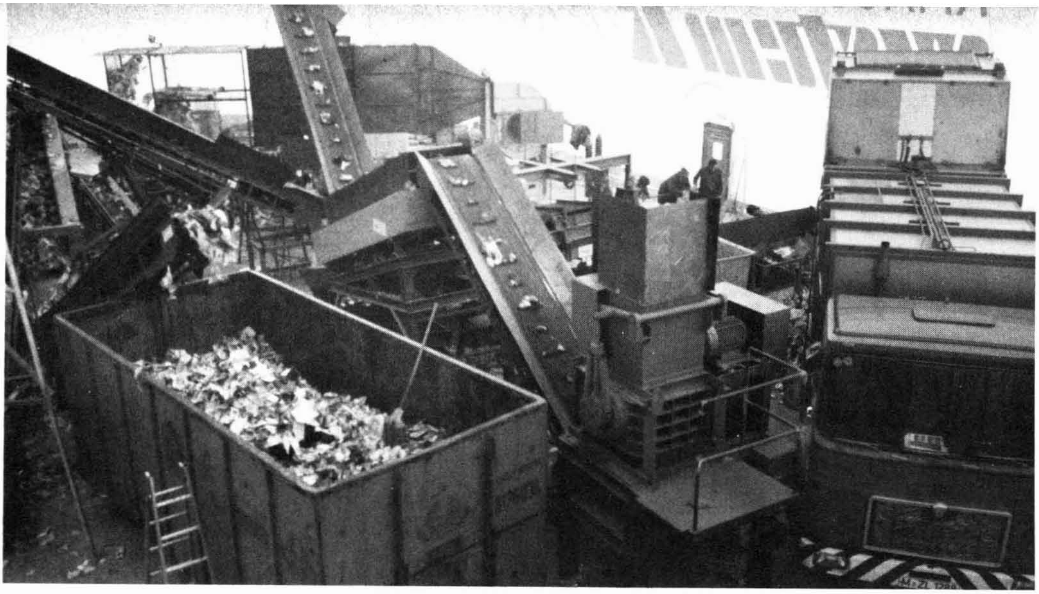
Krauss-Maffei has experimented with separating the plastic film from the paper and using this plastic mixed with filters and/or industrial plastic scrap to make extrusions. Without additional clean up of the plastics, the extrusions are weak; therefore, additional work is being done to produce a more usable recovered plastic.

Holland, TNO/Esmil-Habets

In Haarlem, Holland, private industry (Esmil-Habets) and a government laboratory (Central Technical Institute TNO) are jointly investigating the separation of municipal waste with the



Warren Spring. *This 3–4 tph pilot plant sorts refuse to recover paper, metals, glass and refuse-derived fuel*



Krauss-Maffei. *The pilot system processes 5 tph of refuse to recover paper and metals*

recovery of paper. The reported process flow is for a 15-tph pilot plant. A distinguishing feature of this system is the use of two zigzag air classifiers so that the light fraction from the first is the feed for the second (with sieving in between). The objective of this arrangement is to separate the plastics from the paper in the light fraction from the first classifier so as to produce a usable paper furnish that would be the heavy fraction in the second classifier. To achieve this separation, the moisture content of the mixture of paper and plastics is raised so that the paper becomes the heavy fraction. Separation of Haarlem waste resulted in 3% iron, 25–35% heavy fraction, 20–30% paper and 5% plastics; a high recovery of paper is possible if the Haarlem waste has a composition similar to that in other parts of Holland (Table 1).

Italy, Sorain Cecchini

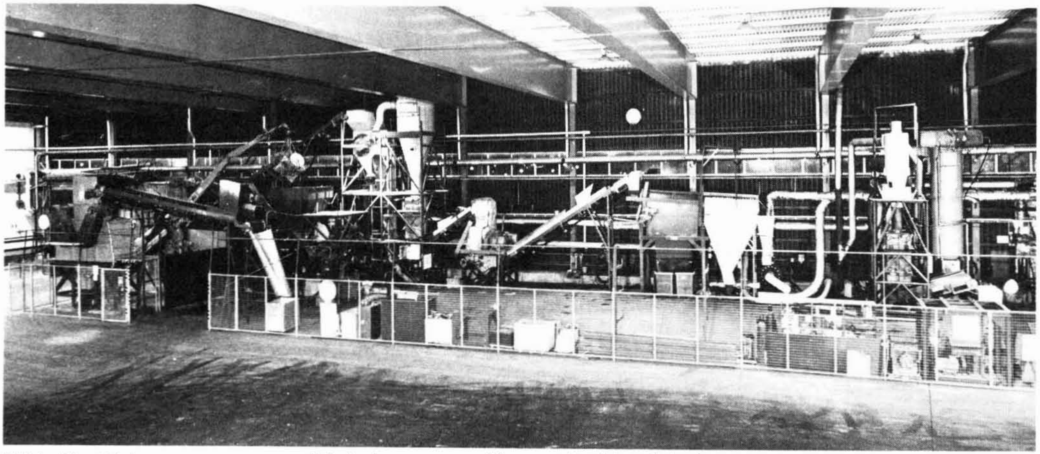
In Rome, the Sorain Cecchini Group operates two full-scale resource recovery plants with capacities of 600 and 1200 tpd (2 shifts). The reported outputs are 2.8% magnetic metals, 13% paper, 16% organic material to animal feed, 24% organic material to compost, 2% plastic and 41.7% incinerated to generate steam. Little technical detail has been made public. No shredding is used; the keys to the operation are the various proprietary classifiers.

It is important to point out that the paper fraction, as opposed to other raw refuse separating systems, contains food waste and bacteria. The paper fraction is pulped at the Cecchini plant; the pulp serves as a good medium for bacterial growth and would have to be used promptly—probably within a few days of preparation.

It is reported that the separated plastic film has been used for miscellaneous extrusions. Also, it is not clear whether mixed municipal waste or wastes collected separately from food markets are used to manufacture the animal feed. Nonetheless, separated organic matter is washed, floated from inorganic contaminants, sterilized (autoclave), dried and pelletized. The product is reported to contain from 14–17% protein and from 7–9% fat. It was reported to the author (August 1976) that plants are under construction in Venezuela and Yugoslavia.

Sweden, Fläkt

A large Swedish firm experienced in air-handling equipment, and pulp dryers, A.B. Svenska Fläktfabriken, operates a 5-tph pilot plant for the recovery of usable paper furnish and steel. Glass recovery by froth flotation could be added. The paper re-



Fläkt. *The 5-tph resource recovery pilot plant recovers usable paper furnish and steel*

TABLE 2.

Comparison of papers manufactured from recovered fiber

Property	Mixed wastepaper	Household wastepaper	Furnish (*left*) and "splinter free" (*right*) furnish from Black-Clawson, Franklin, Ohio		Cecchini, Rome		Krauss-Maffei, Munich	
Degree of pulping, °SR[a]	40	50	24	28	39	45	39	44
Splinters, %	2	1	7	0	4	0	2	0
Long fibers, %	38	34	39	45	29	15	36	37
Short fibers, %	34	21	26	28	26	35	25	25
Fines, %	26	44	28	27	40	50	37	38
Tear length, m	2700	2400	1650	2300	1300	1700	2005	2400
Tear strength, g/cm	9.8	8.8	8.5	8.5	7.3	5.4	9.0	10.0
Bend stiffness, N × mm	0.39	0.41	0.33	0.34	0.75	0.25	0.35	0.36
Bursting strength, kg/cm^2	1.20	—	—	—	—	—	1.25	—
Reflectance	40	42	30	30	35	34	38	38

[a] °SR = Schopper-Riegler.

covered is dry, possibly sterile, and seemingly free of pieces of plastic film that could interfere with the papermaking process.

Household waste is shredded in a flail mill. The milled material is sized through a trommel; material greater than 220 mm is reshredded and the trommel underflow is fed to a zigzag air classifier. Magnetic metals are recovered from the heavy fraction. The light fraction is re-shredded (hammermill or modified flail) and sized through the second trommel. The fraction containing material less than 25 mm is said to contain the putrescibles, and that fraction with greater than 80 mm material much plastic film. The middling (80 × 25 mm) is processed through a pulp flash dryer (a commercial item manufactured by Fläkt) at 130 °C air temperature. This not only dries the paper, but also shrinks remaining plastic film, which is removed by a cyclone. Textiles fall in the pulp dryer and are removed.

Some of the heat-shrunk plastic film, which is not removed by the cyclone, can be removed in a subsequent air classification step that is also said to be capable of separating newspaper from corrugated, chipboard and other similar packaging material. The validity of this claim may be judged by one sample of the news fraction that the author picked from the bin at the operating pilot plant. The only recognizable paper was news, and a 38-gm sample contained 3.4% by wt plastics and cellophane. Most of the pieces of plastic were heat-shrunk (rolled and crinkled). A U.S. user of secondary newspaper later observed that such pieces would be easily removed in their papermill.

Fläkt reports that the composition of the recovered paper is from 50–60% short fibers, presumably newspaper, and the remainder is long fiber; the composition of the steel is Fe, 90%; Sn, 0.4%; Pb, 0.3% and Al, 0.7–6%.

A full-scale plant (120 000-metric-tpy capacity) based on the Fläkt design is scheduled to be built in Holland for VAM-Recycling B.V., a subsidiary of N.V. Vuilafvoer Maatschappij VAM. The latter firm is Holland's largest waste management (disposal and composting) company; it is owned by the Dutch government.

Use of the recovered paper

Almost all of the paper recovered from the various processes contain contraries, such as plastics and textiles. For example, the Warren Spring paper-rich fraction contains 87% paper, 5% plastic and 3% textiles. Presumably, many of the contraries could be removed, especially when processing the recovered furnish in the paper plant, but at some cost. Therefore, depending on its composition, a paper fraction recovered from municipal waste may be *usable*—but not necessarily *saleable*.

In addition to contamination by textiles and plastics, the recovered paper may be mixed with food wastes. Also, it is likely to be wet and thus a suitable medium for bacterial growth and composting. Some of the process operators recognize this possibility and the need to either use the recovered paper within a short time or find a stabilizer to retard the bacterial action. An exception is the paper recovered by the Fläkt process, which is dry. The surviving microorganisms are likely to be inactive; cellulolytic bacteria and fungi are dormant when the paper contains less than about 9% water.

There have been several trials utilizing the recovered paper furnished in mills. Experimental sheets were produced with the fiber recovered by TNO; the Dutch cardboard industry considered the quality of the fibers usable for cardboard production. The paper recovered in Rome (by Cecchini) is pulped on-site and shipped to a paper manufacturer.

The most extensive papermaking trials appear to have been with paper recovered in Munich (by Krauss-Maffei). Some of the properties of the paper produced in these trials are summarized in Table 2. Also, it was reported that the drying in the papermaking machine was sufficient to kill residual bacteria. Paper manufactured on a commercial scale from 100% furnish from the Krauss-Maffei pilot plant was as free from bacteria as normal paper and the incubation time of bacteria on either was the same.

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Monitoring "Rijnmond smog" for alert conditions

To reduce the effects of air pollution episodes, a network of monitoring stations permits the issuance of alerts to enable industry to reduce emissions voluntarily

J. E. Evendijk and P. A. R. Post van der Burg
Central Environmental Protection and Management Agency Rijnmond
Schiedam, The Netherlands

Periods of serious smog and stench accelerated the passage of the Air Pollution Act which, under heavy political pressure, became effective in 1972. Once passed, the law stimulated the integration of all technical expertise on environmental affairs which, until then, had been fragmented in different services in and around Rotterdam, into one environmental agency. This agency, the Central Environmental Protection and Management Agency Rijnmond (in Dutch, abbreviated DCMR), has been in existence four years now and, at the moment, consists of about 150 employees.

Next to drawing up and revising permits under the Air Pollution Act and the Nuisance Act, DCMR's activities in the last few years have stressed the reduction of emissions during smog periods and the prevention of stench waves. For this purpose an elaborate organization has been built up, in which public authorities and industry co-operate closely.

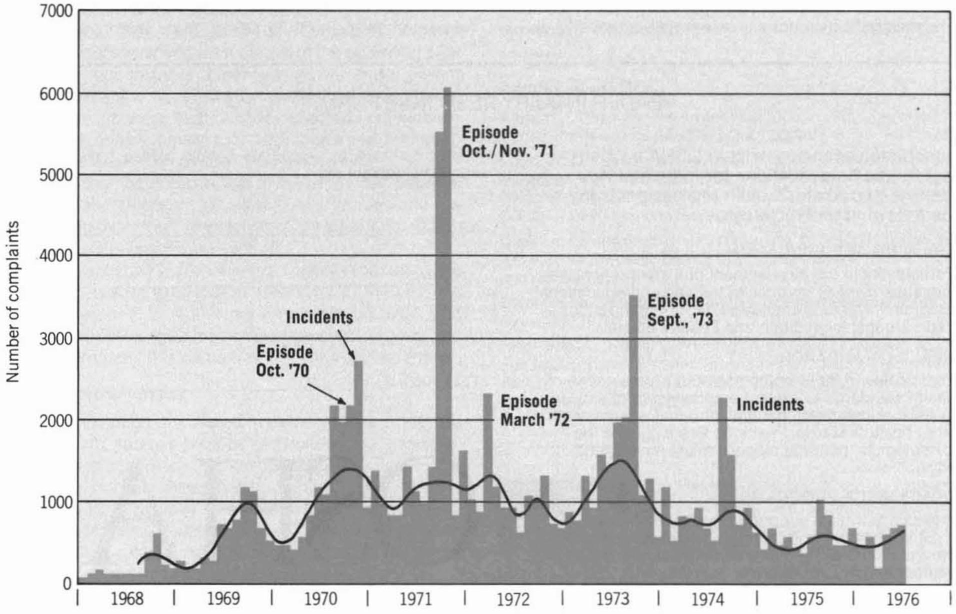
At the center of this organization is the Report and Monitoring Center, which has been in operation since 1968, but is now part of the DCMR.

Air pollution in Rijnmond

Owing to the presence of many factories, the populace of Rijnmond is deeply concerned about air pollution problems. Suggestive drawings showing skulls in the air above industrial and residential areas have appeared; these drawings accurately express the uncomfortable feelings. Verbally these feelings are expressed by the words "stench," "smog" and "dust."

Stench is one of the most undesirable types of air pollution. For the man in the street stench is a serious matter: partly for fear of the consequences to health and partly from annoyance at the growing discomfort of living in a densely populated industrial area with a high standard of living. In most cases, epi-

FIGURE 1
Citizen complaints of air pollution



sodes of noxious odors result from careless operation and industrial breakdowns. But, as these nuisance episodes occur more frequently, the public's tolerance decreases proportionately.

The phenomenon of smog is also considered a highly undesirable side-effect of industrialization, although it does not occur as frequently as stench. Compounding the problem, is the claim by public authorities that they still have insufficient insight into the complex processes that play a part in the phenomenon termed "Rijnmond" smog. This lack of information prevents the authorities from taking the appropriate actions to eliminate smog, and the public, resigned to perceived inaction on the part of the authorities, accepts smog as a part of life.

Dust emissions can cause local nuisances. In many cases these emissions are due to transshipment activities (cereals, ore, coal) in the Rotterdam harbor. The inconvenient and noxious effects are mainly related to the nature of the dust (particle size) and its chemical composition (metals, asbestos, sulfates, nitrates). The citizen recognizes the problem because he has to wash his car more often or he cannot dry his laundry outdoors.

Types of air pollution

Structural air pollution is always present to a greater or lesser extent as a result of the "normal" emissions from heating activities, traffic, and industry. In general, this category of air pollution does not elicit many complaints. Although it seems to have no directly perceptible noxious consequences on public health, this does not mean that no noxious effects occur over the long term.

Accidental air pollution may occur at any time as the result of unforeseeable incidents in industrial operations, such as breakdowns, fires, and explosions. In this case, malodorous and toxic components can be released, which in the most serious cases can be acutely dangerous to the surroundings. In a heavily industrialized area, where large numbers of chemicals are handled, such incidents occur regularly during loading and unloading activities.

Periods of increased air pollution occur when, under certain weather conditions, the polluting components accumulate to levels that sometimes may be ten times the normal level. Moreover, these emissions may react and interact to form even more noxious compounds, as is the case when photochemical smog is formed. It is especially for these periods of increased air pollution that the Rijnmond alert system was developed.

It should be pointed out that the above-mentioned types of air pollution are closely interconnected. If, for instance, structural air pollution decreases, the change of increasing concentrations of pollutants during air pollution episodes will be smaller too.

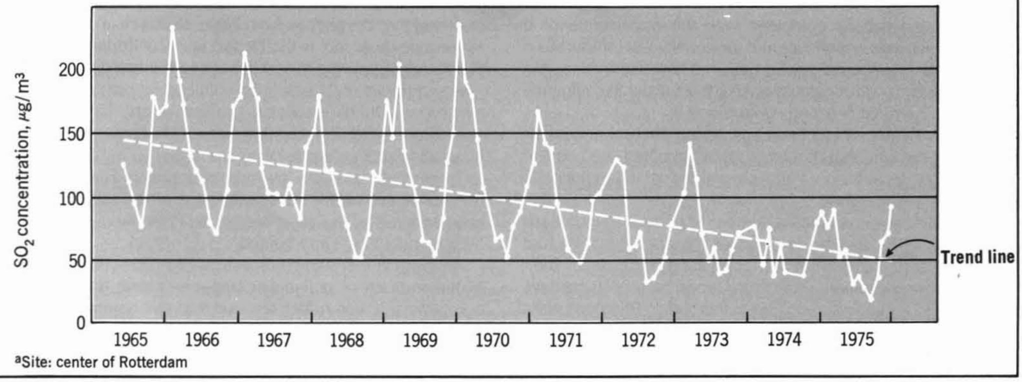
These three types of air pollution have been quantified in terms of the number of complaints received from the population. Figure 1 shows the number of complaints per month that have been registered to the Report and Monitoring Center over the years. The peak values in the months of August through November 1970, September/October 1971, March 1972, July through September 1973, and August/September 1974, result from serious incidents or periods of increased air pollution. The wavy line represents the moving average in which a correction has been made to take into consideration the complaints during serious incidents and air pollution episodes; this line indicates the influence of structural air pollution. These peaks led to the use of the term "Rijnmond smog."

Some monitoring results show a decreasing trend too. Figure 2 shows the course of the average SO_2 concentration per month in the center of Rotterdam. The trend line (structural air pollution) goes down by 0.7 $\mu g/SO_2$ per month.

Together with hydrocarbons, nitrogen oxides (NO_x) are, under certain meteorological conditions, responsible for the occur-

FIGURE 2

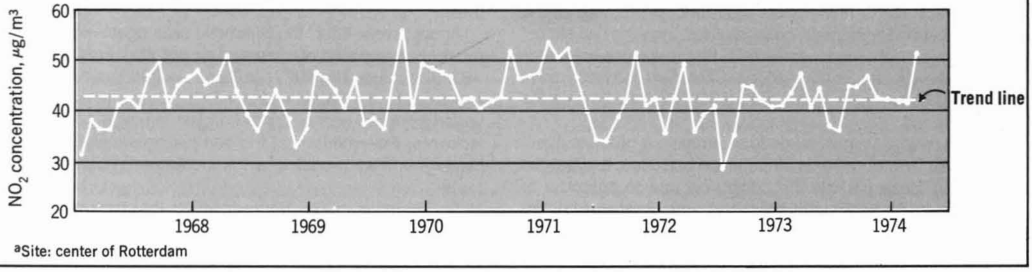
Monthly average of SO_2[a]



[a]Site: center of Rotterdam

FIGURE 3

Monthly average of NO_2[a]



[a]Site: center of Rotterdam

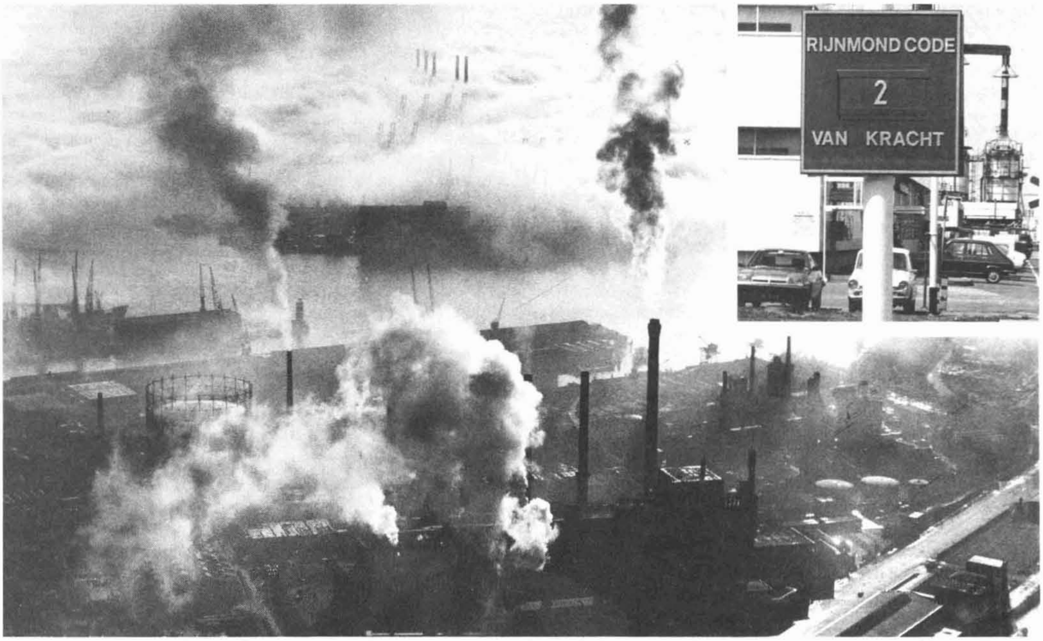


Figure 4. Low-level fog over the Rijnmond area. **Figure 5.** (inset) Announcement of an alert to industry

rence of photochemical smog. Figure 3 shows the average NO_2 level per month for the center of Rotterdam over a number of years. Contrary to SO_2, the course of the trend line in this figure does not significantly differ from zero.

Rijnmond smog

Air pollution usually coincides with the occurrence of a high-pressure area of anticyclonic air-currents. If temperature inversions and low wind speed occur at the same time, the emitted pollutants will accumulate. And, then, under the influence of sunlight chemical reactions take place.

Until now Rijnmond has been spared the photochemical air pollution of the kind that regularly occurs in cities like Los Angeles and Tokyo, at least as far as the extent of the pollution in those cities is concerned.

Rijnmond does experience a number of periods of increased air pollution. In the past, these episodes have resulted in a great number of complaints from the population because of their noxious and inconvenient effects. In December 1952, the days of the notorious London smog, the authorities in Rijnmond were confronted with a number of complaints that exceeded by twice the number received in the following two years.

From the fifth to the ninth of December 1952, a dense fog was observed in Rotterdam. Similar situations occurred at the end of January 1959 (3 days), and in the beginning of December 1962, when a dense fog enclosed Rotterdam and its surroundings. On December 5–6, 1962, temperatures at a height of 100 meters were 10 °C higher than at ground level; there was a distinct inversion. Moreover, on those days, the wind had almost died down entirely as a center of a high-pressure area was crossing the country. In Vlaardingen, Schiedam and Rotterdam, average values of more than 1200 $\mu g\ SO_2/m^3$ for a 24-h period were recorded.

From a medical survey taken to ascertain the possible direct injuries resulting from these air pollution episodes, it appeared that during these periods the admission rate to hospitals of persons over 50 years with heart and lung problems had increased.

Several years later, another case of highly increased air pollution occurred; the date: November 30, 1969. On this date a low-level fog settled over the Rijnmond area in a southeast direction (Figure 4).

Owing to this low-level fog, stacks over 100 meters rose above the fog layer, and did not contribute to the increased SO_2 ground-level concentrations. From this photograph, it can be observed that the plumes from these stacks rose upward, above the ground-level fog. In the Report and Monitoring Center complaints came pouring in that described the episode variously as "nasty acid smell," "blue mist with bad oily smell," and "blue acid haze." On this occasion, the first "alert" for the Rijnmond area was issued. For the first time, industry was officially requested to reduce emissions voluntarily.

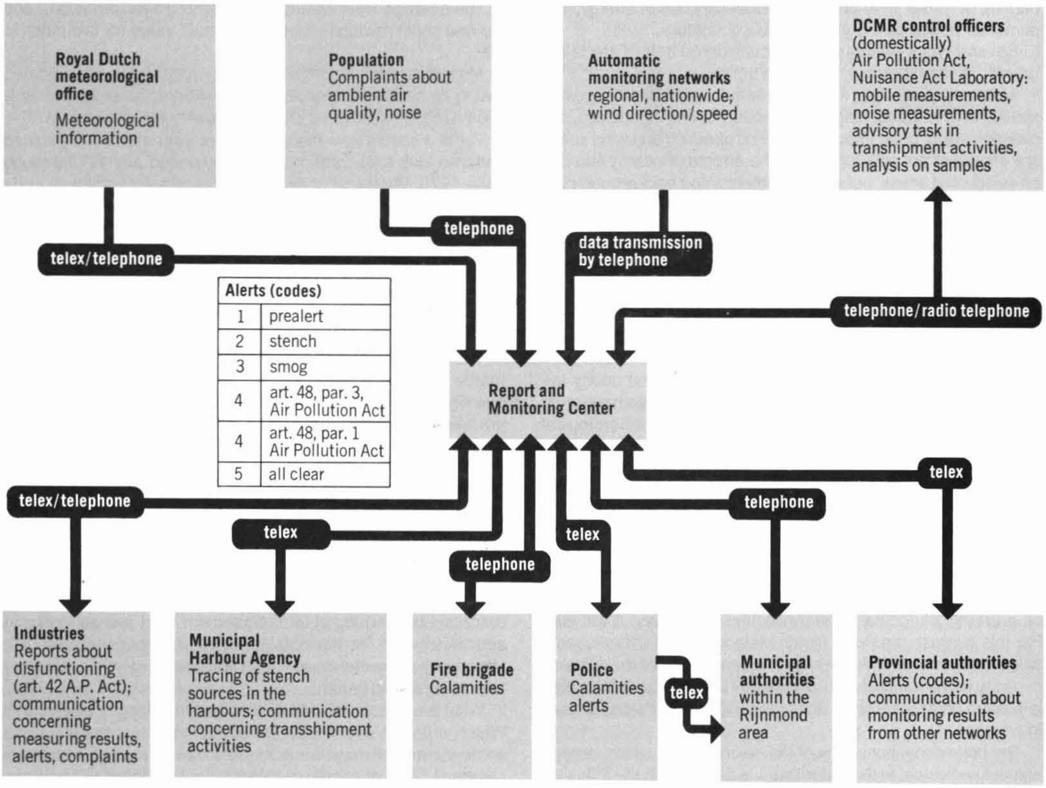
From that date, the periods of increased air pollution in Rijnmond have swiftly succeeded each other, and all have been accompanied by the so-called alerts. From then, also, the term "Rijnmond smog" was coined.

Although at that time there was as yet no insight into the nature of the mixture of polluting components that had caused the complaints, it was rather obvious that this type of air pollution differed from "London smog" or "Los Angeles smog." For example, it was foggy, and the presence of an inversion layer permitted the polluting components to accumulate. Relatively high SO_2 concentrations were measured at ground level. When reconstructing the events, it was not possible to find a satisfactory explanation for the nuisance; lack of sufficient measurements of components other than SO_2 prevented an answer.

About a year later, the Rijnmond area again experienced a relatively long period of increased air pollution. From September 16th to October 7th, 1971, no less than 8000 complaints were registered by the Report and Monitoring Center (Figure 1). These varied from bad odor to dry throat, tingling eyes, headache and sickness. Statements that the complaints resulted from mass hysteria or from prodding by the media were not supported by facts.

The weather in The Netherlands at that time had been influenced by a high-pressure area, which extended over Europe. In the daytime, the late summer weather was fine, at night

How the alert system works



Alerts (codes)	
1	prealert
2	stench
3	smog
4	art. 48, par. 3, Air Pollution Act
4	art. 48, par. 1 Air Pollution Act
5	all clear

temperatures fell to around freezing, while in the morning a low fog occurred. Most of the complaints were received during the morning hours when the fumigation effects occurred; at that time, after sunrise, the ground inversion dissolved from ground level upward. The atmosphere, stable at first, became neutral or unstable, which resulted in the transport of badly polluted air from inversion height to ground level.

SO_2 concentrations in Vlaardingen and Delft were high and ozone levels had increased. As far as could be ascertained, there was no connection between complaints about irritating air and increased ozone levels. This pointed to an active role of polluting components other than those that are normally manifest when photochemical smog is formed.

Presumably polluting components such as sulfur oxides, nitric oxides, sulfates, nitrates, stench components and hydrocarbons had accumulated during the night. By interreactions, products had been formed, some of them of an irritating nature. the presence of ozone has been proved and the hypothesis of sulfuric acid aerosol formation has to be accepted as probable.

Alerts

The objective of issuing alerts is to bring about a temporary reduction in the normal emission pattern during periods of increased air pollution so as to reduce or prevent a nuisance. For these measures to produce the desired effect, it is necessary to reduce the emissions at the right time and at the right spot. It goes without saying, then, that knowledge of the various categories of polluters, the nature and amount of the emissions, and their heights is essential.

Before the Air Pollution Act became effective, arrangements had been agreed upon between the larger plants in Rijnmond and the Report and Monitoring Center concerning voluntary measures, which were to be taken by industry in the event alerts were issued. These arrangements were legalized when the Air Pollution Act came into force.

Under this act, the provincial governor is authorized to take measures, during circumstances of a temporary nature, to control the emissions from sources responsible for the occurring air pollution.

For the practical execution of the Air Pollution Act, the DCMR issues the following alerts (Figure 5) to industry:

Code 1. Meteorological conditions have developed in such a way that a nuisance can be expected the next morning/afternoon/evening/night. Code 1 is a pre-alert, and an appeal to all those concerned to be extra watchful; it allows industry the opportunity to make preparations.

Code 2. In view of the unfavorable meteorological conditions, industry is requested to reduce, by as much as possible, any inconvenient emissions under 40 meters; those, for instance, caused by shipping malodorous materials, cleaning activities, and regenerating catalysts.

Code 3. Weather conditions may develop in such a way that a nuisance from irritating air can be expected. The industry concerned is requested to reduce all inconvenient emissions, including those over 40 meters, to a minimum.

Code 4. The DCMR advises the governor to assume responsibility. Industry must be prepared for obligatory measures to be taken by the governor.

Code 5. All alerts cancelled.

For Code 1, 2 or 3 the measures taken by industry are voluntary ones. These have been worked out for each plant and for each alert separately. In the case of code 4, recommendations can be made to the population, such as to minimize private motorized traffic as much as possible, or to minimize open burning of refuse or to prevent unnecessary use of energy. The demands issued by the governor are obligatory.

Several types of data must be considered before alerts are issued. These types are discussed below.

Meteorological data. Type of weather, wind direction, wind speed, temperatures, height of inversion layers, cloudiness, and radiation are of great importance. Wind direction and wind speed are important not only for tracing the effects of nearby sources on residential areas, but also for determining background concentrations in connection wih polluted air flowing from areas farther away. With easterly winds, there is a greater chance of photochemical smog than with westerly winds. Although increased O_3 and NO_x levels may occur with all wind directions, high-oxidants levels mainly occur with easterly winds. Considerable inversion in the upper air, much sunshine, low wind speed and high maximum temperatures are attendant to relatively high O_3 concentrations.

Figure 6 illustrates the relationship between the hourly average O_3 concentration and the temperatures at three measuring sites in Rijnmond in 1975. It should be noted that meteorological parameters often influence each other. Thus the chance of high maximum temperatures is greatest with southeasterly wind directions.

Another example is the relation between the hourly average NO concentration and windspeed. Here decreasing concentrations occur with increasing windspeed.

The weather forecast forms an important basis on which to determine whether a period of increased air pollution is coming on or, if this period has already occurred, how long it will last. For this purpose the Royal Dutch Meteorological Office uses a color code and the AVA index. Both are measures of the diffusion capacity of the atmosphere during a 24-h period; this information is passed on to the Report and Monitoring Center several days in advance.

The color code, consisting of the colors green, yellow, orange and red, indicates, in the order listed, a decrease in the diffusion capacity of the atmosphere. This code is based on the mixing volume, the cloudiness and the difference between the potential temperature at the upper side of a ground level inversion and the potential minimum temperature.

ranges from 0 (good diffusion) to 100 (poor diffusion). It is based on the potential temperature difference between 500 and 1.5 m, the average wind speed for 24 h (horizontal diffusion), and the maximum mixing height. A "normal" value for this index is 20.

Measuring data. Potential air pollution episodes are indicated mainly by certain meteorological conditions; however, the episode itself is signaled by direct air quality measurements.

Table 1 shows how many times per year alerts were issued and also their total durations. Over the period July 1971 through June 1976, the totals of the alerts issued are as follows: code 1, 125 times with an average duration of 12.8 h; code 2, 102 times with an average duration of 15.1 h; and code 3, 18 times with an average duration of 28.3 h. Code 4 had not been issued until recently. In general, the average duration of code 3 appears to be longer than that of codes 1 and 2. This is probably because code 3 is issued when weather conditions are of a persisting nature.

Table 2 illustrates that the alerts to industry were issued primarily in summer and autumn. Code 3 was issued most frequently in September. The total number of complaints, expressed as a percentage of the total number of complaints over the 5-y period, appears to be highest from August through September. The number of complaints per month is closely related to weather conditions, that is, stagnant conditions. Naturally, it should be remembered that an alert is usually issued before there is any sign of increased air pollution.

When are alerts issued?

Under the Air Pollution Act, the governor can issue general demands concerning plants, equipment, fuel and air polluting activities when, in his opinion, special circumstances of a temporary character make such demands urgently necessary to protect public health.

What are special circumstances and how long is temporary? Which criterion is used for public health? Must there first be some victims or must the admission rate to hospitals have increased? Or must people complain about air pollution and, if so, how many people must complain before the governor acts?

According to the memorandum that is part of the Air Pollution Act and that explains the act, special circumstances are defined as exceptionally unfavorable weather conditions, such as dense fog and temperature inversions.

Before the governor may issue code 4, the following criteria affecting public health have to be considered: the chemical air quality; medical indications; and the pattern of complaints.

Provisional guidance values for a number of air polluting components are mentioned in relation to the alert issued. Certain components (stench components), however, are not measured, and the effect of the interreacting components has not been taken into account in the guidance value of each component separately. For that reason the pattern of complaints and the indications given by the medical authorities play a part in forming a decision on whether to issue code 4 or not. Subjective elements will influence this decision and, in a way, it will be a political decision.

When issuing alerts to industry some subjectivity will be inevitable. No pat formula is available that can consider measuring data, numbers of complaints and meteorological parameters. A number of rules and regulations are available that play a part in issuing alerts. And the Report and Monitoring Center has gained considerable knowledge and experience in the past few years in judging various air pollution situations. This knowledge and experience guarantees that an alert is not issued before all essential data have been weighed and interpreted.

Weighing essential data

Conditions needed for an effective alert system are automatic measuring equipment, short sampling times, and the availability of the measuring results at a central control-point via direct transmission. Only if these conditions are met can more elaborate measures to reduce emissions be considered. It is espe-

FIGURE 6

Relationship of O_3 concentration and temperature at 3 sites

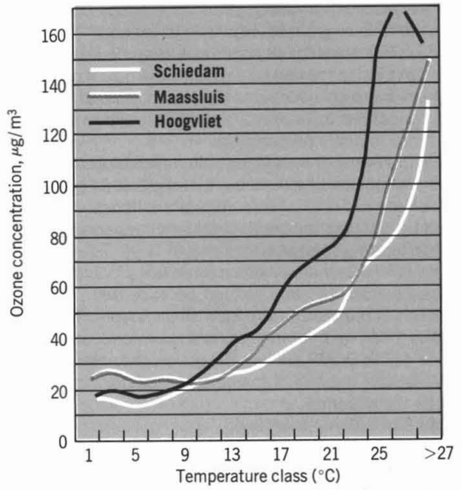


TABLE 1.

Alerts to industry

	1971[a]		1972		1973		1974		1975		1976[b]	
	times	hours	times	hours	times	hours	times	hours	times	hours	times	hours
Code 1	17	213	17	281	33	415	29	340	22	262	7	84
Code 2	15	216	12	246	34	495	17	292	15	182	9	110
Code 3	6	193	3	160	8	148	0	0	1	9	0	0

[a] July through December; [b] January through June

TABLE 2.

Alerts to industry and complaints per month[a]

	Jan.	Feb.	March	Apr.	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.	Total
Code 1	1	3	9	9	3	10	10	25	16	24	5	10	125
Code 2	0	3	6	7	3	9	9	20	15	20	5	5	102
Code 3	0	0	1	0	0	1	3	1	8	4	0	0	18
Total	**1**	**6**	**16**	**16**	**6**	**20**	**22**	**46**	**39**	**48**	**10**	**15**	**245**
Complaints expressed as a percentage of the total number of complaints	5.7	5.0	7.7	5.8	6.6	6.0	6.9	11.5	18.4	14.2	6.2	6.0	100.0

[a] July 1971–June 1976

cially during such episodes that up-to-date measuring data are so important, because it is then that most air pollution models fail. For determining the air quality, an index can be used which, on the basis of one or more components, expresses the air quality by a number. In the U.S. such an air pollution index is often used.

In the Rijnmond area, so-called delta values are calculated from data acquired by the monitoring network. This network, in operation since 1969, is made up of "sniffing poles" and includes 31 measuring stations for SO_2. For each measuring station, the average SO_2 concentration (c) is calculated every hour. Each hourly value is considered in relation to the average hourly concentrations of the same measuring station, with the same wind direction and at the same time of day ($\overline{c}$). The delta value (Δ) is defined as:

$$\Delta = \frac{c - \overline{c}}{\overline{c}}$$

High delta values indicate an accumulation of air pollution. The delta values are based only on SO_2 as an indicator for air pollution, and they have no predicting value. Circumstances are imaginable that result in high SO_2 concentrations, but do not automatically cause high O_3 levels.

In a complex industrial area such as Rijnmond, a great variety of raw materials are used. For that reason other components are measured by the DCMR via automatic data transmission. At three measuring stations (the mammoth stations), NO, NO_2, O_3, standard smoke and a number of hydrocarbons are measured hourly. The intention is to use these measurements for predicting purposes. By means of meteorological forecasts and up-to-date measuring values it may be possible to predict the measuring values to be expected by using a mathematical relation. Based on this statistical approach, early abatement measures can be taken.

Observations by controllers

When judging an air pollution situation, observations made by controllers in the field are important too. Sometimes complaints have to be verified because those who complain are not always able to give a correct description of a situation. An experienced controller can also give important information about the stability of the atmosphere. Thus the form and color of plumes may give an indication about the atmospheric situation. The inversion height can differ from place to place, and some plumes may be able to break through the inversion layer. In this case, the influence of such sources is not observable at ground level, and measurements made at ground level will be on the low side and complaints will decrease in number.

Furthermore, controllers play an important part in checking the abatement measures taken by industry during alerts. For that purpose, checklists of each plant are available and, for each alert, exact measures taken to reduce emissions can be entered. If, for any reason, one or more measures cannot be taken by a plant, direct mention is made of it. All this information is immediately passed along to the Report and Monitoring Center.

Summing up

It can be stated that a great number of factors must be taken into account when deciding whether or not an alert should be issued. In an area with inevitable air pollution, high priority must be given to the prevention of increased air pollution episodes that cause much nuisance to the population. Therefore, an alert system has to be devised and perfected in such a way that the interests of both the populace and industry are served.

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Coordinated by LRE

Keys to photochemical smog control

The idea is to reduce ozone, aerosols, and other secondary pollutants by controlling both HC and NO_x. Here are some suggestions for accomplishing that task

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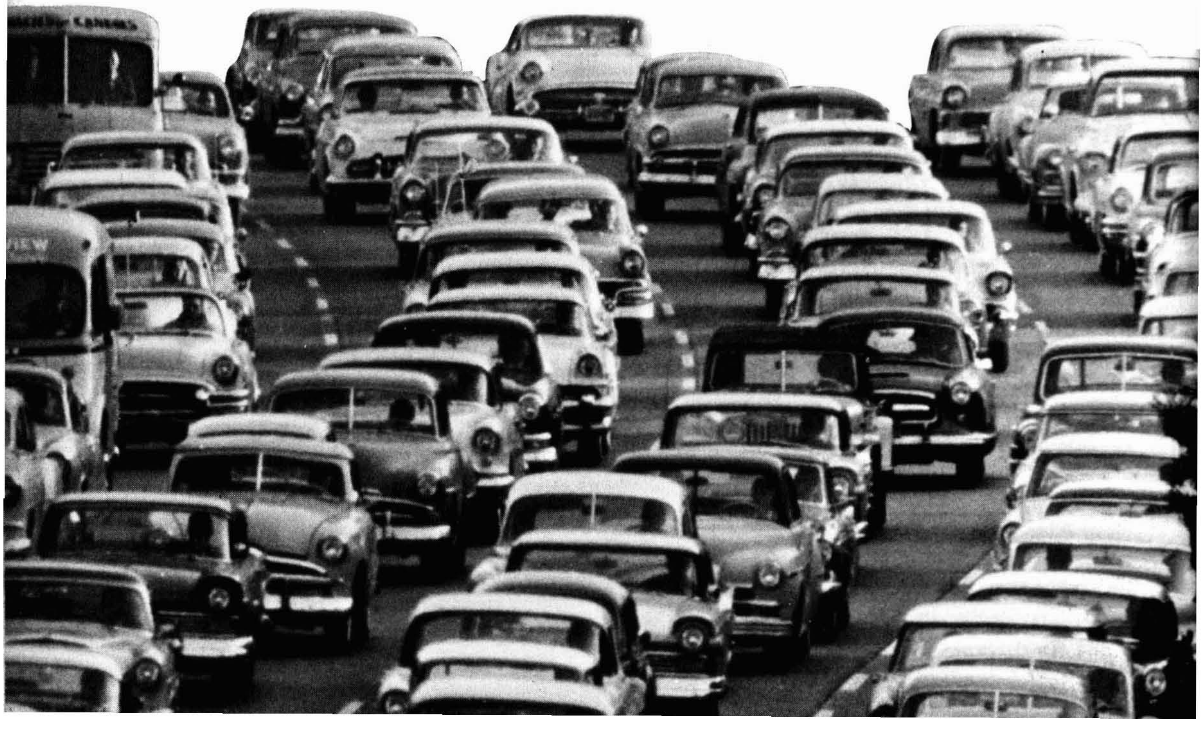
The London type of air pollution, characterized by oxides of sulfur (SO_x) and particulates, has been recognized for centuries. However, in the mid-1940s, the effects of a new kind of oxidizing air pollution, causing eye irritation, plant damage, and visibility degradation became evident in Los Angeles. Subsequently the classic work of Haagen-Smit and his colleagues established that the oxidants involved are formed photochemically by the action of solar ultraviolet radiation on mixtures of hydrocarbons (HC) and oxides of nitrogen (NO_x). These oxidants include ozone, peroxyacetyl nitrate (PAN), nitrogen dioxide (NO_2), and other substances of that nature.

Recent modeling studies predict that during the summer, under favorable meteorological conditions, levels of photochemical oxidant exceeding the U.S. National Ambient Air Quality Standard (NAAQS, 0.08 ppm for one hour) can occur in such diverse regions as Fairbanks, Alaska, or Leningrad, Russia. In fact, oxidant episodes in which levels exceed California's first-stage alert of 0.20 ppm of oxidant (hourly average) are now experienced in, or downwind of, such cities as Tokyo, Rotterdam, and Sydney.

Over the last five years, this rapidly growing problem has generated intense interest and activity not only in the U.S., but internationally, and a number of oxidant control strategies are being developed and implemented. In this control-developing process, the pressing need to accommodate tradeoffs between environmental quality, energy constraints, and economic policies in the air pollution system (Figure 1) has become evident. An additional complicating factor is that the balance between these three factors may vary from nation to nation, and indeed from urban, to suburban, and to rural areas within each country. However, a serious problem common to all existing or proposed control programs is the lack of a comprehensive and reliable data base concerning the causes and effects of photochemical air pollution.

Stationary sources

The first attempts to control photochemical smog, made by the Los Angeles County Air Pollution Control District (LACAPCD) around 1950, dealt primarily with stationary sources, as did those of the San Francisco Bay Area Air Pollution Control District, founded a few years later. One successful action on the LACAPCD's part resulted in the reduction of emissions of butadiene,



an atmospheric precursor to the powerful lachrymator acrolein. This shows that, in certain cases, selective emissions reduction may be cost effective.

In 1966 the LACAPCD implemented the well-known Rule 66, which severely restricted the use of highly photochemically reactive organics as solvents. Today, the term "reactive hydrocarbons," and the symbols HC or NMHC (non-methane hydrocarbons), are commonly used to symbolize all organics except methane and certain perhalogenated compounds, but including alcohols, amines, aldehydes, ketones, ethers, glycols, and halogenated hydrocarbons.

The reactivity of solvents remains today a subject of great concern to control officials, industry, and atmospheric scientists. This concern is based, in part, on research results in several areas (see box).

Pre-1970 reactivity indices emphasized the high reactivity of olefins and di- and tri-substituted aromatics. However, control agencies seem to be adopting the position that, given sufficient time and the right meteorology, all nonmethane hydrocarbons can contribute to photochemical oxidant production. Their concern and, of course, that of industry, is how to incorporate this concept into control programs without causing serious economic impacts.

Why reactivity of organics is of concern

- ***In smog chamber experiments, alkanes, as well as olefins and aromatics, subjected to 9–12-h irradiation periods, appear to generate significant quantities of ozone, although recently it has been suggested that chamber-wall effects may be partially responsible for this phenomenon. On the other hand, a recent analysis of ambient air in Los Angeles indicates that alkanes, presently thought to be of "low" or "zero" reactivity, could well play a role in ozone formation (ES&T, March 1976, p. 256).***
- ***Lengthy irradiation periods occur in summer, especially, and have a particular impact during intervals of stagnant air. They also occur while pollutants are being transported over long distances. This was brought out in studies in California, and at and near St. Louis, Mo. (ES&T, August 1976, p 730; November 1976, p 1085).***
- ***The University of California Statewide Air Pollution Research Center (SAPRC) has proposed a reactivity scale of I–V, based on the rates of reaction of organics with the OH radical. Least-reactive HC, such as methane, would be in Class I, for example, while highly reactive terpenes are in Class V (ES&T, July 1976, p 692).***

Light duty motor vehicles

As the decade of the 1950s ended, it became clear that automobiles were the major source of HC and NO_x emissions in Los Angeles County. Moreover, it was observed that photochemical smog was developing significantly in other air basins throughout California. These observations led to the formation of the State of California Motor Vehicle Pollution Control Board, the predecessor to the present California Air Resources Board (CARB). One of its most important actions was to recommend and enforce 1961 legislation requiring installation of the inexpensive positive crankcase ventilation (PCV) devices on new and used cars.

A second, more complex control step in this direction was the establishment, in 1963, of exhaust emission standards for HC and CO. In 1964, the Board approved four devices for the reduction of HC and CO in exhaust emissions, to be installed on new 1966 cars; three were catalytic converters, and the fourth was a direct-flame afterburner.

Shortly thereafter, automobile manufacturers suggested an alternate, lean-burn method of reducing the HC and CO emissions that would not require catalyst devices or afterburners. This approach was approved by the Board and implemented on California's light duty motor vehicles (LDMV) in 1966, and nationally in 1968. Unfortunately, this approach simultaneously led to large increases in NO_x emissions.

In 1975, when emissions standards became sufficiently stringent for HC and CO, catalytic converters became standard on most U.S. cars sold in California. Interestingly enough, fuel economy of catalyst-equipped automobiles has increased substantially over that of 1973 and 1974 cars, which were known for their poor performance and low "gas" mileage. For example, one major U.S. manufacturer is currently reporting a large increase in sales-averaged fuel economy for its catalyst-equipped

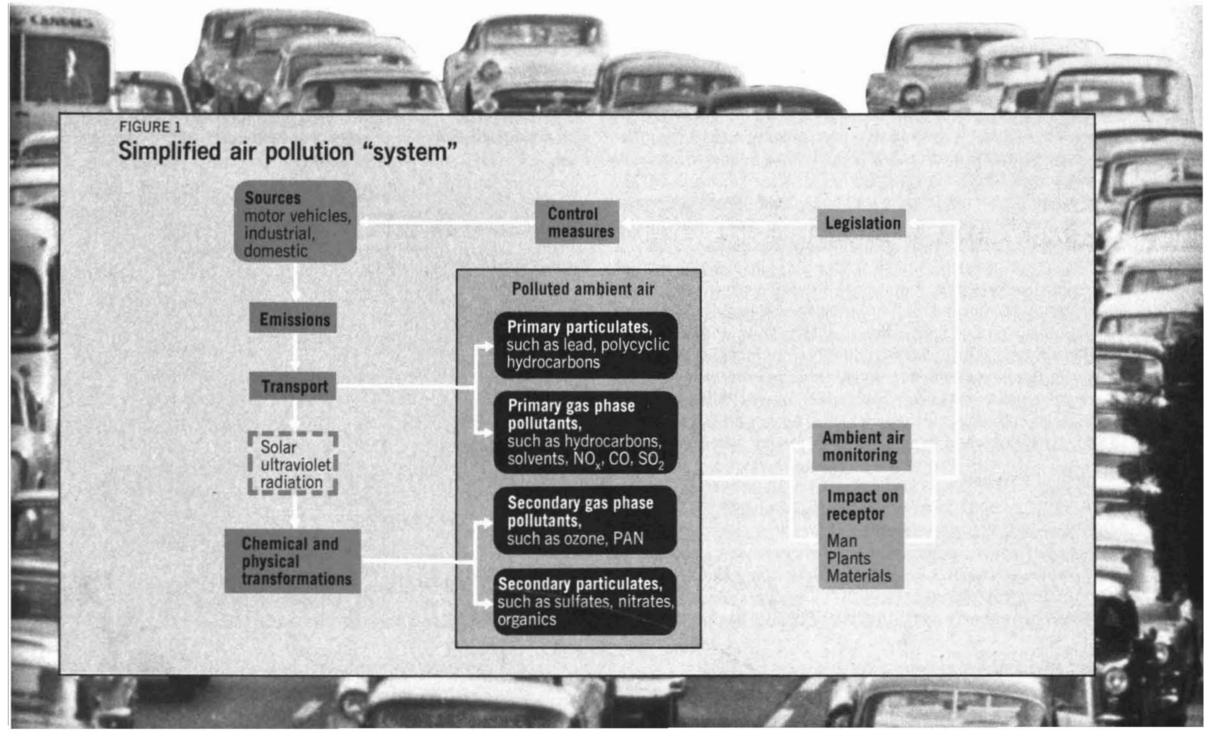
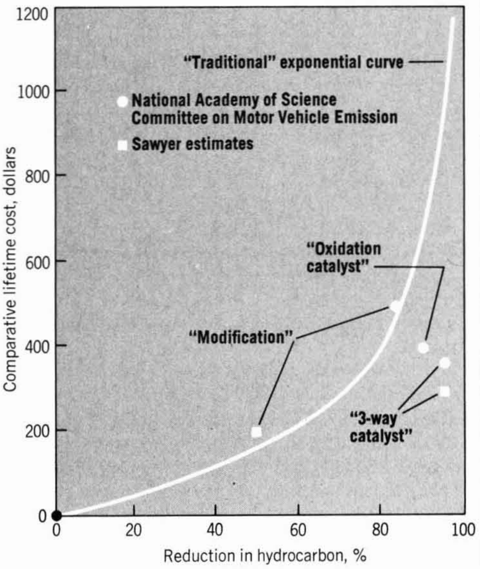


FIGURE 1
Simplified air pollution "system"

FIGURE 2

Pollution control cost assessment



1977 LDMV over comparable 1974 noncatalyst models. What's more, these vehicles meet the strict 1977 California standard 0.4 g/mi HC vs. 3.4 g/mi in 1974.

Still, from an atmospheric chemist's point of view, it seems essential that catalytic afterburners continue to be required by law to have an effective lifetime of at least 5 years or 50 000 mi, not only for CO and hydrocarbons, but also for such oxygenated hydrocarbons as aldehydes, which may be produced by the incomplete oxidation of HC over an old and inefficient catalyst. Thus, formaldehyde and the higher aliphatic aldehydes absorb solar ultraviolet (UV), and are even more effective in initiating and promoting photochemical smog than the parent hydrocarbons.

How much might control of these pollutants cost? Recent experiences with catalytic devices for HC control suggest that the traditional, well-publicized idea that emission control costs rise exponentially with an increasing degree of control may not always be correct (Figure 2). This was pointed out to the author by Robert Sawyer, Professor of Mechanical Engineering at the University of California/Berkeley.

Sawyer's concept is encouraging. Indeed, the emphasis on energy conservation being shown by the Administration of President Carter is perhaps an example of Dr. Sawyer's idea that a "change in lifestyle" might further reduce *overall* costs of emission control. Thus, the reduction in legal speed limits from 70 mph to 55 mph has not only conserved gasoline but also significantly reduced emissions of NO_x from LDMV's, with negligible increases in the HC and CO emissions. Furthermore, if some future combination of legal, economic, and societal constraints, as well as expanded public transportation, reduces the total number of miles driven by the American public, a corresponding decrease in all exhaust emissions will occur.

Oxides of nitrogen

After CO and HC controls were imposed on California's 1966 LDMV's, ambient NO_x levels in downtown Los Angeles increased. Ozone levels dropped concurrently there, but in downwind regions of the South Coast Air Basin, oxidant levels rose at an alarming rate.

These phenomena can be explained by the reaction of ozone with NO, which is the predominant form of the NO_x emitted by automobiles. This reaction lowers the ambient oxidant levels. The subsequent photolysis of NO_2 leads to increase O_3 production during transport of the air parcel downwind. As a result, NO_x controls were required on new LDMV's, starting in 1971 in California, and in 1973 nationally.

However, there is now intense debate as to the appropriate degree of NO_x control on both mobile and stationary sources, and whether this should vary with the specific air pollution problems of a particular area. Thus, California's NO_x emission standards are 2.0 g/mi in 1975 and 1976, 1.5 g/mi in 1977–1979, and 1.0 g/mi in 1980; 0.4 g/mi is proposed for 1982.

To be sure, control needs can differ greatly from region to region. Tradeoffs must be made with respect to technology, economics, and energy. However, for many reasons, NO_x reductions remain important from the viewpoint of an atmospheric chemist.

Sources of nitrosamines, which are suspected carcinogens, and even of their precursors, amines, have not been established in detail. In addition, relatively little is known about the atmospheric levels, or the formation and fate of nitrosamines, if indeed they are synthesized in the polluted troposphere.

One final comment about emissions. A comprehensive, detailed, and accurate emissions inventory is *the* crucial input into any oxidant control strategy, regardless of the approach used to relate emissions to ambient oxidant levels. Even the use of sophisticated computer models is hopeless without a good inventory. Furthermore, these emissions inventories must be *consistent* among the interacting local, state, and national control agencies. Otherwise, serious errors may arise in estimating both the absolute and the relative contributions of various sources in a given air basin, and lead to faulty oxidant control strategies.

Transport

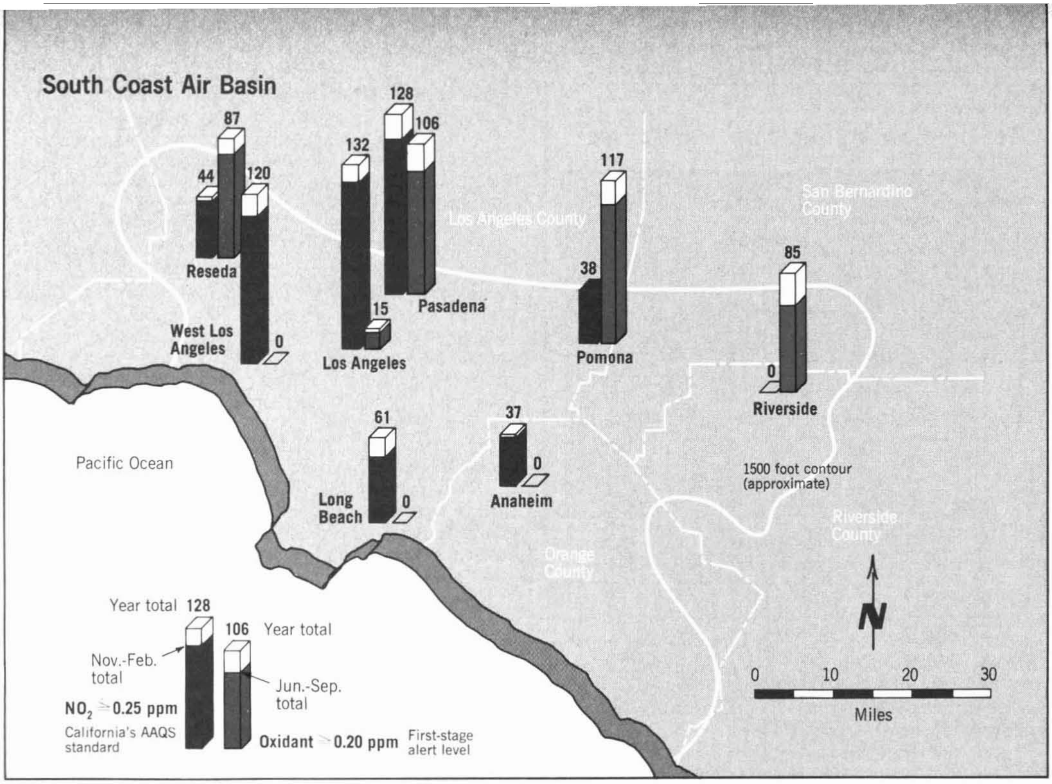
Pollutants emitted in the western and southwestern portions of the Los Angeles Basin significantly impact cities and agricultural regions over 70 mi downwind on the same day. Similar conclusions were subsequently reached in a St. Louis study, as well as in other studies dealing with transport over large regions of the U.S. or western Europe.

Meteorology thus plays a crucial role in establishing ambient pollutant concentrations. Indeed, air quality within an air basin depends upon *where, when,* and *how* one looks at it—that is, the specific location, the period of time and season, and the specific pollutants considered.

In the assessment of the impact of various control strategies, the question is often asked, "Is smog getting better or worse?" As discussed above, the answer for a specific location depends on which pollutant one examines, the time period chosen, and

The importance of NO_x reduction

- ***Although NO_x emissions decrease ozone levels in the immediate area, they seem to raise ozone levels in regions downwind.***
- ***Control of NO_x from stationary and mobile sources decreases ambient levels of toxic NO_2.***
- ***Reduction of NO_x emissions will lower ambient levels of secondary nitrate aerosols formed in photochemical smog.***
- ***NO_x is changed into many compounds, such as PAN, other organic nitrates, and nitric acid, for which no air quality standards presently exist. Though speculative, concern has been expressed that high NO_x levels may be involved in the formation of nitrosamines.***



the meteorology. For instance, in the city of San Bernardino, in 1970, the number of hours with $O_3 \geq 0.20$ ppm (correct by the LACAPCD) was 123 but this dropped dramatically to a low of 17 hours in 1972. However, in 1974 the value rose to 179, the worst in the previous 12 years. Clearly meteorological effects were masking any impact of controls.

Transformations

By the time the amended Clean Air Act was passed in 1970—a monumental piece of legislation—great strides had been made in understanding this exceptionally complex photooxidation system. However, researchers knew little about the roles played by aromatic, aliphatic, and oxygenated HC. Furthermore, results from smog chamber studies, showing much faster-than-predicted rates of disappearance of HC and rates of conversion of NO to NO_2, were not well understood—the so-called "excess rate" problem. Finally, very little is known about transport, and chemical and physical transformations in real polluted atmospheres.

One of the major successes of basic air pollution research was the discovery in the late 1960s of the key role played by the hydroxyl radical and associated species, such as the hydroperoxyl radical (HO_2) in initiating and propagating chain photooxidation. The subsequent work of a number of researchers in many laboratories around the world has led to the development of computer-kinetic models of varying degrees of detail and sophistication, which satisfactorily explain many of the anomalies noted in the 1960s. By use of these models, time-concentration profiles for such major species as HC, NO, NO_2, O_3, and PAN can be generated; these profiles are in good agreement with experimental results from smog-chamber experiments on simulated polluted atmospheres when the hydrocarbons are alkanes or alkenes.

Nevertheless, a few words of caution seem in order. Very few, if any, such computer-kinetic models have been experimentally validated by comparison with smog-chamber experiments conducted with the complex mixtures of alkanes, aromatics, olefins, and oxygenates actually present in urban atmospheres. Also, conditions accurately simulating diurnal variation of light intensity, as well as atmospheric dilution and dispersion during transport were not provided.

Indeed, little is understood even in laboratory studies about the nature, yields, and subsequent fates of the oxidation products of many hydrocarbons, especially aromatics. Since aromatics constitute a significant fraction of gasoline, especially the unleaded type, the problems in applying such kinetic models are obvious. A host of other physical and chemical parameters also need to be better evaluated.

The prime concern

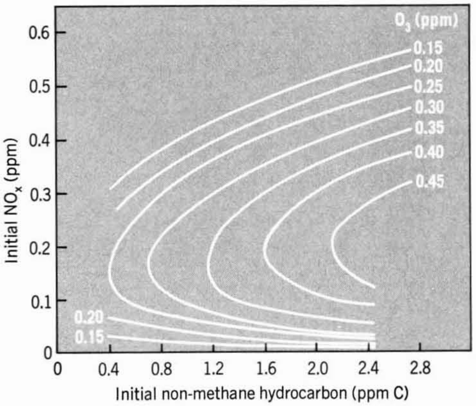
While the possible effects of non-criteria pollutants derived from NO_x and other sources is important, photochemical oxidants remain of prime concern. Thus, control officials are predominantly concerned with the degree, in relative and absolute terms, to which HC and NO_x should be reduced. Although control of HC has been stressed in the past, the EPA is now actively considering the importance of controlling NO_x as well as HC, a position long held by the CARB.

The data considered by these agencies, as well as those, for example in the Netherlands, Japan, and recently Australia, are the classical O_3 isopleths generated through use of chamber data, as well as computer models. While the use of such oxidant-precursor relationships must be approached with caution, these isopleths can nevertheless be important tools. A recent set of isopleths developed at the SAPRC for nine-hour irradiations of a surrogate mixture of HC and NO_x simulating Los Angeles ambient air is shown in Figure 3. Similar isopleths have been generated by other research groups over the past two decades, and while they may differ in an absolute sense, their shapes, and the general conclusions that can be drawn from them, are qualitatively similar.

In applying these data, one must consider where on the O_3-HC-NO_x surface the precursor (i.e., NO_x and NMHC) concentrations fall for a given air basin. For example, if early morning ambient concentrations of NO_x and NMHC in source areas are above the ridge-line in the ozone surface, hydrocarbon control

FIGURE 3

The hydrocarbon/NO_x/ozone relationship



will be more effective in reducing ozone than will NO_x control. This seems to be the case for downtown Los Angeles. If, on the other hand, ambient precursor concentrations in source areas are below the ridge-line, NO_x control can be more effective than hydrocarbon control in reducing ozone.

It is important to recognize that oxidant production in the atmosphere is determined not only by HC/NO_x ratios but also by the *absolute* levels of hydrocarbons and NO_x. Indeed, a fundamental consideration when dealing with varying initial NO_x concentrations is that the only known source of O_3 in the atmosphere is the photolysis of NO_2 followed by the production of ozone. Thus, if one increases NO_x in a photochemical system and integrates ozone concentrations over time and space, an increase in NO_x should result in an increase in the ozone dosage in the *total* integrated volume over time.

Clearly, each situation must be evaluated on a case-by-case basis in formulating cost-effective control strategies, and tradeoffs such as impact on "upwind" and "downwind" oxidant levels must be carefully evaluated. In this respect, the position of the CARB, which emphasizes strict controls on both HC and NO_x, seems prudent.

Simultaneous control of both NO_x and HC in areas suffering from severe photochemical smog should also result in an improvement in visibility, since the formation of secondary sulfate, nitrate, and organic aerosols associated with photochemical smog will be depressed. Thus, by imposing strict HC and NO_x controls, one *might* gain on all fronts–that is, reduced levels of ozone *and* reduced levels of secondary aerosols.

Pollution impacts

It is ironic that far more is known about the impact of photochemical oxidant on plants than on man. Studies over the last quarter of a century have not only amply demonstrated a variety of obvious plant damage symptoms, but have also shown that significant reductions in crop yields can occur without apparent external symptoms, at least those not obvious to the layman. The associated economic impact can be serious, indeed, as recently recognized by cotton growers and other farmers in the southern end of California's San Joaquin Valley when cotton losses were estimated by plant scientists to run as high as $30–40 million in 1975. Clearly, additional research in this aspect of plant sciences can only be highly cost-effective.

The need for an accurate and in-depth data base with respect to the impact on man is especially pressing in the area of long-term chronic health effects of smog. Presently, serious inadequacies exist in models of human dose-response functions, especially for heterogeneous mixtures of pollutants. This is illustrated by the fate of EPA's well-intentioned, but highly controversial CHESS program for elucidating the health effects of ambient SO_2 and associated sulfates. Its recent evaluation by Congressman George Brown's (D, Calif.) House Subcommittee on Atmosphere and the Environment is comprehensive, fair, technically sound, and understanding, but quite devastating.

What is clearly apparent from the Brown report is the fact that accompanying the urgent necessity of obtaining much better information on the biological impact of air pollutants, there is a requirement for extensive and reliable data on the "dose" portion of dose-response curves. This includes a better understanding of the chemical and physical forms, ambient levels, and mechanisms of formation, of not only the criteria pollutants, but also a multitude of non-criteria gaseous and particulate secondary pollutants. These latter include PAN, formic acid, nitric acid, ammonium nitrate, and a multitude of polyfunctional organic compounds found in the particulate phase. Certain of these are, or may be, irritating, toxic, mutagenic, or even carcinogenic.

For example, virtually all aerosol samples collected in three sets of experiments conducted at different locations in the South Coast Air Basin and at different times of the year during current SAPRC studies showed mutagenic activity when examined at the Sanford Research Institute according to the *Salmonella*/microsome test developed by Bruce Ames at the University of California, Berkeley. The only negative result was for a mountain station well removed from the major populated area.

Of course, it must be stressed that mutagenicity in bacteria cannot, and should not, be directly translated into carcinogenicity in man. Moreover, these results are not too surprising, since evidence for possible carcinogenic activity in particulate pollutants in the Los Angeles Basin was presented as early as 1954 by Kotin, and as recently as 1973 by Gordon. In addition, such carcinogenic activity in airborne particulates has been recognized for decades in other urban areas throughout the world. Nevertheless, in an era of justifiable concern over possible environmental causes of cancer, such findings cannot readily be dismissed. It would seem appropriate, therefore, that similar investigations be extended to other cities throughout the world and coordinated. In that regard, the Japanese have recently reported similar mutagenic activity in ambient aerosols.

In the heat of the current debate over the nature and degree of health effects from photochemical air pollution—including the American Petroleum Institute's formal challenge, in December of 1976, of the Federal oxidant air quality standard—it is interesting that the first reported instance of human beings adversely affected by photochemical smog in Australia occurred last year in the Sydney basin. Thirteen children taking part in high school sports events were admitted to a hospital with respiratory symptoms indicative of an excess of ozone. The ozone level near the school at 11 a.m. on the day they were affected was calculated by official air pollution scientists to be about 0.2 ppm.

Although the children were released the next day, the overall impact was significant. For example, the New South Wales State Pollution Control Commission took the bold step of suggesting that the maximum population to be tolerated in the Sydney basin should be 3.5 million—well below the 5 million that is estimated for the year 2000. While one should not make too much of this single episode, it is somewhat sobering. It certainly further illustrates the insidious and ubiquitous nature of photochemical smog.

Research funding changes

Finally, what is becoming truly disheartening to many scientists involved with this problem today is not the extreme complexity of the scientific and societal aspects of photochemical smog, since cost-effective and balanced controls are achievable. Rather, the concern is how the necessary fundamental and applied research programs, especially of a medium- to long-range nature—for example, elucidation of human dose-response curves—will be supported in the future.

Equally important, if not more so, is the question of who will

Japan's NO_x crackdown

Despite an acute energy problem, Japan is continuing with its schedule of strict NO_x controls on both mobile and stationary sources. And in The Netherlands, the belief was recently expressed that NO_x reduction, relative to HC, will lead to the greatest decrease in ozone formation in that country.

support and train present and future generations of graduate students and postdoctorate fellows in the practical and subtle research areas of air pollution science and technology. The funding situation has deteriorated to a significant extent, because of inflation, from that for the vigorous research and training programs in the mid-1960s–early 1970s—including Federal Air Pollution Special Fellowships—to a point at which extramural research funding, for example, in air pollution health effects, is insufficient, and graduate training fellowships are virtually nonexistent.

However, one encouraging development is the role of the National Science Foundation, which, through its RANN and basic programs, has supported applied and basic air pollution research of a medium- to long-term nature—research that is not to a significant extent directed by the regulatory needs of control agencies.

Somewhat ironically, in this era of diminished support of research by public funds, the electric power industry, for example, is greatly expanding its extramural support of air pollution research over the levels existing in the mid-1960s and early 1970s. Indeed, such private funding today constitutes a significant source of support in the U.S. for university air pollution research and associated training through research assistantships and postdoctoral positions.

This increased recognition by industry and public utilities of the need for support of additional research in virtually all aspects of the air pollution system (Figure 1) is highly welcome, particularly since these contracts generally seem no more restrictive than federal or state ones. Indeed, a number of programs will be of a cooperative nature with public agencies, and universities, sharing the resultant data. However, one would think that in view of the enormous and increasing stakes involved, a vigorous and growing research and training effort by the federal government could only be in the best interest of the public and indeed of industry.

Unfortunately, few signs of such an effort are currently on the horizon, and one is left with the interesting question, "By 2001 what fraction of the leaders of the scientific and technical air pollution community will have been trained with support by public funds, and what fraction of the 21st century data bank on health effects, transport, and transformations will have been generated through R&D programs directly derived from taxes?" That question is almost as intriguing as the original space odyssey—and perhaps more relevant today.

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Decontaminating Lake Superior of asbestos fibers

Asbestos removal is fairly straightforward. In U. S. Army tests, best results were obtained by charge neutralization, "bridging," and filtration with an ERDLator Unit

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Department of the Army, Fort Belvoir, Va. 22060

Traditionally, Lake Superior water has been one of the finest raw water sources available in the world. It is cold and clear, and contains very little in the way of microorganisms. It is understandable that the City of Duluth only chlorinates its water, and does not have a filtration process. The Lake Superior water used for all nine test runs was very constant in quality.

The optical turbidity of the raw water averaged only 1.46 JTU. To the naked eye, this water was very clear. This was true, even though the asbestos fiber count during the period of this study varied from 300 000 to 8 300 000 particles per liter. The asbestos fiber results were obtained by three different analytical laboratories, all using the transmission electron microscope, but using a different method for sample preparation of the electron microscope grid.

In reference to the 300 000 to 8 300 000 fibers per liter, the actual length of the fibers was not measured. However, other information in regard to asbestos fibers in Lake Superior water indicates that 90% of the fibers fall in the range 0.06–1.1 microns in length. The tiny asbestos fibers are in the approximate size range of bacteria or the colloidal clay particles found in natural waters.

In addition to numbers and size of the fibers, an important consideration is the electrical charge of the particles. A recent report, "Asbestos in the Great Lake Basin," February 1975, states, "The isoelectric point of chrystotile is at a pH of 11.8. At lower pH values the surface charge is positive; above the isoelectric point the charge becomes negative. Most dispersed materials have a negative surface charge in aqueous systems. Since chrystotile has a positive charge, it attracts or is attracted to most dispersed materials. The isoelectric point of cummingtonite amphibole is 5.2–6.0. Therefore, in most waters the mineral has a negative surface charge represented by a zeta potential of −20 to −40 mv."

The tiny particle size, plus the electrical charge, practically guarantees complete dispersion and minimal settling.

Iron ore production

Three great iron ranges exist in the state of Minnesota—the Vermillion, Missabi, and Cuyuna. For almost 100 years, pockets of pure hematite (Fe_2O_3) were mined from all three ranges and shipped to the steel-producing centers in the East. The hematite was very rich in iron (65% Fe) and was very soft. It could be easily removed by steam shovel and shipped as is. It was frequently called "DSO" (Direct Shipping Ore).

Unfortunately, the days of hematite are numbered: perhaps it will be depleted in less than ten years. However, another source of iron is taconite, an ore that exists in large quantities in the same area. Taconite is a hard, low-grade ore, containing only 25% of finely dispersed iron in the form of hematite or magnetite (Fe_3O_4). Years of experimental research resulted in the development of a practicable process for the up-grading ("beneficiation") of magnetic taconite.

In brief, the taconite is pulverized and subjected to a magnetic separation of the tiny released particles of magnetite. The particles are agglomerated and sintered into pellets containing about 65% Fe. The pellets are shipped to the steelmakers, who actually prefer it to the soft hematite.

About three tons of taconite are processed to produce one ton of taconite concentrate pellets. The remaining two tons are waste tailings of a siliceous nature. Large quantities of water are used during the processing—about 12 000 gallons per ton of taconite pellets.

Several taconite concentration plants are in operation in Minnesota. Most are located on the range, and use recirculation lakes for their processing water. One is located on Lake Superior, and uses Lake Superior water for its processing. In this case, the tailings, including asbestos, are discharged into the lake.

It is estimated that 45 billion tons of magnetic taconite reserves still exist in Minnesota. There is an even larger quantity of the non-magnetic taconite containing the entrapped hematite. A technology for beneficiating non-magnetic taconite has yet to be developed.

As a result of taconite beneficiation, and perhaps other causes, asbestos fiber contamination of Lake Superior has taken place.

Asbestos is technically an amphibole, a complex group of hydrous silicate minerals, containing chiefly calcium, magnesium, sodium, iron, and aluminum. Included in the group are hornblende, cummingtonite, crocidolite, chrysotile, serpentine, williamsite, anthophyllite, tremolite, and amosite. All of these minerals could loosely be described as "asbestos."

Asbestos has about 3000 commercial uses, and is a common industrial commodity. Because of its propensity toward toxicity, a determined effort is underway to keep asbestos out of the life cycle of man.

It has been postulated that asbestos dispersed in drinking water could cause mesotheliomas of the pluera or peritoneum, with an "incubation period" of perhaps 20 years. It is possible that the size and shape of the asbestos particle, in addition to its chemical structure, could cause the disease. In any event, it must be recognized that the present state of knowledge of the public health aspects of asbestos in drinking water supplies is inadequate.

Accepting asbestos contamination of Lake Superior as an unfortunate fact of life, the question arose "Can the U.S. Army, with its specialized knowledge of decontaminating water containing bizarre contaminants such as CBR agents, remove the asbestos from Lake Superior water?" In order to answer this question, a 420 GPH ERDLator Unit was sent to Duluth to determine its effectiveness.

The Unit

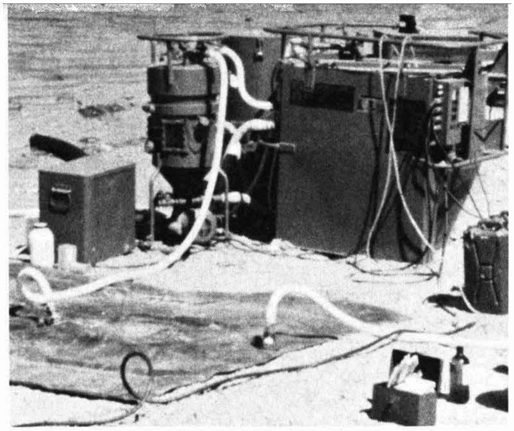
The current, standard, U.S. Army Water Purification Equipment (ERDLator Unit) was designed after World War II to provide transportable, quick-response water purification systems for the modern mobile field Army. The ERDLator equipment is available in four sizes: 420, 1500, 3000, and 10 000 GPH. As noted, a 420 GPH unit was used in the asbestos removal study. Three basic processes normally take place in the ERDLator Unit:

- coagulation
- disinfection
- filtration.

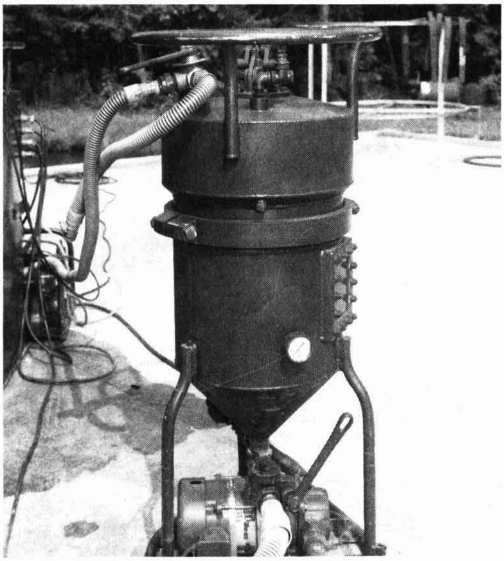
Two major pieces of equipment are involved:

- a conical-shaped solids contact clarifier
- a pressure diatomite filter.

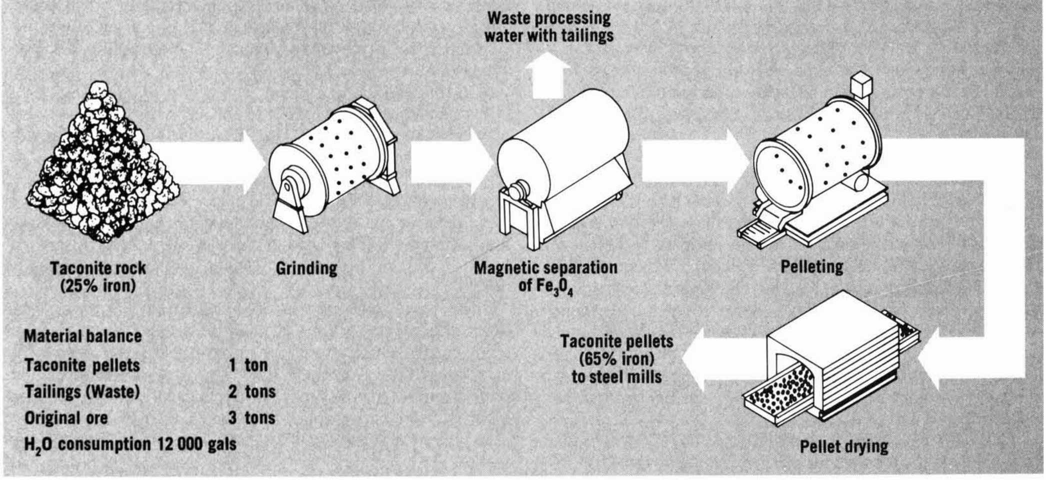
Disinfection takes place concurrently with coagulation, and a positive-free chlorine residual is maintained in the final filtrate.



The unit. *The U. S. Army 420 GPH ERDLator (above) provided continuous water purification by coagulation, disinfection, and diatomite filtration (below) in study of 22 June–1 July 1973*

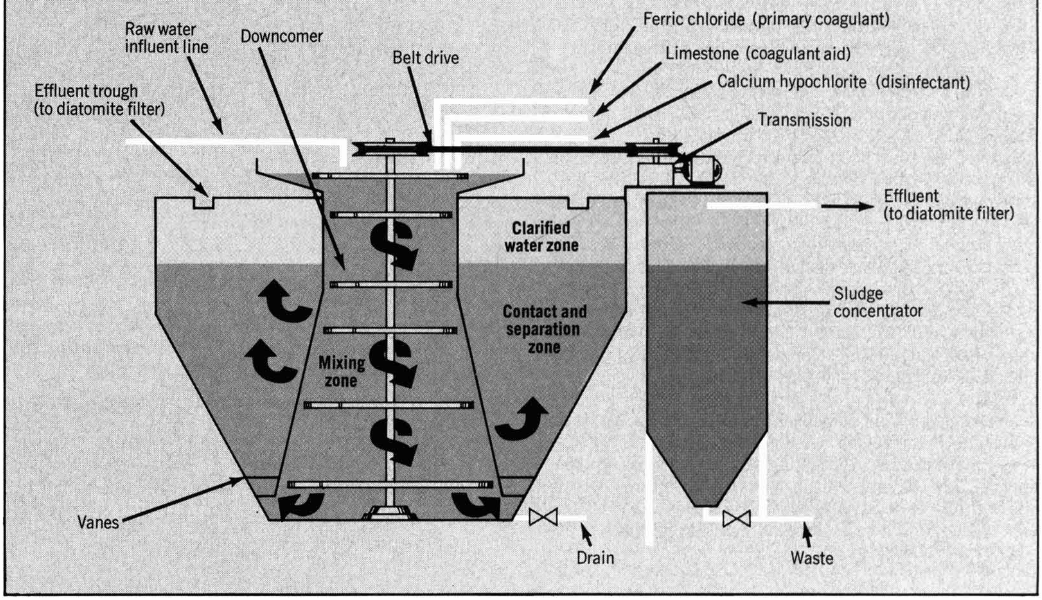


The taconite beneficiation process, basic steps



Material balance	
Taconite pellets	1 ton
Tailings (Waste)	2 tons
Original ore	3 tons
H_2O consumption 12 000 gals	

Contact clarifier, component of mobile water purification unit



The rest of the equipment is supportive in nature (gasoline engine drive electrical generator, storage tanks, and the like). The raw water enters the unit through an aeration assembly, the purpose of which is to release super-saturated air and gases that might cause difficulties by later release, with resulting floating floc. The aerated water enters into a mixing compartment where coagulant, coagulant aid, and calcium hypochlorite are added concurrently at a controlled rate.

The water, plus developing-floc or turbidity aggregates, pass down through a rapid-mix central chamber with agitation. Rotation of the water leaving the rapid-mix chamber is reversed by the fins at the bottom of the clarifier, and the water proceeds upward with a counter-revolving motion through suspended sludge or clarification zone. The residence time in the unit is about 20 minutes. Control of the slurry level in the clarification zone is accomplished by continuous withdrawal of a small amount of floc from the upper portion of the slurry pool.

The unit is designed to hydraulically keep all slurry in suspension with sludge concentration occurring only in a small external concentrator. The coagulated water from the clarifier is collected by an effluent launder ring where it passes to a wet-well storage tank. From the wet storage tank, the water is pumped to a pressure diatomite filter. The diatomite filtration process consists of three basic steps: precoating, filtering, and backwashing.

Before the coagulated water can be filtered, it is necessary to precoat the filter elements. Slurry containing 0.4 lbs of diatomite is added to the filter through the precoat funnel, and water is pumped from the wet well up into the filter. The water rises until it begins escaping through an air release valve, which is then quickly closed for the filter cycle. Air is trapped and compressed in each of the plastic cups of the filter elements and in the dome of the filter shell. As the water is filtered through the elements, the diatomite is deposited on the elements. This operation is called precoating. It is noted that the filter contains four filter elements, each equipped with a polyvinylchloride sleeve of 1 sq ft area. Thus, the precoat loading is 0.1 lbs of diatomite per sq ft of filtering area.

As filtration proceeds, diatomite slurry (body feed) is continuously fed into the incoming water, depositing on the filter elements. The slurry is prepared in a slurry feeder welded to the ERDLator tank. The feeder has a diatomite slurry compartment and a clear-water collection trough with a fixed orifice for constant flow of clear water into the slurry compartment. An air pump is used to furnish a constant flow of air bubbles to the bottom of the tank to provide agitation and to prevent settling of the diatomite. The diatomite slurry is supplied to the wet well near the suction inlet of the filter pump. Body feed maintains the porosity of the filter cake and permits longer filter runs. Eventually, the filter becomes clogged and, in turn, increases the pressure differential across the filter elements. When the filter pressure gage indicates a pressure of 50 psi, the filter is ready to be backwashed.

When the filter effluent valve is in the "backwash" position and the manual release valve is opened suddenly, the air compressed in the filter dome is released. This sudden release of air allows the air compressed in the cups to expand and force water back through the element filter cakes. This rapid reversal of water usually dislodges all the suspended matter from the elements where it settles to the bottom and is drained to waste.

The purpose of the entire ERDLator-Diatomite Filtration process is sixfold:

- clarification
- removal of microorganisms
- removal of tastes
- removal of odors
- removal of toxic materials, and
- removal of color.

Accomplishments of these six objectives is imperative if the finished water is to be used for drinking purposes.

Results

The Army ERDLator unit was operated on Lake Superior water according to nine different variations. Several operational changes involving chemical treatment of the water were made in order to evaluate operating parameters and establish optimum performance of the equipment for this unusual problem. Principal differences in modes of operation were:

- diatomite filtration only—with a coarse grade of diatomite

TABLE 1.

Test runs—operational and analytical data (7 gpm ERDLator unit)

Item	Run no.								
	1	2	3	4	5	6	7	8	9
Mode of operation	Filtration	Filtration	Coagulation filtration	Coagulation filtration	Coagulation filtration	Filtration	Filtration	Coagulation filtration	Filtration
Date (1973)	22 June	23 June	24 June	25 June	26 June	27 June	29 June	30 June	1 July
Hours operation	4	9	7½	6¾	7½	4	3½	4¾	3
Coagulation dosages (mg/liter)									
$FeCl_3$	—	—	57	10	—	—	—	—	—
$CaCO_3$	—	—	214	214	—	—	—	—	—
Ca(OCl)2	—	—	10	10	—	—	—	—	—
Activated carbon	—	—	—	72	—	—	—	—	—
Cationic polymer	—	—	—	—	2	—	—	2	—
Filtration dosages									
Precoat (lbs celite 535)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Body feed (ppm celite 535)	28	28	28	28	—	—	28	—	—
Body feed (ppm Hyflo)	—	—	—	—	28	28	—	28	28
Filtered water									
pH	7.9	7.8	7.5	7.7	7.8	7.8	7.9	7.8	7.8
Alkalinity	43	43	65	95	43	43	43	43	43
Hardness	44	44	95	78	44	44	44	44	44
Conductivity	98	90	217	183	98	92	92	95	92

Note: Analytical data courtesy Duluth Water Works

TABLE 2.

Turbidity, suspended solids, and asbestos fiber data

Run	Turbidity		Suspended solids (x-ray diffraction, mass concn)		Asbestos fibers (transmission electron microscope)							
	JTU	**JTU**	**mg/liter**	**mg/liter**	**Micrograms/liter**				**Millions of fibers/liter**			
					Analyzer A		Analyzer B		Analyzer C		Analyzer C	
	Raw	**Filtered**	**Raw**	**Filtered**	**Raw**	**Filtered**	**Raw**	**Filtered**	**Raw**	**Filtered**	**Raw**	**Filtered**
1	1.54	0.11	0.85	0.31	—	—	—	—	—	—	—	—
2	1.50	0.10	0.86	0.20	—	—	—	—	—	—	—	—
3	1.57	0.08	1.05	0.12+	—	—	—	—	—	—	—	—
4	1.60	0.12	0.87	2.01+	—	—	—	—	—	—	—	—
5	1.23	0.05	0.89	0.06	—	—	—	—	—	—	—	—
6	1.47	0.53	—	—	—	—	—	—	—	—	1.0	0.8
7	1.30	0.38	—	—	3.8	2.2	—	0.1	—	0.7	0.9	0.2
8	1.50	0.22	—	—	7.6	0.1	0.4	0	2.0	0	0.3	0
9	1.45	0.34	—	—	9.6	1.9	8.2	0.2	8.3	3.3	0.8	0.3

Note: All data courtesy EPA

- chemical coagulation followed by diatomite filtration
- chemical coagulation with activated carbon and diatomite filtration
- diatomite filtration with coarse and fine grades of diatomite
- diatomite filtration with introduction of a polymer.

The operating schemes and chemical analyses of the final product water are shown in Table 1. The turbidity and asbestos fiber data for both raw and filtered water are shown in Table 2.

Best results were obtained for Run 8, where all the asbestos content of the raw water was removed. The operating procedure used for this run, is summarized below:

Step 1: Coagulation, 2 ppm cationic polyelectrolyte (added in ERDLator wet well). Step 2: Filtration, precoat, 0.4 lbs celite 535 (Trademark, Johns Manville Co.), Body feed, 28 ppm Hyflo (Trademark, Johns Manville Co.).

It is believed that the mechanism of asbestos removal for Run 8 was fairly straightforward. The positively charged cationic polyelectrolyte neutralized the negative charge on the suspended asbestos fibers. The neutralized particles were then aggregated or "bridged" on the long-chain polymer. The aggregates were removed by the subsequent filtration step.

The results indicate that charge neutralization, bridging, and filtration are the logical approach to the asbestos decontamination of Lake Superior.

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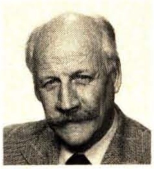

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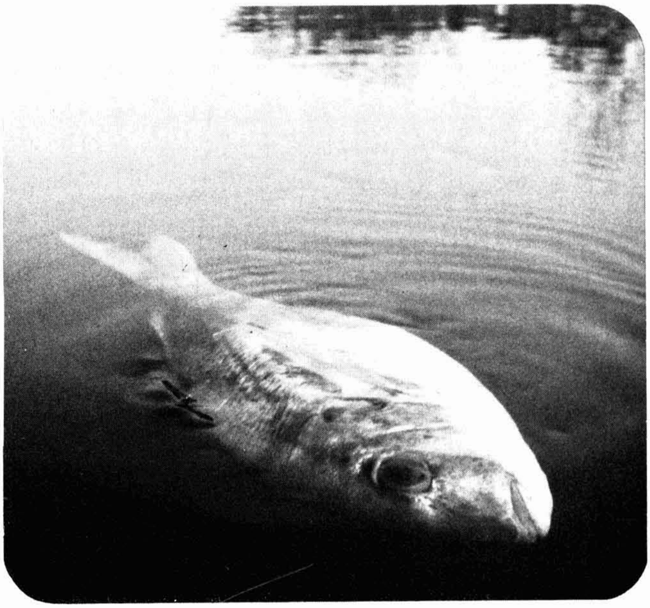

Analysis for Beryllium in Ambient Air Particulates by Gas Chromatography

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■ A chelation–gas chromatographic method was developed to determine beryllium concentrations in particulate matter recovered from ambient air at three locations. The sampling sites were chosen to represent ambient air conditions in rural, suburban, and highly industrialized environments. Background levels of beryllium in suspended particulate matter in air over farming areas in southwestern Ohio ranged from 0.00002 to 0.00006 $\mu g/m^3$. Beryllium levels in urban air near a coal-burning electric power plant and an industrial complex were several times higher than regional background concentrations and were highly dependent on the wind direction.

Beryllium and its compounds are among the most toxic nonradioactive substances found in the environment. An acute form of berylliosis occurs as chemical pneumonitis, with inflammation of the mucosa and submucosa of the respiratory tract. Chronic beryllium disease, which differs clinically from the acute case, causes severe respiratory damage (*1*). One of the suspected mechanisms for toxicity is the inhibition of alkaline phosphatase (*2*).

The highest single input of beryllium into the environment is through the combustion of fossil fuels. This source produces beryllium in suspended particulate materials and volatile forms which are not readily collected and analyzed at the very low levels at which they are toxicologically significant. Fabricating and machining materials containing Be add further to airborne Be levels. These industrial and power plant sources of beryllium are becoming more of a concern to industrial hygienists and environmentalists because of the rapid rate of increase of transforming beryllium from biologically innocuous and unavailable forms such as in coal or in beryllium ores into more available forms scattered throughout man's biosphere.

Reliable quantitative investigation and monitoring of the distribution of beryllium in the environment are thus essential. Meaningful conclusions regarding environmental beryllium can be drawn only if regional background concentrations have been established.

The background concentration of Be in ambient air is low and not well established because of inadequate analytical methodology. There is a need for a very sensitive and accurate analytical technique, including collection and extraction procedures, which will circumvent beryllium blank problems and which can ultimately be used to establish regional background beryllium concentrations. Background assays are also important to establish long period trends which will indicate any changes as a result of man's redistribution of beryllium from locked sources in coal and ore into the environment, particularly into the atmosphere.

The analytical procedure described in detail in the *Federal Register* for the analysis of beryllium in air particulates is the atomic absorption method; however, spectrographic, fluorimetric, and chromatographic or equivalent analyses have also been approved by the EPA (*3*). The chelation–gas chromatographic (GC) method of analysis for beryllium in the environment (*4–6*) has two major advantages over the atomic absorption method—greater sensitivity and virtually no interference from other metals. The GC method of analysis has been utilized in this study, and improved techniques have been developed. Also, methods of dissolution of samples have been studied which do not require the use of hazardous perchloric acid.

Preliminary investigations of gas chromatographic analysis for metals by first forming volatile metal chelates of β-diketones were reported in 1960 (*7*). Since that time, much research has been done, and analytical procedures useful for a variety of matrices are now available (*4–6, 8–16*).

Objectives of the investigation of beryllium analysis in environmental ambient air particulates are to develop and refine methods for the collection and dissolution of ambient air particulates to form aqueous solutions of the beryllium present, to perform quantitative extraction of beryllium by solvent extraction methods, and to develop quantitativemmethods for determination of beryllium by gas-liquid chromatography. A further objective is to use the technique to compare the concentrations of beryllium found in ambient air particulates from rural, urban-industrial, and suburban sampling sites in the same region.

This method for beryllium analysis provides for the quantitative evaluation of only the beryllium within airborne particulates, beryllium compounds which may be adsorbed on the surface of this particulate matter, and any volatile beryllium compounds which are adsorbed on the surface of the filter.

Experimental

Sampling of Ambient Air for Particulates. A Precision Scientific high-volume air sampler, meeting EPA specifications, was used to recover ambient air particulates (*3*). This sampler is designed for the use of filters, 20.3 × 25.4 cm, which are held in place by a frame 2.5 cm wide in both dimensions. The actual area of the filter through which the air passes is 22.9 × 17.8 cm. The instrument flow rate was calibrated and rechecked periodically. The particulates were recovered at a flow rate between 1.22 and 1.30 m^3/min, which is well within the EPA specifications. This flow rate allows suspended particulates having diameters of less than 100 μm to pass to the filter surface. Particles within the size range of 100–0.1 μm diameter are ordinarily collected on glass fiber filters (Fisher Scientific Co., Part No. 1-037-48).

The mass concentration of suspended particulates in the ambient air ($\mu g/m^3$) was measured by weighing the unused filter after heating 1 h at 80 °C to determine the tare weight. The filter was exposed for the desired collection time and reweighed after heating at the same temperature for the same period.

These weights were used to calculate the concentration ($\mu g/m^3$) of suspended particulate mass collected for the volume of ambient air sampled. The amount of air sampled varied with the particulate concentration at the sampling site; urban air contained enough suspended particulates to perform an analysis on a 24-h sampling, but at the rural site it was necessary to sample for as long as 60 h to collect a sufficient amount of particulate matter to allow determination of the beryllium present. Close observation of the flow meter during collection was required to permit any change in line voltage to be taken into account. Initial and final flow meter readings were averaged for calculations of total air volume sampled.

Selection of Sampling Sites. Three sampling sites were selected in western Ohio representing three different ambient air environments in this region: rural, suburban, and industrial-urban. The rural site was in western Preble County. The area is entirely agricultural with no industry within a 10-mile radius and no appreciable industry for 100 miles southwest (direction of prevailing winds). The suburban site was in western Greene County east of Dayton, Ohio. The industrial-urban site was in southwestern Dayton in a heavily industrial area in close proximity to a foundry and less than a mile west of a coal burning power plant (>340 MW). Several other lighter industries are nearby. Figure 1 illustrates the relationships of collection sites.

Selection of Filters. The selection of a satisfactory filtering material on which to collect ambient air particulates was a critical factor in the success of this investigation. The low amounts of beryllium found in ambient air ($2.7–19.5 \times 10^{-5}$ $\mu g/m^3$, Table I) required the extraction of particulates from the entire filter to provide a sufficient beryllium concentration, but the beryllium naturally present in the glass fiber filter was high enough to interfere with the quantitative analysis of the collected sample. Consequently, a treatment procedure was devised to circumvent the high blank beryllium problem.

Leaching of Glass Fiber Filters. The glass fiber filters were carefully rolled to prevent cracking and inserted into a chromatography developing jar 24 cm high and 6 cm in diameter. The unused filter was leached in concentrated nitric acid for 24 h. The filter was then washed in distilled water and dried in an oven at 80 °C before weighing to determine tare weight. This procedure was used to leach the surfaces to reduce the beryllium blank. When this method of leaching was followed by the reflux digestion procedure next described, the beryllium levels found in the blank were lower than in any other procedure.

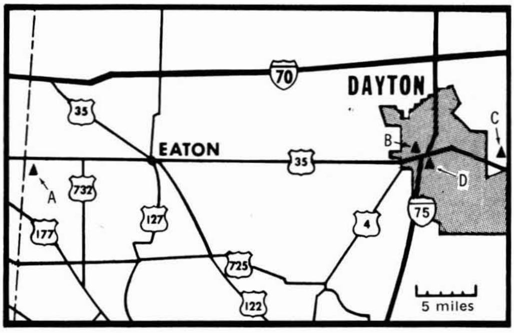

Figure 1. Regional map illustrating relationship of collection sites
A: Rural site, B: urban site, C: suburban site, D: power plant

Digestion of Filter Particulates. One of the objectives of this investigation was to develop techniques in which the use of hazardous perchloric acid in digestion procedures recommended by the EPA could be avoided (*3*). The complex nature of ambient air particulates which contain both organic and inorganic materials requires a specialized digestion procedure, especially when perchloric acid is not used. The total digestion of all beryllium-containing particles is required for ease of chelation and extraction of the beryllium.

Dissolution of Particulates by Reflux Method. The method for dissolution of particulate materials must meet the following criteria:

- All organic material within the particulates must be degraded to form aqueous-soluble beryllium compounds or ionic forms which will lead to the formation of $Be(tfa)_2$ in the extraction step.
- The inorganic compounds must be soluble and any beryllium present must be extracted by trifluoroacetylacetone [H(tfa)] as $Be(tfa)_2$.
- All refractory materials must be dissolved. Fly ash, in which many of the particulates are glassy beads of inorganic materials encapsulating organic material, is particularly hard to dissolve.
- The loss of any volatile beryllium compounds present must be avoided.
- Contaminant (blank) beryllium in reagents and on the surfaces of the filter must be minimized.

These criteria are met in a modified reflux digestion procedure (*6*). The dissolution of the particulates present in the air samples was performed by refluxing the exposed filter for 7 h in an equal volume mixture of concentrated nitric and sulfuric acids. The resulting solution is analyzed for beryllium by solvent extraction and gas chromatography.

The digestion method used in this study is as follows:

- The entire exposed filter was dried for 1 h at 80 °C and weighed to determine the total particulates.
- The entire filter was placed in a 250-ml reaction flask with 20 ml of concentrated nitric acid.
- Twenty milliliters of concentrated sulfuric acid was added, followed by 5 ml of distilled and deionized water.
- The round bottom flask fitted with a 40-cm reflux condenser was heated for 7 h at 80 °C.
- Another 5 ml of water was added from the top of the reflux condenser to wash out any compounds adsorbed on the walls and to bring the total volume of liquid in the flask to 50 ml.
- The liquid was transferred to a 1-oz Boston Round polyethylene sampling bottle after separation from the filter material by pulling the liquid through a Buchner funnel.

Beryllium Blank-Reflux Method. The amount of beryllium blank determined in the processing of a preleached but unexposed filter by the reflux method was 0.047 ppm. This amount of blank beryllium is equivalent to about 4.7% of the beryllium found in the Rural Filter #1 and 2.5% of the beryllium found in Urban-Industrial Filter #4. The blank concentration of beryllium in reagents as well as on the filter material is deducted from the total beryllium measured present in collected particulate samples.

Extraction and Chelation. With the ease of solvent extraction and the sensitivity and selectivity of gas chromatographic determination of ultratrace concentrations of $Be(tfa)_2$, this method appeared to be an excellent technique for the analysis of beryllium in environmental samples. We have analyzed several urban air samples for beryllium by this general method; the following detailed description is an improved modification of the techniques we described earlier (5).

- One milliliter of the filter extract solution was added to an 8-ml culture tube.
- One milliliter of EDTA-buffer solution was added. The solution was prepared by dissolving 5.15 g of disodium ethylenediaminetetraacetic acid (EDTA), 85.00 g of sodium acetate, and 6.25 ml of glacial acetic acid in 500 ml of distilled water.
- A quantity (1.5–2.5 ml) of 12 N NaOH was used to bring the pH to 6, which is optimum for the quantitative extraction of $Be(tfa)_2$.
- A Teflon-coated magnetic stirrer was used to agitate the solution while the sample was heated to 80 °C in an oil bath for 30 min. (This step was performed to ensure that other metals present were converted to the EDTA chelates, which are water-soluble and do not interfere with the beryllium analysis. Beryllium is not complexed by EDTA to any appreciable extent in competition with trifluoroacetylacetone.)
- The buffered solution was washed twice with 2-ml portions of benzene to remove nitrobenzene which seriously interferes with the gas chromatographic analysis. It is formed when benzene reacts with residual HNO_3 remaining in the buffered aqueous solution (step 2).
- The buffered solution was allowed to react with an equal volume of a 0.8 M solution of trifluoroacetylacetone in benzene for 15 min while shaking the flask with a "wrist-action" shaker.
- The organic layer containing the $Be(tfa)_2$ chelate was decanted and washed for 15 *seconds* with 2 ml of 0.1 N NaOH to remove any unreacted H(tfa) which would interfere seriously with the measurement of $Be(tfa)_2$ in the gas chromatographic analysis. The organic phase must be separated immediately to prevent serious losses of beryllium into the alkaline aqueous phase.
- One-microliter aliquots of the organic phase were injected into the gas chromatograph for analysis, and peak heights were compared with those determined intermittently for standard solutions of $Be(tfa)_2$ dissolved in benzene.

Gas Chromatographic Instrumentation. Many of the metal chelates are thermally labile; therefore, care must be taken to avoid column conditions under which they will undergo appreciable decomposition. The formation of highly volatile trifluoroacetylacetone chelates permits the use of injection port and column temperatures low enough that thermal decomposition can be avoided. Also the fluorine atoms impart high sensitivity to electron capture detectors. The instrument employed allowed use of direct on-column sample injection, and glass or Teflon columns.

The instrument conditions used in this study were: instrument: Hewlett-Packard Model 402 research chromatograph with a titanium tritide electron capture detector; column: 1.2 m × 4 mm i.d. glass packed with 3.8% Union Carbide UC W98 on Gas Chrom Z, 80–100 mesh; column temperature: 110 °C; detector temperature: 200 °C; carrier gas: prepurified nitrogen at 60 ml/min with a purge gas of 90% argon, 10% methane at 10 ml/min; and electrometer setting: gain 10, attenuation 32.

Standardization. The standards were made by weighing resublimed $Be(tfa)_2$ on a Cahn electrobalance and dissolving this compound in Mallinckrodt Nanograde benzene. **Caution:** Owing to the high toxicity of most beryllium compounds when inhaled, great care should be taken when weighing and handling $Be(tfa)_2$. Fresh standard solutions were prepared (every two weeks) from stock solutions containing 9.25×10^{-6} g/ml. Fresh stock solutions were prepared every two months. $Be(tfa)_2$ gradually decomposes and/or is adsorbed on the walls of the volumetric flasks in significant amounts ($<1 \times 10^{-7}$ g/ml) at the low concentrations. The degradation is indicated by the appearance of a new extraneous peak at a slightly longer retention time that that of $Be(tfa)_2$ and a concomitant reduction in the height of the $Be(tfa)_2$ peak. The volumetric flask used to store the standard solution was silanized to reduce degradation and absorption of the $Be(tfa)_2$.

GC Analysis of Standards and Unknowns. An inherent problem encountered with use of the electron capture detector is the deleterious effect of certain compounds on detector response. The injection of an unknown complex which contains several compounds may temporarily affect the sensitivity of response of the detector to subsequently eluted compounds. If this situation occurs, standards analyzed at the beginning and at the end of a series of injections of the unknown will have differing response values, manifested by a change in slope or displacement of the original calibration curve. To obtain complete calibration curves between determination of every unknown is impractical; therefore, a sampling method was adopted to compensate for temporary changes in sensitivity.

A sequence of injections was used in which two standards which produce peak heights smaller and larger than the unknown were followed by injection of the unknown sample. This sequence of injections was repeated at least five times for each sample. The mean of peak heights from five analyses of each standard and the mean of the peak heights from five unknown analyses were determined. From the concentration of $Be(tfa)_2$ in the standard solutions and the resulting peak heights, the concentration of $Be(tfa)_2$ in the unknown could be determined. The computation was performed on an Olivetti-Underwood Programma 101 computer-calculator from continually updated two-point calibration curves obtained over a narrow concentration range approximating the concentration of the unknown. This method of operation simplified calculations and enhanced the accuracy and precision of the analysis. Complete calibration curves were periodically obtained to determine the linear range of the detector and to ensure that the standards and unknowns fell in this range.

Results and Discussion

Figure 2 is a chromatogram resulting from the extraction of beryllium as $Be(tfa)_2$ from an aqueous digest of particulates collected at the urban site. Table I is a summary of data from analysis of ambient air suspended particulates for beryllium content. As subsequent discussion will show, the beryllium levels in urban air near a coal-burning power plant and an industrial complex are several times higher than regional (rural) background levels and are highly dependent on wind direction.

Three glass fiber filters were analyzed from three different collection periods at each of the three sites (Figure 1). Each filter was processed by the reflux dissolution method described earlier, with a total of 50 ml of the digest solution resulting. One-milliliter aliquots of this filter particulate digest solution were used in the determination of beryllium. Five aliquots were individually treated with benzene–trifluoroacetylacetone and analyzed. A mean of the beryllium concentration found in the five aliquots was determined and is shown in Table I. The total volume of air processed is given in the second column of Table I. The suspended particulate weight per cubic meter of air was determined by weight difference of the filter in the usual manner. The concentration of beryllium determined in the filter digest solution was used to calculate the weight of beryllium per volume of ambient air

($\mu g/m^3$) and ultimately to determine the concentration of beryllium in the suspended particulate matter.

The concentrations of suspended beryllium determined in ambient air ($\mu g/m^3$) at various sites over nine different collection periods are listed in Table I, column 4. Due to limitations in collection equipment available, the three filters used to collect particulates at each site were exposed during three different time periods; therefore, only location differences can be compared. There is a significant difference between the beryllium levels measured at the rural site ($2.7–5.8 \times 10^{-5}$ $\mu g/m^3$) vs. those at the urban site ($10.4–19.5 \times 10^{-5}$ $\mu g/m^3$). The levels varied more ($4.0–7.2 \times 10^{-5}$ $\mu g/m^3$) at the suburban site but were not greatly different from the levels observed for the rural filters. On the other hand, there appear to be no clear trends in the total particulate matter weight.

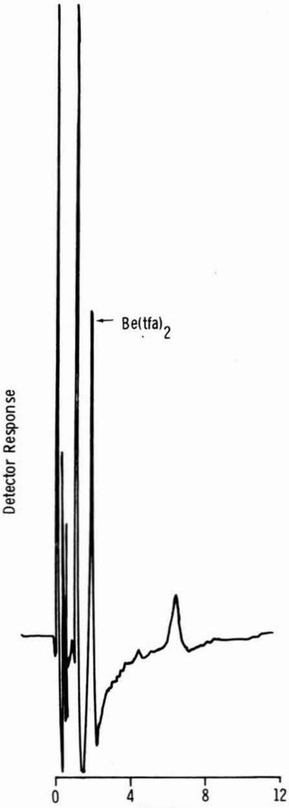

Figure 2. Gas chromatogram of extract from glass fiber filter after recovery of ambient air particulates for 24 h at urban site

These data indicate that the beryllium concentration may increase as the particulate loading decreases or vice versa. This would be expected if different particulate sources containing varying concentrations of beryllium were involved. However, the concentration of beryllium in particulates appears to be coupled with wind direction and the relation of the sampling site to the power plant and industrial area of the city. The beryllium concentration in suspended particulates is relatively constant at the rural collection site, 0.66–1.1 ppm, irrespective of wind direction, and is in the same concentration range as found in farm soil in the region.

The beryllium concentration in the urban-industrial particulates was highest (2.8 ppm) when the wind was from the east, the direction of the city power plant and a highly industrial area; it was least when the wind was from the west and northwest (1.5–1.9 ppm), blowing across farmland and suburban areas with little industry.

The suburban sampling indicated a similar relationship. A 0.7-ppm level was measured when the wind was from the east (farmland), but a threefold increase (2.2 ppm) was found when the wind was from the west and southwest, the direction of Dayton's power plant and heavy industries. The suburban Filter #9 contained nearly as high a concentration of beryllium (1.6 ppm) when the wind traveled across the city from northwest and west, again from the direction of the power plant and industrial area.

The Student's t test was used to determine the significance of differences between the beryllium concentration in particulates collected at the urban and rural sites. The comparison indicated significance at the 95% confidence level. A comparison of the concentration of total particulates between the same two sites also indicated significant differences at the 95% confidence level.

Soil samples from each of the three sites were analyzed for beryllium content. The samples were taken from subsurface layers of soil to ensure that soil was obtained without including any fallout from air particulates. The analytical data are reported in Table II.

Comparisons of beryllium in soil and beryllium in particulates collected from ambient air are made in Table II. The beryllium in the rural soil sample is within the range of the ambient air particulates, so one might conclude that the

Table I. Beryllium Found in Ambient Air Particulates by Chelation–Gas Chromatographic Method

Filter no.	Air vol, m^3	Particulates, $\mu g/m^3$	Be, $\mu g/m^3$ 10^{-5} [a]	Be in particulates, ppm	Wind direction
			Rural		
1	4180	57.4	5.8 ± 1.4	1.0 ± 0.2	SE
2	4490	63.4	4.2 ± 1.4	0.66 ± 0.2	S, N, E, SE
3	4545	24.2	2.7 ± 0.6	1.1 ± 0.3	SW, W, NW, E
			Urban-industrial		
4	1815	104.7	19.5 ± 4.6	1.9 ± 0.3	W, N
5	1815	68.9	10.4 ± 2.6	1.5 ± 0.3	N, NW
6	1882	50.4	13.9 ± 6.2	2.8 ± 0.9	E
			Suburban		
7	3876	55.5	4.0 ± 1.8	0.72 ± 0.06	E
8	4604	32.5	7.2 ± 1.4	2.2 ± 0.3	W, SW, S
9	4619	35.0	5.5 ± 2.0	1.6 ± 0.1	W, NW, S

[a] Mean of five determinations.

Table II. Beryllium Determined in Subsurface Soil and Comparison with Suspended Air Particulates

Soil sample	Sample wt, g	Be, ppm Soil	Be, ppm Particulates, air
Rural	0.1220	0.95[a]	0.66–1.1
Urban	0.1027	0.57	1.5–2.8
Suburban	0.1090	1.15	0.7–2.2

[a] At least three analyses were made on each soil sample.

particulates collected and analyzed in this sample are primarily fugitive dust of particles of surface soil. The beryllium concentration in the urban soil (and in the soil throughout the region) is well below that in the ambient air particulates collected in the city, indicating that other sources are contributing higher concentrations of beryllium in particulates. For example, we have found beryllium in fly ash collected from three different power plants to be from 10 to 25 ppm. The beryllium concentration in soil at the suburban site falls within the wide range observed in the particulate matter collected at that site. The collection for which the particulate Be concentration most nearly matched the soil Be level was made on the day when the wind was in the east from farmland.

Since the applicability of this method to the determination of minute amounts of beryllium has been established, it would be of interest to study the sources, transport, and fate of this highly toxic metal in the biosphere more extensively.

Acknowledgment

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Method for Simulating Plume Centerlines from Tall Stacks

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■ The Tennessee Valley Authority has maintained an SO_2 monitoring network at the Paradise power plant since 1963 to record 15 meteorological variables at one location in the network, plus the SO_2 concentration at 14 locations. The large number and 5-min time interval between measurements make these data potentially useful for dynamic modeling. The 5-min wind direction and velocity were used to construct a plume centerline for each interval. This line was then fit with a polynomial, and the distances from it to each of the stations were computed. The resulting concentration and distances were then used to construct a distribution function which appeared normal in character. These curves had a standard deviation close to those predicted from the Pasquill curves. Calculated concentrations at the stations for each time interval were compared with the actual data to calculate a sum of squares which asymptotically decreased as more points were averaged.

The largest, single nationwide source of sulfur dioxide emissions is electric power generating plants which account for 45.5% of such emissions (*1*). The problem is compounded by the fact that this SO_2 is released at a point rather than being uniformly distributed over a large area. Concentration levels of sulfur dioxide in the ambient air that cause adverse health and material effects have been established (*2, 3*), and ambient air quality standards based on these levels have been set.

One approach to emission control involves the use of tall stacks and fuel switching or load reduction during periods of atmospheric stability not conducive to dispersion. The effectiveness of this approach depends largely on the ability to predict the ambient SO_2 levels that will result from a given set of emission factors and meteorological conditions. The role of mathematical models in describing the dispersion of pollutants emitted from a tall power plant stack has, therefore, become very significant.

Sulfur dioxide levels, wind direction, and velocity in the vicinity of the TVA Paradise coal-fired power plant (*4, 5*) were used to establish the efficacy of the proposed plume centerline simulation technique. The choice of this power plant was made on the basis of its remote location in reasonably flat terrain, its tall stacks acting as a point SO_2 source, its use of 4–5% sulfur coal to produce up to 2500 MW of power, and the existence of an SO_2 monitoring network near the plant since 1963 (*4, 5*). As an example, the TVA reported that combustion of 23 295 tons of coal per day resulted in 1793 tons per day of SO_2 emitted by the stacks to the atmosphere.

From a literature survey it became apparent that little has been done in the area of relating source and meteorological variables to receptor concentrations in the vicinity of coal-fired power plants on a dynamic or short-term average basis such as an hour or less. There also was disagreement in the literature as to how well existing (primarily Gaussian) models apply to the dispersion from very tall stacks.

The objectives of this study were to analyze the data by various methods to determine how well existing types of models fit the data as a function of the time averaging period, to determine if a linear superposition of the effects of the variables gives meaningful results in terms of the level of the source variable at the receptor point, and to determine how much of the receptor signal can be attributed to a given source variable.

Table I. Variables Recorded by Paradise Meteorological and Sulfur Dioxide Monitoring Network (at 5-Min Intervals)

Scan field no.	Variable	Elevation, ft
1	Wind speed, mph	360
2	Wind direction, degrees	360
3	Standard deviation of variable 2	360
4	Wind speed	44
5	Wind direction	44
6	Solar radiation	4
7	Total radiation	4
8	Temperature	360
9	Temperature	44
10	Temperature	4
11	Dew point	4
12	Rain	4
13	Atmospheric pressure	4
14	Standard deviation of horizontal wind direction	360
15	Standard deviation of vertical wind direction	360
16–30	SO_2 monitoring stations	

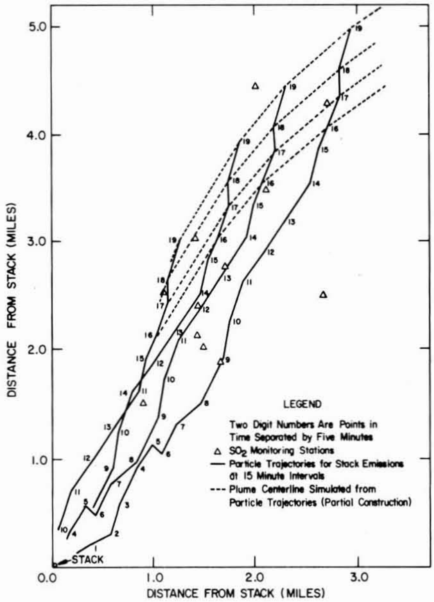

Figure 1. Example of procedure used to construct plume trajectories from parcel trajectories

Because of the small fraction of a year that SO_2 readings attributable to the power plant were recorded by the network, only the first objective could be attained. Although some results for the second and third objectives are available (*6*), it is difficult to draw conclusions confidently from these.

Data Acquisition and Description

The Air Quality Branch of the Tennessee Valley Authority in Muscle Schoals, Ala., initially supplied hourly average values of the 29 variables listed in Table I as recorded by the Paradise network during 1970. The SO_2 monitoring network is comprised of 14 stations all located within a 22.5° compass sector with respect to the plant. Originally, the network was thought to be positioned in the direction of the prevailing winds; however, subsequent records indicated that the wind direction was fairly uniformly distributed around 360°, and the wind would blow over the network approximately 23 days a year.

Examination of the hourly concentration data made it apparent that during the winter, considerable background SO_2 interference was present from coal that was burned in the area for home heating. Because some of these sources were as close as 150 ft to the monitoring sites, data measured during the winter months were not useful for this study. Outside of the winter months, there were few instances of measurable SO_2 concentrations during the night, since night-time low-level radiation inversions prevented the plume from reaching the ground.

After elimination of the winter data, and days for which data were not available, there were only eight days during the year 1970 with data that could be used for analysis, and for these readings occurred during 5 or 6 h out of 24. Thus, of the 10^5 potential 5-min readings during 1970, only about 500 were nonzero or did not occur during a period of high background interference.

Comparison of the 5-min readings and hourly averages for wind speed and direction showed that the use of hourly averages gave a very misleading picture of the location of the plume centerline. In general, the wind vector tended to rotate back and forth across the network. Typically, at the beginning of an observation period it would be on one side of the network and at the end of the hour it would have moved at least the 22.5° necessary to traverse across the network. Figure 4 shows this effect clearly. On some days the wind vector would go across the network and return to its starting point in an hour or less.

The meteorological data also showed that the 360-ft readings for wind speed and direction had a smaller random component than the 44-ft data. Thus, it was decided that the 5-min reading of these two variables at 360 ft would be used to construct 5-min plume trajectories. These trajectories would then serve as centerlines for subsequent predictions of the 5-min SO_2 concentrations at the monitoring stations.

Determination of Plume Trajectories from 5-Min Meteorological Observations

The hour average wind direction was judged to be an inadequate representation of the plume trajectory; therefore, the location of the plume centerline was determined by the following procedure.

A parcel of gas containing the SO_2 released from the stack at the beginning of each 5-min period was assumed to move horizontally along a vector in the direction of the wind at 360 ft as measured for that 5-min period. The length of the vector in miles was the wind speed at 360 ft in miles per hour multiplied by the time period, $\frac{1}{12}$ h. The parcel trajectories, as illustrated in Figure 1, were constructed by adding the 5-min travel vectors which occurred consecutively in time. A complete picture for 1 h would result in 12 separate paths. Because of the close proximity of these, only four separated by 15 min are shown in Figure 1. The numbers on that figure correspond to a real time period; thus, the trajectories represent the paths followed by parcels released from the stack at time periods 0, 3, 6, and 9 corresponding to 0, 15, 30, and 45 min.

It was then possible to construct the plume trajectory at any point in time by joining positions representing that point in time on successive parcel trajectories. Such trajectories were constructed for points determined at each 5-min interval (Figure 1).

Third order polynomials were fitted to the points on the instantaneous plume trajectories described in the previous paragraph to construct smoothed plume trajectories.

With the equation for the plume centerline and the locations of the monitoring stations, it was easy to derive an expression for the normal distance from the plume centerline to each station as shown below, where the variables are defined in Figure 2.

$$y = f(x) = a_0 + a_1x + a_2x^2 + a_3x^3 \qquad (1)$$

$$d^2 = (y_1 - y_3)^2 - [(y_2 - y_3)^2 + (x_2 - x_1)^2]$$

x_2, y_2 are unknown. Minimize $d^2 = [(y_1 - y)^2 + (x_1 - x)^2]$.

Taking the second derivative and setting it equal to zero gives

$$0 = 2(y_1 - a_0 - a_1x - a_2x^2 - a_3x^3) \times (-a_1 - 2a_2x - 3a_3x^2) - 2x_1 + 2x \qquad (2)$$

Equation 2 was solved using Newton's iteration scheme. A graphic example of distance from plume centerline to station is shown in Figure 3.

Figure 4 shows the movement of the plume across the SO_2 monitoring network for hours 15 and 16 of day 129. This plot also shows the average wind direction for the hour [WD(J)] and the previous hour [WD(J-1)]. Computer programs to perform all of these calculations including the distance from the station to the plume and the coordinates of the intercept of the shortest distance between the station and the plume are given by Jones (6). From these plots, the use of the hour average wind directions for determining the distance of the plume from the stations during the hour would result in large errors in comparison with the constructed plume trajectories. The relative distance between points on the plume trajectory contained valuable information because this distance corresponds to a 5-min release from the stack. The magnitude of this distance corresponds to the stretching out or dilution of the plume due to the wind velocity; however, no manageable procedure was developed to determine this distance for the segment intersected by the normal line from the monitoring station to the plume centerline. The crosswind distance between successive centerlines is also an important variable and could be incorporated with the distance variables previously mentioned into an area variable which would represent both radial and crosswind dilution.

Estimation of Plume Crosswind Concentration Distribution from Plume Trajectory Data

To test the effect of using these more realistic plume trajectories, the crosswind SO_2 distribution was examined by constructing a printplot of SO_2 concentration (Y-axis) and distance from the plume centerline (X-axis). Data points for all the stations on day 129 are shown in Figure 5. The data were then divided into cells equispaced on the X-axis, and cell means were calculated so that the distribution was more apparent.

The distribution of the data was very close to the Gaussian (7) form for most stations, and the maximum concentration value was generally observed to occur close to zero distance, indicating that the calculated plume trajectories were rea-

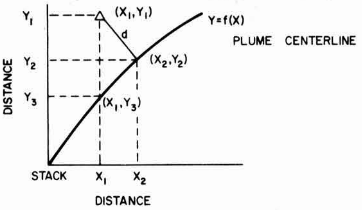

Figure 2. Geometry of normal distance d from station to plume centerline

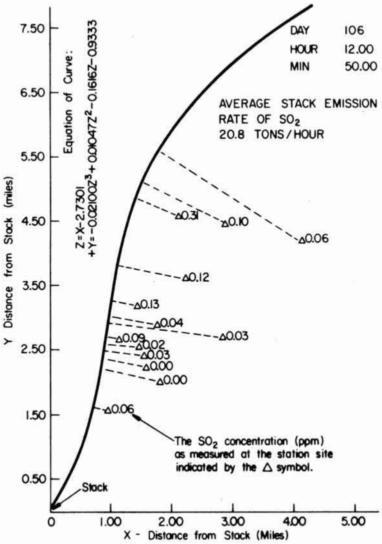

Figure 3. Example of plume trajectory, distances to monitoring sites, and SO_2 concentrations

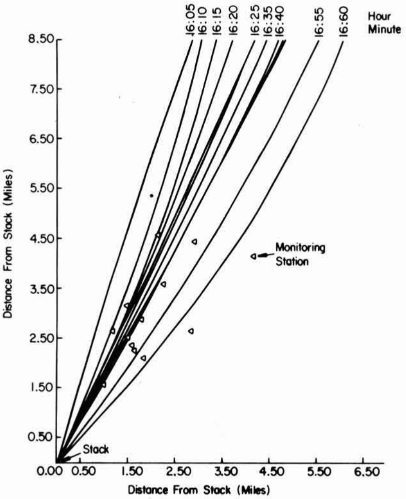

Figure 4. Smoothed plume trajectories for hour 15 day 129

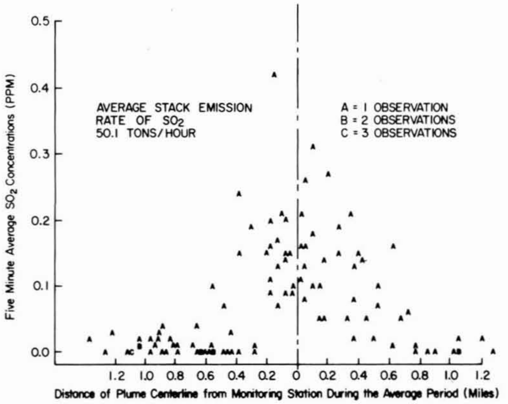

Figure 5. Crosswind SO_2 concentration distribution at station 12, day 129

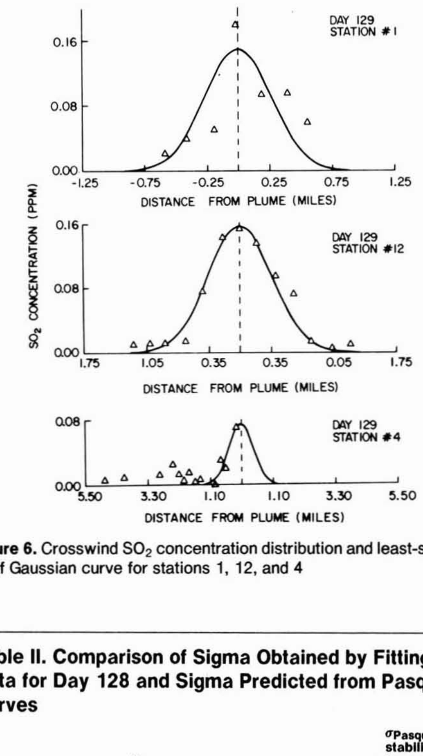

Figure 6. Crosswind SO_2 concentration distribution and least-squares fit of Gaussian curve for stations 1, 12, and 4

Table II. Comparison of Sigma Obtained by Fitting Data for Day 128 and Sigma Predicted from Pasquill Curves

Station no.	Y_{max} Obsd	Y_{max} Pred	σ_{NLIN}, m	$\sigma_{Pasquill}$ stability category, m A	$\sigma_{Pasquill}$ stability category, m B
1	0.089	0.083	0.68	0.54	0.41
9	0.146	0.117	0.82	0.82	0.62
8	0.089	0.083	0.89	0.76	0.58
7	0.084	0.083	0.79	0.74	0.56
2	0.114	0.112	0.82	0.95	0.72
11	0.332	0.278	1.12	0.95	0.72
5	0.025	0.038	1.34	1.02	0.80
12	0.180	0.150	1.13	1.13	0.88
14	0.042	0.032	1.35	1.33	1.00
13	0.095	0.099	1.87	1.35	1.02
3	0.030	0.031	1.66	1.50	1.12

sonably accurate. If we consider that the wind speed and direction measurements were made at a point several hundred feet lower in elevation and almost 7 km downwind, the results are indeed encouraging. The wind velocity and direction variables measured at an elevation of 44 ft gave substantially different results and were not usable in constructing trajectories.

The standard deviation and the maximum concentration were computed to construct a Gaussian curve for each station. A standard nonlinear least-sqares program was used to evaluate σ and C_{max} in the equation:

$$C_{pi} = C_{max} \exp(-x_i^2/2\,\sigma^2) \qquad (3)$$

so that

$$\sum_{i=1}^{N} (C_{oi} - C_{pi})^2 = \text{minimum}$$

where x_i is the calculated distance from the plume centerline, and C_{oi} is the observed SO_2 concentration. The cell averages for the eight days were plotted. Typical results are shown in Figure 6. Station 1, which shows the poorest fit, is located closest to the stack, and its results are strongly influenced by where the plume actually comes down in the network. Station 12 gives almost a perfect fit which reflects the fact that it is located where all the meteorological variables are measured and in the center of the network. Station 4, the most distant, consistently had the lowest C_{max}. The effect of being on one side of the network also is shown by the lack of readings on the positive distance side.

The C_{max} and σ^2, estimated from the data using Equation 3, were compared with those using the Pasquill curves given in Turner (*8*) for atmospheric stability. Results for day 128 are shown in Table II. Stability classification A best represented this day, and the erroneous use of B classification would have resulted in a larger deviation of σ than the difference between the sigma values for stability A and those fit to the data.

For day 106 using all the 5-min observations without averaging results in a sum of squares of approximately 0.006; using 10 points reduces this to 0.004, and 50 points further reduces this to 0.0004. Gaussian models are not suitable for prediction during periods of turbulent vertical mixing such as occurs during an inversion breakup. Averaging of the data tends to smooth the fluctuations and provide better agreement with the Gaussian predictions.

Conclusions

Examination of the SO_2 data from the fixed monitoring network for the TVA Paradise Power plant has shown that only a few days out of each year give readings useful for analysis purposes. This is caused by meteorological conditions such as low level night time inversions which prevent the plume from reaching the ground and an almost uniform wind rise. In addition, the winter stack emissions were confounded with ground level SO_2 emissions from home heating.

The network showed little effect of distance since over half the stations were within 2½ to 3½ miles of the stack. The rate of movement of the plume across the network and previous plume history are important in modeling a point SO_2 source. This was particularly evident when comparing the SO_2 concentrations predicted from the simulated plume trajectory with the actual concentrations. These crosswind average concentrations followed a Gaussian distribution with a standard deviation following the Pasquill curves for the meteorological conditions studied. Best agreement on all days occurred at the meterological tower where all the meteorological variables were measured as well as the ground level SO_2 concentration. Finally, ground level measurements of the wind velocity and wind direction at low to moderate wind speeds are not sufficiently accurate for modeling purposes. The ground temperature, terrain, and low level objects tend to introduce very large fluctuations in these variables. Analysis shows that the signal-to-noise ratio is small—not a desirable characteristic for modeling purposes.

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Partition Coefficient and Bioaccumulation of Selected Organic Chemicals

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■ An empirical equation is established to relate the experimental *n*-octanol/water partition coefficients to the aqueous solubilities of a wide variety of chemicals including aliphatic and aromatic hydrocarbons, aromatic acids, organochlorine and organophosphate pesticides, and polychlorinated biphenyls. Such a correlation, covering more than eight orders of magnitude in solubility (from 10^{-3} to 10^4 ppm) and six orders of magnitude in partition coefficient (from 10 to 10^7), allows an assessment of partition coefficient from solubility with a predicted error of less than one order of magnitude. A correlation is observed between the bioconcentration factors in rainbow trout and the aqueous solubilities for some stable organic compounds.

The current emphasis on the environmental impact of both agricultural and industrial chemicals has resulted in an increased reliance on the physical and chemical properties of these compounds to assess their environmental behavior. The *n*-octanol/water partition coefficient, for example, has proved useful as a means to predict soil adorption (*6*), biological uptake (*18*), lipophilic storage (*10*), and biomagnification (*21, 24, 25, 27*). Unfortunately, the partition coefficients of many compounds of environmental significance are not always available despite a recent extensive compilation (*20*). Assessment of partition coefficients from a more readily available physical parameter would be useful.

By definition, the partition coefficient expresses the equilibrium concentration ratio of an organic chemical partitioned between an organic liquid (e.g., *n*-octanol) and water. This partitioning is, in essence, equivalent to partitioning an organic chemical between itself and water. Consequently, one would suspect that a correlation might exist between the partition coefficient and the aqueous solubility. An equivalent correlation has been demonstrated earlier by Hansch et al. (*13*) for several classes of organic liquids of relatively low molecular weights whose aqueous solubilities generally fall in the high ppm (mg/L) range. In the report of Hansch et al., however, most partition coefficients of the organic liquids were assessed from the π constants of the substituents in relation to some parent compounds since the experimental values were not determined.

It would be of interest to test this correlation using the experimental data on various types of pesticides and industrial chemicals. This correlation would be useful as it serves not only as an indication of the interrelationship between these two physical parameters but also as a convenient means to predict a reasonable partition coefficient from the aqueous solubility. For example, it has been noted that partition coefficients reported for a given pesticide (e.g., DDT) often differ more than several orders of magnitude (*21, 28, 33*). The use of this correlation will help clarify questionable data. In our present studies we are reporting a satisfactory relationship between measured partition coefficients and aqueous solubilities for a wide variety of chemicals. By combining the relationships of partition coefficient to aqueous solubility and to biomagnification (*21, 24, 25, 27*), a correlation between biomagnification and aqueous solubility as reported by Lu and Metcalf (*21*) and Metcalf et al. (*25*) is supported. In the present report, a similar correlation is demonstrated for several stable organic compounds using the biomagnification data in rainbow trout from Neely et al. (*27*).

Experimental

The aqueous solubilities of 2,4,5,2′,5′-PCB, 2,4,5,2′,4′,5′-PCB, and six organophosphate pesticides were determined at room temperature. The method consisted of equilibrating a quantity of the compound with water by determining the concentration at different time intervals until saturation was achieved. The water used in the solubility study was passed through a 1 × 7 cm XAD-2 column to remove organic impurities. The chemical was dissolved in approximately 10 mL distilled ether and swirled onto the walls of a flask, evaporating the ether and leaving the compound deposited on the walls. Water was added and stirred slowly to avoid disturbing the coated walls. Aliquots of the aqueous solution were removed via a sintered-glass filter immersed in the solution (*16*) and analyzed at regular intervals with GLC until no further change in concentration was noticed. Preliminary values of the water solubilities of 4,4′-PCB and *p,p*′-DDE were also determined under similar conditions except that samples taken for analysis were equilibrated for a shorter time interval. The determined solubilities for the latter two compounds, however, are in reasonably good agreement with the reported literature values (*3, 34*).

The partition coefficients of the three PCB's and 12 organophosphates were determined by the following method. A stock solution of approximately 1 mg/mL compound in *n*-octanol was prepared. A 2-mL aliquot and 20 mL of water were shaken for 16 h at 20 °C in a closed 25-mL Corex centrifuge tube. After equilibration and centrifugation (17 500 rpm, 37 000 G at 20 °C for 20 min), the two phases were separated and extracted or diluted as necessary to analyze by GLC. The *n*-octanol used was distilled several times to remove trace amounts of impurities which tended to produce emulsions. Formation of emulsions gives poor phase separation and results in a wide scatter in the partition coefficients. It is essential to analyze the concentrations in both phases for a compound of low aqueous solubility when determining the partition coefficient, since the compound may adsorb on the glass walls of the container. All compounds were analyzed on a Tracor 550 GLC equipped with a Ni^{63} electron capture detector. The columns used were as follows: DDT and PCB's—a mixed phase 1.5% OV-17/1.95% OV-210 on 60/80 Gas-Chrom Q, 2 mm × 2 ft glass column; organophosphates—5% OV-225 on 60/80 Gas-Chrom Q, 2 mm × 2 ft glass column or >0.2% Carbowax 20M on 80/100 Chromasorb W, 2 mm × 2 ft glass column (*1*).

Results and Discussion

Table I shows a list of the experimental values for the aqueous solubilities and *n*-octanol/water partition coefficients for various types of chemicals. A plot of log (partition coefficient) vs. log (solubility in water) using the experimental values obtained in this laboratory as well as values cited in the literature is shown in Figure 1. The solubility values from the literature were taken from a temperature range of 10–30 °C and the partition coefficient values at room temperature. Our solubility and partition coefficient values were determined at 20 °C except the solubilities of the two PCB's which were done at 24 °C. A satisfactory linear relationship is observed between the log (partition coefficient) and log (aqueous solubility), which extends to more than eight orders of magnitude in solubility (10^{-3} to 10^4 ppm) and six orders of magnitude in partition coefficient (10 to 10^7). The regression equation shows:

$$\log K = 5.00 - 0.670 \log S \tag{1}$$

where K = *n*-octanol/water partition coefficient and S = aqueous solubility, in μmol/L. The corresponding statistical analysis of variance table is as follows:

Source	DF	Sum of squares	Mean square
Total	33	74.3	2.25
Regression	1	72.1	72.1
Residual	32	2.24	0.0699

$R^2 = 0.970$; $F = 1030$; $\alpha = 0.005$

Table I. Solubilities and Partition Coefficients of Various Compounds

Compound	Solubility in water, ppm	Log (*n*-octanol/H_2O partition coeff)
Benzene	820 (22 °C)[12]	2.13[11]
Toluene	470 (16°)[12]	2.69[11]
Fluorobenzene	1540 (30°)[12]	2.27[11]
Chlorobenzene	448 (30°)[12]	2.84[11]
Bromobenzene	446 (30°)[12]	2.99[11]
Iodobenzene	340 (30°)[12]	3.25[20]
p-Dichlorobenzene	79 (25°)[12]	3.38[19]
Naphthalene	30[12]	3.37[15]
Diphenyl ether	21 (25°)[19]	4.20[19]
Tetrachloroethylene	400 (25°)[19]	2.60[19]
Chloroform	7950 (25°)[19]	1.97[14]
Carbon tetrachloride	800[12]	2.64[22]
p,p'-DDT	0.0031[5]–0.0034[4] (25°)	6.19[28]
p,p'-DDE	0.040 (20°)	5.69[28]
Benzoic acid	2700 (18°)[12]	1.87[11]
Salicylic acid	1800 (20°)[12]	2.26[14]
Phenylacetic acid	16600 (20°)[12]	1.41[11]
Phenoxyacetic acid	12000 (10°)[12]	1.26[11]
2,4-D	890 (25°)[19]	2.81[11]
2,4,5,2',5'-PCB	0.010 (24°)	6.11
2,4,5,2',4',5'-PCB	0.00095 (24°)	6.72
4,4'-PCB	0.062 (20°)	5.58
Phosmet	25 (25°)[23]	2.83
Malathion	145 (20°)[23]	2.89
Fenitrothion	30[23]	3.38
Dicapthon	6.25 (20°)	3.58
Parathion	24[23]	3.81
Phosalone	2.15 (20°)	4.30
Methyl chlorpyrifos	4.76 (20°)	4.31
Dialifor	0.18[17]	4.69
Ronnel	1.08 (20°)	4.88
Chlorpyrifos	0.4 (23°)[7]	5.11
Dichlofenthion	0.245 (25°)[32]	5.14
Leptophos	0.0047 (20°)	6.31

Equation 1 allows an estimation within one order of magnitude of the partition coefficient of a given compound from its aqueous solubility.

The scatter of points in Figure 1 reflects the following two factors: temperature and analytical procedure. The temperature effect on the partition coefficient is generally about 0.01 log unit per degree near room temperature (*20*). The temperature effect on the solubility will be within the same order of magnitude. This corresponds to about a 25% change in either the partition coefficient or the aqueous solubility for every 10° variation in temperature. The maximum temperature effect would account for a deviation of no more than 50% or a factor of two in the plot. Varied analytical methods employed in the determination of the partition coefficient or the solubility account for the larger discrepancy in the literature values (*16, 20, 29*). Anomalies due to molecular structure can also be a possible cause. However, more information in this line is needed to make fair conclusions. In spite of the difficulty in analyzing some relatively unstable or insoluble chemicals, the experimental data in Figure 1 show an acceptable fit. It is of interest to note that such a correlation covers many classes of chemicals from hydrocarbons and organic halides to aromatic acids, pesticides, and PCB's. It also spans chemicals of different polarities (from nonpolar to polar) and of different molecular states (both liquid and solid).

The partition coefficient is defined in the form:

$$K = a_0/a_w \cong C_0/C_w \tag{2}$$

where a_0 and a_w refer to the activity, and C_0 and C_w to the concentration in the *n*-octanol and water phase. The close fit of the aromatic acids suggests that these compounds show no significant dissociation or dimerization in the system. The latter is in agreement with the findings of Fujita et al. (*11*) who reported an insignificant difference in the measured K values of benzoic acid with log K changing from 1.88 to 1.81 when the concentration in octanol phase varied from 10^{-2} to 10^{-4} M. Similar findings were reported for phenoxyacetic acid and phenylacetic acid. Considering that the p*K*a of these acids are in the neighborhood of 4, one would expect no more than a few percent dissociation in the aqueous phase. Obviously, it would be doubtful that Equation 1 would apply for salts, strong acids, and bases since the activities of these solutes in this case cannot be approximated by their concentrations.

The magnitude of the partition coefficients covered in Figure 1 ranges from less than 10^2 for unsubstituted aromatic acids to 10^6 for PCB's and organochlorine pesticides. Hydrocarbons and organic halides fall in the range from about

10^2 to about 2×10^3 and organophosphate pesticides from 10^3 to 10^5. Leptophos shows an exceptionally high partition coefficient and low solubility in comparison with other organophosphates. Since the partition coefficient has been used in assessing the environmental and biological activities of the chemical, Equation 1 can provide a preliminary basis for a rapid evaluation of the probable behavior and fate of the chemical simply from its aqueous solubility, since this is generally more readily available and better established.

Equation 1 also will clarify some of the questionable partition coefficients reported for several chemicals. Although the aqueous solubility reported for DDT ranges from about 0.2 to 1000 ppb (μg/L) (*2, 4, 5, 26, 30, 31*), at this time it is accepted that the actual value is between 1 and 5 ppb. The published partition coefficient varies from about 9×10^3 to 1.6×10^6 (*21, 28, 33*). The accepted DDT solubility in the low ppb range would, according to Equation 1, predict a K value in the million range. The value of 1.6×10^6 calculated by O'Brien (*28*) is in good agreement with this estimate. Low K values have been reported for many compounds: 1 030 for aldrin, 13 560 for hexachlorobenzene (*21*), and 16 037 for 2,4,5,2′,5′-PCB (*25*). According to the reported solubility of about 6 ppb for hexachlorobenzene (*21*), the authors would predict a K value of 1.5×10^6 which concurs with the value of 1.5×10^6 as calculated by Neely et al. (*27*). Based on the reported solubility values for 2,4,5,2′,5′-PCB from 10 ppb of this laboratory to about 20 ppb of Metcalf et al. (*25*) and of Wallnofer et al. (*34*), the authors' experimental K value of 1.3×10^6 is in good agreement with that predicted from Equation 1.

As previously stated, the partition coefficient is related to physical adsorption on solids, biomagnification, and lipophilic storage. Equation 1 would extend those correlations to cover compounds using their aqueous solubilities without requiring the partition coefficient data.

The adsorption-solubility relationship may be understood by considering the (physical) adsorption of a chemical from aqueous solution. As adsorption is an exothermic process in which the adsorbate condenses from the bulk phase onto the adsorbed phase, an increase in solubility with increasing temperature would result in a reduction of the amount adsorbed. For compounds of comparable molecular size with different solubilities, the one with lower solubility, i.e., lower hydrophilicity, would tend to be adsorbed more favorably at a given equilibrium concentration, provided such adsorption is not complicated by other geometric effects (*8, 9*).

The correlation of biomagnification in mosquito fish (*Gambusia affinis*) with the aqueous solubilities of chemicals has been reported for some PCB's, DDT, DDE, aldrin, and many other organic compounds (*21, 25*). As an additional illustration, the authors are presenting a similar correlation in Figure 2 utilizing the reported biomagnification data of some selected organic chemicals in rainbow trout (*Salmo gairdneri*) (*27*). The solubilities of biphenyl and 2,4,2′,4′-PCB in Figure 2 are obtained from Bohon and Claussen (*35*) and Wallnofer et al. (*34*), respectively.

The regression equation shows:

$$\log(\mathrm{BF}) = 3.41 - 0.508 \log S \qquad (3)$$

where BF = bioconcentration factor in rainbow trout and S = aqueous solubility in μmol/L. The associated statistical analysis of variance table is as follows:

Source	DF	Sum of squares	Mean square
Total	6	6.93	1.15
Regression	1	6.44	6.44
Residual	5	0.484	0.0968

$R^2 = 0.930$; $F = 66.6$; $\alpha = 0.005$

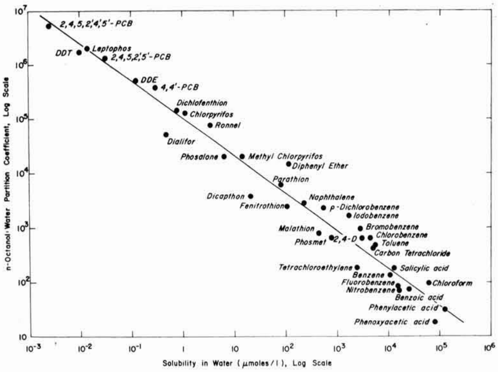

Figure 1. Partition coefficients and aqueous solubilities of various organic chemicals at room temperature

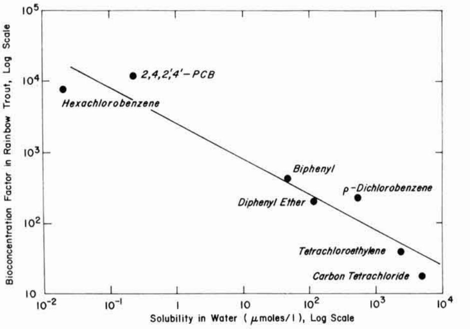

Figure 2. Aqueous solubilities and bioconcentration factors of organic chemicals in rainbow trout

The utility of the lipophilic storage-partition coefficient correlation has been demonstrated in the treatment of several cases of human poisoning involving the organophosphate dichlofenthion (*10*). The relatively high partition coefficient for this compound provided an explanation of the anomalous symptomology observed after ingestion. It was postulated that fat deposition with the resultant slow release into the circulatory system was the probable cause of the prolonged toxic manifestations. Leptophos, with a partition coefficient of more than an order of magnitude higher than dichlofenthion, should exhibit similar behavior. An estimation of these partition coefficients from their available solubilities would be of value in understanding the unusual toxicological features encountered and the prescription of appropriate prolonged antidotal therapy.

An attempt has been made to illustrate a few interrelationships of the physical and chemical properties which guide the behavior and fate of chemicals in the environment. Hopefully, these correlations will prove useful for environmental scientists in assessing data and considering the possible effects of chemicals on the environment.

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Chlorination Reactions of Fulvic Acids in Natural Waters

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■ Chlorination of both drinking waters and wastewaters leads to the generation of various chlorinated degradation products of natural fulvic acids. Fulvic acids constitute the bulk of the organic matter in colored surface or ground waters. Meta-dihydroxybenzene structures are proposed as main reactive sites of the molecule. Experimental evidence is presented for possible reaction pathways leading to haloforms and other chlorinated by-products.

In 1974 Marx (*1*) gave particular notice to some disquieting effects on health as a result of chlorination of drinking water as observed in New Orleans by the group of Laseter.

Earlier in the year Harris and Page (*2*) had published statistical evidence for the carcinogenic properties of some micropollutants in drinking water from the Mississippi River. Some months later Dowty et al. (*3*) reported on their findings of 13 volatile halogenated organic compounds in tap water. At least five of these were detected in the blood plasma of local consumers of the water. Rook (*4*) in the meantime reported experimental evidence for the formation of haloforms as by-products of chlorination of naturally colored waters. Rook demonstrated that fulvic acids that impart the yellow color to the water are precursors for haloforms when treated with chlorine. Even traces of bromine generated by oxidation of the bromide ions in the water during chlorination produce analogous effects. Consequently, all colored water that is chlorinated, whether surface or ground water, must contain these micropollutants, ironically introduced by a process to protect the consumers from waterborne diseases.

In 1975 the ubiquity of haloforms in chlorinated waters was duly confirmed by EPA's nationwide reconnaissance survey for halogenated organics (*5*). In all of the surveyed water treatment plants employing chlorine for disinfection, chloroform was present in the finished water. Positive correlations existed between haloform concentrations and the total organic matter content in the untreated water.

Fulvic Acid Structures

In the following report we shall give more evidence in support of our earlier experimental data obtained with resorcinol and aqueous peat extract as model substances for fulvic acids.

Since the classical studies of Oden, who in 1919 distinguished the group of yellow acids as a subgroup of humic acids, many researchers have contributed to the identification of the natural yellow acids in water environments with fulvic acids from the soil. Oden's classification is still generally used. It differentiates three groups according to solubility dependent on pH. The group that remains in solution at pH 1 is named fulvic acids. Fulvic acids are essentially small sized humic acid molecules.

Wilson (*6*) concluded from ultraviolet measurements that fulvic acids are the major component of organic color in surface waters. Black and Christman (*7*), in an extensive study covering 10 different sources of naturally colored waters, concentrated and fractionated the total amount of hydrophilic organic matter, which had been freed from fats, waxes, and fatty acids by preliminary ether extraction. They separated humic and hymatomelanic acids by precipitation with HCl. The dry weight of these two precipitates made up for about 10% of the total dry weight of hydrophylic organic matter. The remaining organic solutes were considered to be fulvic acids, though other polysaccharides, peptides, tannins, and smaller organic molecules systematically were not excluded from this fraction.

Since the waters under investigation were mostly unpolluted waters characterized by high contents of natural color, it seemed plausible that the previously named contaminants represented only minor impurities in the dried residues of the fulvic acid fractions. The dry weight accounted for 83–90% of the total hydrophylic organic residue. On these good grounds Black and Christman concluded the predominance of fulvic acids in naturally colored waters. This predominance was later supported by Packham (*8*) in England who used specific isolation techniques with anion exchange resins and by the Russian workers Shevchenko and Taran (*9*) and Fotiev (*10*) who applied liquid chromatography.

In polluted waters the composition of organic matter is quite different. Sontheimer (*11*) recently published results of a fractionation analysis of total dissolved organic carbon (DOC) of water from the lower river Rhine. Application of appropriate separation techniques of DOC gave, for periods of high river flow, the following main components: 36% small molecule biodegradables, 42% humic and fulvic acids, 10% sulfonated lignins, 7% smaller sulfonated aromatics, and 5% chlorinated organic compounds. During periods of low flow the percentages shifted toward man-made pollutants; the latter three groups increased to 53%.

Humic acids according to Dragunov (*12*) and Kleinhempel (*13*) consist of polymers of polyhydroxybenzenes, polyhydroxybenzoic acids, benzene polycarboxylic acids, sugars, and small amounts of N-bases.

Humic acids and fulvic acids both give identical monomeric by-products in various degradation methods surveyed by Schnitzer and Khan (*14*). Examples of degradation products generally found are resorcinol, phloroglucinol, pyrogallol, catechol, orcinol, 2,6-dihydroxytoluene, *o*- and *m*-phtalic acids, and 3,5-dihydroxybenzoic acids.

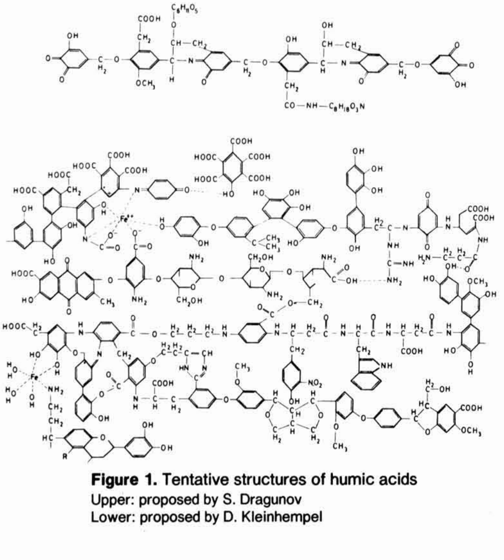


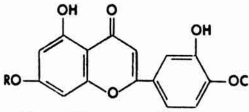
Figure 1. Tentative structures of humic acids
Upper: proposed by S. Dragunov
Lower: proposed by D. Kleinhempel

To establish a reaction pathway for chloroform from its precursor, knowledge of the structure is necessary. It is still not exactly known in which way the monomers are linked together. Dubach and Mehta (*15*) stated that no two molecules of humic acids are exactly identical. Figure 1 shows two tentative structures for fulvic acids; the upper model in Figure 1 is that of Dragunov (*12*). The second structure in Figure 1 is a more recent proposal of Kleinhempel (*13*). Many variations on this theme may be invented.

In the author's view, hydroxylated aromatic rings with two free meta-positioned OH-groups are available active sites for haloform formation.

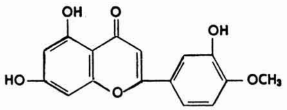
Model Substances

To test this assumption we investigated the ability of some smaller natural glycosides containing the proposed active sites. For that purpose, we have chosen hesperidin and its aglycon hesperetin, a flavonoid occurring in citrus fruits; secondly, the related glycoside rutin occurring in several plants; and thirdly, phlorizin, which is found in roots of Rosaceae. The latter is a model substance for chalcones. Chalcones are C_6–C_3–C_6 structures: two phenyl groups linked by a C_3–ketone. They have been found in black liquor, the degradation product of the Kraft pulping process of wood. In native lignins their presence has not been reported.

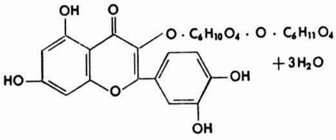


R = D-Glucose + L-Rhamnose

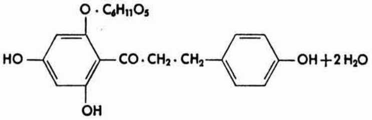
Hesperidin



Hesperetin



Rutin



Phlorizin

All of these biological products contain the proposed active site: two meta-positioned hydroxylgroups. Only hesperidin contains one OH and one *O*-glucoside group. In the author's opinion, these types of configuration may well represent active sites in fulvic acids.

Because of the very low solubility these compounds had to be tested in great dilution. The haloform test was performed by reacting 5×10^{-6} molar solutions with tenfold excess of chlorine allowing a reaction period of 2 h at 20 °C, with pH kept at 7.2. The chloroform yield was measured by head space gas chromatography. The results are given in Table I.

All model substances tested gave quite high amounts of $CHCl_3$. Hesperetin with two free OH-groups gave nearly twice the yield in comparison with hesperidin. This may be explained by the etherization of one of the OH-groups. Phlorizin and rutin behaved as expected.

The above-mentioned similarities of these natural substances, with some special parts of fulvic acids combined with the clear-cut haloform reaction, corroborate our assumption that the most readily reacting site is the carbon between 2 meta-OH-groups. If we consider the structural model of Kleinhempel (Figure 1), we find very few of these sites. This is in accordance with the experience that chlorination of natural waters containing 12 mg organic precursor with 8 mg/L chlorine at pH 7 yielded 0.12 mg $CHCl_3$. The carbon content of fulvic acid is about 50%. In this case, 6 mg of organic carbon, that is expressed in moles as 0.5 mmol total carbon, yielded 0.001 mmol $CHCl_3$. This means that only one out of 500 carbon atoms has been transformed into chloroform under the given conditions.

In experiments with peat extracts in higher concentrations, yields up to 1:100 were measured. The rate of $CHCl_3$ formation in a typical experiment is given in Figure 2. The reaction conditions were watery peat extract diluted to 22.2 mg/L total organic carbon, treated with 3.1 mmol/L chlorine, buffered at pH 7.15, temperature 20 °C.

The molar yield on the vertical axis is expressed as the ratio millimoles of $CHCl_3$ per mole of initial precursor carbon. The shape of the curve reflects nonuniform reaction kinetics; roughly two phases may be distinguished. During the first 15 min a rapid start was observed followed by a much slower secondary phase. This slow phase continued for 24 h. The ultimate yield then was, in duplicate measurement, 20 and 21 mmol/mol. After 48 h, 21 were found. In this experiment 33% of the ultimate yield was obtained within 5 min, and 60% after 1 h reaction time. This slow but constant second reaction could not fully be explained by the lower residual chlorine concentration after first "chlorine demand" had been satisfied. After ½ h the residual chlorine had diminished to 50% of the initial concentration. From thereon Cl_2 further remained near constant for the next 24 h.

Table I. Yields of $CHCl_3$ Molar % from Model Substances 5 $\times$ 10^{-6} Molar in Water After 2-h Reaction with Excess Chlorine, pH 7, Temp 20 °C

Hesperidin	30–32%
Hesperetin	50–56%
Rutin	65–70%
Phlorizin	90–94%
Duplicate experiment	

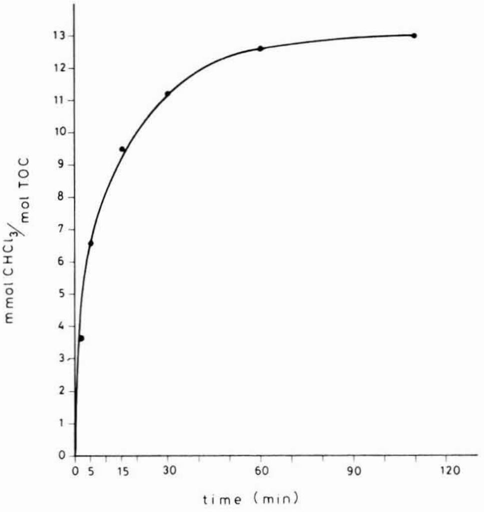


Figure 2. Rate of $CHCl_3$ from fulvic acids TOC 22.2 mg/L, chlorine 0.003 mol/L, pH 7.15

The slope of the secondary phase of $CHCl_3$ production was about 1% of the average over the first 15 min. It is tempting to conclude to a dichotomy in reaction mechanisms of both phases. To find causative factors, further experimentation was needed.

Experiments with Hydroxybenzenes as Model Substances

The experiments described in the preceding section indicated that hydroxylated benzene moieties of fulvic acids readily undergo a haloform type of reaction when treated with chlorine water.

Treatment of fulvic acids in watery solutions with halogens in neutral or alkaline conditions essentially is an oxidative halogenating degradation method which effects drastic alterations by simultaneous oxidations and substitutions. Such a complex system of simultaneously proceeding reactions of quite different types will result in a variety of degradation products. Chloroform may well be a major product generated from a specially reactive site, or as well, just one of many byproducts of secondary or side reactions. Also in chlorination tests with single uncomplicated polyhydroxybenzenes, various reactions will compete. Substitutions, oxidative ring fissions or even ring contractions, and other fragmentations may occur. Reaction conditions such as excess of one of the reaction partners, or pH, will determine which type of reaction will prevail.

In contrast, aliphatic methylketones give a kinetically well-defined haloform reaction, based on the fact that the rate determining step is the initial enolization. Still, we want to find a mechanism which accounts for the positive effect of increased pH on haloform production rates from OH-substituted aromatic rings. For this purpose, a number of model substances were tested for $CHCl_3$ yield with pH as the variable condition. The model substances were chosen to match with known moieties present in humic acids. The compounds tested are listed in Table II. The test conditions were: concentration of organic precursor 0.001 M, chlorine 0.012 M, temperature 15 °C, reaction time 2 h, pH buffered at 7 and 11, respectively. The $CHCl_3$ yields measured are given in Table II as molar percentages.

The results allow the following interpretations and conclusions. The increase in haloform production at pH 11 from meta-substituted compounds 1,3-dihydroxynaphthalene (naphtoresorcinol) 3,5-dihydroxybenzoic acid, 3,5-dihydroxytoluene (orcinol) and the mono-pentylether of phloroglucinol is striking. Resorcinol itself already gave high yields at pH 7 because it reacts faster than related meta-dihydroxybenzene derivatives. In separate experiments with resorcinol the reaction at pH 7, temp 15 °C had reached 60% completion in the first 5 min. We consider halogenation to be electrophilic substitutions. Furthermore, hydroxyl groups and *O*-alkyl groups are activating, ortho and para directing substituents. Hence the carbon atom between two meta-positioned OH- or OR-groups is activated from both sides.

In pyrogallol, cathechol, hydroquinone, and phenol, there are no such positions. Phloroglucinol, however, contains three OH-groups and three activated carbons evenly distributed. That $CHCl_3$ is less produced at high pH may be misleading. Still phloroglucinol is duly halogenated. However, the substitution is followed immediately by fragmentation into CO_2, dichloroacetic acid, and tetrachloroacetone, as observed by

Zincke (*16*) in 1889. We were able to confirm this qualitatively by GC–MS analysis of ether extracts of reaction mixtures of phloroglucinol with chlorine water. Two large peaks were found that were identified with dichoroacetic acid and tetrachloroacetone. $CHCl_3$ was not present. If we transform one of the OH-groups into OR, the activating −I, +T effect is hardly changed. However, the monoether changes the character of phloroglucinol so as to react as a resorcinol. This change of behavior is especially pronounced in the alkaline region. This observation may be explained if we realize that etherization blocks the ionization of phenolic OH. The phenoxide O^- is one of the strongest activating substituents, combining both the +I, +T effect.

Further evidence for this phenoxide-ion theory was obtained by reacting the mono- and dimethylethers of resorcinol. At pH 7 the monoether 1-hydroxy-3-methoxybenzene gave 10% of the theoretical yield of $CHCl_3$, and the dimethylated derivate 1,3-dimethylbenzene gave no $CHCl_3$ at all.

If we compare the meta-hydroxylated compounds with ortho- and paradihydroxybenzenes, the experimental evidence indicates that the carbon atom between two ortho hydroxyl groups is the best suited to function as an active site for $CHCl_3$ formation.

The observation that catechol and hydroquinone gave small traces of $CHCl_3$ at pH 7 indicates that in the complexity of degradation reactions, minor amounts of $CHCl_3$ might be generated by secondary pathways. These pathways were obviously favored by increased pH, as shown by the experiments at pH 11.

It is noteworthy to observe the identical behavior of hydroquinone and quinone. The latter compound cannot form phenoxide-ions. According to classical studies by Zincke and Fuchs (*17*), the main chlorination pathway leads first to chloranil. This absorbs another chlorine to a cyclic dione which in turn is disrupted into dichloromaleic acid and trichloroethylene.

The aim of the present study was to find a reaction mechanism valid for the pH range of practical water chlorination, i.e., near neutrality. In the author's view, by-reactions with quinones may be one possible explanation of the slow secondary phase in the graph of Figure 2. However, the lower residual chlorine concentration (50% after 1 h) also reduces the speed of any further reactions.

Putting all the evidence together, we conclude that the most reactive sites for the haloform reaction with fulvic acids are meta-dihydroxylated benzene moieties. The increased rate of haloform production induced by high pH also observed with fulvic acids may be explained by the initial rapid formation of more phenoxide ions. However, apparently other slower oxidative disruptions of alpha-chlorinated quinonoid intermediates seem to take place in the secondary phase in Figure 2. Two compounds behaved differently in that increased pH caused a decrease of $CHCl_3$ formation. Apparently, in these structures high pH favored the formation of larger oxidative cleavage products.

Table II. Comparison of $CHCl_3$ Yields from Model Substances 0.001 M, Chlorine 0.012 M, 2 h, 15 °C

	pH 7, %	pH 11, %
1,2-Dihydroxybenzene	0.5	6
1,3-Dihydroxybenzene	85	100
1,3-Dihydroxynaphthalene	42	100
1,4-Dihydroxybenzene	1.5	14
1,4-Quinone	2	13
3,5-Dihydroxytoluene	10	32
3,5-Dihydroxybenzoic acid	32	96
Pyrogallol	0	7
Phloroglucinol	60	1.5
Phloroglucinol monopentylether	15	89
Phenol	0	1
1-Hydroxy-3-methoxybenzene	10	4
1,3-Dimethoxybenzene	0	9
3-Hydroxybenzoic acid	6	1

Further Chlorinated Degradation Products

Since we consider chloroform to be only one of the possible chlorinated degradation products caused by chlorination of naturally colored waters, further analysis and identification of such products were undertaken.

Experiments with excessive chlorination were carried out with peat extracts containing 180 mg of total organic carbon per 100 mL, which were chlorinated with 20 mmol Cl_2 during 2 h at pH 7, at room temperature. At the end of the period the reaction was stopped by addition of sodium sulfite. The chlorinated degradation products were extracted with 10 mL diethylether. After drying on Na_2SO_4 the ether extracts were concentrated to 1 mL. Two-microliter aliquots were injected into the gas chromatograph–mass spectrometer combination.

The main peak was identified with chloral. Additional peaks of moderate size were found, comprising chloroform, dichloromethane, dichloroacetic acid, trichloropropylene, chloroisopentanol, tetrachloro- and pentachloroacetone.

In another experiment, water samples from the Rotterdam storage reservoir were excessively chlorinated, allowing a contact period of 60 h with 50 mg/L chlorine at pH 7.5. The total organic carbon of the water was 6 mg/L, which is much lower than in the experiment with peat extract. The gas chromatogram of the ether extract showed 25 large peaks that had never been observed in the water chlorinated under normal plant chlorination conditions where only 4 mg/L chlorine is dosed. After a contact time of ½ h the residual chlorine is reduced by activated carbon.

The compounds identified by mass spectrometry comprised several alpha chlorinated C_4 and C_5 ketones, polychlorinated acetones, chloral, chlorinated butanol, and further compounds listed in Table III.

Some of these compounds are identical with the degradation products detected by Glaze and Henderson (*19*) in an excessively chlorinated wastewater. These authors reacted secondary effluent with 2 g chlorine/L for the period of 1 h. From the compounds listed, the following were identical: tetra-, penta-, hexachloroacetones, haloforms, dichloroacetate, and dichloromethoxytoluene. We found trichlorophenol only in chlorinated peat extract. The degradation product 3-chloro-2-methylbutene is probably a dehydrated form of our chloroisopentanol.

Our conclusion is that excessive chlorination of waters is just one more degradation method of humic substances. In normal water treatment the chlorine doses are restricted to about 1–10 mg/L which apparently keeps these nonvolatile degradation products in the submicrogram per liter level. The volatile haloforms, however, are an exception; they are generated in concentrations of 0.01–0.1 mg/L.

Reaction Mechanisms

In our further effort to describe the degradation pathway of fulvic acids, we used a suggestion given by Moye (*18*). He obtained pentachlororesorcinol in good yield by chlorination of resorcinol in chloroform. The resulting dione I in Figure 3 proved to be unstable in water. It was hydrolytically split to the acid II, which in turn decarboxylates readily to give III, which is the enol of 1,1,3,5,5-pentachloropent-4-en-2-one IV.

Table III. Degradation Products Identified by MS in Heavily Chlorinated Water from Rotterdam Storage Reservoir

Chloroform
Trichloroethylene
Trichloropropane
Chloroisobutanol
Dichloroacetic acid
Tetrachloroacetone
Pentachloropropane
Hexachloroacetone
Trichloropentanone
Trichloroacrolein
3-Chloro-2-methylbutanol
Trichloropentanol-1
Dichloroethylbenzene
Tetrachloroisobutanol
Pentachloroisopentanol
Dichloromethoxytoluene
Chlorodimethylbutanol
Dichloromethoxytoluene (isomer)
Chlorinated dinaphthol
Chlorinated methoxylated stilbenes

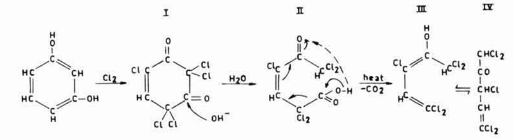


Figure 3. Degradation of pentachlororesorcinol, according to Moye

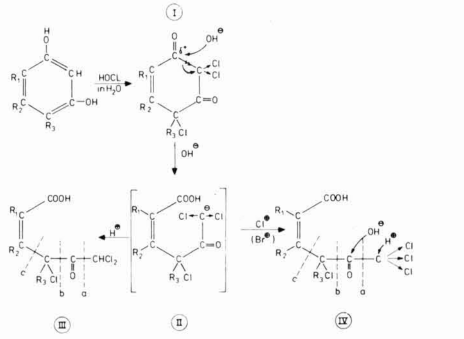


Figure 4. Proposed degradation pathways of fulvic acids and resorcinol

Cl$^+$ represents in a simplified way any electrophilic halogenating species of series XOH_2^+, X_2, HOX, X_2O

Moye confirmed this by mass spectrometry. The degradation pattern suggested by Moye for the pentachlororesorcinol is valid when this compound has been obtained as a result of chlorination with dry chlorine of resorcinol in aprotic solvents.

For chlorination in aqueous solutions we propose a slightly different pathway, illustrated in Figure 4. Here, the resorcinol-type moiety of fulvic acids may be substituted by R_1, R_2, R_3. One or two of these may be the fulvic acid matrix molecule, and the others H, OH, OCH_3, or COOH. If R_1 is fulvic acid, R_2 is OH, and R_3 is H, we have a phloroglucinol built in fulvic acid. If R_1 or R_2 represented fulvic acid and R_3 is H, we have a resorcinol moiety linked to fulvic acids, etc. The proposed pathway is a fast chlorination of the carbon atoms that are activated by ortho OH-substituents, or phenoxide ions in an alkaline environment. The haloform reaction initially will give the intermediate carbanion II, which is rapidly halogenated further to product IV, or alternatively protonated to III. Both III and IV undergo further hydrolytical or oxidative fissions, here indicated by the dotted lines a, b, or c.

Cleavage a represents the final stage of the usual haloform reaction, leading to $CHCl_3$, or in the presence of bromine to mixed bromo-chlorohaloforms. If iodine is present, iodination will occur as well. Cleavage III a explains the small amounts of CH_2Cl_2 found in chlorinated water. Cleavage c represents a haloform-like fission leading to tetrachloroacetone or penta- and hexachloroacetone if R_3 is H. Oxidative and hydrolytic cleavages along the dotted line b are responsible for the degradation products chloral, di-, or trichloroacetic acid. It should be kept in mind that other hydroxybenzenes also contribute, e.g., phloroglucinol can degrade into tetrachloroacetone, and para-quinone into dichloromaleic acid and trichloroethylene, and so on. By excessive chlorination of both natural waters and peat extracts, we also found trichloroethylene. This product may originate from hydroquinone linked to fulvic acid by R_1, if R_2 is H and R_3 is OH instead of the meta-positioned OH, pictured in Figure 4. The proposed scheme explains most of the chlorinated degradation products of fulvic acids that actually have been found.

Acknowledgment

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Nitrogen Dioxide Photolysis in the Los Angeles Atmosphere

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■ Atmospheric measurements of k_1, the rate of NO_2 photolysis, were made in El Monte, Calif., by use of a tubular quartz reactor to measure directly the conversion of NO_2 to NO in an N_2 atmosphere. A least-squares treatment of the data from September 1975 resulted in the following empirical relationships for predicting k_1 from standard UV radiometric data. $0° <$ Solar zenith angle $< 40°$: k_1 (min^{-1}) = 0.079 (1/cos z) + 0.002 × radiometric UV (mW/cm^2); $40° <$ solar zenith angle $< 90°$: k_1 (min^{-1}) = 0.16 (1 − cos z) + 0.088 × radiometric UV (mW/cm^2). Ultraviolet intensities corresponding to k_1 values greater than 0.4, 0.3, and 0.2 min^{-1} can persist for periods of 8, 10, and 12 h, respectively, during the weeks around the summer solstice. Both the high photochemical light intensity observed and its extended time duration indicate that the potential for ozone formation in the atmosphere is greater than utilized in most previous "smog chamber" studies. This result suggests that the application of existing smog chamber data in such areas as solvent reactivity may have to be reinterpreted.

A number of early measurements of the total ultraviolet radiation present in polluted atmospheres has been reported in previous studies (*1, 2*). These studies, however, did not measure the primary quantity of interest in our understanding of photochemical air pollution, the intensity of ultraviolet radiation leading directly to the photodissociation of nitrogen dioxide. The quantity is important because the production of oxygen atoms in this process and their subsequent recombination with oxygen via the reactions defined below,

$$NO_2 + h\nu\ (\lambda < 4400\ A) \rightarrow NO + O \qquad (1)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$

are the only steps known to lead directly to the production of ozone in polluted atmospheres.

In most of the earlier investigations, either chemical actinometers or ultraviolet radiometers were used to make the light intensity measurements. These devices have disadvantages in their ability to measure directly the primary quantity of interest because of their limited spectral response and/or their lack of total "volumetric" sensitivity to ultraviolet radiation.

With the introduction of chemiluminescent NO_x analyzers, however, improved measurements of k_1, the rate of NO_2 photolysis, have been made. Jackson et al. (*3*) have reported a continuous technique that determines the rate of NO_2 photodissociation by measuring the nitric oxide formed as nitrogen dioxide traverses a tubular quartz, plug flow reactor containing low concentrations (e.g., 1 ppm) of nitrogen dioxide in air. Sickles and Jeffries (*4*) modified this technique for measuring k_1 by using a spherical, quartz batch flow reactor and by photolysis of nitrogen dioxide in nitrogen. The use of a cylindrical quartz tube or quartz sphere has the advantage that the reactor itself, to a good approximation, is equally responsive to light from all directions and is therefore less sensitive to the orientation effects that tend to reduce the actual measurement. Jackson et al. (*3*) estimated the light loss due to orientation effects of the tubular reactor to be less than 5%, while Sickles and Jeffries (*4*) suggest that the UV light intensity determined in the sphere is still less dependent on orientation. One study (*3*) uses the value 93% as the overall transmission factor for quartz and simply applies a correction factor of 7% to their calculations to account for this radiation which is absorbed or reflected by the reactor walls.

In this paper we examine some of the theoretical factors involved in calculating the quantity k_1 in a plug flow reactor. In addition, we report some recent measurements of k_1 in the South Coast (Los Angeles) Air Basin of California and examine their relationship to the type of ultraviolet radiometer frequently used to measure ultraviolet radiation. The implications of these measurements for the production of ozone are briefly considered.

Experimental

Method and Apparatus. The apparatus and method used in this study were similar to those utilized by Jackson et al. (*3*) where nitrogen dioxide/air mixtures were photolyzed. To increase the sensitivity of the method, however, a mixture of nitrogen dioxide in nitrogen was used in this work. The apparatus consisted of a 2.2 cm × 1 m quartz tube mounted 21 cm above a utility box containing two flow meters (Fisher and Porter Co.) and two low-pressure line regulators (Matheson Gas Products) which were used to maintain a stable and constant flow rate throughout the day. The flow meters were calibrated both in the laboratory and in the ambient atmosphere with a wet test meter. There was little or no apparent change in calibration under these conditions. The utility box (56 × 33 × 26 cm) was brown in color and was not expected to reflect UV radiation. The albedo of the roof of the building upon which the measurements were taken was 7–10% at noon. The instruments were exposed to ambient temperatures during the measurement period. Nitrogen dioxide gas, 100 ppm in nitrogen (Matheson Gas Products), was diluted to 2 ppm for these measurements. All tubing connections were made of Teflon. Measurements of nitric oxide and total nitrogen oxides were made with a chemiluminescent NO–NO_x analyzer (Model 14D, Thermo-Electron Corp.).

Solar ultraviolet radiometric measurements were made with a UV radiometer (the Eppley Laboratories, Inc.) with a full bandwidth sensitivity from 2950 to 3850 A and a half-power bandwidth sensitivity extending from 3100 to 3700 A. This radiometer was calibrated against a second UV radiometer which, at the beginning of the study, had been newly calibrated by the Eppley Laboratories, Inc.

The equation used to calculate the rate of nitrogen dioxide photolysis was a modification of the equation used by Jackson et al. (*3*) for a plug flow reactor.

$$k_1 = \frac{\Delta(NO)}{(NO_2)} \times \frac{F}{V} \times \frac{1}{\Phi} \times \frac{1}{T} \qquad (A)$$

In this equation, Δ(NO) is the measured increase in the nitric oxide concentration (ppm) as a result of photolysis, (NO_2) is the nitrogen dioxide concentration (ppm), F is the total flow rate in the tubular reactor (l./min), V is the volume of the quartz reactor, Φ is the effective quantum yield for the production of nitric oxide upon photolysis, and T is the overall transmission factor of the quartz tube for UV light.

The last two parameters are examined further in the text below. The nitrogen dioxide concentration used in the calculation of the parameter, k_1, is given by the following relationship

$$(NO_2) = (NO_2)_{final} + 1/2\ \Delta(NO)$$

where $(NO_2)_{final}$ is the resultant NO_2 concentration determined after the NO_2/N_2 gas mixture has traversed the quartz tube. This quantity is a good approximation to the average NO_2 concentration during the period that the NO_2 gas traverses the photolysis tube.

Typical NO_2 concentrations were on the order of 1–2 ppm, typical gas flow rates were on the order of 3 l./min, and typical values for $\Delta(NO)$ ranged from 0 to 0.2 ppm.

Calculation of Quantum Yield Factor. The calculation of the quantum yield factor, Φ, given in Equation A is straightforward, based on the chemistry of the reaction system. The primary chemical reactions of interest for the photolysis of nitrogen dioxide in a nitrogen atmosphere are given in Table I. Other reactions were found to be unimportant for our conditions. The effective quantum yield is given by the following expression:

$$\Phi = \frac{\text{Rate of NO appearance}}{\text{Rate of } NO_2 \text{ photolysis}}$$

$$\Phi = \frac{k_1(NO_2) + k_3(NO_2)(O) - k_5(O)(NO)(N_2) - k_6(NO_3)(NO)}{k_1(NO_2)} \qquad (B)$$

This equation can be simplified by assuming an instantaneous steady state for the concentrations of O and NO_3 to yield

$$\Phi = 1 + \frac{k_3(NO_2) - k_4(NO_2)(N_2) - k_5(NO)(N_2)}{k_3(NO_2) + k_4(NO_2)(N_2) + k_5(NO)(N_2)} \qquad (C)$$

For a wide range of initial conditions, i.e., for initial nitrogen dioxide concentrations of from 1 to 4 ppm in nitrogen, and initial nitric oxide concentrations of from 0 to 0.3 ppm in nitrogen, the quantum yield factor reduces to a constant term

$$\Phi = 1.61 \pm 0.07$$

The error limits represent the maximum deviation from the value of 1.61 for the concentration ranges defined above. Calculations were made at a temperature of 300 K and an atmospheric pressure of 750 torr. This value of Φ was determined for the set of rate constants given in Table I which was chosen based on the best available data. The critical rate constant is that for Reaction 4 which considerably reduces the quantum yield factor from the maximum value of 2.0. Consideration of other values for this reaction (see, for example, ref. *8*) could alter this factor by a small amount. Inclusion of N_2O_5 chemistry would alter the value of Φ slightly. However, this effect would be within the experimental errors in the measurements.

Calculation of Geometry Transmission Factor. Concern has been expressed (*4*) over the most appropriate geometry to be used for the quartz photochemical reactor for the direct determination of k_1. The problem arises from a consideration of the Fresnel equation, which can be used to predict the fractions of light refracted and reflected at the interface of two transparent media. For natural sunlight (unpolarized radiation) at a single interface, this equation reduces to the following form:

$$R = \frac{\sin^2(i-t)}{2\sin^2(i+t)} + \frac{\tan^2(i-t)}{2\tan^2(i+t)}$$

where R is the reflection coefficient for natural sunlight at the interface, i is the angle of the incident radiation on the surface, and t is the angle of the refracted or transmitted radiation.

The intensity of the refracted ray will equal the quantity $(1 - R)$ times the intensity of the incident ray. For light transmitted through an air-quartz-air interface, the Fresnel equation predicts the behavior shown in Figure 1, which gives the light transmission properties of quartz. For a normal or zero degree angle of incidence, 93% of the radiation at 3700 A will be transmitted. The percent transmission decreases slowly to 90% as the angle of incidence increases to 40° and drops off rapidly to a value of zero for an incident angle of 90°. The figure indicates that for light incident on a photochemical reactor of any geometry, considerations of both refracted and reflected radiation must be made, particularly for angles of incidence greater than 40°.

The model used to calculate the geometry transmission factor for ultraviolet radiation penetrating to the interior of the tubular or the spherical *reactor* is given in Figure 2. The figure shows an incident ray of light, $\bar{I}_0$, at an arbitrary angle of incidence, i, striking a circular cross section of the reactor.

Table I. Principal Reactions in Photolysis of NO_2 in Nitrogen

Reaction	Rate constant
(1) $NO_2 + h\nu\ (\lambda < 4400\ A) \rightarrow NO + O$	(To be determined)
(3) $O + NO_2 \rightarrow NO + O_2$	$9.1 \times 10^{-12\ a}$
(4) $O + NO_2 + N_2 \rightarrow NO_3 + N_2$	$8.2 \times 10^{-32\ b}$
(5) $O + NO + N_2 \rightarrow NO_2 + N_2$	$9.6 \times 10^{-32\ c}$
(6) $NO_3 + NO \rightarrow 2\ NO_2$	$8.7 \times 10^{-12\ d}$

[a] Units: cc/molecule/s (*5*). [b] Units: $(cc/molecule)^2$/s (*6*). [c] Units: $(cc/molecule)^2$/s (*7*). [d] Units: cc/molecule/s (*6*).

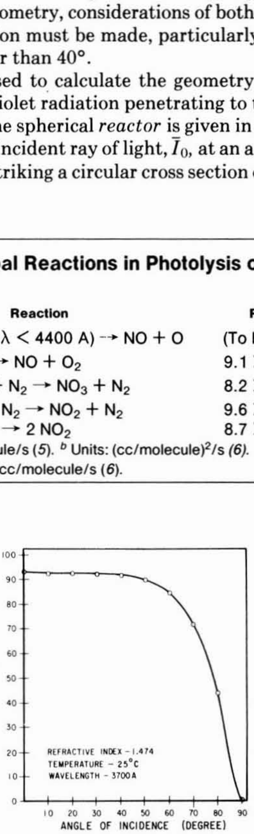

Figure 1. Light transmission properties of quartz vs. angle of incident radiation for air-quartz-air interface

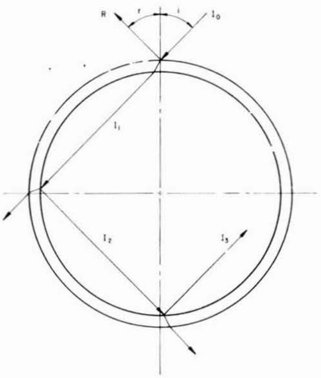

Figure 2. Light ray diagram for spherical or infinite tubular reactor

Also shown are the reflected light ray, $\bar{R}$, the transmitted light ray, $\bar{I}_1$, and the internally reflected light rays, $\bar{I}_2$ and $\bar{I}_3$. The problem is one of calculating the relative contribution of the internally reflected light rays, $\bar{I}_2, \bar{I}_3, \ldots \bar{I}_\infty$, which also contribute to the overall light intensity within the reactor. These rays compensate for the loss of the light ray, $\bar{R}$, which is initially reflected from the surface and therefore does not contribute to the photodissociation of nitrogen dioxide within the tube.

The intensity of reflected and refracted light from an air-quartz-air interface is given by (*9*)

$$\bar{I}\,(\text{reflected}) = \bar{I}_0\left(\frac{2R}{1+R}\right) = \bar{R} \qquad \text{(D)}$$

and

$$\bar{I}\,(\text{refracted}) = \bar{I}_0\left(\frac{1-R}{1+R}\right) = \bar{I}_1 \qquad \text{(E)}$$

and the contributions to the total light intensity within the reactor are given by

$$\bar{I}_1 = \bar{I}_0\left(\frac{1-R}{1+R}\right)$$

$$\bar{I}_2 = \bar{I}_1\left(\frac{2R}{1+R}\right)$$

$$\bar{I}_3 = \bar{I}_2\left(\frac{2R}{1+R}\right)$$

$$\bar{I}_{n+1} = \bar{I}_n\left(\frac{2R}{1+R}\right) \text{ for } n > 0$$

The total light intensity can be found from

$$\begin{aligned}\bar{I}_{\text{total}} &= \bar{I}_1 + \bar{I}_2 + \bar{I}_3 \ldots + \bar{I}_n + \ldots \\ &= \bar{I}_0\left(\frac{1-R}{1+R}\right) + \bar{I}_0\left(\frac{1-R}{1+R}\right)\left(\frac{2R}{1+R}\right) \\ &+ \bar{I}_0\left(\frac{1-R}{1+R}\right)\left(\frac{2R}{1+R}\right)^2 + \ldots = \bar{I}_0\left(\frac{1-R}{1+R}\right)\sum_{n=0}^{\infty}\left[\frac{2R}{1+R}\right]^n\end{aligned} \qquad \text{(F)}$$

The summation in the final expression has a solution commonly encountered in physical problems, i.e.,

$$\sum_{n=0}^{\infty}(X)^n = \frac{1}{1-X} \quad \text{for } -1 < x < 1$$

For $X = (2R/1 + R)$, one finds that

$$\bar{I}_{\text{total}} = \bar{I}_0; \text{ therefore, } T = 1 \qquad \text{(G)}$$

i.e., the internally reflected light ray will *exactly* compensate for the reflected light lost initially. This result indicates that no transmission correction factor need be applied under ideal conditions where the tubular reactor is infinite in length, where there is no inlet/outlet system, and where there is no significant light loss due to UV light absorption by nitrogen dioxide.

Although it has not been previously noted in the derivation, it should be pointed out that this result will hold for any incoming ray of radiation, provided the reactor is either spherical or tubular. For a finite tubular reactor, an "end correction" can be made to account for both the internally reflected light lost at the ends and the light not entering the reactor at the ends. This correction should be proportional to the area of the end caps and inversely proportional to some complex function of the length and diameter of the tube. In this study no end correction was determined since it was expected to be small (*3*).

Note also that there is an "end correction" for the spherical reactor as used by Sickles and Jeffries (*4*) which consisted of an inverted, round bottom quartz flask. Equation G will be valid only when an infinite number of reflections are permitted within the flask. The well at the bottom of the spherical reactor, however, acts as a sink for radiation, thus prohibiting further internal reflections after the light ray has entered the well. The result is a slightly lower light intensity within the flask, the correction for which will be proportional to the ratio of the area of the well and the internal area of the sphere. A priori it is difficult to determine which correction would be smaller since the occurrence of any internal reflection reduces the magnitude of the correction. Furthermore, although it is expected that the sphere will be less directionally sensitive than the cylindrical tube, the curvature and large size of the sphere present much the same problem for the calculation of the light transmission properties of the sphere as for the cylindrical tube.

Results and Discussion

Experimental Comparison of Tubular and Spherical Reactor Geometries. The effect of reactor geometry on the value of k_1 was studied in a series of measurements whereby a spherical reactor of the type used by Sickles and Jeffries (*4*) and a tubular reactor described above were used. The experiments were carried out on relatively cloudless days in March and April 1976 with intensities followed radiometrically. During the course of the experiment the use of the tube and the sphere was alternated with all other parameters kept constant. Another comparison was made indoors within a conventional smog chamber with blacklight fluorescent lighting.

The equation used for the calculation of k_1 with the data from the spherical reactor is as follows:

$$k_1 = \frac{F\cdot(\Delta\text{NO}_2)}{2\cdot V\cdot(\text{NO}_2)} \times \left[1 + R_1 + R_2\frac{(\Delta\text{NO})}{(\text{NO}_2)}\right]$$

where $R_1 = 0.268$ and $R_2 = 0.25$ (*4*). The results for these comparative tests are presented in Table II which indicates that the tube reactor yields a consistently higher value of k_1 compared to the sphere. The difference in k_1 between the spherical and tubular reactors can be at least partially explained by differences in flow and mixing. The spherical reactor is basically a stirred flow reactor and requires thorough mixing for maximum efficiency of NO_2 conversion. The tubular reactor on the other hand is a plug flow-type reactor which does not require complete mixing. This effect was corroborated by experiments which showed the k_1 value measured in the spherical reactor to be flow dependent yielding higher k_1 values at higher flow rates, while the k_1 values measured in the tubular reactor were flow independent.

Atmospheric Measurements. Figure 3 is a plot of the diurnal variation of k_1 for three days in September 1975. The data exhibit the expected maxima during the midday period, in addition to secondary variations in the light intensity due to changes in cloud cover and aerosol content of the atmosphere. Some atmospheric haze occurred on the three mea-

Table II. Comparison of UV Measurements from Tubular and Spherical Flow Reactors

UV source	Observed k_1 (min^{-1}) Tube	Sphere	k_1 ratio
Atmosphere	0.429	0.352	1.22
Atmosphere	0.382	0.356	1.07
Atmosphere	0.364	0.332	1.10
Atmosphere	0.351	0.329	1.07
Atmosphere	0.202	0.181	1.12
Smog chamber	0.338	0.321	1.05

surement days, leading to visibility reduction in the San Gabriel Valley area where the monitoring took place.

To gain more insight into the relationship between the k_1 measurement and the measurement of the Eppley UV radiometer, a comparison of the two measurements was made as shown in Figure 4. The data indicate that the relationship between k_1 and the UV radiometer is not linear as reported earlier (*3*). Instead, there is some curvature at the higher k_1 values which correspond to the midday readings. From a theoretical viewpoint, it is not expected that a linear correlation should occur since the UV radiometer is not equally sensitive to light reaching the diffuser from each angle of incidence, while the transparent quartz tube or spherical reactor is less directionally sensitive. Because of the Lambertian or cosine dependence of the UV radiometer to incoming radiation, it is expected that light striking the radiometer from an angle near the horizon would have a weighting factor near zero. Therefore, the standard UV radiometer is expected to underestimate the total UV light present in the atmosphere, particularly as the sun leaves its zenith position and approaches the horizon.

It is desirable to obtain a relationship between the UV radiometer measurement and the k_1 measurement to correct the UV radiometer measurements to the k_1 measurement, a parameter important from an air pollution standpoint; therefore, it was decided to investigate the diurnal dependence of the ratio of these measurements. Figure 5 is a plot of this ratio as a function of time of day for the three days. The agreement between the three days is satisfactory, and the curves are nearly symmetric about the solar noon axis as expected. If the correlation between these two parameters were linear, the ratio would be constant for all times of the day. However, there does exist a smooth variation in the relationship between the ratio and the time, with the minimum appearing at solar noon. The symmetry of this plot suggests that a dependency corresponding to some function of the zenith angle would provide an effective method for displaying the data.

Figure 6 is a plot of the ratio vs. the function $(1 - \cos z)$ where z is the solar zenith angle. Also given in the figure is the fit of the data to the function $(1/\cos z)$. These functions were chosen because they are simple functions and exhibit the necessary minimum at solar noon as shown by the data. Furthermore, the function $(1/\cos z)$ has an established basis in Lambertian optics where the projected heating load or area of a light beam on a surface is proportional to the cosine of the angle of incidence. The results of the least-squares fit to the data points are given below in Equations H and I for the fitting functions $(1 - \cos z)$ and $(1/\cos z)$, respectively.

$$k_1 = [0.079\ (1/\cos z) + 0.022] \quad (\text{for } 0° < z < 40°) \times \text{radiometric UV (mW/cm}^2) \qquad \text{(H)}$$

$$k_1 = [0.16\ (1 - \cos z) + 0.088] \quad (\text{for } 40° < z < 90°) \times \text{radiometric UV (mW/cm}^2) \qquad \text{(I)}$$

The estimated error in these equations is 10%.

It is clear from Figure 6 that the ratio does show an increasing trend with increasing zenith angle. As noted earlier, the variation in the experimental data appears to be related to changes in scattered radiation due to changes in the atmospheric aerosol content. Increased levels of atmospheric aerosol yield a more constant value for the ratio at a value near 0.1 during the daylight hours.

The expressions given above can be used to calculate the diurnal variation of k_1 on peak smog potential days. Figure 7 gives a comparison of the *peak* UV radiometric data (hourly averages) collected during June–July 1975, when the direct measurement of k_1 was not made, and the value for k_1 calculated from Equations H and I above. The data show that the k_1 value remains high (above 0.2 min^{-1}) for a greater portion

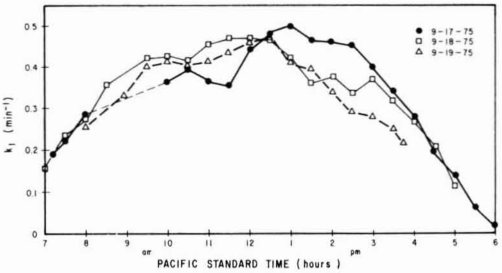

Figure 3. Diurnal variation of rate of NO_2 photolysis, k_1, at El Monte, Calif., during September 1975

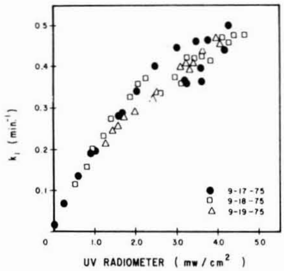

Figure 4. Comparison of experimental rate of NO_2 photolysis, k_1, to radiometric UV measurement taken at El Monte, Calif.

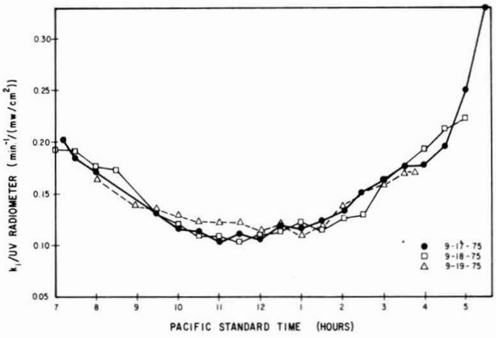

Figure 5. Diurnal variation of ratio of NO_2 photolysis rate, k_1, to radiometric UV measurement at El Monte, Calif.

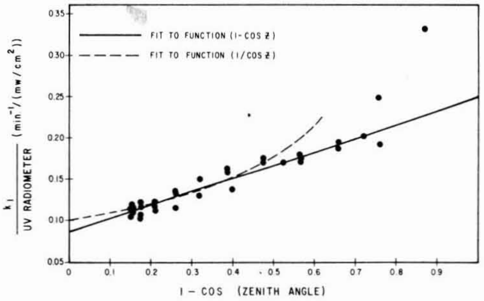

Figure 6. Dependence on zenith angle of ratio of NO_2 photolysis rate, k_1, to radiometric UV measurement

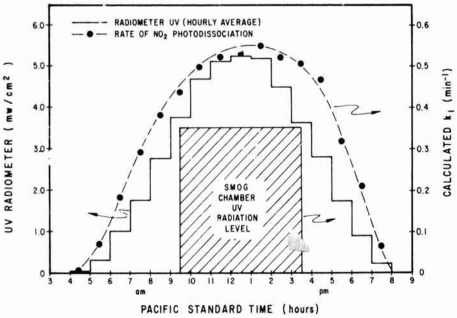

Figure 7. Estimation of rate of NO_2 photolysis, k_1, during summer solstice

Radiometric UV data for June–July 1975 (bar graph); calculated k_1 for June–July 1975 (data points); and maximum UV flux used in environmental chamber studies (shaded area)

of the day relative to the UV radiometric measurement. For example, the k_1 values are above 0.2, 0.3, and 0.4 min^{-1} for 12, 10, and 8 h, respectively. These data show that irradiation times in the southern California area are potentially very long. The dashed line in Figure 7 shows a maximum at 1 p.m. (PST) rather than 12 p.m. (PST), as would normally be expected. This result is attributed to the morning fog or haze that was present during this period. Aerosol present in the atmosphere tended to reduce the UV intensity during the morning measurements. Therefore, the peak k_1 reading at solar noon may be higher than the calculations (dotted line) indicate.

The data obtained on the three monitoring days of September 18–20, 1975, can be compared to data presented by Jeffries et al. (*10*) which were taken during a similar time period a year earlier (1974) at Chapel Hill, N.C. Chapel Hill has a latitude of 35°N which is similar to that of El Monte, Calif. (34°N). However, because these data were obtained one year apart under different atmospheric conditions and using a spherical quartz reactor, they cannot be compared on a one-to-one basis. The diurnal trends and UV intensity levels reported show excellent agreement with the measurements in this work, with the exception that the peak k_1 values obtained during solar noon at Chapel Hill were slightly lower by approximately 8–9%. The peak values for k_1 in this work varied from 0.47 to 0.50 min^{-1}, while the peak k_1 values reported by Jeffries et al. (*10*) varied from 0.43 to 0.46 min^{-1}. With the present information, it is not possible to determine whether this difference is due to differing atmospheric conditions or to differences in other parameters such as ground albedo occurring at each of the measurement sites. We feel that the ranges of the measurements are in good agreement.

Conclusions

The ratio of the total photochemical UV radiation to the UV radiation measured by standard radiometric techniques varies throughout the day, i.e., the use of standard radiometric UV measurements underestimates the contribution of scattered radiation to the available photochemical radiation. An empirical relationship between these two quantities has been derived for the case where nitrogen dioxide is photolyzed by ultraviolet radiation in the Los Angeles atmosphere (Equations H and I). Based on the results discussed above, it is clear that there is available in the atmosphere a significantly greater level of UV radiation than customarily used in 6-h smog chamber simulations. The duration of this period of high atmospheric UV intensity is also substantially longer than the customary 6-h irradiation period used in smog chamber simulations. These factors are particularly troublesome when determining the reactivity of organic compounds as measured by ozone production. Longer smog chamber irradiation times of over 6 h will increase the relative reactivity of compounds which were previously considered to be of low or moderate reactivity by providing more time to generate additional ozone.

Because the production of free radical intermediates contributing to ozone formation in photochemical air pollution is strongly dependent on the photodissociation of nitrogen dioxide, it is reasonable to conclude that the extension to the ambient atmosphere of most previous smog chamber results will tend to underestimate organic photochemical reactivities occurring in the real world. Existing data will have to be reinterpreted, to the extent that this is possible, to account for both the low UV intensity and the unrealistically short irradiation times used.

Acknowledgment

We thank Carlo Bonamassa for his aid in reducing the data.

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Comparative Kinetics of High-Temperature Reaction Between H_2S and Selected Metal Oxides

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■ Initial rates for the reactions between H_2S and MnO, CaO, ZnO, and V_2O_3 over a temperature range of 300–800 °C were determined in a thermobalance reactor. All reactions were first order with respect to H_2S and obeyed the Arrhenius equation. The relative magnitude of reaction rates determined was MnO > CaO $\approx$ ZnO > V_2O_3. MnO possessed favorable properties for a high-temperature desulfurization process, and additional research in this area is recommended.

Numerous reactions between solid metal oxides and H_2S at high temperature are reported in the literature (*1*). Such reactions form the basis of past processes for coke oven gas purification using iron oxide (*2, 3*), existing processes for ammonia synthesis gas desulfurization (*4*), and developing processes for sulfur removal from gases produced from coal or residual oil gasification (*5*). Success in the last application is particularly important if coal gasification technology is to achieve optimal development.

Although the reactions are well known, basic kinetic data are quite sparse, the notable exception being the work by Ruth et al. (*6*) on the H_2S–dolomite system. Several reasons for the scarcity of kinetic studies may be cited. Perhaps of greatest importance is the emphasis placed upon rapid process development with little priority assigned to studying the basic phenomena. In addition, gas-solid kinetic studies are inherently difficult, both from the experimental and data interpretation aspects.

In a previous paper, Westmoreland and Harrison (*7*) reported on a thermodynamic investigation of the desulfurization feasibility of a large number of elements at conditions representative of future high sulfur coal gasification. Eleven metals and their oxides were identified as possessing desulfurization potential over at least a portion of the range of operating conditions of interest. In this paper we are reporting comparative kinetic measurements for four of the candidate oxides—MnO, ZnO, CaO, and V_2O_3.

Experimental

Operating Conditions. Initial rates of chemical reaction were determined over a temperature range of 300–800 °C at 1 atm total pressure. H_2S concentration was varied from 1.9 to 7.0 mol %. Hydrogen was added to the reactive gas in a ratio of 5 mol H_2/mol of H_2S, both to simulate the reducing atmosphere found in coal gases and to prevent the decomposition of H_2S at high temperature. Separate tests at low temperatures (<500 °C) where H_2S decomposition should be unimportant showed that the H_2 did not measurably alter the H_2S–metal oxide kinetics. Nitrogen constituted the remainder of the gas feed.

Equipment. A thermobalance apparatus shown schematically in Figure 1 and described completely by Westmoreland (*8*) was utilized as the reactor. Reactive and diluent gases were supplied from regulated cylinders and monitored through calibrated rotameters equipped with needle valves for flow control. Nitrogen entered the system through the balance mechanism housing, thus serving the dual purpose of protecting the balance mechanism from corrosion and diluting the reactive gases. H_2S and H_2 entered through a side tube, mixed with the nitrogen, and flowed downward over the solid reactant. The solid was contained in a platinum pan suspended from the balance by nichrome wire. Temperature was monitored and controlled by shielded chromel–alumel thermocouples positioned immediately below the sample pan.

Kinetic data were analyzed on the basis of unit surface area of the reactive solid. Surface areas were measured using the dynamic BET method on a Perkin-Elmer Model 212D sorptometer. The chemical composition of solid reaction products was determined by x-ray diffraction using copper K-alpha radiation on a Phillips Electronic Instruments x-ray diffractometer.

Materials and Material Pretreatment. Nitrogen (99.99% purity), hydrogen (99.95%), and hydrogen sulfide (99.5%) were taken directly from gas cylinders.

In all tests, reagent grade metal oxide powders were used so that complications due to competing reactions with impurities could be avoided. Each metal oxide was initially sieved with that fraction passing 100 mesh retained for experiment. Following sieving each metal oxide was subjected to differing pretreatment conditions as described below.

Manganese oxide (MnO_2) was reduced by hydrogen at 800 °C to MnO, the thermodynamically stable oxidation state in a coal gas atmosphere. Similarly, V_2O_5 was reduced in hydrogen at 550 °C to V_2O_3, the stable form of vanadium. Calcium oxide was pretreated by heating to 500 °C in an inert atmosphere to ensure total removal of volatile impurities. Thermobalance tests using the reagent grade zinc oxide showed no volatile impurities present so that no pretreatment step was included. The reductions and heat treatments were carried out outside the thermobalance reactor; treated samples were stored in a vacuum desiccator until use. The specific surface area of the treated samples was measured and used in the kinetic analysis. Table I summarizes the pretreatment steps and reports the results of surface area measurements. The low specific surface area of MnO is caused by rapid sintering which occurs at the high pretreatment temperature. The effects of the large variation in specific surface area were partially offset in kinetic experiments by using larger quantities of the low surface area solids.

Mass Transfer and Diffusion Considerations. Conver-

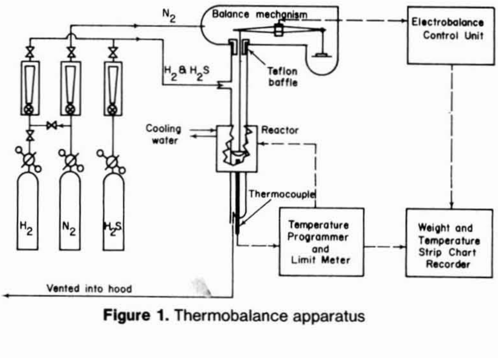

Figure 1. Thermobalance apparatus

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Table I. Pretreatment and Specific Surface Area of Solid Reactants

Original sample		Pretreatment conditions	Treated sample	
Species	Source		Species	Surface area, m^2/g
MnO_2	Mallinckrodt	H_2 reduction at 800 °C	MnO	0.32
V_2O_5	Fisher	H_2 reduction at 550 °C	V_2O_3	3.1
CaO	Fisher	Heated to 500 °C under inert gas	CaO	17.3
ZnO	Matheson Coleman & Bell	None	ZnO	4.9

sion of metal oxide to metal sulfide produces an increase in mass which is directly proportional to the fractional conversion of the oxide. Consequently, the slope of the thermobalance response curve of sample weight as a function of time (see Figure 2 for a typical curve) is directly proportional to the global reaction rate. The elimination of both external mass transfer and product layer diffusion resistances is required if the measured global rate is to be equal to the intrinsic chemical reaction rate.

In this study, product layer diffusion was rendered unimportant since only initial reaction rates were considered. As shown in Figure 2, the response curves were characterized by an initial linear increase in mass with time (neglecting the transient period when reactive gases were initially introduced). During this linear period, it may be assumed that the total surface area of solid available for reaction is proportional to the specific surface area reported in Table I. As time and fractional conversion increase, the slope of the response curve decreases and asymptotically approaches zero. The decreasing slope may be attributed to a combination of decreasing reactant surface area and increasing diffusional resistance through a product layer of increasing thickness.

External mass transfer resistances are lessened as the volumetric flow rate of gas past the sample is increased and the initial mass (surface area) of solid available for reaction is decreased, either singly or in combination. Practical limits on both gas flow rate and sample mass are imposed by the interactions of aerodynamic effects and balance sensitivity.

The proper combination of sample size and volumetric flow rate was determined experimentally. For a fixed sample size and flow rate, the apparent first order reaction rate constant was calculated from the measured initial global reaction rate. The assumption that the kinetics were first order with respect to gas was verified independently. As the ratio of sample size (proportional to surface area) to flow rate decreased, a point was reached where the apparent first order rate constant became independent of the ratio. This point was taken to be indicative of minimal mass transfer resistance and the point at which the apparent rate constant became equal to the intrinsic rate constant. The concept is illustrated in Figure 3 for two temperatures, T_1 and T_2. As indicated, higher reaction temperature requires lower values of the surface area to flow rate ratio before external mass transfer is rendered unimportant.

In general, the elimination of mass transfer effects was achieved for all reactions studied at reaction temperatures at or below 500 °C. Above this temperature mass transfer could not be totally eliminated for all reaction systems. This aspect is discussed in additional detail below.

Analysis of Data

The chemical reactions studied may be represented by the general stoichiometric equation

$$a_{A_1}A_1 \text{ (gas)} + a_{S_1}S_1 \text{ (solid)} \rightarrow a_{A_2}A_2 \text{ (gas)} + a_{S_2}S_2 \text{ (solid)} \quad (1)$$

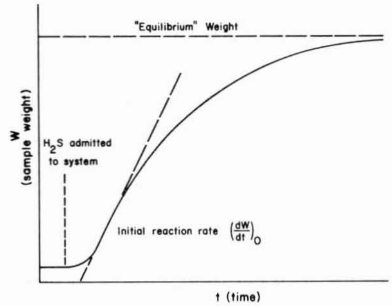

Figure 2. Typical thermobalance response curve

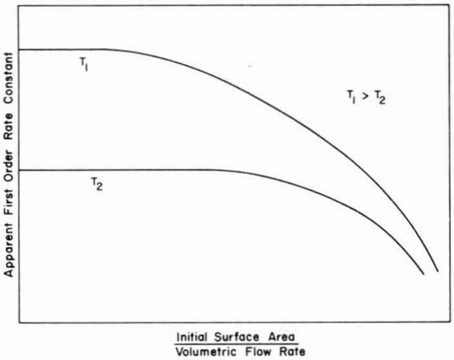

Figure 3. Elimination of external mass transfer resistance

where a_A and a_S are stoichiometric coefficients for gaseous and solid species (negative number for reactants). In the absence of both diffusional and mass transfer resistances, we postulate an intrinsic initial reaction rate expression of the form

$$R_0 = a_{A_1} k'_S C'_{S_{10}} C^N_{A_{10}} \quad (2)$$

where R_0 is the initial molar rate of production of species A_1 per unit surface area of S_1, k'_S is the intrinsic rate constant per unit surface area, $C'_{S_{10}}$ is the initial molar concentration of S_1, $C_{A_{10}}$ is the bulk fluid concentration of A_1, and N is the reaction order with respect to A_1.

Experimentally, the initial intrinsic reaction rate may be calculated from the measured slope of the thermobalance response curve by the equation

$$R_0 = \frac{(a_{A_1}/a_{S_1})(dW/dt)_0}{m_0\alpha_0\left[M_{S_1} + \frac{a_{S_2}}{a_{S_1}}M_{S_2}\right]} \quad (3)$$

where $(dW/dt)_0$ is the initial rate of change of weight (Figure 2), m_0 is the initial mass of solid reactant, α_0 is the specific surface area of solid reactant, and M_{S_2} and M_{S_1} are molecular weights of solid product and reactant.

Initial intrinsic reaction rates calculated from Equation 3 were then utilized in Equation 2 to examine the rate constant and the order of the reaction with respect to the gas.

Results

The order for all reactions studied was determined to be one. Figures 4 and 5 illustrate typical results at both high and low temperature for the MnO–H_2S and ZnO–H_2S systems, respectively. The linearity of the experimental data is, in general, quite good. It should be pointed out that high-temperature linearity illustrated in Figures 4 and 5 in no way proves the absence of mass transfer effects. It is easily shown (*9*) that first order chemical reactions carried out at conditions where mass transfer is important maintain apparent first order behavior.

The rate constants determined from Equation 2 with $N = 1$ were found to obey the classical Arrhenius relationship

$$k_S' = k_0 e^{-E/RT} \quad (4)$$

at conditions where mass transfer effects were unimportant. In the above equation k_0 is the Arrhenius frequency factor, E is the activation energy, R is the gas constant, and T is the absolute temperature.

Figure 6 shows the resultant Arrhenius plot for the MnO–H_2S reaction. As discussed previously, mass transfer was shown to be unimportant below approximately 500 °C. This temperature corresponds to the beginning of deviation from linearity in Figure 6. The straight line represents a nonlinear least-squares fit to the experimental points obtained at or below 500 °C. The Arrhenius constants shown on the figure represent the parameters of the straight line.

The Arrhenius dependence for the other reactions was similar to that illustrated in Figure 6, although the particular combination of the rate constants and solid reactant properties permitted extension of the range of linearity to approximately 700 °C for both the CaO–H_2S and ZnO–H_2S systems. Arrhenius constants for all reaction systems are summarized in Table II. Although the magnitudes of the activation energies are relatively small, they are in line with values reported for other gas-solid reactions by Costa (*10*).

Special comments regarding the V_2O_3–H_2S reaction are necessary. No reaction was detected below 400 °C, whereas from 400 to 650 °C the rate was considerably less than found in other systems. The maximum reaction temperature of approximately 650 °C was imposed by the melting temperature of product V_2S_3. For these reasons, the Arrhenius constants for vanadium in Table II are based upon minimum data and should be considered less reliable than the constants for the other reactions.

Maximum temperature in the ZnO–H_2S system was limited to about 750 °C because of the formation of metallic zinc vapor above this temperature. Such behavior was predicted from thermodynamics (*7*) and has also been reported experimentally at somewhat higher temperature by Beveridge (*11*).

A final word of explanation is needed regarding the stoichiometry of reactions shown in Table II. Thermobalance experiments which measure weight changes provide only indirect proof of reaction stoichiometry, and this only when the reaction is carried out to completion so that measured total

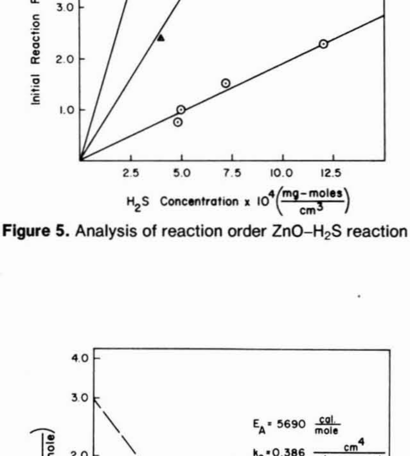

Figure 5. Analysis of reaction order ZnO–H_2S reaction

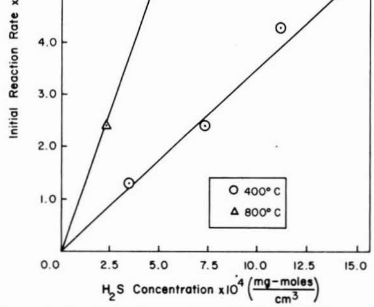

Figure 4. Analysis of reaction order MnO–H_2S reaction

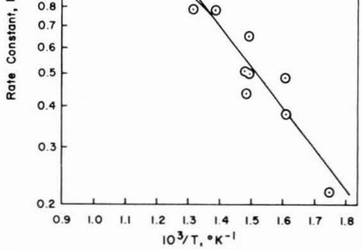

Figure 6. Arrhenius plot MnO–H_2S reaction

Table II. Arrhenius Constants for High-Temperature Desulfurization Reactions

Reaction	Temp range, °C	Arrhenius constants	
		k_0, cm^4/min mg mol	E, cal/mol
$MnO + H_2S \rightarrow MnS + H_2O$	300–800	0.386	5690
$ZnO + H_2S \rightarrow ZnS + H_2O$	300–750	0.095	7240
$CaO + H_2S \rightarrow CaS + H_2O$	300–800	0.038	5160
$V_2O_3 + 3H_2S \rightarrow V_2S_3 + 3H_2O$	400–650	0.017	8834

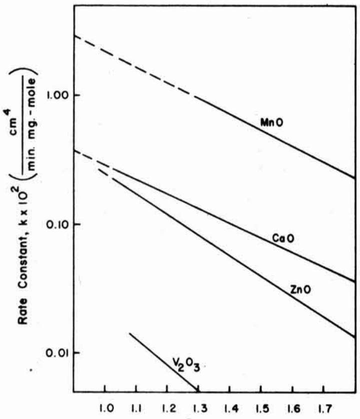

Figure 7. Comparative Arrhenius plots

weight changes may be compared to values calculated from postulated stoichiometry. In this study selected solid products from each system except vanadium, both partially and totally reacted, were qualitatively analyzed using x-ray diffraction. In all cases only the initial metal oxide and/or the product metal sulfide were identified, thus providing independent verification of the stoichiometry. Vanadium stoichiometry was based solely on thermodynamic analysis and the observed mass changes.

Discussion

The Arrhenius plots for each reaction are shown together in Figure 7. One may observe that the intrinsic reaction rate of H_2S with MnO is approximately one order of magnitude greater than the rate of reaction with either CaO or ZnO and two orders of magnitude greater than the reaction rate with V_2O_3. This observation is quite significant.

CaO in the form of calcined limestone or half-calcined dolomite is currently being emphasized in the effort to develop high-temperature H_2S removal capability (*5*). However, the product gas from coal gasification contains sufficient CO_2 so that $CaCO_3$ is preferentially formed over CaS below the calcination temperature. At approximately 900 °C, where CaS can be formed, problems with materials of construction, regeneration of spent oxide, and maintenance of high solid surface area have been reported.

On the other hand, ZnO cannot be used above about 700 °C because of the formation of zinc vapor. In addition, the regeneration of spent ZnO has proven unfeasible, and current use is limited to situations where the sulfur content is quite low, thus permitting once through operation.

MnO, in addition to exhibiting higher intrinsic reaction rates as reported here, possesses none of the limitations of the CaO and ZnO systems. $MnCO_3$, which is much less stable than $CaCO_3$, would decompose in a coal gas atmosphere around 400 °C, thus, from a thermodynamic viewpoint, permitting operation from that temperature up to approximately 1100 °C (*7*). None of the metallic vapor problems associated with ZnO is known. From this combination of favorable properties, it appears that MnO does indeed have high-temperature H_2S removal potential. Additional reaction and regeneration studies certainly appear warranted.

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Formation of Toxic Products from a #2 Fuel Oil by Photooxidation

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■ Oxygenated compounds toxic to baker's yeast and relatively soluble in water were formed upon simulated environmental ultraviolet irradiation of a #2 fuel oil. Toxicity reached a maximum within 24 h and appeared to be principally due to reactive peroxides; addition of a mild reducing agent (thiacyclohexane) eliminated a large percentage of the light-induced toxicity. On continued irradiation, other classes of toxic compounds were produced. Carbonyl compounds (largely derived from benzylic hydrocarbons) and phenols increased at approximately linear rates for at least seven days. The phenolic compounds present in the original oil were largely destroyed and replaced by higher-boiling phenols (including hydroxyl-substituted aryl ketones). Quinones were not detected. The acids present included some with phenolic substituents.

Petroleum spills present acute hazards to aquatic communities. Large spills have been highly publicized, and ecological damage caused by them has been thoroughly documented (*1*). Environmental transformations of spilled petroleum are complex and incompletely understood. Although some toxic hydrocarbons are relatively volatile and disappear from a spill within a few hours (*2*), others persist and are concentrated by aquatic organisms (*3*). Surface slicks may be biologically or chemically degraded to some degree, may form stable emulsions or tarry lumps, or may be stranded on shores or in sediments (*4*). Finally, some hydrocarbons and oxygenated compounds are relatively soluble in water and may be leached from spills.

Recent evidence indicates that some oil products become much more toxic to algae (*5*), fish, and marine invertebrates (*6*) after exposure to light and air and that the toxic principles are extractable by water (*6*). We undertook a study of the formation of toxic substances by simulated environmental photooxidation of the same fuel oil used in an earlier bioassay study (*6*).

Experimental

The #2 fuel oil was obtained from a local supplier. As shown by gas chromatography (Figure 1), it contained predominantly *n*-alkanes ranging from C_{10} to C_{22}, corresponding to a boiling range from 175 to 320°.

Mass spectral analysis of the oil (courtesy of R. J. Pancirov, Exxon Research) indicated a hydrocarbon composition of 77% saturated and 23% aromatic compounds. For the photooxidation experiments, the oil (150 mL, 124.9 g) was poured into a Pyrex tray (15.8 × 25.5 cm). An identical sample, loosely covered with aluminum foil, served as a dark control.

The light source was a water-cooled Ace-Hanovia 200-W medium-pressure mercury vapor lamp which emitted 7.6 W (30% of its total output) in the near-UV region (280–400 nm). To ensure that no light of less than 280 nm wavelength was transmitted, a Pyrex filter (2.0 mm thick, in the form of a sleeve around the lamp) was employed. The lamp was positioned 30 cm from the surface of the oil film, providing UV light energy of 0.038 gcal/cm^2/min. Intensity measurements were made with a Blak-Ray long wave UV meter calibrated to an Eppley pyrheliometer. During the experiment the light was left on continuously. Thus, the total UV irradiation received in 24 h approximated that received on a bright summer day at 40°N latitude (55 gcal/cm^2/day). The temperature of the two sample trays was virtually identical at all times and ranged from 21 to 23°.

Samples were removed at intervals for analysis of peroxides by iodometry (*7*), phenols by nitrosation (*8*), and acidity (*7*). Production of total carbonyl compounds was monitored by infrared (IR) spectroscopy; the intensity of the 1700 cm^{-1} band was compared to that of a series of standards prepared by diluting a stock solution of 1-tetralone in CCl_4. Turbidity was monitored at 725 nm; at this wavelength the starting oil had an absorbance of less than 0.01 in a 1-cm cell.

In some photooxidation experiments, thiacyclohexane (10 μL, 97 μmol) was added to 1.0 mL of irradiated oil containing 20–40 μmol peroxide/mL. Complete destruction of peroxide occurred within 1 min as shown by thin-layer chromatography (TLC). Samples treated with thiacyclohexane, untreated irradiated samples, and appropriate controls were used for toxicity studies.

Toxicity of the oil was determined by adding 0.25-mL samples to 25.0 mL of a freshly inoculated (about 1×10^6 cells/mL) culture of baker's yeast, *Saccharomyces cerevisiae*. In our study we chose to monitor yeast (rather than some other microorganism) because it is a eukaryote and is similar in its cellular organization to higher aquatic forms. The yeast stocks were grown in a defined medium containing basal salts, vitamins, and glucose (1%) as sole carbon source. Cultures were incubated in duplicate on a reciprocal shaker for 48 h at room temperature. Growth was measured turbidimetrically (OD_{600}) and expressed as a percentage relative to duplicate control cultures. Growth inhibition by fractionated samples and pure compounds was tested similarly, except that acetone solutions were added to the yeast cultures. An equal volume of acetone was added to the control cultures.

At the end of the irradiation experiment (165 h), the remaining oil (25 mL) was decanted from a precipitated film of insoluble amber resin and poured into 300 mL of hexane, giving a small quantity of insoluble material having an IR spectrum nearly identical to that of the amber resinous precipitate. Recovery of additional oxidized material was achieved by passing the diluted, irradiated oil over a column of neutral alumina. Hydrocarbons were eluted with hexane and discarded; polar substances were eluted with hexane–

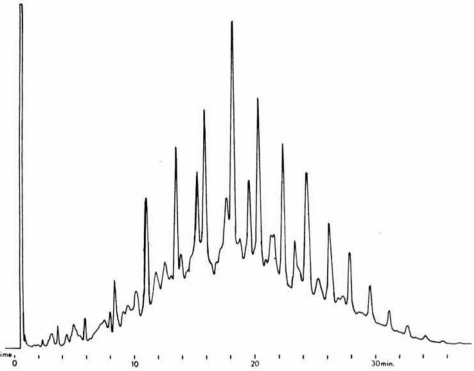


Figure 1. Gas chromatogram of #2 fuel oil
Column: 10% OV-1, temperature program 55–275°, 6°/min

ether (3:2). The combined polar material (2.85 g) was dissolved in 25 mL CH_2Cl_2, and acidic compounds were extracted by shaking with aqueous NaOH (0.25 M, containing 6% NaCl) under N_2. A weakly acidic (mainly phenolic) fraction was separated by adjusting the pH of the NaOH extract to 7.0 and reextracting the weak acids into CH_2Cl_2. Stronger acids were extracted into CH_2Cl_2 at pH 3.5. The NaOH-insoluble (nonacidic) fraction was further separated by silica column chromatography, followed by rechromatography of the more polar silica eluates on alumina.

The extracts and column fractions were characterized by standard techniques: silica TLC, spot tests, IR and UV spectroscopy. Solvents for TLC were: phenolic fraction, 70:30 pentane/Et_2O: nonacidic fraction, CH_2Cl_2: acidic fraction, 90:25:4 PhH/dioxane/HOAc. Naphthenic acids were obtained by acidifying a mixture of their sodium salts (Eastman). Glass GC columns (0.4 × 180 cm) were packed with silicone oil (10% OV-1, 3% OV-210) stationary phases on acid-washed Chromosorb W. Most of the individual compounds used as standards and in model reactions were purchased from Aldrich and recrystallized before use. Tetralin hydroperoxide (*9*) and 3-(2-hydroxyphenyl) propionic acid (*10*) were synthesized by literature methods.

Results

Within 12 h after the start of the experiment, the irradiated #2 fuel oil became noticeably turbid. Turbidity continued to increase for about three days (Figure 2), whereupon the fine particulate material gradually coalesced and settled to the bottom of the reaction vessel, forming a resinous film. IR spectroscopy of the precipitated material indicated that it was highly oxidized relative to the starting oil; absorptions for alcohols, carbonyl compounds, and carboxylic acids were evident.

In a preliminary experiment in which the oil film was layered over water and irradiated, the oil-insoluble precipitated material was extractable from the water by the aqueous phase, as shown by an IR spectrum of material extractable from the water by $CHCl_3$.

Rates of formation of oxygenated compounds were monitored for 165 h (Figure 3). Peroxides were formed at a roughly linear rate (without an initial induction period) for ca. 90 h and then declined slowly from a maximum of 73 meq/L. Hydrogen peroxide, which has been shown by TLC to be produced by UV irradiation of tryptophan (*11*), was not detected by TLC; all of the peroxides detected were relatively nonpolar.

Phenolic compounds were present in the starting oil at a concentration of 600 mg/L (based on phenol). After an initial decline, phenol content increased linearly, reaching a final concentration of 3.2 g/L. The initial oil had negligible acidity. During irradiation, acids were produced; after 91 h, maximum acidity (7.86 mmol H^+/L) was observed. Because of possible contributions by sulfonic, monocarboxylic, and polycarboxylic acids with indeterminate pKa's, the concentration of acidic compounds could not be determined accurately.

Total carbonyl compounds, including carboxylic acids (90 mg/L in starting material), likewise increased in the irradiated oil throughout the experiment, reaching 1.0 g/L (6.8 mmol/L based on 1-tetralone). There were no significant changes in toxicity, turbidity, acidity, or content of peroxides, phenols, or total carbonyl compounds in the control (dark) oil. Extraction of the 165-h crude photoproduct gave 174 mg strongly acidic, 99 mg phenolic, and 1362 mg nonacidic material.

The IR spectrum of the acidic fraction (Figure 4) indicated that it probably contained lactones (1775 cm^{-1}) as well as free acids. Phenolic acids were present, as shown by positive diazotized sulfanilic acid, Prussian blue, and $FeCl_3$ TLC spray tests. The low R_f's (0.47–0.62) of the phenolic acid spots indicated that they were more polar than a sample of petroleum naphthenic acids, which appeared at R_f 0.66. Substituted salicylic acids have been previously identified as crude oil photoproducts (*12*). The acid fraction had relatively high toxicity to yeast (Figure 5).

The IR spectrum of the phenolic fraction (Figure 6) showed an intense band centered at 1700–1705 cm^{-1} due to carbonyl compounds. In the TLC pattern, three major spots (one of which was intensely fluorescent) were observable at R_f's 0.59–0.77. The positions of the spots were characteristic of compounds having polarities intermediate between 1-naph-

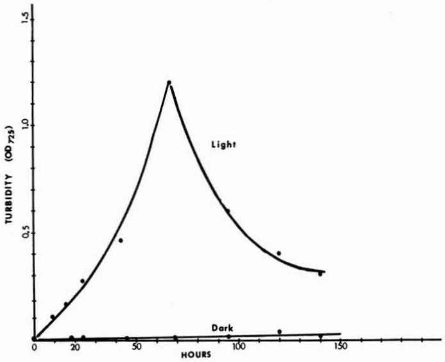


Figure 2. Development of turbidity during irradiation of #2 fuel oil

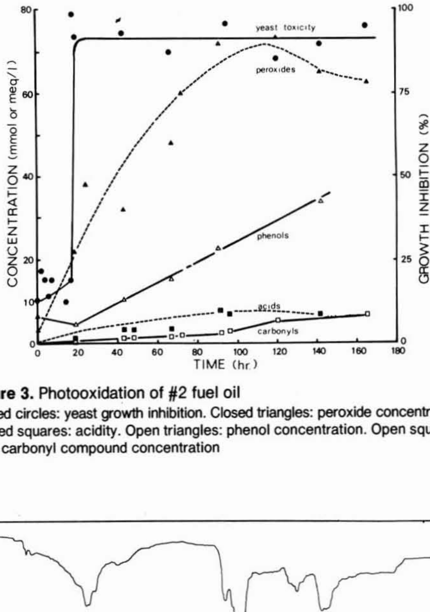


Figure 3. Photooxidation of #2 fuel oil

Closed circles: yeast growth inhibition. Closed triangles: peroxide concentration. Closed squares: acidity. Open triangles: phenol concentration. Open squares: total carbonyl compound concentration

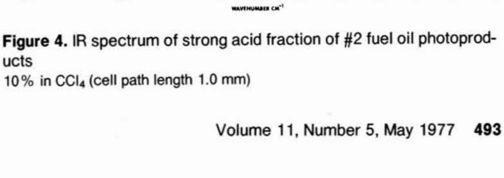


Figure 4. IR spectrum of strong acid fraction of #2 fuel oil photoproducts

10% in CCl_4 (cell path length 1.0 mm) thol (R_f 0.78) and dihydroxyphenols (catechol, R_f 0.50; resorcinol, R_f 0.38; hydroquinone, R_f 0.36). All three spots gave positive spray tests for phenol and carbonyl functionality; thus, both groups were probably present in many of the compounds producing the spots. Further evidence for this hypothesis was provided by the GC patterns (Figure 7) of the phenolic fractions of the stock oil and of the photoproduct. Almost all of the phenols of the starting fuel oil had boiling points below that of the internal standard, thymol (234°), but after irradiation there was a marked shift to higher-boiling compounds. A plausible explanation for these observations is photooxidation of phenols having nuclear alkyl substituents to arylcarbonyl compounds; *p*-hydroxyacetophenone, e.g., has a boiling point about 100° higher than *p*-ethylphenol.

In a previous study of fuel oil photooxidation (*13*), newly formed compounds having two oxygen atoms were identified by mass spectoscopy and tentatively assigned structures having two phenolic hydroxyl groups. In our investigation we were unable to demonstrate the presence of such substances; an alternative explanation would be compounds of the same empirical formula having one phenolic hydroxyl and one arylcarbonyl group.

The phenolic fraction was moderately inhibitory to yeast growth (Figure 5). Column chromatography of the nonacidic fraction afforded a number of yellow subfractions differing in polarity. These subfractions were characterized by TLC and by IR and UV spectroscopy. The TLC pattern showed several yellow spots which gave positive spray tests for ketones and (in a few instances) for aldehydes. Quinones were not detectable by spot test methods. The IR spectra of all the subfractions had carbonyl (1670–1720 cm^{-1}) absorption, and the more polar subfractions also contained hydroxylic compounds.

The UV spectra of several of the subfractions were similar to those of authentic fluorenone (Figure 8) and alkyl-substituted fluorenones (*14*). The GC pattern (Figure 9) of the silica column subfraction having an R_f on TLC equivalent to that of authentic fluorenone was extraordinarily complex, but had a large peak corresponding to fluorenone. Upon coinjection of authentic fluorenone, a single peak was still observed. At concentrations of 400 mg/L, some growth inhibition of yeast was observed with all the silica and alumina subfractions tested (Figure 5).

In model photooxidation studies, several compounds known to occur in #2 fuel oil were irradiated in decane solution under conditions identical to those used for oil irradiation. Fluorene, tetralin, and acenaphthene were converted in part to the corresponding ketones. 1-Naphthol and 2-methyl-1-naphthol gave low yields of naphthoquinones; however, when 1-naphthol was dissolved in the #2 fuel oil and irradiated, no quinone was formed. Quinones were not produced from phenol, *m*- or *o*-cresol. Biphenyl, phenanthrene, 1-methylnaphthalene, and 1,2,4-trimethylbenzene appeared to be inert to the irradiation.

Growth inhibition studies with oil fractions and with pure compounds are summarized in Figure 5. In general, all of the oxidized oil fractions inhibited growth to some extent at 400 mg/L, but only the acid fraction was highly active (>20% inhibition) at 100 mg/L. All of the pure compounds tested, except for *p*-hydroxyacetophenone, displayed some toxicity to yeast at 10^{-4} M. Fluorenone was most active (68% growth reduction after 48 h), but tetralin hydroperoxide had greater short-term toxicity (100% growth reduction at 24 h, compared to 79% for fluorenone).

In Figure 3, growth reduction by the irradiated oil and the rates of formation of four oxygenated species are plotted as a function of irradiation time. Particularly noteworthy is the substantial increase in toxicity between 10 and 20 h irradiation.

Addition of thiacyclohexane to oil which had been irradiated for 20 h reduced its toxicity markedly (from 92% growth inhibition to 17%). Oil exposed to light for a longer period (ca. 2 weeks) was reduced only to 48% growth inhibition (from 98%) by thiacyclohexane; the compound had no effect on the toxicity of control samples.

Discussion

Autoxidation of petroleum products has been a well-recognized phenomenon for many years, and a great deal of effort has been put forth by the petroleum industry to develop inhibitors of the process. Photooxidation of petroleum is less

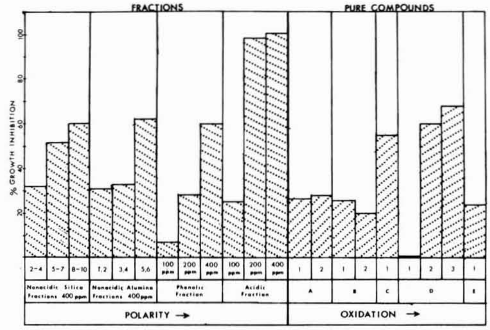


Figure 5. Growth inhibition of yeast by fractions of #2 fuel oil photoproducts and by pure substances

Hydrocarbons: A-1 fluorene, A-2 naphthalene. Phenols: B-1 *p*-cresol, B-2 1-naphthol. Hydroperoxide: C-1 tetralin hydroperoxide. Carbonyl compounds: D-1 *p*-hydroxyacetophenone, D-2 *p*-hydroxybenzaldehyde, D-3 fluorenone. Acid: E 3-(2-hydroxyphenyl) propionic acid

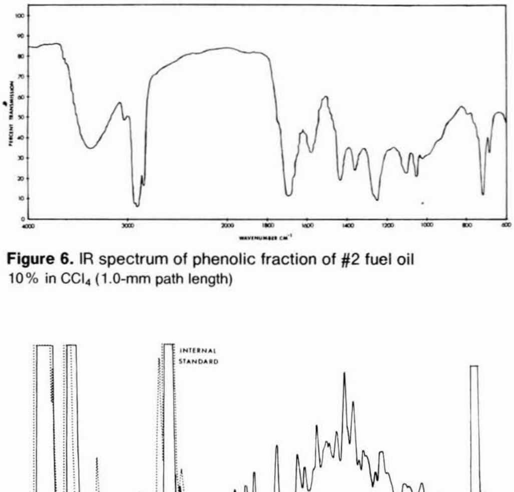


Figure 6. IR spectrum of phenolic fraction of #2 fuel oil

10% in CCl_4 (1.0-mm path length)

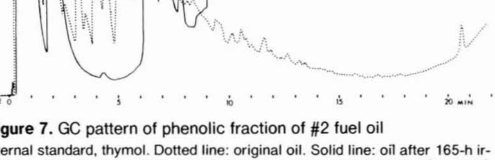


Figure 7. GC pattern of phenolic fraction of #2 fuel oil

Internal standard, thymol. Dotted line: original oil. Solid line: oil after 165-h irradiation. Column: 3% OV-210, temperature program 4 min hold at 80°; to 250° at 10°/min well understood. There have been only a few investigations of photooxidation in films of crude oils (*15–17*) and oil-related products (*12, 13, 18–20*). Carbonyl compounds (*18, 21*) and other oxygenated derivatives (*12, 13, 15, 16*) have been observed in artificially or naturally weathered petroleum.

Since many of the known toxic constituents of petroleum are relatively water-soluble, there has been increasing emphasis on its water-extractable fraction. Aromatic hydrocarbons (*3, 4, 22–25*), phenols and other alcohols (*23, 25*), and ketones (*23*) have been demonstrated in water extracts of various petroleum products. The toxicity of a few simple phenolic compounds to aquatic organisms has been studied in some detail (*26*), but less is known concerning the polyalkylated phenols, naphthols, and related compounds found in petroleum (*27*). Aryl ketones and phenols having nuclear carbonyl substitution have also been little studied. *p*-Hydroxybenzaldehyde, produced by a marine bacterium (*28*) and by some higher plants (*29*), has been reported to have powerful antimicrobial and phytotoxic activity; our data show that it also retarded yeast growth, but the structurally related *p*-hydroxyacetophenone had no activity.

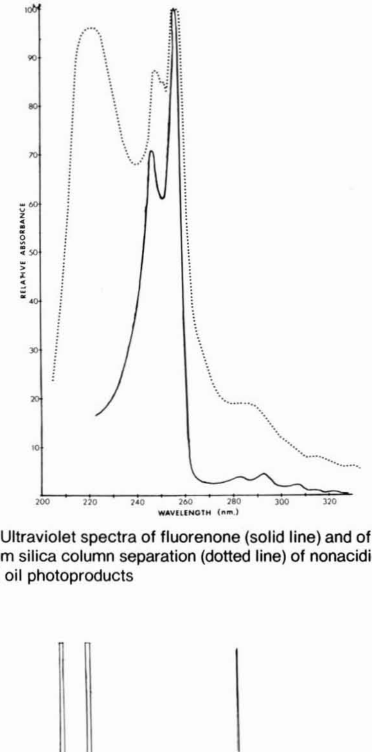


Figure 8. Ultraviolet spectra of fluorenone (solid line) and of fractions #8–10 from silica column separation (dotted line) of nonacidic fraction of #2 fuel oil photoproducts

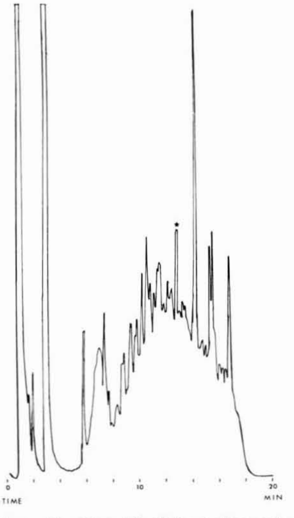


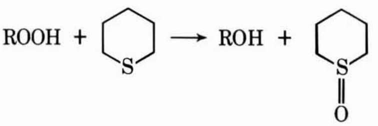
Figure 9. GC pattern of fractions #8–10 from silica column separation of nonacidic fraction of #2 fuel oil photoproducts

Starred peak corresponds to fluorenone. Column: 3% OV-210, temperature program 100–250°, 8°/min

Some phenolic acids are likewise toxic at low concentrations to higher plants, due to their disruptive effects on cell membranes (*30*). Aged oils containing acids and peroxides are also injurious to higher plants (*31*).

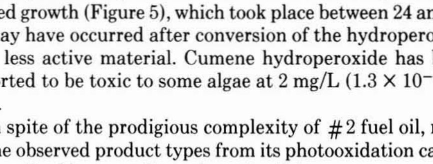
Although aging or weathering of oil spills has usually been considered to lead to reduced toxicity, due largely to evaporation of acutely toxic low-boiling hydrocarbons (*3, 32*), our results and those of others (*5, 6*) demonstrate that photooxidative processes acting on surface films can lead to materials highly toxic to aquatic organisms.

It is likely that peroxides and acidic materials were responsible for much of the phototoxicity of #2 fuel oil. The early (ca. 20–40 h) acute toxicity was evidently due almost entirely to reactive peroxides, as it could be reversed by addition of the easily oxidized thiacyclohexane:



Fuel oil irradiated for a longer period contained appreciable concentrations of oxidized substances other than peroxides and retained considerable toxicity after thiacyclohexane treatment.

Hydroperoxides likely to be produced by irradiation of petroleum products are those of benzylic hydrocarbons such as tetralin, indan, fluorene, cumene, and their alkyl derivatives. Phenols having *p*-substituents also form hydroperoxides when photooxidized in the presence of a sensitizer (*33*):



Tetralin hydroperoxide had the highest short-term toxicity toward yeast of any substance tested in this study. The observed growth (Figure 5), which took place between 24 and 48 h, may have occurred after conversion of the hydroperoxide to a less active material. Cumene hydroperoxide has been reported to be toxic to some algae at 2 mg/L (1.3×10^{-5} M) (*34*).

In spite of the prodigious complexity of #2 fuel oil, most of the observed product types from its photooxidation can be rationalized by a small number of well-known processes.

Fluorene (I, cf. Figure 10, or another reactive polycyclic compound) could be converted by long wavelength UV to an excited state and decay to radical II. Combination with atmospheric oxygen would afford hydroperoxy radical III. Abstraction of a hydrogen atom from compounds similar to those in Figure 11 would give hydroperoxide IV and a chain-propagating radical also capable of autoxidation, leading to products of the types indicated (*35*).

Fluorene hydroperoxide (IV) could collapse to fluorenone (V) (*36*) or cleave heterolytically under the influence of Lewis acids (*37*) to electropositive hydroxyl, an active hydroxylating agent toward electron-rich aromatic hydrocarbons.

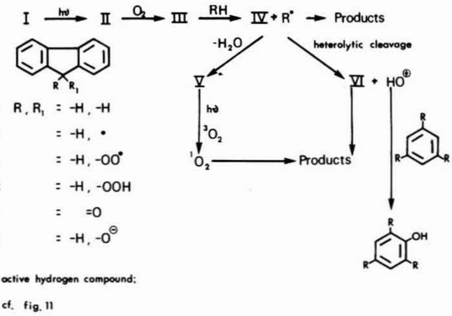


Figure 10. Proposed mechanism of #2 fuel oil photooxidation

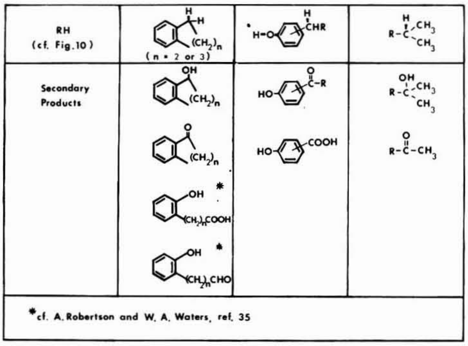


Figure 11. Active hydrogen compounds in #2 fuel oil and some of their likely products of photooxidation

Fluorenone has been used as a sensitizing dye for production of singlet oxygen (*38*), a species of considerable interest for its ability to add to double bonds and condensed aromatic nuclei and to cleave some types of aromatic and heterocyclic rings (*39, 40*). Such reactions may also be important in the photooxidation of #2 fuel oil, which also may contain other potential photosensitizers such as 1-naphthol (*41*).

Inhibition reactions are undoubtedly significant in the environmental photochemistry of some oil spills. Preliminary evidence suggests that the toxicity of a Nigerian crude oil is not greatly affected by exposure to light (*6*). One possible explanation for this observation is that crude oils normally have increased sulfur content relative to refined products. Organosulfur compounds, particularly the heterocyclic sulfides common to crude oils (*42*), are known to be effective inhibitors of radical reactions. Furthermore, such compounds are readily converted to sulfoxides by hydrogen peroxide (*43*) and by photooxidation (*16*). Because addition of a heterocyclic sulfide to peroxide-containing fuel oil reduces its toxicity significantly, it is conceivable that similar compounds could be used in the field to mitigate the environmental impact of spills of refined oils.

Acknowledgment

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Chromatographic Investigation of Inositol Phosphate Esters in Lake Waters

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■ Alkaline bromination of destabilized foam and concentrated Lake Mendota water followed by measurements of organic P (Po) and inositol in gel permeation chromatography (GPC) fractions gave evidence for the presence of inositol phosphate (IP) esters. The relative distribution of Po and inositol in GPC fractions by use of Sephadex G-25 favored the lower IP esters (ITriP, IDiP, IMP). Based on results from GPC analysis of nontreated foam and lake water, the IP esters were associated with high-molecular-weight organic matter. The percentages of total P present as IP esters averaged 19 and 26 for the foam and lake water, respectively. Estimated spring and summer IP concentrations in Lake Mendota were 3–15 μg P/L.

Although organic phosphorous (Po) frequently comprises a major fraction of the phosphorus in lake waters, relatively little is known about the nature and behavior of organic phosphorus in lakes. Naturally occurring Po compounds in lakes are thought to be largely associated with biological matter and thus are particulate in nature (*1, 2*). Endoplasmic Po which likely exists, at least fleeting, in the "dissolved" phase as a result of cellular excretion or decay consists of nucleic acids, phospholipids, phosphoproteins, nucleotide enzymes, sugar phosphates, and their degradation products (*3*). Phosphonic and aminophosphonic acids occurring as subunits of certain soluble and insoluble structural proteins may accumulate in natural waters due to the hydrolytic stability of the C—P bond (*3*). Limited information presently exists on the identity of important naturally occurring Po compounds in the "dissolved" phase. Much of the difficulty is related to the lack of suitable analytical methods.

Recent investigations of the nature of indigenous Po have emphasized either the biologically important Po pool or the more refractory components. Kuenzler (*4*) used thin-layer chromatography to separate 8–11 Po compounds from axenic algal cultures, but none was identified. Watt and Hayes (*5*) spiked lake water with $^{32}P-PO_4$ and isolated six ^{32}P-containing species, three of which were concluded to be nucleotides or polynucleotides based on adsorption by charcoal. Lean (*6, 7*), using ^{32}P-labeling and gel permeation chromatography (GPC), found that ^{32}P equilibrated rapidly with lake water to form a labeled particulate fraction containing most of the added ^{32}P, small amounts of a high-molecular-weight colloidal P component (>5 000 000), and a labile, low-molecular-weight species (~250 mol wt) excreted by seston. Most of the labeled, nonparticulate P in lake water was in the form of colloidal P.

Naturally occurring Po compounds of a more refractory nature were studied by Minear (*2*). Using GPC, he found that up to 20% of the recoverable "dissolved" Po from axenic algal cultures was high-molecular-weight matter (>50 000), consisting primarily of DNA and its fragments. Similar investigations of freeze-dried lake water samples yielded comparable results.

More recently, Minear and Walanski (*8*), McEntyre and Minear (*9*), and Weimer (*10*) established that algae were a potential source of the lower inositol phosphate (IP) esters which are known to accumulate in lake sediments. Using enzymatic techniques, Herbes et al. (*11*) found that up to 50% of the Po in lake water was hydrolyzable by phytase and occurred in both low- and high-molecular-weight fractions. The enzymatic behavior of the hydrolyzable Po agreed with that for inositol hexaphosphate. However, the lack of specificity of the phytase enzyme, as reflected in the hydrolysis of other Po esters in lake waters, suggests that the presence of inositol-P has not been adequately established.

Since inositol phosphate (IP) esters comprise 1–58% of soil Po (*12*) and 12–63% of lake sediment Po has been detected in both rooted aquatic plants and free-floating algae (*10*), it is likely that IP-esters exist in the "dissolved" state in lake water. However, IP-esters probably do not occur as free compounds but are likely associated with refractory organic matter of varying molecular weight. The purpose of this investigation was to evaluate the existence and concentrations of the inositol-P esters in lake waters using the techniques of alkaline bromination and gel permeation chromatography.

Experimental

Lake foam samples were collected in the fall of 1974 along southern and eastern Lake Mendota where foam lines generated by northwest winds intersected with the shoreline. Samples were collected in aluminum containers and allowed to destabilize overnight in the dark at 4 °C. Portions of the highly colored, destabilized foam were membrane-filtered (0.45 μm) and stored in polyethylene containers in the dark at 4 °C.

Water samples were collected in the "deep hole" area of Lake Mendota in 1974 and 1975 with a preequilibrated, Plexiglas, van Dorn sampler, membrane-filtered (0.45 μm) within 1 h of collection, and frozen in polyethylene containers. Thawed water samples were concentrated using an ultrafiltration apparatus (Amicon Corp.) with a UM-05 membrane having a nominal molecular-weight cutoff of 500. Nitrogen gas was used as the pressurizing agent. Concentration factors of ~50–100 were attained.

The bromination procedure used to investigate IP esters was similar to that developed by Cosgrove (*13*) for soils as modified by Minear and Walanski (*8*) for studies of algal extracts. Five mL of destabilized lake foam (filtered or nonfiltered) or filtered concentrated lake water was added to 50-mL test tubes containing 3–5 mL each of Br_2-saturated distilled water and 5 N NaOH. The mixture was heated in a boiling water bath for 1–1.5 h, cooled, neutralized by dropwise addition of concentrated HCl, and membrane-filtered (0.45 μm). Samples of the filtrate were retained for analysis and were stored frozen in the dark to inhibit hydrolysis of IP esters. The neutralization step resulted in the formation of a dense precipitate containing 0–70% of the initial P. Alkaline bromination is reported to oxidize natural organic matter and hydrolyze most Po compounds to orthophosphate, but to leave inositol phosphates largely unaffected (*8*).

The molecular-size distribution patterns of native or alkaline brominated samples were determined primarily on Sephadex G-25 in a 2.5 × 70 cm column operating in the ascending mode. The eluant consisted of 0.5 N NaCl plus 10^{-4} N NaOH. An ISCO Model 312 constant flow pump was used to achieve constant flow rates of 50–60 mL/h. Fractions were collected automatically with Gilson Spherical Model SB1 fraction collector. The void volume (Vo) was determined with Blue Dextran-2000 and deoxyribonucleic acid (DNA), and the

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inclusion volume (Vi) determined with orthophosphate. Samples were injected in-stream via a six-way control valve with a 5-mL sample loop.

Phosphorus measurements were made by the method of Murphy and Riley (*14*) as modified by Eisenreich et al. (*15*). Absorbance measurements were performed on a Beckman DU or Beckman 25 spectrophotometer using either 1- or 5-cm semimicro cells vs. a reaction blank. Inositol was detected in chromatographic fractions by the Feigl spot test (*16*) following IP hydrolysis. Inositol present initially does not survive the alkaline bromination/digestion step.

Results and Discussion

Inositol phosphate esters result from the replacement of one to six OH groups of inositol (1, 2, 3, 4, 5, 6-cyclohexanehexol) with orthophosphate anions. A common IP ester in soils is inositol hexaphosphate (IHP) in which six PO_4^{-3} groups have replaced OH groups on the cyclohexane ring. IHP has also been commonly called phytic acid or phytin (Ca, Mg salt).

Inositol phosphate (IP) esters have been separated and measured in soils, lake sediments, and plant extracts by anion exchange techniques (*10, 13*). Identical chromatographic behavior between an isolated organic P (Po) fraction and a particular IP standard has been considered sufficient evidence for identification. Bromination prior to anion exchange chromatography was introduced by Cosgrove (*13*) to oxidize soil organic matter without hydrolyzing IP esters. Minear and Walanski (*8*) applied alkaline bromination to algal culture extracts followed by gel permeation chromatography (GPC) to separate IP-esters by molecular size. This technique, modified slightly for the analysis of destabilized foam and concentrated water samples, was used in this investigation.

Sephadex G-25 with an eluant of 0.05 N NaCl plus 10^{-4} N NaOH adequately separated the high and lower esters of inositol P. Figure 1A shows the elution behavior of DNA, inositol hexaphosphate (IHP), inositol monophosphate (IMP), and orthophosphate (Pi) on Sephadex G-25. The elution volumes of 140 ± 5 mL (DNA) and 260 ± 5 mL (Pi) correspond to the void volume (Vo) and the inclusion volume (Vi), respectively, of the packed column. IHP and IMP elute at 170 ± 5 and 225 ± 5 mL, respectively. IMP elutes in a broadened peak as compared to IHP and exhibits some tailing.

To evaluate whether the alkaline bromination procedure affected the elution behavior of inositol P compounds, standard IHP and IMP solutions were subjected to alkaline bromination and chromatographed on Sephadex G-25 (Figure 1B). The recoveries of the IHP and IMP averaged 87 and 45%, respectively, in duplicate experiments. Whereas the IHP sample maintained an elution pattern similar to the standard, IMP exhibited a major peak at 220 mL, corresponding to the standard and two small peaks occurring at elution volumes (higher apparent mol wt). Minear and Walanski (*8*) have speculated that small quantities of inositol-containing, condensed phosphates were formed in the alkaline bromination step. The recovery value of 45% for IMP following alkaline bromination was due primarily to hydrolysis to Pi, rather than to the formation of high-molecular-weight matter. As shown in Figure 1B, IHP is significantly less susceptible to hydrolysis by alkaline bromination than is IMP.

Three additional model Po compounds were also subjected to alkaline bromination to evaluate the oxidizing efficiency of the reaction. Glucose-6-phosphate, adenosine monophosphate, and deoxyribonucleic acid were converted quantitatively to Pi. Apparently, the alkaline bromination procedure eliminates interference from simple Po compounds in the chromatographic analysis of inositol-P esters. Inositol not associated with inositol-P esters was also destroyed by the alkaline bromination procedure.

Since only the hexa- and monoinositol phosphate esters were commercially available (Sigma Chemical Co.) for determination of elution volume on Sephadex G-25, the elution volumes of the penta- through di-inositol-P esters were estimated.

The elution volumes (Ve) and distribution coefficients (Kav) were first determined experimentally for IHP and IMP. Assuming that the distribution coefficient (Kav) for a homologous series of IP-esters is a linear function of log (molecular weight), the Kav for unknown IP esters was estimated from a plot of log (molecular weight) vs. Kav by linear regression analysis using equation (*17*):

$$\mathrm{Kav} = \frac{\mathrm{Ve} - \mathrm{Vo}}{\mathrm{Vt} - \mathrm{Vo}}$$

where Ve is the elution volume, Vo is the exclusion volume, and Vt is the total bed volume.

Table I lists the elution volumes and distribution coefficients for inositol phosphates on Sephadex G-25. The elution volumes shown for IPP (inositol pentaphosphate) through IDiP (inositol diphosphate) are calculated and represent only estimates. However, this technique has been applied successfully to a study of IP-esters in algal cultures (*8*).

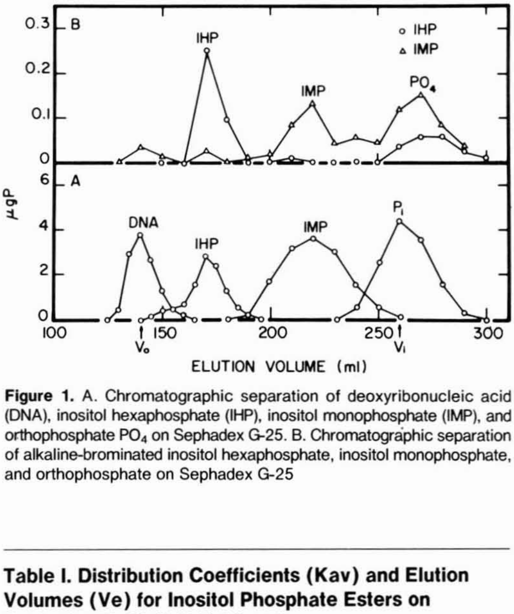

Figure 1. A. Chromatographic separation of deoxyribonucleic acid (DNA), inositol hexaphosphate (IHP), inositol monophosphate (IMP), and orthophosphate PO_4 on Sephadex G-25. B. Chromatographic separation of alkaline-brominated inositol hexaphosphate, inositol monophosphate, and orthophosphate on Sephadex G-25

Table I. Distribution Coefficients (Kav) and Elution Volumes (Ve) for Inositol Phosphate Esters on Sephadex G-25 (2.5 × 60 cm)

Compound[a]	Mol wt	Log mol wt	Kav	Ve
IHP	660	2.819	0.1942	170
IPP	580	2.763	0.2436	178
ITetP	500	2.699	0.3000	186
ITriP	420	2.623	0.3669	197
IDiP	340	2.531	0.4480	209
IMP	260	2.415	0.5502	225
BD-2000	...	....	....	140 (Vo)
DNA	...	....	....	140 (Vo)
PO_4	...	....	....	260 (Vi)

[a] IHP, inositol hexaphosphate; IPP, inositol pentaphosphate; ITetP, inositol tetraphosphate; ITriP, inositol triphosphate; IDiP, inositol diphosphate; IMP, inositol monophosphate; DNA, deoxyribonucleic acid; PO_4, orthosphosphate; BD-2000, Blue Dextran 2000.

The relatively low degree of chromatographic resolution of GPC when using large diameter columns limits the reliability of identifications of IP-esters based on GPC alone. The presence of organic P in samples after alkaline bromination in addition to positive tests for inositol in hydrolyzed fractions was considered indirect but strong positive evidence for the lower or higher IP-esters.

Prior to molecular-size fractionation of alkaline-brominated samples, untreated, filtered (0.45 μm) samples of destabilized lake foam and concentrated lake water were chromatographed in Sephadex G-25 (Figure 2). The elution behavior of foam samples shown in Figure 2A and B indicates that >80% of the P eluted in peaks corresponding to the exclusion volume of the column. Fractionation of the same samples on Sephadex G-75 indicated that 70–80% of the P was >70 000 mol wt. Following P analysis of subfractions, eluant corresponding to volumes less than and greater than 180 ml was combined and tested for the presence of inositol. Inositol was detected in only the high-molecular-weight fractions. The sensitivity of the Feigl spot test for inositol is ~2.5 μg.

The phosphorus elution patterns exhibited by the concentrated water samples (Figure 2C and D) indicated the presence of high-, intermediate-, and low-molecular-weight P. In each of these two cases, a large proportion of the P eluted as if it were orthophosphate (260 mL). The Feigl spot test for inositol was performed on combined fractions less than and greater than 180 mL as described above. Again, the reddish-brown spots suggestive of inositol were noted only in the high-molecular-weight fractions. Spot tests for inositol were performed on all destabilized foam and water samples, and in each case, inositol was detected only in the high-molecular-weight peak.

Alkaline Bromination Studies

Wind-generated lake foam in Lake Mendota was greatly enriched in high-molecular-weight dissolved C, N, and P and significant quantities of dissolved organic P (DOP) (*18*). Based on the high levels of organic C, N, and P and total protein (Biuret analysis), the lake foam was concluded to be of natural origin. The Langmuir circulation patterns responsible for the accumulation of lake foam suggest that organic components of lake foam originate as surface-active material scavenged from the mixing layer, with small amounts originating from the atmosphere. Thus, the organic matter in Lake Mendota foam is considered to be largely autochthonous.

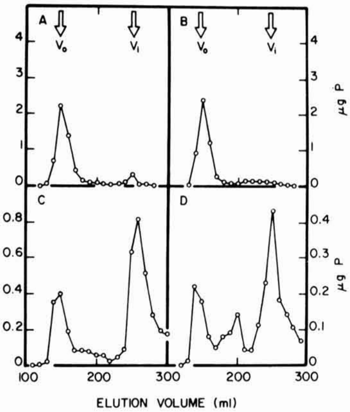

Figure 2. Fractionation of destabilized, filtered lake foam and concentrated water filtrates on Sephadex G-25

A. Lake Mendota destabilized foam, 11-22-74; B. Lake Mendota destabilized foam, 12-02-74; C. Lake Mendota concentrated water, 4-10-75, 1 m; D. Lake Mendota concentrated water, 5-01-75, 2 m

The Sephadex G-25 chromatographs of alkaline brominated, destabilized, foam samples are shown in Figure 3. Both filtered (F) and nonfiltered (NF) samples were investigated to evaluate the contribution of particulate matter to the inositol phosphate levels. Each chromatogram shows the total dissolved (TDP) and dissolved reactive P (DRP) levels in each fraction with organic P estimated by difference. The occasional higher Po levels in filtered over nonfiltered samples were attributed to greater losses from precipitation of P in the nonfiltered samples during the neutralization step.

The alkaline-brominated foam samples exhibited Po peaks in an elution region corresponding to the lower esters of inositol (ITriP, IDiP, IMP). An example of this behavior is shown in Figure 3D where peaks occurring between 200 and 225 mL likely correspond to IDiP and IMP. Chromatographic fractions between 190 and 230 mL, combined for analysis by the Feigl test, gave positive results for inositol. Combined eluant

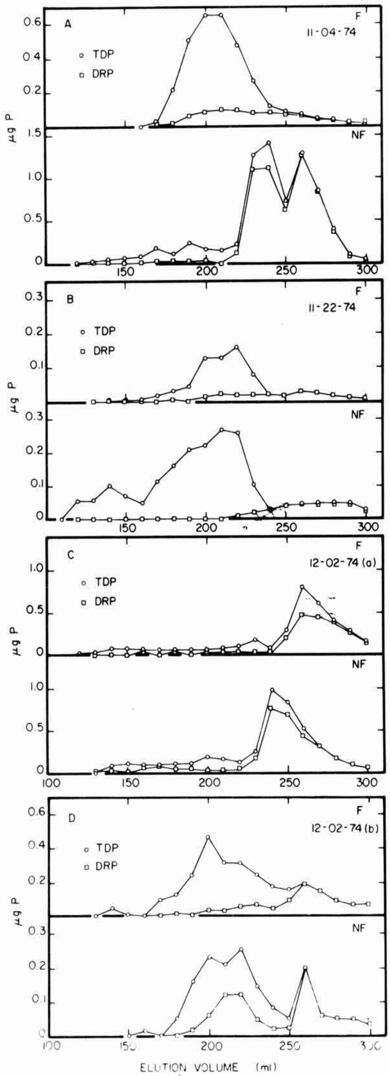

Figure 3. Fractionation of alkaline-brominated, destabilized foam samples from Lake Mendota on Sephadex G-25 (F, filtered; NF, not filtered)

fractions less than 190 mL and greater than 230 mL gave negative results, although inositol could have been present below the detection limit. Apparently, the high IP esters (IHP, IPP, ITetP) were not present in measurable quantities in the 12-02-74 (B) sample.

Other foam samples exhibited similar chromatographic behavior, except for the 11-4-74 sample (Figure 3A). In this case, the filtered foam sample gave significant quantities of Po from 180 to 230 mL, but the spot test indicated only small amounts of inositol were present. Peaks for the nonfiltered sample occurred at 170 and 190 mL, corresponding to the elution volumes of the higher IP esters (IHP, IPP, ITetP) and gave positive Feigl tests; Po also occurred at 220–240 mL. Slight variations in elution volume of peaks in filtered vs. nonfiltered samples represent small changes in ionic strength resulting from Br_2 additions and neutralization of base. Comparison of the filtered and nonfiltered samples for 11-4-74 suggests 1) the higher esters were present only in the particulate phase, 2) hydrolysis of higher esters to lower esters occurred predominantly in the filtered samples, or 3) oxidation of noninositol Po species by alkaline bromination was not complete. Little evidence can be presented to support any one hypothesis, although a combination of 1) and 2) is likely since the IHP standard was hydrolyzed to a small degree by the alkaline bromination procedure. However, hydrolysis appears to be more prevalent for the lower esters. Evidence suggestive of IMP (*8, 9*) and IHP (*10*) in algal cells, the major contributors to particulate P in lake systems, has been reported. Since standard solutions of model Po compounds of varying complexity and Po in water concentrates and destabilized foam (except for 11-4-74) were quantitatively converted to Pi during alkaline bromination, Po remaining following treatment was likely inositol-P esters only.

Evidence for partial formation of high-molecular-weight matter in the experimental procedure is shown in Figure 3B. The 11-22-74 sample shows most of the IP to occur as lower esters as in previous samples, with some Po appearing as high esters (positive Feigl test). The chromatogram of the nonfiltered sample showed a peak at the exclusion volume of the column. Fractions representing 130–160 mL of repeated runs were combined, and testing for inositol proved positive. Inositol at the Vo in this sample is likely an artifact of the alkaline bromination procedure because this was not observed in the other samples.

Thus, for the foam samples, alkaline bromination followed by measurements of Po and inositol in GPC fractions gave evidence for the presence of IP esters. The relative distribution of Po and inositol following alkaline bromination favored the lower esters ITriP, IDiP, IMP). Based on fractionation of nonbrominated, filtered foam samples (Figure 2A and B), the IP esters were apparently associated with high-molecular-weight matter, a hypothesis suggested previously for water (*11*) and soil (*19*).

The estimated IP concentrations in lake foam and percent of total-P are presented in Table II. The IP concentrations were estimated as the Po remaining after vigorous alkaline bromination and GPC of the samples, using only samples in which inositol was detected. These values should be considered as maximum values since interference from unoxidized, noninositol-P could not be readily evaluated on an absolute basis. The percentages of IP esters compared to total-P ranged from 4.5 to 36.9% and averaged 19.2 ± 13%.

Lake water concentrations of IP esters as reflected by their presence in foam could not be calculated due to lack of information concerning the scavenging efficiency of foam. As a result, filtered lake water was concentrated by factors of 67–102× by ultrafiltration techniques and subjected to alkaline bromination and GPC procedures. The percentages of IP present calculated as DOP remaining and giving positive Feigl spot tests compared to total-P ranged from 20.6 to 31.5% and averaged 26.1 ± 4.5% (Table II). Since the dissolved P concentrations for these samples ranged from 0.035 to 0.093 mg P/L and DOP levels ranged from 30 to 60% of these values, the estimated IP concentration in Lake Mendota during late spring and summer is in the range of 0.003 to 0.015 mg P/L.

Figure 4 depicts the elution patterns of alkaline-brominated water concentrates on Sephadex G-25. The samples taken at 1.0 m on 6-11-74 (IVA) and 5-1-75 (IVB) show small but distinctive Po peaks at 200 mL and diffusely distributed Po between 210 and 250 mL. Fractions corresponding to elution volumes of 190–220 mL collected on duplicate runs were combined and found to contain inositol based on the Feigl spot

Table II. Estimated Concentrations of Inositol Phosphate in Destabilized Lake Foam and Concentrated Water

Sample	Phosphorus in original sample, mg/L				% P recovered[a]	IP concn,[b] mg/L	% IP of total P
	TP	TDP	DOP	DRP			
			Foam				
11-04-74 NF[c]	3.75	3.19	2.13	1.06	~100	0.32	8.5
F					39	0.89	23.7
11-22-74 NF	4.40	2.87	1.86	1.01	46	0.52	11.8
F					27	0.20	4.5
12-02-74 NF	1.30	....	....	....	~100	0.47	36.2
(a) F					~100	0.48	36.9
12-02-74 NF	4.20	3.66	1.21	2.45	49	0.29	6.9
(b) F					81	1.05	25.0
			Water				
6-11-74 (×100)[d] (1 m)		1.03	....	....	62	0.32	31.5
4-11-75 (×67) (2 m)		2.84	....	....	51	0.73	25.8
4-11-75 (×83) (20 m)		1.52	....	....	53	0.40	26.3
5-01-75 (×102) (1 m)		1.78	....	....	42	0.37	20.6

[a] Total P recovered through the alkaline bromination and GPC procedures. [b] Inositol P (IP) concentrations were calculated as the quantity of organic P remaining after GPC of alkaline brominated samples and verification by the Feigl spot test. [c] NF, nonfiltered; F, filtered (0.45 μm). [d] Represents concentration factor.

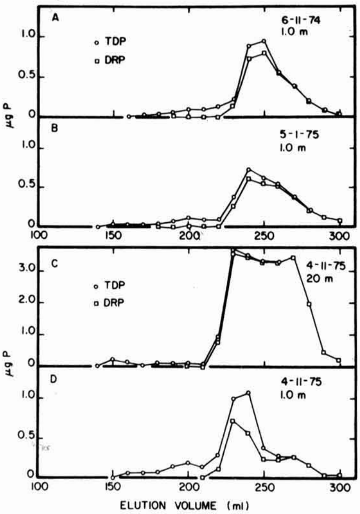

Figure 4. Fractionation of alkaline-brominated, concentrated water samples from Lake Mendota on Sephadex G-25

test. No significant Po concentrations were noted in the elution region of the higher IP esters.

Lake Mendota water samples taken at 2 and 20 m under the ice on 4-11-75 were alkaline brominated and fractionated on Sephadex G-25 (Figure 4C and D). Results for Po combined with a positive Feigl test indicate that the 1-m sample contained a significant quantity of IP, as compared to the 20-m sample (Table II). Temperature and P measurements in the water column clearly showed that the surface water was warmer, more highly colored, and had higher P concentrations than the lower strata. Runoff induced by warm spring rains prior to ice-out on Lake Mendota apparently carried soil organic matter to the lake. Since the higher esters predominate in soils (*10*), the predominance of the lower esters in this sample suggests that either rapid hydrolysis of the higher IP esters occurs in soil runoff or the distribution in runoff favors the lower esters. If the latter is true, Weimer's (*10*) hypothesis that the lower esters dominate in sediments as a result of in-lake production by aquatic plants is in doubt. The lower esters could occur in sediments as a result of soil erosion and runoff. Since Weimer did not actually investigate the IP content of soil runoff, the lower IP esters could be the major IP form. Whether the dominance of lower IP esters in this water sample is the result of enhanced mobility in soil is unclear. Perhaps the higher esters are more strongly retained by soil components than the lower esters as a result of a greater number of exposed, reactive phosphate groups.

Lake Sources of Inositol Phosphorus

The major sources of inositol phosphates to lakes are thought to be soil runoff and in-lake production by rooted aquatic plants and free-floating algae (*8–10*). Although lake sediments have a high proportion of Po as IP, it is unlikely that a significant quantity is released to the overlying waters, even under anaerobic conditions. Weimer (*10*) has calculated that ~17 000 and 20 000 kg/year of inositol polyphosphate enter Lake Mendota from algal and soil input, respectively. In addition, he found that the average higher IP ester to lower ester ratio found in lake sediments (0.59) is remarkably close to the weighted average ratio based on algal and soil input (0.62). For this calculation, a higher ester to lower ester ratio of 1.14 and 0.29 was assigned to soil and algal sources, respectively. Data obtained in this report suggest that lower esters may be the dominant IP form in soil runoff. If this is true, the high ester to low ester ratio found for lake sediments may reflect a greater input of IP from runoff as compared to in-lake production by algae and macrophytes.

The form in which the IP ester occurs in water may be important when considering rates of chemical and microbial hydrolysis or decomposition. Soil IP is found to be partly associated with high-molecular-weight organic matter and Fe and Al oxides (*19, 20*). Herbes et al. (*11*) found that up to 50% of lake Po was hydrolyzable by phytase and associated with both low- and high-molecular-weight fractions. The enzymatic rate of hydrolysis was similar to that for inositol hexaphosphate. The results from this investigation indicate the lower inositol phosphate esters are the dominant forms in filtered and nonfiltered foam samples and in filtered, concentrated lake water. The IP in both instances was associated with high-molecular-weight matter.

Acknowledgment

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Sources of Tar Pollution on Israeli Mediterranean Coast

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■ A survey was made to find the sources of tar balls polluting the Mediterranean coast of Israel. Samples were collected fortnightly from eight stations along the shore from September 1973 to January 1975. According to chromatographic analysis, 76% of the tar balls were formed from weathered crude oil (GC-1) + crude oil sludge (GC-2), 18% from weathered fuel oil (GC-3), 4% were greatly weathered, and 2% of the samples were unidentified. According to the vanadium/nickel ratio and sulfur contents, 96% of the tar balls formed from GC-1 + GC-2 were from Middle Eastern sources. The degree of weathering of the samples showed that 46% of the tar balls formed from GC-1 + GC-2 were exposed at sea for about a fortnight, 41% for more than two months, and 13% probably for one to two years.

The Mediterranean is a closed basin sea with well-defined oil transport lanes. Along its southern shore are the oil producing countries Algeria, Libya, and Egypt. Israel, Lebanon, and Syria, on its eastern shore, have pipelines for transporting Persian Gulf and Iraqi oil to the Mediterranean. This study was made to assess the relative contribution of North African and Middle Eastern crude oils to the pollution of the Mediterranean shore of Israel.

Crude oil is a complex mixture of hydrocarbon compohents including saturated straight and branched chains, saturated and aromatic rings, and heterocyclic compounds. The chemical characteristics of each type of petroleum indicate its source (in this study, "source" is defined as the geographical source of the crude oil). North African crude oils usually differ from Middle Eastern crudes, particularly in the ratio of vanadium to nickel and in the percentage by weight of sulfur. Nickel and vanadium are present in the crude oils in the form of metallo-organic complexes. Sulfur is in the form of nonvolatile organic compounds practically insoluble in water (*1*).

Spilled crude oils are altered by evaporation, by dissolution, and by chemical or biochemical attack. The effects of these processes on the chemical composition of the oil can be predicted (*2*). There is an increase in proportion of vanadium and nickel during natural deterioration of spilled oils. However, due to the identical chemical form by which the metals are bound, the V/Ni ratio remains the same (*3–5*).

In studies made after the Torrey Canyon accident (*3*), the investigators concluded that the sulfur content of weathered crude oil is about 15% lower than the unweathered. Davis and Gibbs (*5*), however, found that the sulfur content remained the same through a two-year experiment.

An important parameter for an indication of the age of the tar ball is the degree of weathering, for which no technique has been developed to provide an unambiguous answer (*6*). The approximate time elapsed since the crude oil was exposed to weathering is an important parameter in determining the source of the oil pollution. A criterion is given for estimating the age based on experimental results.

Methods

Samples were collected fortnightly from September 1973 to January 1975 at eight stations on the Israeli coast. Three samples were taken at each station at 200-m intervals along the shore. The tar balls were collected from the tar strip closest to the waterline. Each sample was stored separately in a small plastic container.

For analysis, each tar ball was divided in half, and the central portion of each half was removed and treated identically. Only the tar that did not come in contact with the container was used. The weighed samples were dissolved in 10 ml toluene and centrifuged. The solution over the water and sand layers was decanted and used in gas chromatographic, vanadium/nickel, and sulfur analyses.

The gas chromatograph (Varian Model 1840) was programmed from 80 to 320 °C at 4 °C/min. The column packing was 3% SE-30 on Varaport 30; FID was used. Seven unweathered crude oil samples from the Persian Gulf and two samples from the Sinai were examined, and their chromatograms obtained. Two samples of crude oil sludge and four samples of unweathered fuel oil from local sources were analyzed, and their chromatograms obtained. These chromatograms served as model patterns for the classification of the chromatograms made from the tar balls collected from the shore.

Vanadium and nickel were determined by methods described by the Institute of Petroleum Standardization Committee (*7*). The metal concentrations were measured on a Techtron AA-5 (atomic absorption spectrophotometer). For sulfur the supernatant was evaporated to dryness, and the sulfur content determined according to the ASTM-D15S2 high temperature method with a "Leco" induction furnace and "Leco" sulfur titrator.

The degree of weathering of the sample is indicated by the appearance of the first *n*-hydrocarbon on the chromatogram. By our definition, the first *n*-hydrocarbon is that whose peak height is at least 10% of the height of the C_{20} peak:

$$\text{Height of first } C_n > \frac{\text{Height of } C_{20}}{10}$$

Results and Interpretation

Classification of Chromatograms. Brunnock et al. (*3*) and Ramsdale and Wilkinson (*8*) listed three types of beach pollutants from oil spilled or discharged at sea: weathered crude oil, crude oil sludge, and fuel oil. In this study the authors have grouped the chromatographic results into four classes. The four types of chromatograms, described below, are obtained consistently from the various tar samples taken from Israel's beaches.

GC-1: Weathered Crude Oil (*Figure 1*). Typical of this group is the steep rise in the hydrocarbon peaks at the beginning of the chromatogram, which has a maximum of its *n*-paraffin concentration at about C_{20}.

GC-2: Weathered Crude Oil Sludge with Bimodal Distribution (*Figure 1*). This group is similar to GC-1 and differs from GC-3 in that there is no hump; however, there are two distinct maxima at about C_{20} and above C_{30}. The first maximum usually has the same characteristics as group GC-1.

GC-3: Weathered Fuel Oil (*Figure 1*). Unweathered fuel oil also has two maxima. The second maximum is characterized by a very large hump of unresolved components (isoparaffins, naphthenes, aromatics, and polycyclics) on which relatively small peaks of n-hydrocarbons are superimposed. In weathered samples of fuel oil, the hump is large and distinct.

GC-4: Highly Weathered Oily Residue (Figure 1). This type is characterized by very low peaks and an unresolved hump. From such a chromatogram, it is impossible to identify the type of oil residue from which the tar balls have been formed.

All tar samples were examined by means of a gas chromatograph, and their chromatograms compared with model pattern chromatograms of the unweathered samples. The four types and the percentage of each in the tar samples are summarized in Table I. Seventeen tar ball samples did not fit any of the model pattern chromatograms and therefore were not classified. These divisions form the basis for tracing the tar ball origin (in this study, "origin" is defined as the means, i.e., accidental spill, tank washing, by which the pollutant is introduced into the sea).

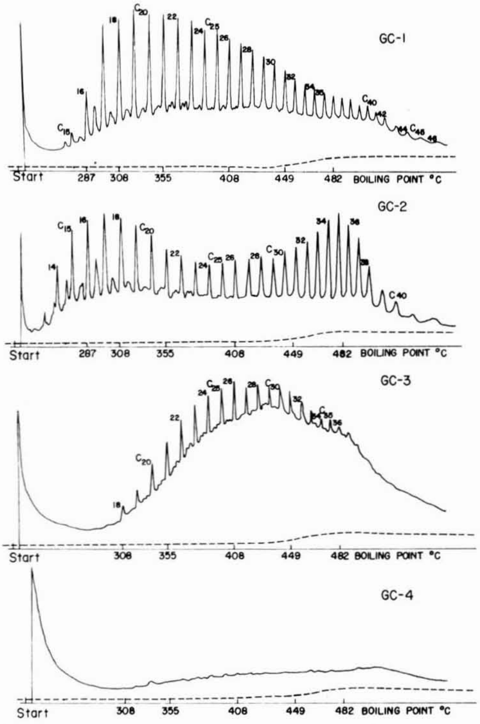

Figure 1. Gas chromatographic types used as models for classifying chromatograms of tar balls

GC-1 weathered crude oil, GC-2 crude oil sludge, GC-3 weathered fuel oil, GC-4 highly weathered oily residue

Table I. Four Types of Tar Chromatograms and Their Quantity

Chromatographic types	No. of samples	% of tar samples
GC-1 weathered crude oil	149	19
GC-2 crude oil sludge with bimodal distribution	451	57
GC-3 weathered fuel oil	139	18
GC-4 highly weathered oily residue	32	4
Unidentified samples	17	2
Total	788	100

GC-1 and GC-2 are specific for residues resulting from activities related to crude oil transport, tank washing, and discharge of slop tanks. GC-3 includes all maritime vessels and onshore facilities such as power stations. In group GC-4 the paraffin chain is destroyed, maybe as a result of the high degree of weathering; thus, its classification into one of the previously mentioned groups was not possible.

The bimodal tar chromatogram GC-2 is the dominant type (57%) in the samples analyzed. Butler et al. (*9*) found 33% bimodal tar chromatograms among the tar balls collected on the Bermuda beaches. In the Gulf of Mexico, 32% of the pelagic tar showed a bimodal tar chromatogram (*10*). From the data in Table I, weathered crude oil and crude oil sludge together have a much larger share in the tar ball pollution than does weathered fuel oil. The percentage of tar balls formed from GC-1 + GC-2 is 76%, whereas the percentage of GC-3 is only 18%.

Figure 2 shows the monthly fluctuation in the four types of chromatograms during 17 months. GC-1 and GC-2 appear throughout all the months of the survey. GC-3 did not appear during three months. However, it is noteworthy that GC-4 did not appear throughout December 1973 and the months April–September 1974.

Vanadium/Nickel Ratio and Sulfur Content. As mentioned earlier, crude oils from Middle Eastern and North African (Algeria, Libya) sources have different vanadium/nickel ratios and sulfur contents, making it possible to identify the sources of pollution.

Data from literature (*3, 11, 12*) on vanadium/nickel ratio and sulfur % contents for Libyan, Algerian, Egyptian, Sinai, and Middle Eastern oils (including the Persian Gulf) were plotted on a log-log chart (Figure 3). Each type of oil was given a symbol, and then a line could be drawn separating the Algerian-Libyan groups of oils from the Middle Eastern groups, The Egyptian-derived oil is closer in its characteristics to the Middle Eastern crude oil than to the other North African crude oils, although it lies between both groups (Figure 3). However, as most Egyptian oil was used internally (*13*), very little was released to pollute the sea. This chart (Figure 3) serves as a model pattern for identification of tar balls based on our analysis.

The results obtained from the analysis of the V/Ni ratio and sulfur contents have been cataloged and divided according to chromatographic types GC-1 to GC-4. Figure 4 shows V/Ni ratio vs. sulfur % contents on a log-log graph. The line separating two groups as in Figure 3 was drawn to divide every one of the four subgraphs into two parts. Since weathered crude oil (GC-1) and crude oil sludge (GC-2) were derived from the same origin, they were analyzed together. Ninety-six percent of the 600 samples of the two types were situated above the dividing line. Since these data satisfy the qualifications de-

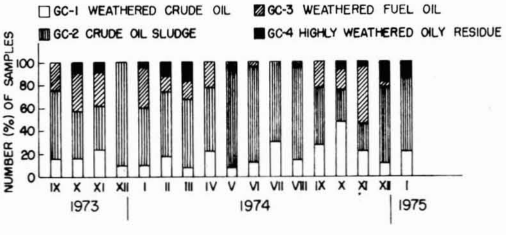

Figure 2. Monthly distribution of chromatographic types collected on Israeli coast

scribed for Middle Eastern oil, this oil probably came from the Middle East. Four percent of the data were found below the dividing line. According to the observations made by Brunnock et al. (*3*) on sulfur degradation, the derivation of the samples examined from the Mediterranean shore of Israel may be from the Middle Eastern groups.

Individual samples which fell in areas on the chart characteristic for Libyan and Algerian oils were too few to allow conclusive determination.

GC-3 represents fuel oil. As such, it is an artificial refinery product. Placing it into one of the previous geographical groups does not prove its descent from this geographic area. Moreover, ships fill their tanks with fuel at various ports of the world. Therefore, no attempts were made to find the geographical source of the GC-3 type profile in this study.

The points on the GC-4 subgraph are situated in the upper parts and correspond with Middle Eastern oil. However, it is unknown to which of the chromatographic types GC-4 belongs, and since this profile is only 4% of the total number of samples examined, it is not further considered.

Degree of Weathering. The age of the tar ball is defined as the period of time from the oil spill to sample collection. This parameter is considered important in determining the source of the oil pollution. The degradation process of the spilled oil is affected by several environmental factors, among them temperature, sunlight intensity, and wind. The variability of the environmental factors contributes to the difficulties in establishing a formula or set of rules for defining the age of a tar ball.

Several experiments have been conducted to study the disappearance rate of the low-boiling paraffin fraction. Zafiriou et al. (*14*) found that within a few hours, paraffins up to C_{10} (n-decane) had volatilized from spilled crude oil and that n-hydrocarbon chains up to C_{13} (n-tridecane) had disappeared in a few days. After a year, the paraffins up to C_{17}–C_{18} (n-heptadecane and n-octadecane) were no longer present. Blumer and Sass (*15*) reported that the degradation process is rapid initially and stabilizes at C_{16}–C_{17} (n-hexadecane and n-heptadecane) after six months. In the West Falmouth oil spill, the paraffins up to C_{18} (n-octadecane) were degraded after 16 months. In preliminary experiments carried out by Ravid and Oren (*16*), on the fifth day after the spill, paraffins up to C_{12} (n-dodecane) had disappeared. The paraffin degradation reached C_{14} (n-tetradecane) in two weeks and C_{16} (n-hexadecane) after two months.

In this study the appearance of the first n-hydrocarbon was examined according to the various chromatographic types: weathered crude oil (GC-1), crude oil sludge (GC-2), and weathered fuel oil (GC-3).

The assumption has been made that GC-1 and GC-2 have the same origin; thus, from Figure 5, the first n-hydrocarbon range of C_{13}–C_{17} occurs in the greatest number of samples. The degradation reached paraffin C_{14} in 277 (46%) samples. From the data of Ravid and Oren (*16*), this corresponds to approximately a two-week exposure at sea. The group with the first n-hydrocarbon C_{15}–C_{16} occurred in 249 (41%) samples or after about two months of weathering. The distribution of the first n-hydrocarbon for GC-3 (Figure 5) is distinctly different. This chromatographic profile is representative of fuel oil which is a blend and may not contain a significant number of low-boiling paraffins in the unweathered sample.

In Figure 6 the first n-hydrocarbon is plotted according to the month in which the sample was collected. There appears to be a seasonal cycle. Tar samples in which the first n-hydrocarbon was C_{13}–C_{14} decreased in the winter months, reaching a minimum in December. This (C_{13}–C_{14}) first n-hydrocarbon increased in the summer with a maximum in June. There is insufficient seasonal data to interpret this observation especially since it is assumed that hydrocarbon evaporation increases with increase in temperature.

Discussion and Conclusions

The authors are aware that classification of the various chromatograms by means of model pattern chromatograms

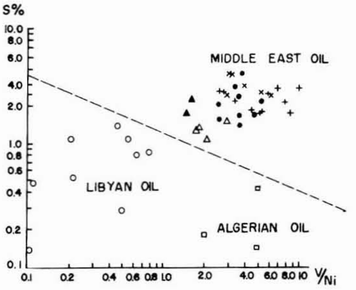

Figure 3. Chart based on data in literature on sulfur contents vs. vanadium/nickel ratio showing geographical sources of crude oil

North African oil: □ Algerian, ○ Libyan, △ Egyptian. Middle Eastern oil: ● Iranian, × Kuwait, + Saudi Arabian, ▲ Sinai

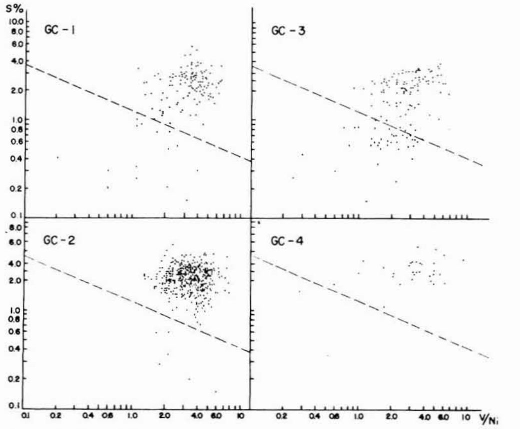

Figure 4. Chart GC-1 to GC-4 showing sulfur contents vs. vanadium/nickel ratio of data obtained from sampled tar balls

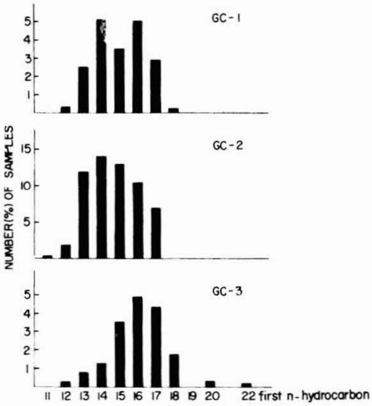

Figure 5. Degree of weathering of tar balls based on first *n*-hydrocarbon appearing in chromatogram

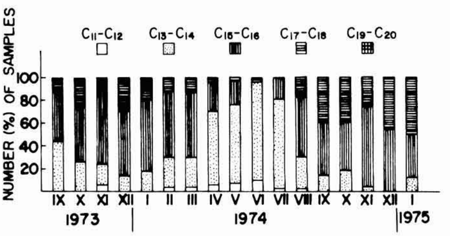

Figure 6. Monthly distribution of degree of weathering (based on first *n*-hydrocarbon) of tar balls collected on Israeli coast

is imperfect. Moreover, there was an insufficient amount of standard material for making model pattern chromatograms, especially for unweathered crude oil sludge and fuel oil not of Israeli production.

It was impossible to identify the origin of the 17 samples which did not fit any of the model patterns. Hence, vanadium/nickel ratios and sulfur percentages of these samples were not examined.

However, the vanadium/nickel ratios and percentage by weight of sulfur were examined for the highly weathered oily residues exposed for a long time at sea, as the authors wished to check whether these residues were of North African source. By use of Figure 4, these residues also appeared to be of Middle Eastern sources.

The results suggested that for the period studied, the geographical source of 96% of the tar balls (only two types: GC-1 and GC-2) was the Middle East.

The degree of weathering and the environmental effects on tar balls are important factors in tracing the source of tar balls. More information is required on these factors before the results of this study can be fully interpreted. There is insufficient data on the evaporation of the low-boiling paraffins in hot climates. This problem concerns, in particular, the observations plotted in Figure 6, i.e., the high percentage of relatively fresh tar samples collected during the summer months. A second problem, that might be related to the first, is the lack of highly weathered (GC-4) samples in the months April–September.

A study is now in progress to observe the changes occurring in exposed crude oil and fuel oils.

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Anatomy of Two Ozone Transport Episodes in the Washington, D.C., to Boston, Mass., Corridor

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■ During the summer months of 1975, the Interstate Sanitation Commission, in cooperation with the States of New York, New Jersey, and Connecticut and the Brookhaven National Laboratory, conducted a series of studies to characterize ozone transport in the Washington, D.C., to Boston, Mass., corridor. Periods of ozone concentrations above 120 ppb in the New Jersey–New York–Connecticut area were generally preceded by a surface wind shift from a northwest quadrant to a southwest quadrant. On several occasions prior to the wind shift, significantly lower values of ozone (between 30 and 60 ppb) were observed over the area. Synoptic surface weather maps indicated that the shift to a southwest flow preceding these episodes of increased ozone concentrations frequently corresponded to the onset of the return flow around a high-pressure system. An in-depth analysis of two such occurrences during July and August is presented. The arrival and movement of the high concentrations of ozone are supported by continuous surface ozone monitoring data, aerial ozone measurements obtained during the morning and afternoon, meteorological soundings examining local conditions, and air trajectory analyses demonstrating the mesoscale movement of particular parcels of air.

Surface ozone data from New York, New Jersey, and Connecticut collected during the past three years indicate that there are generally four or five episodes of elevated ozone per month during May through August. They generally persist for 1–8 days, but 3–4-day episodes are the most frequent (*1*). These episodes are generally associated with a single air mass and terminate as a new air mass moves into the region (*2*). Stations separated by hundreds of miles but under the influence of the same high-pressure system generally have similar ozone levels (*2, 3*). Studies have also indicated that the area of highest ozone within a high-pressure system usually occurs in the southwestern or western sector of the high-pressure system (*3, 4*). This is consistent with observations in the Northeast which indicate that highest ozone levels are reached when under the influence of southwest winds on the return flow around the high-pressure system (*1, 5*).

On July 21 and August 18, 1975, cold fronts passed through the Northeast. With northwest flows prevailing on July 22, August 19 and 20, ozone levels were generally low (less than 80 ppb) over the entire region. However, on July 23 and August 21, the ozone levels increased dramatically even though this area was under the influence of the same high-pressure system which persisted on the previous day. The purpose of this paper is to characterize the changes in the meteorological parameters associated with these sharp increases in ozone concentrations, document the onset of high ozone levels across the region, and employ trajectory analyses to determine possible source regions of the high ozone.

Methodology

Surface ozone values were obtained from monitoring networks operated by the States of Connecticut, New York, New Jersey, Pennsylvania, and Maryland (Figure 1). Aerial ozone measurements presented in this paper were obtained in conjunction with two other studies, and the experimental details have been described elsewhere (*6, 7*). Briefly, aerial sampling was conducted using a Cessna 172 single-engine aircraft. Flights on August 20 and 21 originated simultaneously from Trenton, N.J., and Stratford, Conn., while the flights on July 22 originated from Trenton. Ozone measurements were obtained using a portable AID chemiluminescent ozone monitor.

Trajectory analyses were conducted by the Atmospheric Sciences Division at Brookhaven National Laboratory. Each trajectory, forward and backward, is comprised of a series of segments of length $\bar{u}\Delta t$, where Δt is 3 h and $\bar{u}$ is calculated as follows: Winds from sites in the National Weather Service upper-air observation network are considered within a 300-nautical mile distance and are weighted by the inverse square of the distance to the site. Winds at each site considered are averaged within the specified layer. For these runs the surface layer is specified (here taken to be from the surface to 1000 m). Trajectories are commenced from the specified point every 6 h and continue for 5 days or until significantly off the North American continent. For backward trajectories, termination at rather than commencement from the specified point occurs every 6 h. Motion is constrained to the layer, and thus vertical motion is ignored.

The possible errors involved in the trajectory calculations consist of three types: meteorological data measurement errors, wind field interpolations between observations, and the use of rawindsonde data which measure instantaneous rather than mean wind. In a recent study, Buoni et al. (*8*) concluded that although the calculated trajectories can be in substantial

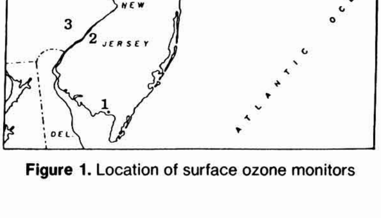

Figure 1. Location of surface ozone monitors

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[2] Department of Environmental Protection, State of Connecticut, State Office Building, Hartford, Conn. 06115.

[3] Department of Environmental Protection, State of New Jersey, P.O. Box 2809, Trenton, N.J. 08625.

[4] Department of Environmental Conservation, State of New York, 50 Wolf Road, Albany, N.Y. 12233.

error, a high degree of accuracy can be achieved in cases of uniform persistent flow. They further concluded that in most cases the error appears to be smaller than the plume dispersion resulting from theoretical Gaussian diffusion.

In all but one of the trajectory calculations used in this paper, persistent uniform flow existed. However, according to the second conclusion of Buoni et al. (*8*), even if the trajectory missed, it would usually be by less than the width of the plume, and the emissions from the source would still be expected to reach the target. That the winds are averaged over the boundary layer would tend to mitigate the turbulence errors, and the uniformity of the wind fields would tend to diminish the errors associated with the space-time interpolation.

Additional calculations indicate that the standard error (one sigma) involved in the trajectories used in this paper is less than 1 nautical mile per hour of travel time.

Results on July 22 and 23

Meteorology. During the day on July 20, a cold front passed through the region and was followed by a brisk northwesterly wind. The combination of a deep low-pressure system over northern Maine and a weak high-pressure system over the Ohio Valley maintained the northwest flow on the 21st. The high-pressure system had entered the United States from the Pacific Northwest on the 17th.

The high continued to move eastward on the 22nd, and the pressure gradient weakened. The wind on the morning of the 23rd was from the west and gradually backed around to the southwest. By 0200 h, the high was centered off the coast, and the pressure gradient increased due to a rapidly developing low over the western Great Lakes. These conditions produced mostly clear to partly cloudy skies over the study area with increasing wind on the 23rd.

Ozone. The period including the 22nd and 23rd of July was characterized by a sudden increase in the ozone levels on the 23rd. On July 22nd (Table I) the maximum ozone detected at the surface monitoring stations was generally less than the standard of 80 ppb and occurred between 1500–1800 h. The time is significant because no pattern for the movement of the ozone maxima could be established. This technique of moving peaks has been used to establish transport in other studies (*1, 5, 9, 10*). Since the maximum observed ozone values across the region are fairly uniform (≈60 ppb), it appears that there was little influence from local anthropogenic sources (within approximately 20–70 km) at most sites.

Flights were conducted on this day above High Point, N.J., to obtain vertical profiles of ozone at 0800, 1100, and 1600 h (Figure 2). Ozone values detected from 2000 to 9000 ft above sea level were fairly uniform, indicating the presence of a well-mixed atmosphere without local urban influence. These ozone levels should be indicative of the ozone contained in the air mass prior to entering the region. According to the trajectory in Figure 3a, possible sources of some of the ozone or its precursors could have been cities in the Midwest.

Although the large scale trajectory for 2000 h on 7/23 (Figure 3b) shows that the overall flow is still from the west-northwest and is very similar to that observed on 7/22, the ozone values approximately doubled (Table I). The reason is thought to be due to the slower transport time of the air parcels. The trajectories on 7/22 indicate a transport time of approximately 24 h from the Cleveland area to the New York area. On 7/23 the trajectory indicates a 42-h transport time. The effect of the slow movement of the air parcels would permit a greater accumulation of precursors.

As the air parcels reached the Washington, D.C.–Boston, Mass., corridor on 7/23, they began to move toward the NE (Figure 4), and the ozone increased substantially throughout the area. For the most part, the maxima occurred in New Jersey between 1600–1700 h. In Connecticut the maxima were detected progressively later with the earliest recorded in the southwestern section, and the later maxima occurred in the eastern and northern sections.

Because of the urban plume, there are several anomalies in the time of the ozone maximum. A 0800-h trajectory from New York City–Northeastern New Jersey area indicates that the morning rush hour emissions from this area arrived in the Bridgeport and New Haven areas around 1600 h. This corresponds to the time the maximum values of 245 and 315 ppb, respectively, were observed.

Table I. Surface Ozone Data, ppb

	Date ozone, hour of maximum		
Site	7/22	7/23	8/21
1. Bivalve, N.J.	90:13, 17	125:22	145:13
2. Camden, N.J.	84:17	. . .	104:13
3. Norristown, Pa.	74:15	157:17	. . .
4. Allentown, Pa.	93:12	204:16	142:17
5. Chester, N.J.	75:15	140:16	170:18
6. Scranton, Pa.	51:15	142:18	. . .
7. High Point, N.J.	58:17	130:23	. . .
8. Eisenhower Pk, N.Y.	20:23	104:16	88:16
9. Mamaronack, N.Y.	80:24	111:15	85:17
10. Babylon, N.Y.	30:22	127:17	116:16
11. Bridgeport, Conn.	85:13	245:16	98:18
12. Danbury, Conn.	65:13	150:15	120:17
13. New Haven, Conn.	65:15	315:16	105:19
14. Middletown, Conn.	55:18	275:18	105:20
15. Hartford, Conn.	55:14	145:18	75:21
16. Groton, Conn.	. . .	150:18	130:23
17. Windsor, Conn.	55:14	135:23	60:22
18. Eastford, Conn.	65:12	175:17	100:24

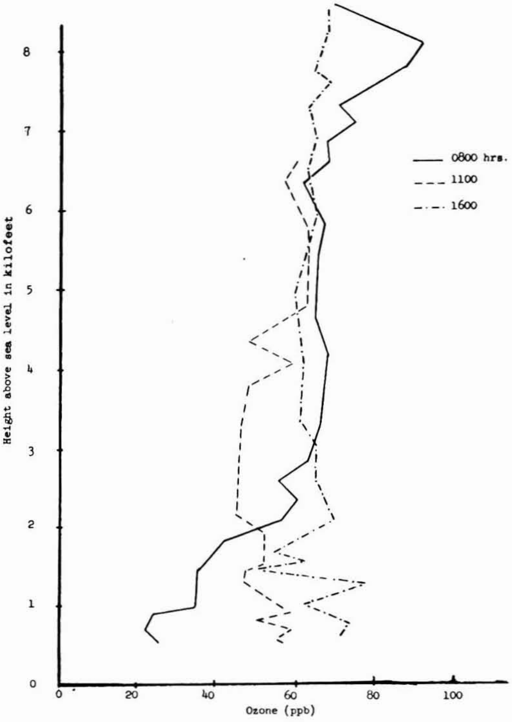

Figure 2. Vertical ozone profiles at High Point, N.J., on 7/22

Results on August 20th and 21st

Meteorology. On August 20th a high-pressure center which had been located over Lake Superior on the 19th drifted southeastward over Pennsylvania and provided a northwest flow over the region with generally fair to partly cloudy skies. The center then moved rapidly southeastward and was located off the coast in the afternoon on the 21st, and a south-southwest flow was established from the surface to the 5000-ft level. This was accompanied by an increase in moisture and a broken cloud cover.

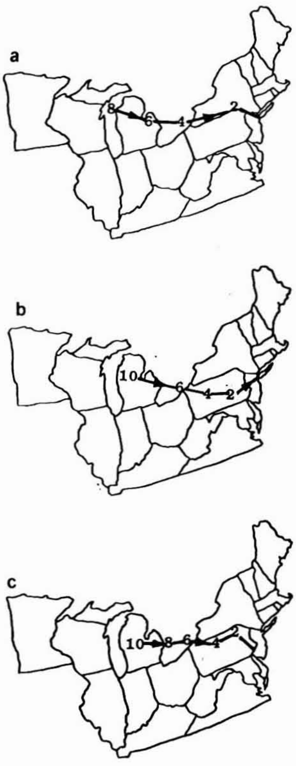

Figure 3. Long-range backward trajectories
Numbers indicate previous position at 6-h intervals. For example, 1 indicates position 6 h previous, 2 indicates 12 h previous. All time e.d.t. a: Backward from New York on 7/22 at 1400, b: backward from New York on 7/23 at 2000, c: backward from Philadelphia on 8/20 at 2000

Figure 4. Forward and backward trajectories from New York City on 7/23 at 2000

Ozone. During this period, surface ozone measurements were supplemented by three aircraft flights on the 20th and four on the 21st. These flights originated from Stratford, Conn., and Trenton, N.J., and included simultaneous triangular patterns around the Philadelphia metropolitan area and the New York metropolitan area.

The afternoon flight data collected on 8/20 are shown in Figure 5a. Upwind (to the northwest) of the two major metropolitan areas, the ozone values range between 69 and 94 ppb. The backward trajectory from Philadelphia (Figure 3c) suggests that the path of these air parcels traveled in a south-southeasterly direction through southern New York State and northern Pennsylvania. Although the trajectory passed over primarily rural areas, the ozone levels were still close to the Federal Ambient Air Quality Standard.

Downwind of the major metropolitan areas, the ozone concentrations were substantially higher. Downwind of the Philadelphia–Camden area, the maximum ozone observed on the flight was 101 ppb, while on the surface at Bivalve, 125 ppb was observed at 1600 h. The forward trajectory originating from Philadelphia on 8/20 at 0800 h confirms the direction of the local transport (Figure 6).

On the morning of the 21st, these high concentrations persisted over the extreme southern portion (Figure 5b) of the flight area but not over New York City. South of Philadelphia the ozone concentrations ranged from 107 to 122 ppb, while north of Philadelphia extending into Connecticut, they ranged from 20 to 70 ppb. Winds aloft and at the surface overnight and into the morning were light, and little transport occurred. Between 1100 and 1200 h on the 21st, the winds shifted, and a very strong south-southwest flow was established over the region from the surface to 3000 ft. During the afternoon the skies over the region were partly cloudy (ranging 0.3–0.6 cloud cover), and hazy sunshine persisted. As a result, the meteorological conditions were conducive for ozone synthesis and transport. The sequence of events is shown dramatically in Figures 6 and 7, forward trajectories for Philadelphia and Washington, respectively. The beginning of the 2000 h forward trajectory from Philadelphia on August 20th shows a small spiral circulation which lasted for 18 h. However, between 1100 and 1300 h there was rapid movement up the corridor as the southwesterly flow became firmly established.

As the wind shifted, it appeared that the air containing the high ozone over the southern part of the region moved rapidly northeastward throughout the New York City area around 1430–1500 h (Figure 5c). Since the wind shift at Philadelphia occurred around 1100 h, the air south of Philadelphia traveled about 80 miles in 3½–4 h (20–25 mph). The rapid advection from the southwest is further confirmed by radio sonde data from Ft. Totten which showed that by 2000 h the winds through the mixing layer ranged up to 50 mph from the southwest. The highest concentration of the ozone detected during the afternoon flights in Connecticut was 184 ppb recorded at 1700 h. These high concentrations were significant because in the morning the concentrations in Connecticut were only 40–60 ppb and at takeoff in the afternoon (1347 h), the concentrations were only 80–85 ppb. This suggests that the northeastward progression of high ozone values continued during the latter portions of the flight through New York City into Connecticut.

Surface observations of ozone also supported the rapid movement of the ozone front (Table I). At Ancora the ozone rose rapidly between 1100 and 1200 h from 29 to 67 ppb and reached a maximum of 101 ppb between 1200 and 1300 h. Further north in New Jersey, Bayonne reached 73 ppb between 1300 and 1400 h, and the ozone continued to rise until

1800 h when it reached 100 ppb. Traveling further northeastward, Bridgeport, Conn., reached 60 ppb at 1400 h and 90 ppb by 1500 h. In New Haven, Conn., the ozone levels did not reach 70 ppb until 1700 h and peaked with 105 ppb at 1900 h. All these sites demonstrated rapid increases in ozone, but most significant was the time at which it occurred. The correlation of the ozone peak with time along this southwest to northeast direction demonstrated the transport. In New Jersey most maxima occurred between 1300–1500 h, between 1600–1900 h in New York City and lower Connecticut, and between 2000–2400 h in northern Connecticut. The 8/20, 2000-h trajectory from Washington, D.C., indicates that the late ozone peak observed in northern Connecticut could have been partially due to precursor emissions as far south as Washington, D.C.

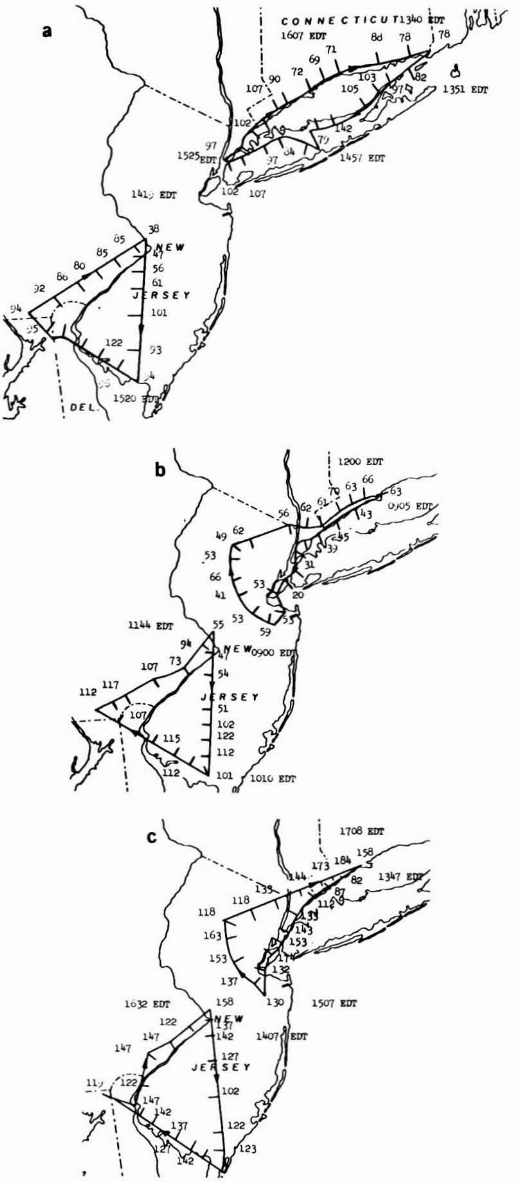

Figure 5. Aerial ozone measurements at 1000 ft above ground
Ozone in parts per billion. a: Afternoon flights on 8/20, b: morning flights on 8/21, c: afternoon flights on 8/21

The high ozone levels in Connecticut are a result of ozone synthesis from precursor emissions in the corridor plus the ozone transported into the corridor. Since the ozone levels over extreme southern New Jersey were on the order of 120 ppb, while levels of 180 ppb were observed over Connecticut, it appears that at least 60 ppb net ozone was synthesized en route.

Discussion and Conclusions

Air parcels traveling from the midwest and air parcels traveling across New York State from Canada were observed to contain substantial ozone concentrations by the time they entered the corridor extending from Washington, D.C., to Boston, Mass. On 7/22 and 7/23 the air parcels arriving from the Midwest contained approximately 60 and 130 ppb, respectively. The difference between these ozone levels is thought to be a result of the slower travel time on 7/23. On 8/20 the ozone concentrations in the air parcels which traveled through New York State were between 69 and 94 ppb.

Downwind of the Philadelphia–Camden metropolitan area and the New York City–northeastern New Jersey metropolitan area, the concentrations were higher, resulting in violations of the Federal Ambient Air Quality Standard on 7/22 and 8/20.

Because of the number of large urban areas in the corridor, the ozone problem appears to be amplified on southwest winds. (Traveling from the southwest to the northeast, the following major urban areas are located in the corridor: Washington, D.C., Baltimore, Md., Wilmington, Del., Philadelphia, Pa., Trenton, N.J., the New York City metropolitan area which includes northeastern New Jersey and southeastern Conn., and Boston, Mass.) On 7/23 the ozone concentrations in the parcels approaching the central section of the corridor from the northwest were on the order of 130 ppb. When the wind shifted to the southwest and these parcels were apparently advected up through the corridor, the ozone reached 315 ppb in southern Connecticut.

On 8/20 the winds were more northerly than on 7/22, and the wind shift from northwest to southwest was more gradual. The parcels upwind of Philadelphia contained approximately 85 ppb of ozone. Downwind of Philadelphia the concentration increased to around 100 ppb. The trajectories indicate that the parcels then traveled southwestward and then westward and entered the corridor near Washington, D.C., before moving northeastward. Upon approaching the Philadelphia area on the morning of 8/21, these air parcels contained approximately 120 ppb of ozone. By the time these parcels reached Connecticut later in the day, ozone levels of 185 ppb were observed.

The above analysis suggests an additive effect of sequential urban emissions on the ambient ozone concentration contained in an air parcel and shows the complex movement of the air parcels. Both of these observations illustrate the necessity for a multiregional control strategy for ozone precursors.

The data indicate that long-range ozone transport can be significant. A program is currently being designed to compare surface ozone data with trajectory analysis for the entire Midwestern and Northeastern sections of the U.S. during the summer of 1976. This program will also include reaction modeling.

A number of recent studies emphasizing chemical modeling (*11–13*) have sought to explain high ozone incidents in rural areas. It is our contention that detailed meteorological analysis is also essential to determining the origin of regional ozone. We have included two-dimensional trajectory analysis, ver-

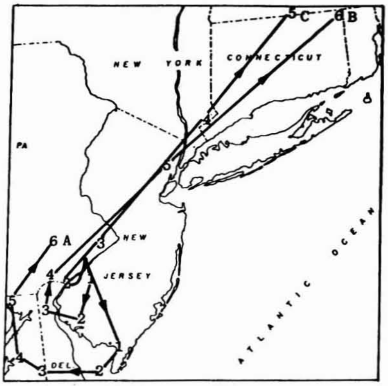

Figure 6. Forward trajectories from Philadelphia on 8/20 originating at A: 0800, B: 1400, C: 2000

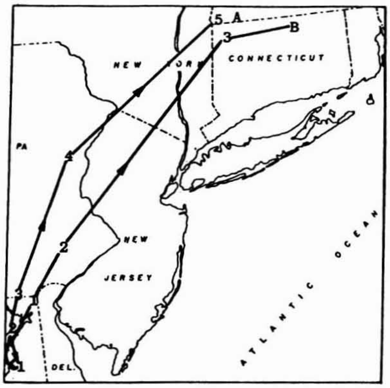

Figure 7. Forward trajectories from Washington, D.C., at A: 8/20, 2000; B: 8/21, 0800

tical aircraft sounding, and multiple ozone station observations in the present study. More definitive studies must also include cosmogenic radionuclides, three-dimensional trajectories, and stratospheric–tropospheric interaction analyses to quantify the role of stratospheric injection of ozone.

Acknowledgment

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Generation of Accurate Halocarbon Primary Standards with Permeation Tubes

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■ A number of permeation tubes for generating low concentration primary standards are tested for 18 halocarbons, and the permeation rate data are presented. In most cases, permeation tubes offer a satisfactory technique for the generation of accurate primary halocarbon standards.

Because of the serious environmental impact of ambient halocarbons (*1–3*), it has become imperative that the atmospheric concentration levels of these pollutants be determined with utmost accuracy. Halocarbons are a relatively new group of pollutants generally present in the clean atmosphere at an extremely low concentration range of about 1–1000 ppt (10^{-12} v/v) (*3*). Generation of known low-level concentration mixtures for use in development and calibration of instruments is a critical part of this research. In a recent workshop on halocarbon measurements, it was discovered that interlaboratory calibrations were uncertain by as much as a factor of two, which was considered unacceptable (*4*). However, in almost all cases, halocarbon primary standards at ppt levels were generated from pure materials with subsequent multiple dilutions. On the basis of the experience in our laboratories, at extremely low concentrations such procedures are tedious and inaccurate. The errors are due to a number of reasons, but surface sorption and heterogeneous reactions are probably the most significant at very low concentration levels. In a continuing research program to determine the atmospheric fates of halogenated compounds, permeation tubes (*5*) were used to obtain primary halocarbon standards at an error of 10% or less. Results presented here are based on experimental data obtained at SRI over a four-month period.

Experimental

Permeation tubes (3.2 in. long) for 18 halocarbons of interest, constructed from standard FEP Teflon tubing of varying thicknesses, were obtained from AID Inc. (Avondale, Pa.). The methods of manufacture and sealing of permeation tubes are proprietory (AID, private communication) but are very similar to those used by O'Keeffe and Ortman (*5*) in principle. Each permeation tube was contained in a specialized glass holder (Figure 1) which was held in a 37-L water bath (18 × 12 × 10.5 in.) maintained at 31.0 ± 0.05 °C. Permeation holders were flushed constantly with a purge gas flowing through at a rate of approximately 15 mL/min. The purge gas used was prepurified helium and was further passed through a sequence of traps containing charcoal, anhydrous calcium sulfate, and molecular sieve. The permeation holder inlet coil length was adequate to allow a helium flow rate of as much as 5 L/min over the permeation tubes without causing any heat transfer problems. All tubing materials were either aluminum or glass. Fittings were either brass Swagelok or all glass ball joints.

Permeation tubes were weighed at least once a week and in many cases twice a week on a semimicro (10^{-5} g) balance. The water bath was filled to a constant level every week with additional water at 30–32 °C to make up for evaporation losses.

Results and Discussion

Table I lists the 18 halocarbons for which the permeation tubes were tested. This table also provides information on the wall thickness used for each tube, its permeation rate in ng/min and ppb/min/L (ng = 10^{-9} g; ppb = 10^{-9} v/v) of diluent gas, its performance, and the conditioning time. In all cases, a conditioning period of up to six weeks was required before a constant permeation rate could be established. As a general rule, for a given compound the conditioning time increased with increasing wall thickness of the permeation tube.

The permeation rates were obtained statistically as slopes of the least-squares error line used to fit the weight vs. time data. The error criterion used was the standard error of the slope using the *t distribution chart* at the 95% confidence limit (*6*). The permeation rate was defined as

$$\text{Permeation rate (ng/min)} = b_1 \pm \{[v(b_1)]^{1/2} t_{1-\alpha/2}(N-2)\}$$

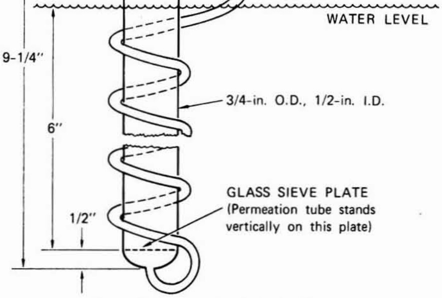

Figure 1. Permeation tube holder

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Table I. Permeation Rate Data for Halocarbon Primary Standards

Compound	Tube wall thickness,[a] in.	Permeation rate, ng/min—95% confidence limit	Mean permeation rate, ppb/L/min (25 °C, 1 atm)	Status[b]	Conditioning time, weeks
CH_3Cl	0.125	1350.0 ± 80.4	653.6	S	<1
CH_2Cl_2	0.030	580.0 ± 34.2	166.8	S	<1
$CHCl_3$	0.030	132.0 ± 12.7	27.0	S	1–2
CCl_3F (F11)	0.030	1050.0 ± 78.4	186.9	S	5–6
CH_3Br	0.030	2020.0 ± 102.2	520.2	S	1–2
CH_3I	0.030	256.6 ± 9.6	44.2	S	5–6
$COCl_2$	0.125	2460.0 ± 183.6	607.6	S	1–2
C_2H_5Cl	0.030	460.0 ± 37.8	174.4	S	1–2
CH_2CHCl	0.062	1170.0 ± 64.1	457.7	S	1–2
CH_2ClCH_2Cl	0.030	71.3 ± 6.0	17.6	S	1–2
$CHClCHCl_2$	0.030	246.0 ± 20.1	45.7	S	1–2
$CClF_2CClF_2$ (F114)	0.030	14160.0 ± 240.0	2025.6	S	1–2
CCl_2FCClF_2 (F113)	0.030	480.0 ± 49.6	62.6	S	5–6
CCl_2CCl_2[c]	0.030	64.8 ± 26.1	9.5	U	...
CCl_4[d]	0.030	...	...	U	...
CH_3CCl_3[d]	0.030	...	...	U	...
CH_2BrCH_2Br[d]	0.030	...	...	U	...
CCl_2F_2 (F12)[e]	0.125	...	...	U	...

[a] Tubes were made of FEP Teflon tubing (3.2 in. long) and were maintained at 31.0 ± 0.05 °C. For tubes with wall thickness of 0.125 in., the tube o.d. was 0.375 in.; for all others the o.d. was 0.250 in. [b] S = satisfactory; U = unsatisfactory. [c] There are short time periods when CCl_2CCl_2 permeation tubes perform satisfactorily; however, errors of less than 10% are difficult to obtain. TFE Teflon is expected to perform better and will be tested. [d] Leak rate is too slow to quantify accurately and may be used as a secondary standard. [e] Leak rate is too fast at 31 °C; new permeation tube is under test.

with a confidence interval of $100\ (1 - \alpha)\%$ where b_1 is the average permeation rate, ng/min; N is the number of data points; and $[v(b_1)]^{1/2}$ is the standard error of regression coefficient.

Note that 13 out of the 18 permeation tubes tested worked satisfactorily and resulted in errors of 10% or less. Over shorter time periods of, say a month, this error could be further reduced. From Table I, at a flow rate of 1 L/min of the diluent gas, halocarbon mixtures could be obtained in a concentration range of 17 ppb (10^{-9} v/v) to 654 ppb, depending upon the compound of interest. However, a flow rate of 5 L/min of the diluent gas was quite satisfactory, resulting in primary standards in the 3–130 ppb range.

To obtain mixtures at the ppt levels, a maximum of one dilution (dynamic or static) is necessary if one uses these tubes. In many cases, even this need not be done. We tested the response of a Perkin-Elmer 3920 gas chromatograph, equipped with two frequency-modulated electron capture (EC) detectors (Ni-63) held at 300 °C. These detectors have a linear response to halocarbons at least in the ppb to sub-ppb concentration range. Figure 2 shows the linearity of the frequency-modulated EC detector using CCl_3F injections in the 0–20 pg (pg = 10^{-12} g) sample range (a typical 10.0-mL sample of clean air at 110 ppt CCl_3F concentration contains about 6.2 pg of CCl_3F). This linearity cannot be taken for granted, however, and should be tested for each system.

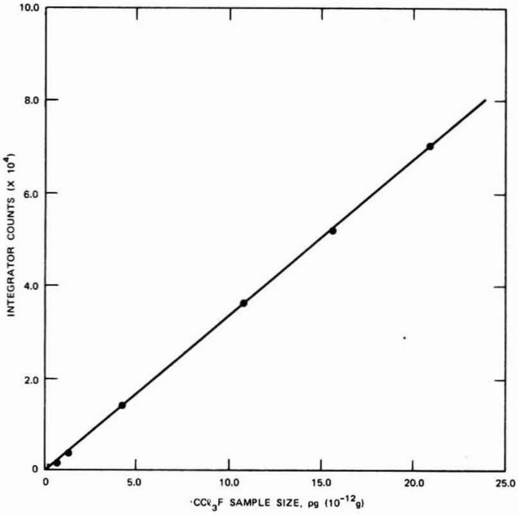

Figure 2. Demonstration of linear response of frequency-modulated EC detector

At least five out of the 18 tubes were found unsatisfactory. In the case of CCl_2CCl_2, the data were quite scattered, and errors were often as high as 50%. However, for all of the tubes where the performance was considered unsatisfactory (except CCl_2F_2), by using GC analysis the permeation rates were constant although too small to be accurately determined by gravimetric methods. All of these tubes may work satisfactorily at higher temperatures of 60–70 °C, but this creates additional problems of temperature and humidity control and was not considered an acceptable option. A literature search indicated that TFE Teflon often permeates at a rate that is about 10 times faster than FEP Teflon (7). Permeation tubes made from TFE Teflon may be found satisfactory for CCl_2CCl_2, CCl_4, CH_3CCl_3, and CH_2BrCH_2Br and are currently under study. In the case of the FEP CCl_2F_2 tube, the permeation rate was too fast, and the tube was empty in about one week. While this tube performed satisfactorily at 15 °C (permeation rate 3700 ng/min), we are in the process of testing specially designed permeation tubes ("bulb type") to allow adequate operation at 31 °C.

On the basis of our experience, if halocarbon measurements are to be conducted at errors of less than 10%, permeation tubes offer a satisfactory technique for obtaining accurate low concentration primary standards from which secondary standards could be generated and used for in-field calibrations.

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Loss of ^{14}C and ^{3}H from Liquid Scintillation Counting Vials

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■ Observations of significant losses of $^{14}C–CO_2$ and $^{3}H–H_2O$ from liquid scintillation counting solutions under certain conditions are reported, and evidence is presented for migration of these radioactive species through the walls of polyethylene counting vials.

Weimer and coworkers (*1*) recently reported that dilute aqueous solutions of $^{32}P–PO_4^{-3}$ and $^{14}C–CO_3^{-2}$ lost activity, as measured by liquid scintillation counting, because of precipitation or volatilization of the radioactive species from a dioxane base cocktail. A similar observation concerning loss of activity from dilute aqueous $^{14}C–HCO_3^-$ solutions in Aquasol (a premixed cocktail available from New England Nuclear Corp.) was reported by Iverson and coworkers (*2*). In the present communication, observations corroborating those of Weimer and Iverson with respect to volatilization of $^{14}C–CO_2$ are reported, and evidence is presented which indicates that there is appreciable migration of $^{14}C–CO_2$ and $^{3}H–H_2O$ through the walls of polyethylene counting vials. Liquid scintillation counting is a standard technique for monitoring levels of ^{3}H and ^{14}C in the environment (*3, 4*). Such environmental samples are typically of low specific activity and require long counting times. Migration of ^{3}H or ^{14}C from the counting vials can introduce serious counting errors and cause contamination of equipment.

Work in our laboratory involved the counting of dilute solutions (about 10^{-4} M) of ^{14}C as Na_2CO_3 and of ^{3}H as H_2O in commercially prepared cocktails ("Ready-Solv VI" from Beckman Instruments; "Insta-Gel" from Packard Instruments Co.) or in a dioxane base cocktail (8 g butyl-PBD, 100 g naphthalene, diluted to 1 L with dioxane). Low potassium glass vials and polyethylene "Poly-Q" vials (both from Beckman Instruments) were used to contain the counting solutions.

The dilute Na_2CO_3 solutions stored in glass vials (which were opened periodically to withdraw samples) lost ^{14}C activity at rates up to 90% in a one-month period. As Weimer suggests, this loss is probably due to volatilization of CO_2. The addition of ethanolamine in a cocktail (either Insta-Gel or Ready-Solv VI) caused the activity level to remain constant over periods of several months. This observation agrees with that of Iverson who used phenethylamine as a CO_2 absorbant. We further found that if $Ca(OH)_2$ was added so that $CaCO_3$ was formed, no loss of ^{14}C activity was observed. Thus, it appears that dilute aqueous $^{14}C–CO_3^{2-}$ solutions do not retain their activity unless some steps are taken to prevent volatilization of $^{14}CO_2$. In contrast with this experience with $^{14}CO_2$, we have observed no loss of ^{3}H activity from H_2O stored in glass vials.

Appreciable losses of ^{14}C and ^{3}H activity from unopened polyethylene vials were also observed, both from dilute aqueous solutions and from cocktails containing small aqueous samples. Typical loss rates from Insta-Gel or Ready-Solv VI spiked with 50 λ of dilute $^{14}C–Na_2CO_3$ and 50 λ of $^{3}H–H_2O$ were about 10% of the ^{3}H activity and about 50% of the ^{14}C activity in a three-day period. These loss rates were sufficiently severe to preclude the use of polyethylene vials for low activity samples requiring long counting times if either commercial cocktail were used. As noted above, loss of $^{14}CO_2$ was prevented if ethanolamine or $Ca(OH)_2$ was added to the vial contents.

Several experiments were performed to determine whether the activity was escaping from the polyethylene vials or being removed from the solution by an adsorption phenomenon. When the vial was immersed in Ready-Solv VI to a level slightly below the cap, appreciable quantities of the ^{3}H and ^{14}C from the contents of the vial appeared in a few days in the surrounding fluid. The arrangement used prevented any material leaking through or around the vial cap from getting into the cocktail surrounding the bottom part of the vial. Thus, the activities were migrating through the vial wall when it was immersed in the cocktail. To learn whether this migration would occur if the vial were not in external contact with the cocktail, a vial loaded with Ready-Solv VI and ^{14}C and ^{3}H aqueous spikes was placed in a closed vessel containing a reservoir of Ready-Solv VI which was not in contact with the vial. After standing at room temperature for five days, both ^{14}C and ^{3}H were found in the cocktail in the reservoir. The results of these experiments led us to conclude that the previously observed losses of activity from the polyethylene vials were due to migration of the radioactive material through the walls of the vials. Apparently, this migration is in part a

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function of the cocktail composition, because we did not observe loss of ^{14}C or ^{3}H activity from aqueous solutions mixed with the dioxane base cocktail described above.

Our experience indicates that with certain cocktails, polyethylene vials may not be satisfactory containers. Care should be exercised in the selection of counting cocktails and vials to avoid measurement errors and contamination problems due to migration of activity through the vial walls.

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Further Developments in Oxidation of Methane Traces with Radiofrequency Discharge

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■ The radiofrequency discharge, previously shown to oxidize trace levels of methane in oxygen, was studied with contaminated air at 50, 600, and 760 torr. As with oxygen, the concentration of methane traces could be reduced by several orders of magnitude, and no organic reaction products were detected in the effluent; however, substantial concentrations of NO_x (0.1–6%) were formed during treatment. The concentration of NO_x was decreased by using a large diameter electrode. There is evidence that the process will oxidize N_2 and NO as well as organic impurities in oxygen or oxygen/inert gas atmospheres.

Recently, we reported that a radiofrequency glow discharge could be used to effect almost complete removal of contaminative methane traces from oxygen (*1*) over a wide range of pressure (50 torr to 1 atm) and concentration (70–8000 ppm). Unlike many other methods of purification, the fraction of methane removed was insensitive to concentration within this range, even at high degrees of removal (99%) and very low concentration. The device was proposed as a means for removing trace contaminants from closed environments such as spacecraft or from "zero gas" used as a standard for monitoring equipment.

In the previous investigation, only contaminated oxygen was studied. We have now extended that work to air, which contains methane traces, and report the formation of NO_x in air which is so treated. An analysis of the thin film which forms on the reactor wall (*1*) is also given.

Experimental

The basic apparatus and reactor have been described in detail (*1, 2*). A mixture of dry air or dry oxygen and methane is formed in a dynamic dilution system (Figure 1) and metered into the reactor. The reactants and products have been analyzed by use of a gas chromatograph with a dual thermal conductivity/flame ionization detector.

In addition to this analysis, the product stream from the air discharges was routinely analyzed for total nitric oxides. For this purpose, a sample of the reactor effluent was collected in an evacuated bomb containing 25 cm^3 of 0.003 N H_2SO_4/0.3% H_2O_2 solution and chilled to 0 °C with an ice bath. The samples collected at subambient pressure were back-filled to atmospheric pressure with oxygen and set aside for 24 h. NO and NO_2 are thus converted into nitrate in solution. To each sample was added 0.5 ml of 5 M KF ionic strength adjuster, and an Orion Model 93-07 ion selective electrode was used to determine the nitrate concentration.

An attempt was made to analyze ozone from two oxygen discharges at atmospheric pressure by iodometry (Table I). The treated stream passed through an extra coarse gas dispersion tube immersed in 300 ml of 0.2 M KI solution buffered with 0.1 M boric acid. The iodine thus formed was titrated with 0.1 N $Na_2S_2O_3$.

During these experiments the TC filament detector was operated at high current giving increased sensitivity over that of our previous investigation. This enabled us to detect and thus confirm the presence of CO_2, CH_4, and NO_2 with the TC detector, although these chromatograms were not quantitative or entirely reproducible due to the consequent oxidation of the filament.

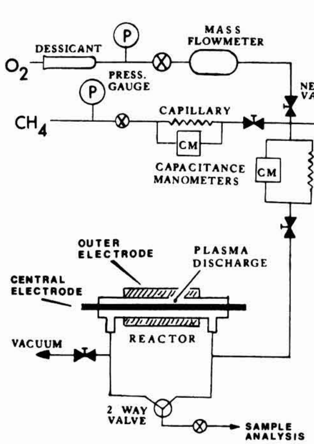

Figure 1. Apparatus

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Results

The degrees of methane removal achieved in air (Figure 2) are comparable to those obtained using an oxygen atmosphere. However, nitric oxides were formed in air, and the observed concentrations (Figures 3 and 4) would be unacceptable for an atmospheric purification process. The iodometric analyses were positive (Table I), but not large enough to indicate the presence of ozone (see Discussion section). In any case, traces of ozone would not detract from the utility of this process since they are readily removed by heterogeneous catalytic decomposition.

The chemical analysis did not differentiate between various nitric oxides (NO, NO_2, etc.). At 600 and 760 torr, the bomb samples generally were amber in color which indicates NO_2; however, at the observed levels (0.1–7% total NO_x), NO is rapidly oxidized to NO_2. Thus, the presence of NO_2 in the effluent air stream does not imply that it is produced within the discharge.

As was previously reported for oxygen (*1*), the inner glass wall of the outer electrode developed a thin, transparent, brownish film which appeared to quickly attain a steady-state thickness. This coating was visibly denser when it formed in the air discharges, especially at 600 and 760 torr, but it tended to lighten when an oxygen discharge was subsequently operated. As before, the electrical operating characteristics were constant with time throughout each experiment (20 min to 3 h) and were insensitive to flow rate and methane concentration.

A quartz reactor unit used in the experiments with a 0.079-cm electrode was sectioned to characterize the film formed on the inside surface. Samples of the inner quartz wall were taken from two different longitudinal locations and were scanned for carbon, chromium, iron, nitrogen, and silicon with a Hewlett-Packard Model 5950A x-ray photoelectron spectrometer. One section of the tube was taken from a location which was always in the discharge zone and where the tint of the film was darkest. Another section was taken from a position where the edge of the plasma zone had been and where the film was faintest. Except for silicon, the above elements were detected in almost the same abundance ratio in both samples (C:Cr:Fe:N = 1.3:0.77:3.6:0.32). The lighter sample indicated silicon in a relative abundance of 0.13 (referred to the above), whereas the more intense signal from the darker sample did not show a noticeable silicon peak. There were two oxidized forms of carbon (286.4 and 288.4 eV), as well as a principal peak at 285.0 eV (relative abundance 0.14:0.22:1).

Table I. Nominal Residence Times for Typical Conditions[a]

	50 W, ms	240 W, ms
50 Torr $F = 6875$ cm^3/min	4–10	10–10
600 Torr $F = 533$ cm^3/min	3–6	15–60
760 Torr $F = 452$ cm^3/min	No data	20–80

[a] $\tau = V/F$ was computed using approximate volumes, V, filled by visible discharge with a 0.318-cm electrode and a feed rate of 420 cm^3-stp/min at room temperature and discharge pressure (F). Lower figures are for air, and higher values for oxygen. To a good approximation, τ was inversely proportional to feed rate with other variables held constant.

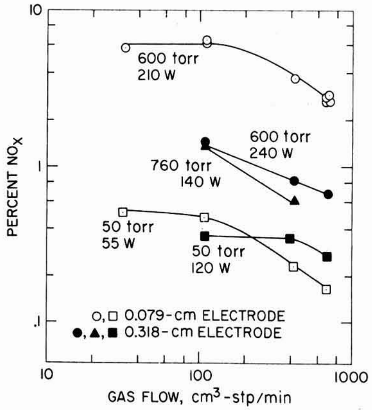

Figure 3. Nitric oxides formation vs. air flow rate

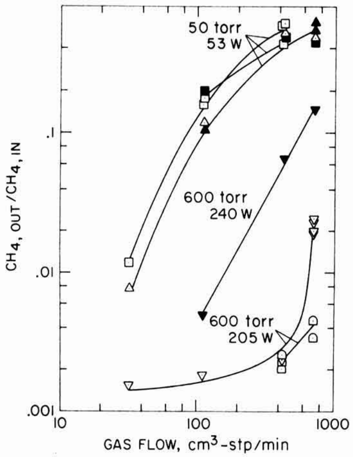

Figure 2. Methane removal vs. flow rate

(△, ▲, ▽) air; (□, ■, ⊙) oxygen. Open points for 0.079-cm central electrode. Shaded points (▲, ■) denote 0.318-cm central electrode

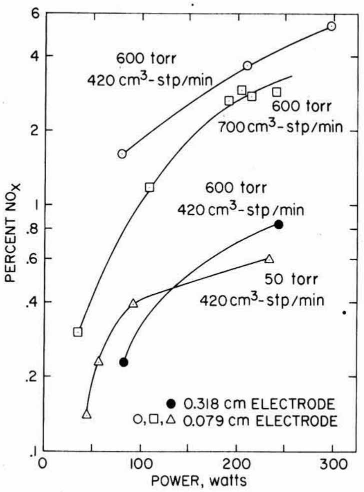

Figure 4. Nitric oxides formation vs. power

Discussion

The presence of carbon and nitrogen is consistent with our previous identification of the film as a polymeric deposit (*1*); the nitrogen apparently was incorporated during the air discharges. Evidently, there is a plasma-chemical mechanism whereby iron and chromium are transported from the central electrode to the quartz wall (and in the reverse direction since the film thickness does not increase indefinitely).

The nitric oxide concentration increases with decreasing flow rate, increasing pressure (hence, increasing residence time), and increasing power, but appears to approach a steady concentration as the residence time is increased at a fixed pressure and power level. Nominal residence times (based on room temperature and the actual volume of active discharge—see ref. *1*) for typical conditions are presented in Table I. Since the electrode size does not have much effect on the degree of methane oxidation (*1*), a large electrode diameter can be used to minimize the production of nitric oxides in the presence of nitrogen.

NO_x is an undesirable by-product when the objective is to remove trace contaminants from air; however, the oxidation of nitrogen is a positive result when applying the process to produce "zero" oxygen or for the purification of oxygen/inert gas atmospheres in the absence of nitrogen. Since a minor component, methane, and a major constituent, nitrogen, are both oxidized by the discharge, it seems reasonable to expect that traces of nitrogen will also be oxidized.

The oxygen used in these experiments (aviator's breathing oxygen) contained approximately 0.05% N_2 (Ar ~ 0.2%, CH_4 ~ 14 ppm, water ~ 3.2 ppm, CO_2 ~ 0.8 ppm, N_2O ~ 0.6 ppm), but we made no attempt to measure nitric oxides in the effluent of the treated oxygen. Nevertheless, the studies of Malt'sev, Eremin, and their coworkers (*3, 4*) provide support for our suggestion that nitrogen will be oxidized when it is a minor component of the feed stream. These investigators found that NO_x (reported as NO) was formed from N_2/O_2 mixtures in glow discharges at low pressure (50–400 torr) and that the fraction of oxidized N_2 increased from about 4% when $N_2{:}O_2 = 4$ to 25% when $N_2{:}O_2 = 0.25$.

The iodometric analyses of the treated oxygen stream (Table II) indicates the presence of NO_2 and/or O_3. NO is nearly insoluble and would not be detected by this analysis. However, NO_2 will produce a response equivalent to 10–30% of an equimolar quantity of ozone (*5*). The complete oxidation of the N_2 impurity in aviator's breathing oxygen would produce $[NO_2] \sim 0.1\%$ and thereby give an iodometric response equivalent to 0.01–0.03% of O_3, the range of our results. If nitrogen emerged from the reactor as NO and if $[O_3] \sim 0.01\%$, this NO would be entirely converted to NO_2 by the fast reaction ($k_{300} = 1.65 \times 10^{-14}$ cm^3/s):

$$O_3 + NO = NO_2 + O_2 \qquad (1)$$

or to higher oxides (*6*). We may therefore exclude the possibility that O_3 and NO were both present. During these absorption experiments the reactor effluent was vented into the laboratory, but the odor of ozone was not detected as it almost certainly would have been at the concentrations in Table I. Therefore, the data are consistent with 300–1000 ppm NO_2 in the effluent. The probable presence of NO_2 rather than NO is significant because the latter is relatively inert, whereas NO_2 and higher oxides are effectively absorbed by certain molecular sieves (*7–9*). Thus, the discharge may be useful for removing NO as well via oxidation to NO_2.

Table II. Oxidant Analysis at 1 atm and 700 cc-stp/min

Power, W	Equivalent ozone concn, %
102	0.015
230	0.028

Conclusions

Contaminative methane traces are oxidized in air as well as in oxygen. Unfortunately, the removal is accompanied by the formation of NO_x; unless this by-product can be minimized by changes in reactor design and operating conditions, the utility of the discharge purification process will be restricted to atmospheres in which nitrogen is not a major component. This oxidation of nitrogen can be a useful result in applying the process to produce "zero" oxygen or for the purification of oxygen/inert gas atmospheres.

Acknowledgment

We thank James C. Carver for performing the ESCA analyses.

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INDUSTRY TRENDS

Combustion Engineering, Inc. (C-E) and Pollution Control-Walther, Inc., have signed an agreement by which C-E will acquire the latter firm. Maximum aggregate purchase price is about $5.35 million.

Nuclear Engineering Co., Inc. (Louisville, Ky.) has established a National Chemical and Toxic Waste Division. The company operates three Class I chemical and toxic waste disposal sites in the U.S.

Peabody International Corp. (formerly Peabody Galion) has reached agreement in principle to merge with Weatherford International Inc. (Houston, Tex.), specialists in oil field equipment/services.

Hayden, Harding & Buchanan Inc. (Boston, Mass.) announced that a $20 million water pollution control facility it designed for the City of Manchester, N.H., is a nominee for the 1977 Outstanding Civil Engineering Achievement Award of the American Society of Civil Engineers.

Nalco Environmental Sciences (Northbrook, Ill.), an operating group of Nalco Chemical Co., has opened its fourth U.S. Regional Laboratory at Burlingame, Calif., in the San Francisco Bay area.

Metcalf & Eddy is designing a plant for the City of Marlborough, Maine, which will use ozone instead of chlorine to disinfect sanitary wastewater. Ozone for the 500 000-gpd plant will be generated by an electron beam accelerator.

A **Camp Dresser & McKee** study on New York–New Jersey Wastewater Sludge Management won for the firm the Consulting Engineers Council of New England award for engineering excellence.

A **Manufacturing Chemists Association** (Washington, D.C.) spokesman told a Senate subcommittee that some provisions of the Clean Air Act "are rapidly leading our nation to untimely and overly restrictive limitations on industrial growth."

The **Electric Power Research Institute** (Palo Alto, Calif.) has awarded Babcock & Wilcox Co. (Alliance, Ohio) $1.6 million to devise new methods for reducing NO_x emissions at coal-burning power plants.

The **Bionetics Corp.** (Hampton, Va.) received a potential $350 000 contract with the EPA to operate an analytical support laboratory at the EPA Environmental Research Center in Athens, Ga.

Air Pollution Industries, Inc. (Englewood, N.J.) will furnish a venturi scrubber system for dust removal for an existing 250-tpd black liquor recovery boiler at Weyerhaeuser Co. (Pine Bluff, Ark.).

Environmental Research & Technology, Inc. (Concord, Mass.) has won a $160 000 contract from the U.S. Bureau of Land Management to analyze oceanographic data and make recommendations concerning Atlantic Ocean Outer Continental Shelf oil/gas development.

Bethlehem Steel Corp. has broken ground for the largest portion of a $36 million two-phase water pollution control project at Bethlehem, Pa. The facility will treat 11 000 gpm.

Southern California Edison Co. says that solar devices can become important energy savers, but much more research and "massive subsidies" are needed to support immediate major market penetration.

Goodyear (Akron, Ohio) is providing technical assistance in using old tires as part of a new artificial reef near Marathon, in the Florida Keys.

The **Atomic Industrial Forum** (Washington, D.C.) noted that nuclear plants produced electricity to meet needs generated by the recent very cold winter, unhampered by the cold, sudden price rises, or fuel scarcity.

Drew Chemical Corp. (Parsippany, N.J.) is part of a consortium developing an economical cost-oil fuel mixture aimed at softening the effects of rising oil prices. General Motors organized the consortium.

Scott Environmental Technology, Inc. (San Bernardino, Calif.) has an EPA contract to assess the adequacy of current state-of-the-art continuous source level hydrogen sulfide monitoring systems.

The **Chemical Industry Institute of Toxicology** (Research Triangle Park, N.C.) announced that Amoco Chemical Corp. (Naperville, Ill.) has joined it. The institute thus has 27 company members.

United Air Specialists, Inc. (Cincinnati, Ohio) has merged with Allied Air Products Co., Inc. (Newberg, Oreg.), an energy conservation equipment maker. Terms were 292 000 shares of United common stock for all share of Allied.

The **Raymond/Bartlett-Snow/Ehrsam Division** of **C-E Process Equipment** (Chicago) will install a system to produce fertilizer from sewage sludge for Talon Construction Co. (Addison, Tex.), which, in turn, has a contract to do so from the City of Fort Smith, Ark.

NUS Corp. (Rockville, Md.) has announced the opening of an office at Clear Lake City, Tex., in order to expand NUS' regional operations, and reinforce the company's long-term commitment to the Houston area.

The **Solar Energy Industries Association** (Washington, D.C.) announced that solar energy installation guidelines are now being included in national air conditioning standards.

The **Carborundum Co.,** Filter Media Division (Niagara Falls, N.Y.) has received the John C. Vaaler Award (Top Honors) for a seamless tube filter bag for air pollution control. The award is sponsored by *Chemical Processing Magazine*.

Combustion Equipment Associates, Inc. told security analysts that their ECO-FUEL II will run 16 million Btu/t, or more, about equivalent to Montana coal. Sulfur content is 0.3–0.5%; ash, 7%. The fuel is immediately available in the eastern U.S.

General Electric has received a $6.7 million ERDA contract to evaluate and develop materials for very high temperature reactors, and other components of gas-cooled nuclear reactors.

Research-Cottrell has received a contract to design and fabricate an electrostatic precipitator (336 815 acfm, 454 °F) for the Tennessee River Pulp & Paper Co. Mill at Counce, Tenn. Guaranteed efficiency is 99.65%.

Stanley Consultants, Inc. (Muscatine, Iowa) will provide engineering design and specifications for new municipal sewage treatment facilities for the town of Dayton, Ind.

The **Sverdrup Corp.** has been formed at St. Louis, Mo., to streamline environmental and other services the 4400-employee firm performs. It is an outgrowth of Sverdrup & Parcel and Associates, Inc., which becomes an operating company of the new firm.

American Air Filter Co., Inc. will provide an AAF-Elex Electrostatic precipitator, valued at about $6 million, to Saskatchewan Power Corp. The 1.2 million cfm precipitator will be installed on a turn-key basis.

Castle Associates (Deerfield, Ill.), which is in the field of sound-level meters, has opened two new offices—one in Chicago, and one near Paris, France—and is also making special models to meet specific needs.

MikroPul Corp. (Summit, N.J.), a subsidiary of U.S. Filter Corp., will supply two MikroPul fabric dust collection systems, valued at about $1.11 million, to the Mapleton, Ill. foundry of Caterpillar Tractor.

Marine Construction & Design Co. (Seattle, Wash.) is installing five Model 101 stationary "oil skimmers" to remove oil from water flows at Mississippi Power & Light Co. They will remove No. 6, lubricating, and hydraulic oils.

Lear Siegler, Inc.'s Environmental Technology Division (Englewood, Colo.) has announced the availability of a gas cooling system that permits the recovery of thermal energy.

AVCO Everett Research Laboratory, Inc. (Everett, Maine) has a $1.7 million ERDA contract to produce conceptual design and engineering specifications for a coal-fueled magnetohydrodynamic (MHD) test facility to be located in Montana.

The **National Association of Recycling Industries, Inc.** (New York, N.Y.) has asked a federal court to overturn a recent Interstate Commerce Commission decision which said that freight rates on recycled materials are not discriminatory.

Monsanto Enviro-Chem Systems, Inc. (St. Louis, Mo.) has introduced sulfuric acid plant designs to help steel producers control SO_2 emissions from coking operations, and reduce plant costs, as well.

Jacobs Engineering Co. has received a contract for detailed engineering of two multimillion-dollar SO_2 sludge waste treatment facilities from IU Conversion Systems. Jacobs is headquartered in Santa Monica, Calif.

Gelman Instrument Co. (Ann Arbor, Mich.) has formed a new Air Analysis Division. Gelman is in the filtration and analysis fields, and also makes laboratory diagnostic equipment and supplies.

Radian Corp. (Austin, Tex.) has a $98 653 contract from ERDA to advise on selection of proper, corrosion-resistant materials for use in the development of geothermal energy.

URS Corp. (San Mateo, Calif.) has acquired McPhee, Smith Rosenstein Engineers (Norwood, N.J.) for $1.1 million in cash and notes. The engineering firm specializes in planning/design of wastewater treatment facilities.

Neptune Microfloc, Inc. has a $585 000 contract to supply two water treatment systems to Fluor Nederland, B.V., for use in gas conditioning plants in Iran.

Penberthy Houdaille Water and Wastewater Systems Division of Houdaille Industries is henceforth to be known as Pentech Houdaille, and is located at Cedar Falls, Iowa.

Hager Laboratories, Inc. (Denver, Colo.) now offers complete analytical services, by mail, in the field of occupational health. Services cover asbestos, silica, solvent vapor, dust, metals, and other analyses. Special mailers are furnished.

NEW PRODUCTS

O_2 analyzer remote controller
The remote control unit allows the user to operate the oxygen analyzer from a central control room. The unit allows the user to activate automatic or manual calibrations and range selections of 0–2.5%, 0–10%, or 0–25% oxygen. Lear Siegler **101**

Airborne asbestos sampler
The personal sampling kit contains all the equipment needed for on-site assessment of individual workers' exposure to airborne asbestos dust. C.F. Casella & Company Ltd. (London) **102**

Automatic weighing systems
The in-line conveyor belt scales allow accurate measurement of material loading on the belt regardless of volume or belt speed. The systems are especially designed to meet the requirements of wastewater and sewage treatment plants. AutoWeigh, Inc. **103**

Gas chromatograph
The microprocessor-controlled gas chromatograph can store and execute up to 15 user-variable programs and have three fixed programs that provide for pneumatic control element routines. All parameters are programmable on a time basis. Packard Instrument Co. **104**

Carcinogen glove box
The enclosure is equipped with both HEPA and charcoal exhaust filters and is especially designed for handling gaseous radioisotope and carcinogenic materials. The exterior controls, glove ports and access door have been engineered to promote comfort and efficiency for the operator. Labconco Corp. **105**

Chlorine dioxide generator
Suitable for use as a disinfectant on high-quality secondary effluents and tertiary effluents whose operating limits are 25–150 psi at 35–70 °F. Generating capacities are 10, 25, 50, 100, 200, 500 and 1000 lb/day chlorine dioxide. Sodium chlorite metering pumps are furnished in accordance with generator's capacity. The sodium chlorite tank capacity varies with the size of the metering pump, and ranges from 105–500 gal. CIFEC (10, Avenue de la Porte Molitor, 75016 Paris, France) **106**

Fog generator
Produces a low-hanging, long-lasting dense fog, mist or fast surface spray for control of disease-carrying insects. These devices may be used for fogging sewers and testing boilers and pipelines for leaks. TIFA, Ltd. **107**

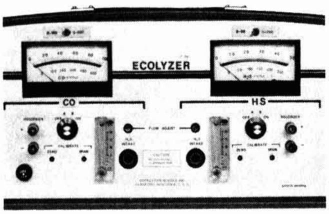
Scale/corrosion inhibitor
The product is designed for use in open evaporative recirculating cooling systems. It comes as a dark brown liquid that is soluble in water in all proportions. The pH of a 1% solution is 11.9. It is normally used in dosages of 25–75 ppm. Mogul **108**

Sound level meter
The unit is portable and battery operated and features A and C weighing scales with fast and slow meter response. The measuring range is 36–120 dBA with eight selective increments. Thermo-Systems **109**

IR spectrometer
This unit functions as an industrial monitor-analyzer with the ability to act as a mobile field test system. It can specifically function as a toxic gas detector and a control area monitor, but can also operate as a research laboratory IR spectral analyzer. EOCOM **110**

Photoacoustic spectrometer
The manufacturer claims that this instrument can measure the absorption spectra of opaque solids and liquids. Human skin, blood smear, crystals, leaves and metal powders can now be routinely analyzed. Princeton Applied Research **111**

Hydrographic surveying system
The system measures and automatically displays horizontal, slope and vertical distances; it has the capacity to measure horizontal and zenith angles. Hewlett-Packard **112**



Toxic gas analyzer
The portable instrument can measure carbon monoxide and H_2S simultaneously or independently in the presence of a wide range of interfering gases. Detection ranges for CO are 0–50 and 0–10 000 ppm; for H_2S, 0–10 and 0–5000 ppm. Energetics Science **113**

Monitoring station
The portable unit permits up to 27 different sensors to measure wind, temperature, precipitation, radiation and pressure. The collected digital data are stored until transmitted by phone, radio or hardwire. Towner Systems **114**

Air sampling/monitoring system
The system consists of five-layer impervious gas-sampling bags and a small sampling pump. Sampling bags are available in sizes ranging from 2–170 liters. The pump's normal rate varies from 450–7200 pulses/h. Calibrated Instruments **115**

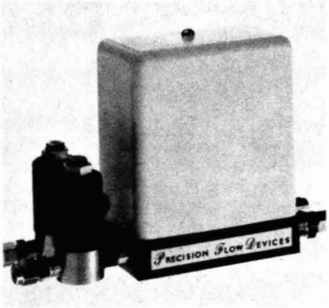
Micro-flowmeter
This liquid flowmeter utilizes a ring-shaped rotor less than 1/16-in. in diameter that floats freely in suspension in a vortex chamber. Flow range is less than 1 mL/min to 150 mL/min. Bearingless Flowmeter Company **116**

Flame photometric detector
The unit detects total sulfur in up to 10 sulfur compounds present simultaneously in a gaseous stream in concentrations as low as 5 ppb. It is designed for use with systems monitoring or controlling air pollution. Process Analyzers **117**

Wet scrubber
The electrified unit combines electrostatic precipitation of sub-micron particles with conventional scrubbing of particles over 1 micron. The system complies with federal regulations that cover particulate emissions and exhaust opacity. RP Industries **118**

Integrating flowmeter
Accurately measures and records open channel flow in manholes and streams. It can be used as a portable unit or off of line power for stationary use. It is capable of triggering automatic samplers at intervals, based on volume. ISCO **119**

Toggle valves
Valves are designed to provide instant flow control on chromatographs and mass spectrometers. Orifice sizes are 1/8 in. and 1/4 in.; maximum operating pressure is 800 psig; temperature range is −40 to 200 °F. Hoke **120**



Mass flow controller
This dual-channel flow controller both measures and controls the mass flow rate of gases. Control accuracy is within ±0.2% of setpoint; full-scale accuracy is ±2%. The flow channels function together or independently. Precision Flow Devices **121**

Gas chromatograph
The column oven cover contains dual injection ports, detectors and columns. The modular instrument is designed to permit the separation of low-boiling compounds without the need for sub-ambient accessories. Packard Instrument Company **122**

Air velocity meter
Designed to detect and measure low-velocity air flows, the unit also indicates air temperature up to 50 °C. Air velocity ranges are 0–5 m/s and 0–0.5 m/s. Aikenwood **123**

Sensor blower weather cover
This system operates in conjunction with the company's opacity monitoring system. The enclosure gives the stack-mounted transmissometer added weather protection; a filter assembly in the base of the enclosure assures clean filtered air for the regenerative blower air purge system. Dynatron **124**

Discharge control system
This system is designed to prevent the discharge of oily bilge water into inland waterways. It is intended for use on ships 26 ft and longer. Keene **125**

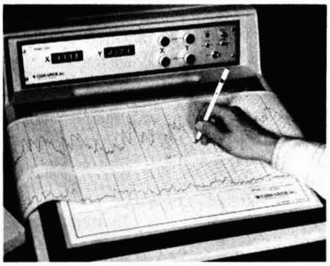
Ion flux meter
The battery-operated instrument measures air ion-flux density (current flow) with a range of 1×10^{-4} to 1×10^{-13} amperes. It is bipolar, input protected and operates from −5 to +50 °C. It finds application in air monitoring studies. Santek **126**

Scanning calorimeter
The differential scanning calorimetry is a rapid, simple, thermal analytical device, which in combination with the company's thermal analyzer measures the heat flow into or out of materials and determines at what temperature physical or chemical changes occur. The sensitivity of the instrument is 0.005 mcal/s/in. Du Pont **127**

Vertical elutriator
This air monitoring instrument is designed to determine concentrations of airborne cotton dust to NIOSH specifications. General Metal Works **128**

AA spectrophotometer
The double-beam model provides baseline stability, and ease of background correction. The all-reflective optical system permits constant focus at all wavelengths. The double-beam unit automatically compensates for variations in source intensity and electronic drift. Varian Instrument **129**

Cooling system controls
The panels provide inhibitor feed control in proportion to makeup, in addition to pH and total dissolved solids (TDS) control. The panels prevent scale formation that can reduce heat-transfer efficiency. Each panel includes a TDS and pH controller, with indicating meters and chart recorders. The Mogul Corp. **130**



Digitizer system
The pressure-sensitive digitizer tablet interfaces with a variety of minicomputers, calculators and terminals. Information from graphs, strip charts and photographs can be entered directly into data processing systems for on-line reduction and storage of data. Elographics **131**

Dust collectors
The pulse-jet-type collector's capacity ranges from 16 filter bags to 144 bags, from 151–1696 ft^2. There are no moving parts and there is a positive cleaning cycle. The collector can operate under temperatures ranging from 270–450 °F, depending on the fabric construction of the bags. Peabody International **134**

Data acquisition expander
These modules are designed to increase the input capacity of 16-channel and 8-channel acquisition systems to 48 single-ended and 24 differential channels, respectively. Datel Systems **135**

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

NEW LITERATURE

Gas chromatography. Brochure describes a photoionization detector that can be used on any gas chromatograph. Applications include detection of sulfur- and nitrogen-based compounds, organometallics, hydrogen sulfide, and others. HNU Systems, Inc. **151**

Reverse osmosis. Literature tells about new "Sepralator," a spiral-wound membrane module, for reverse osmosis and ultrafiltration applications. Drawings and descriptions are given. Osmonics, Inc. **152**

Energy-saving scrubber. Bulletin 401 describes venturi scrubber with high efficiency and low power consumption and operating costs. Capacities and dimensions are given. The W. S. Sly Manufacturing Co. **153**

Vacuum filters. Bulletin 315-412 covers rotary drum vacuum filters to assure efficient solids dewatering, dryer cakes, and greater filtration rates. Design data covers 12 types of sludge. Envirex. **154**

Liquid chromatography. Comprehensive brochure lists monitors and accessories for liquid chromatography, and describes a spectrofluorometric detector. Spectrophotometers are also listed. Schoeffel Instrument Corp. **155**

Sludge processing. Brochure describes SLUDG-A-TRON IV Centrifuge for municipal, industrial, and other sludge processing. Noise levels meet and better OSHA standards. The Western States Machine Co. **156**

PCB detection. Application Note AN 176-20 discusses PCB detection by gas chromatograph/mass spectrometer, especially in foodstuffs and human tissue. Hewlett-Packard **157**

Nuclear equipment. Catalog lists nuclear instruments, equipment, devices, and accessories, and covers particulates, aerosols, decontamination, radioactive gas, and medical devices. Atomic Products Corp. **158**

Aerators. Brochure describes "Xodar 360" submarine and bottom diffusion-type aerators for efficient oxygen-to-water transfer. Mechanisms are discussed. Xodar Corp. **159**

Environmental services. Booklet lists environmental services, typical projects, and clients. Clayton Environmental Consultants, Inc., a service of Marsh & McLennan, Inc. **160**

Filter silencers. Product Catalog No. 242 illustrates and describes small air filters and filter silencers in a wide range of sizes. Capacity 15–1050 cfm, particle size to 10 μ, 93% efficiency. Universal Silencer **161**

IR spectrometer. Brochure describes Series 7000 FT-IR System for infrared (IR) spectrometry. Very easy operation. Accessories are also listed. Nicolet Instrument Corp. **162**

Filters. Cleanable filter guide provides comprehensive data for the selection, specification, and application of stainless steel filters. Applications in pharmaceuticals, nuclear power, coal gasification, and others. Pall Trinity Micro Corp. **163**

Water test kits. Education Catalog lists test kits and apparatus for almost any aquatic ecology educational program in the classroom or field. Hach Chemical Co. **164**

Flying insect control. Form No. 77-12 describes control for flying insects that meets OSHA rules, and has no down-time, residue, reapplication, or inconvenience. Insects are electrocuted. Flintrol, Inc. **165**

Pure water. Bulletin describes reverse osmosis systems that handle 800 and 1600 gpd. Capital/operating costs are reduced. Millipore Corp. **166**

H_2S monitor. Literature describes ECOLYZER 6000, which can respond to hydrogen sulfide (H_2S) within 30 s, even in presence of interfering gases. Detects 0–320 ppm. Energetics Sciences, Inc. **167**

Filtration. Brochure, " 'Nomex' For Air Filtration," describes industrial air filtration materials, and their properties and performance. Guidelines are given for filter media selection. Du Pont **168**

Fabric shaker. Technical Bulletin MT-2 describes shaker that removes and captures material from fabric filters. Clean air is exhausted to the atmosphere. MikroPul Corp. **169**

Sewer rehabilitation. Brochure tells how polyethylene lines are the most economical and effective way to rehabilitate deteriorating sewer lines. Case histories are given. Ace Pipe Cleaning, Inc. **170**

Laboratory safety. Original, unpublished overview by T. W. Edwards includes helpful list of OSHA contacts. Article on pH meters is also available. Markson Sciences Inc. **171**

Filter/carbon purifier. Description and application information discuss Submerged SUBX Filter System with a carbon treatment system added to remove damaging organic impurities. Sethco Mfg. Corp. **172**

Industrial safety. Catalog lists 4000 safety products that meet OSHA specifications. These cover noise, fumes, dust, and many other regulated substances and conditions. Industrial Safety and Security Co. **173**

Environmental newsletter. Newsletter briefly lists new procedures for analyzing pollutants in air and water, with organics analysis down to parts-per-trillion level. Ask for "Environmental Notes." Waters Associates **174**

Oil skimming. Brochure describes oil spill skimmers ranging 28–120 ft. In use by contractors, oil companies, and U.S. Navy; one type usable in open ocean. Marine Construction & Design Co. **175**

Sludge disposal. Bulletin R-1 describes a new line of thermal sludge destructors that oxidize wastes to inert ash without polluting the atmosphere. Maximum capacity exceeds 300 gal/h. Met-Pro Systems, Inc. **176**

Plant models. Information describes a Flocpress mobile demonstration plant for dewatering relatively dilute sludge. It helps customers evaluate the best attacks on sludge. Infilco Degremont Inc. **177**

Ocean instruments. New 1977 catalog lists buoys, sounding equipment, biological accessories, a hydrocarbon profiler, and other oceanographic instruments and systems. InterOcean Systems, Inc. **178**

Control weirs. Technical brochure describes popular types of fabricated slide gates and control weirs, with features, specifications, and applications. Coldwell-Wilcox Co. **192**

Glassware washers. Catalog AIC-2516 lists fully automatic glassware washers, controls, water systems, and sterilizers. AMSCO **193**

Plastic balls. Plastic balls have application for valves, irrigation, water treatment, paper mills, and other uses. High strength. Can sometimes replace metal balls; many usable from cryogenic levels up to above 500 °F. Chemplast, Inc. **194**

Water pollution control. New edition of brochure describes company's consulting/designing services in water pollution control. Representative projects are listed. WESTON Environmental Consultants-Designers **195**

Fuel cells. Reports EM-335 and EM-336 discuss technology and economics of fuel cells. EPRI Records and Reports Center, P.O. Box 10412, Palo Alto, Calif. 94303 (write direct).

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

BOOKS

Marine Pollutant Transfer. H. L. Windom, R. A. Duce. vii + 391 pages. D. C. Health & Co., 125 Spring St., Lexington, Mass. 02173. 1976. $21.95, hard cover.

This book contains material presented at the Pollutant Transfer Workshop, held at Skidaway Institute of Oceanography, near Savannah, Ga., early last year. Among topics covered are heavy metal transport, halocarbons, DDT and PCB's, light hydrocarbon flux, and petroleum residues. The Workshop's aim was to evaluate existing knowledge of marine pollutant transfer, and make recommendations for future research.

Energy and the Environment: A Structural Analysis. Anne P. Carter, Ed. xvii + 262 pages. The University Press of New England, Box 979, Hanover, N.H. 03755. 1977. $12.50, hard cover.

One of the biggest tasks facing this nation is increasing the energy supply without intolerable environmental disruption. In discussing approaches to the task, this book looks at problems of electric power, the paper industry, steel, and engineering data. Coal gasification, pollution abatement, and economic growth are also considered.

Thermal Ecology II. Gerald W. Esch, Robert W. McFarlane, Eds. ix + 404 pages. Energy Research and Development Administration, P.O. Box 62, Oak Ridge, Tenn. 37830. 1976. $11, paper.

As more power is produced, more heat and warm water could be released to the environment. This work looks at effects on ecosystems, thermal tolerance of organisms, fish behavior, and other pertinent subjects. It groups much of the new data gathered on thermal ecology into one comprehensive volume.

Commercial Organic Flocculants. Josef Vostrčil, František Juračka. vii + 521 pages. Noyes Data Corp., Mill Rd., at Grand Ave., Park Ridge, N.J. 07656. 1976. $24, hard cover.

This book presents in tabular form commercial sources, availability, and principal applications of organic flocculants on a worldwide basis. A very complete listing of trademarks, and generic and chemical names is given.

Land Application of Waste Materials. v + 313 pages. Soil Conservation Society of America, 7515 Northeast Ankeny Rd., Ankeny, Iowa 50021. 1976. $10, paper.

Land treatment/disposal of wastes is considered as an alternative in meeting 1983 "best available" standards. But what is the capacity of soils to accept such wastes, which contain many different forms of pollutants and pathogens? This book contains 22 symposium papers that consider how land disposal can be done, especially in a way that enhances plant growth without damaging land resources.

National Institute of Environmental Health Sciences Research Programs. Stock No. 017-051-00002-4. 63 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1977. $1.05, paper.

This pamphlet describes the mission of the NIEHS, and summarizes its research programs for 1976–1977. Among topics covered are mutagenesis, toxicology, pharmacology, international activities, and research resources. An understanding of the efforts and accomplishments of NIEHS scientists is given.

Economics and the Environment. Allen V. Kneese. 285 pages. Penguin Books, 625 Madison Ave., New York, N.Y. 10022. 1977. $3.50, paper.

Pollution has become a most pervasive problem of economic development. The author explains why. He also provides case studies of environmental management, and examines the countervailing urge to pursue economic development "at any cost," as often seems to occur in the developing world. The book considers some possible solutions to the conservation-development dilemma, and these could comprise social breakdown, a police-type state, war, or a rationally managed approach.

Our Energy Future. Don E. Kash et al. xxii + 489 pages. University of Oklahoma Press, 1005 Asp Ave., Norman, Okla. 73019. 1976. $5.95, paper.

Research, development, and demonstration (RD&D) is one response to the oil embargo of 1973–1974. This book looks at energy RD&D concepts, how RD&D is oriented toward trying to relieve U.S. energy constraints, and what the most rational funding for energy RD&D might entail.

Pollution Control for Agriculture. Raymond C. Loehr. xiii + 383 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1977. $17, hard cover.

Increasing constraint is being placed on the extent to which agriculture is allowed to pollute. This book covers changing practices, impacts, aerobic and anaerobic treatment, utilization of agricultural wastes, nitrogen control, physical/chemical treatment, and many other pertinent topics.

Assessment of the Arctic Marine Environment. D. W. Hood, D. C. Burrell, Eds. xi + 468 pages. University of Alaska, Institute of Marine Science, Fairbanks, Alaska 99701. 1976. $25, hard cover.

Ecological processes in the Arctic zone are uniquely stressed by conditions of light, cold, and ice. They must be understood better. This book, containing symposium papers, helps to shed some light on the understanding of the fragile Arctic marine ecosystem, and man's effects upon it, especially in view of the search for hydrocarbon energy sources in that part of the world.

Remote Sensing of Environment. Joseph Lintz, Jr., David S. Simonett, Eds. xix + 694 pages. Addison-Wesley, Advanced Book Program, Reading, Mass. 01867. 1976. $27.50, hard cover.

Aircraft and spacecraft can provide increased efficiency in environmental assessment, and natural resource evaluation and development. This book contains 20 contributions on the subject, is essentially nonmathematical, and can serve as a graduate text in the field. Agriculture, forestry, hydrology, and oceanography are among the numerous subjects covered.

Smoke, Dust and Haze: Fundamentals of Aerosol Behavior. S. K. Friedlander. xvii + 317 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1977. $16.95, hard cover.

With aerosol behavior becoming an increasing matter of concern, a text on the subject was needed, and this book fulfills that need. It covers the field of small particle behavior that causes aerosols to have their distinct theoretical character. Practical material on emission sources, plumes, and pollution are presented.

Air Monitoring Survey Design. Kenneth E. Noll, Terry L. Miller. vii + 296 pages. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1977. $22.50, hard cover.

Air monitoring must not only be thorough and properly done; it must also be cost-effective. This book provides a complete guide to air monitoring, including modeling, sample collection, design of systems, and data reporting. It goes much further than most works on the subject, which concern themselves mainly with instrumentation and analytical procedures.

Pesticides in the Environment. Vol. 3. Robert White-Stevens, Ed. xiv + 366 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, N.Y. 10016. 1977. $38.50, hard cover.

In this continuing series, Volume 3 emphasizes herbicides, and the impact of their use on weeds, fungi, bacteria, and insect pests. More specifically, it covers the role of herbicides in crop production, forest management, and preservation of stored grain and grain products.

Sensible Sludge. Jerome Goldstein. 176 pages. Rodale Press, 33 E. Minor St., Emmaus, Pa. 18049. 1977. $5.95, hard cover. Ask for order no. 529.

Is sludge a boon or a bane? Most think of it as a bane, but properly treated sludge—particularly the organic components—can be of real help to the land, as in strip-mine reclamation, gardens, farmland, and the like. Tax dollars for expensive disposal might be saved, as might large sums presently spent on synthetic fertilizers and energy. This book explains how sludge can be more than just a worrisome commodity.

World Energy Outlook. 106 pages. OECD Publications Center, Suite 1207, 1750 Pennsylvania Ave., N.W., Washington, D.C. 20006. 1977. $12.

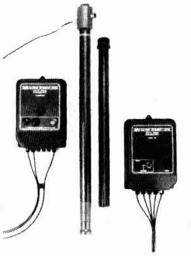
Acute risks lie in permitting current energy trends to continue, this report warns. What is needed is a way in which vigorous energy policy action can bring about a better balance between supply and demand by 1985. The report suggests ways to achieve this goal.

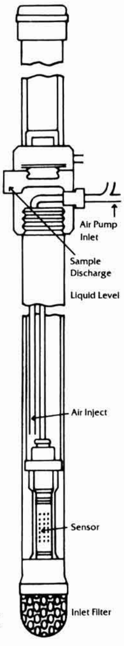
Ekistics on Water. Periodical issue. Ekistics, Page Farm Rd., Lincoln, Mass. 01773. 1977. $3.

If continued water supplies are to be assured in the future, the time to start taking action is now. This publication assesses the world water situation, which it considers critical, and emphasizes the need for local self-sufficiency. It also looks at relations between water quality, soil conservation, and forestation; water/sewer policies for suburbs; rural water supply self-help, water supply protection through sewerless sanitation, and similar topics. Ekistics is published by the Athens Center of Ekistics (Greece).

The Sanibel Report. John Clark. 308 pages. The Conservation Foundation, 1717 Massachusetts Ave., N.W., Washington, D.C. 20036. 1977. $9 (add 10% for postage/handling).

What happened when people living on a Florida island whose ecology imposed natural limits on growth revolted against runaway development? This book tells how the people of Sanibel Island in the Gulf of Mexico took matters into their own hands, and drew up plans that called for a population limit of 25 000 (the original plan was for 100 000); wetlands protection, conservation of water and natural systems, and other environmental values. It presents a case study of how the carrying capacity of a natural system can be determined, and plans drawn up accordingly.





MEETING GUIDE

May 16–19 Fort Collins, Colo.
National Conference on Irrigation Return Flow Quality Management. EPA and Colorado State University

Write: U.S. EPA, Robert S. Kerr Environmental Research Laboratory, P.O. Box 1198, Ada, Okla. 74820

May 18–19 Grand Forks, N.D.
Ninth Biennial Lignite Symposium. ERDA and the University of North Dakota

Environmental considerations of the technology and utilization of low-rank coals will be discussed. *Write:* ERDA, Grand Forks Energy Research Center, Box 8213, University Station, Grand Forks, N.D. 58202

May 18–21 New Orleans, La.
National Solid Wastes Management Association Equipment and Technology Exposition. National Solid Wastes Management Association (NSWMA)

Write: NSWMA, 1120 Connecticut Ave., N.W., Suite 930, Washington, D.C. 20036

May 18–21 Fontana Dam, N.C.
18th Annual Fontana Conservation Roundup. Tennessee Valley Authority

Theme is "Energy and Energy Resource Conservation—Obstacles and Opportunities." *Write:* Bob Sloan, Fontana Village Resort, Fontana Dam, N.C. 28733

May 19–20 Kenner, La.
Eighth Annual Symposium on Applied Chromatography. American Chemical Society/Louisiana Section

Write: Val James, c/o Hewlett-Packard, Box 840, Kenner, La. 70063

May 22–26 Atlanta, Ga.
Noise Control Seminar. TAPPI

Write: W. B. Manning, TAPPI, One Dunwoody Park, Atlanta, Ga. 30341

May 22–27 New Orleans, La.
1977 American Industrial Hygiene Conference. American Industrial Hygiene Association (AIHA)

Write: AIHA, 66 South Miller Rd., Akron, Ohio 44313

May 23 Washington, D.C.
Environmental Regulations and the Chemical Industry. The Energy Bureau Inc.

Write: Registrar, The Energy Bureau Inc., 101 Park Avenue, New York, N.Y. 10017

May 23–25 Morgantown, W. Va.
Institute for Coal Utilization. College of Engineering/West Virginia University

Write: Fred Galli, Institute for Coal Utilization, College of Engineering, Room 421, West Virginia University, Morgantown, W. Va. 26506

May 23–25 Houston, Tex.
Fugitive Emissions: Measurement and Control. EPA's Industrial Environmental Research Laboratory, Research Triangle Park

Write: Joanne King, The Research Corporation of New England, 125 Silas Deane Highway, Wethersfield, Conn. 06109

May 23–25 New Orleans, La.
ISA Power Industry Division's National Symposium. Instrument Society of America

Environmental topics will be discussed. *Write:* John Coles, New Orleans Public Service, 1600 S. Peters Street, New Orleans, La. 70130, or Harold E. Hendler, Taylor Instrument Process Control Division/Sybron Corporation, 95 Ames Street, Rochester, N.Y. 14601

May 23–25 St. Louis, Mo.
National Conference on Water. United States Water Resources Council

Write: 1977 National Conference on Water, Water Resources Council, 2120 L Street, N.W., Suite 800, Washington, D.C. 20037

May 24–26 St. Louis, Mo.
National Conference on 208 Planning and Implementation. U.S. EPA

Write: Office of Water Planning and Standards, Water Planning Division, U.S. EPA, Washington, D.C. 20460

May 27–29 Aspen, Colo.
Aspen Energy Forum 1977. Roaring Fork Resource Center and Pitkin County Government

Theme is "Solar Architecture." *Write:* Roaring Fork Resource Center, P.O. Box 9950, Aspen, Colo. 81611

May 30–June 3 Washington, D.C.
1977 Spring Meeting. American Geophysical Union (AGU)

A session will be devoted to "Weather Dependence of Energy Demands and Energy Consumption." *Write:* AGU, 1909 K St., N.W., Washington, D.C. 20006

June 1–3 Storrs, Conn.
International Symposium on Pathobiology of Environmental Pollutants—Animal Models and Wildlife as Monitors. Northeastern Research Center for Wildlife Diseases, the University of Connecticut and others.

Write: George Migaki, D.V.M., Registry of Comparative Pathology, Armed Forces Institute of Pathology, Washington, D.C. 20306

June 6–7 Washington, D.C.
The Second National Conference on the Interagency Energy/Environment R&D Program. EPA, ERDA, NIEHS and others

Write: Ms. Kathleen E. Dixon, Conference Coordinator, Vitro Laboratories, Silver Spring, Md. 20910

June 6–8 Stevens Point, Wis.
American Chemical Society's 11th Great Lakes Regional Meeting. American Chemical Society

Write: W. B. Gitchel, Zimpro, Inc., Rothschild, Wis. 54474

June 6–8 Washington, D.C.
Engineers' Public Affairs Forum. National Society of Professional Engineers (NSPE)

Environmental issues will be discussed. *Write:* National Public Affairs Forum, c/o NSPE, 2029 K St., N.W., Washington, D.C. 20006

June 6–10 Fallen Leaf Lake, Calif.
3rd Annual Underground Coal Conversion Symposium. Lawrence Livermore Laboratory

Write: Dr. Douglas Stephens, Lawrence Livermore Laboratory, P.O. Box 808, L-502, Livermore, Calif. 94550

June 6–10 Orlando, Fla.
Annual Meeting of the American Section of the International Solar Energy Society, International Solar Energy Society

Write: American Section, International Solar Energy Society, 300 State Rd. 401, Cape Canaveral, Fla. 32920

June 7–9 Columbia, Mo.
11th Annual Conference on Trace Substances in Environmental Health. University of Missouri

Write: D. D. Hemphill, 411 Clark Hall, University of Missouri, Columbia, Mo. 65201

June 13–15 Ann Arbor, Mich.
1977 Specialty Conference on Geotechnical Practice for Disposal of Solid Waste Materials. American Society of Civil Engineers (ASCE)

Write: Prof. D. H. Gray, Civil Engineering Department, University of Michigan, Ann Arbor, Mich. 48109

June 19–21 Pasadena, Calif.
Earthquake Engineering and Soils Dynamics Specialty Conference and Exhibit. American Society of Civil Engineers (ASCE)

Write: A. J. Favata, Convention Dept., ASCE, 345 E. 47th St., New York, N.Y. 10017

June 19–22 Grand Island, N.Y.
51st Colloid and Interface Science Symposium: Aerosols and Particulate Dispersion. American Chemical Society and the State University of New York at Buffalo

Write: Prof. David T. Shaw, Laboratory for Power and Environmental Studies, State University of New York at Buffalo, 4232 Ridge Lea Rd., Buffalo, N.Y. 14226, or Prof. Warren C. Kocmond, Desert Research Institute, University of Nevada, Reno, Nev. 89507

June 19–22 Denver, Colo.
Conference on the Development and Commercialization of Breeder and Fusion Reactors. Atomic Industrial Forum, Inc. (AIF)

Write: AIF, 7101 Wisconsin Ave., N.W., Washington, D.C. 20014

June 20–21 Minneapolis, Minn.
ASTM Symposium on Quantitative and Statistical Analyses of Biological Data in Water Pollution Assessment. American Society for Testing and Materials (ASTM)

Write: Dr. Kenneth L. Dickson, Center for Environmental Studies, Virginia Polytechnic Institute and State University, 1020 Derring Hall, Blacksburg, Va. 24061

June 20–22 Columbia, Mo.
Water Resources Management and Outdoor Recreation. American Water Resources Association (AWRA)

Write: Dr. Carl D. Settergren, School of Forestry, Fisheries and Wildlife, University of Missouri, Columbia, Mo. 65201

June 20–24 Minneapolis, Minn.
ASTM Committee D-19 on Water. American Society for Testing and Materials (ASTM)

Write: ASTM, 1916 Race St., Philadelphia, Pa. 19103

June 21–22 Denver, Colo.
Energy Management in Buildings. New York University's School of Continuing Education

Write: Ms. Heidi E. Kaplan, Information Services Manager, Dept. 14NR, New York Management Center, 360 Lexington Ave., New York, N.Y. 10017

June 24–26 Amherst, Mass.
2nd Annual Toward Tomorrow Fair. University of Massachusetts and others

Alternative energy technologies will be displayed. *Write:* Erna Koch or Michael Maguire, Fair Coordinators, Toward Tomorrow, 200 Hills House North, University of Massachusetts, Amherst, Mass. 01003

June 26–July 1 Henniker, N.H.
Corrosion and Deposits from Impurities in Combustion Gases. The Engineering Foundation

Write: The Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

Courses

May 16–20 Research Triangle Park, N.C.
Source Sampling Seminar. Entropy Environmentalists, Inc.

Fee: $350. *Write:* John A. Parrish, Jr., Manager of Technical Services, P.O. Box 12291, Research Triangle Park, N.C. 27709

May 23–25 Washington, D.C.
Loan Guarantee Program: Financing Energy Conservation Opportunities in Existing Buildings. The George Washington University

Fee: $360. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

May 23–25 Albany, N.Y.
Air Pollution Field Enforcement, Course No. 444. Air Pollution Training Institute (APTI)

Fee: $66. *Write:* Registrar, APTI, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

May 23–25 Chapel Hill, N.C.
Water Supply Engineering: Quality, Treatment, Management. University of North Carolina

Preregistration is requested. Fee: $100. *Write:* Dr. Singer, Dept. of Environmental Sciences and Engineering, University of North Carolina at Chapel Hill, School of Public Health 201 H, Chapel Hill, N.C. 27514

May 23–26 Kansas City, Kans.
Statistical Evaluation of Air Pollution Data, Course No. 426. Air Pollution Training Institute (APTI)

Fee: $88. *Write:* Registrar, APTI, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

(*continued on page 526*)

May 23–27 Bronx, N.Y.
Biological Waste Treatment. Manhattan College

Fee: $325. *Write:* Kathryn King, Program Coordinator, Environmental Engineering and Science Program, Manhattan College, Bronx, N.Y. 10471

May 23–27 Bronx, N.Y.
Mathematical Modeling of Natural Water Systems. Manhattan College

Fee: $325. *Write:* Kathryn King, Program Coordinator, Environmental Engineering and Science Program, Manhattan College, Bronx, N.Y. 10471

May 23–27 Cincinnati, Ohio
Planning Monitoring Activities in Water Quality Management Programs, Course No. 161.2. EPA

Fee: $110. *Write:* Registrar, National Training and Operational Technology Center, MOTD, OWPO, WHM, U.S. EPA, Cincinnati, Ohio 45268

May 31–June 1 Washington, D.C.
Optimizing Your Responses to OSHA. Daniel P. Boyd & Co. and Dunn Technology, Inc.

Fee: $395. *Write:* Rosemary Meehan Dunn, Dunn Technology, Inc., 204 Columbia St., Newport Beach, Calif. 92663

June 2–3 Milwaukee, Wis.
Safety in Solid Waste Collection. University of Wisconsin–Extension

Fee: $125. *Write:* John Reindl, Dept. of Engineering, University of Wisconsin–Extension, 432 North Lake St., Madison, Wis. 53706

June 2–3 Pittsburgh, Pa.
Stack Sampling Procedures. Research Appliance Co. (RAC)

Fee: $175. *Write:* Ralph J. Bulger, General Manager, RAC, Route 8, Gibsonia, Pa. 15044

June 6–9 Columbus, Ohio
Control of Gaseous Emissions, Course No. 415. Air Pollution Training Institute (APTI)

Fee: $88. *Write:* Registrar, APTI, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

June 6–10 Research Triangle Park, N.C.
Ambient Air Quality Monitoring Systems (Planning and Administrative Concepts), Course No. 463. Air Pollution Training Institute (APTI)

Fee: $110. *Write:* Registrar, APTI, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

Call for Papers

June 1 deadline
U.S. Antarctic Research Program Proposals. National Science Foundation

Grant award notifications will be made beginning October 1, 1977. Proposals should be submitted in accordance with instructions found in NSF's Grants for Scientific Research (NSF 76-38). *Write:* Division of Polar Programs, National Science Foundation, Washington, D.C. 20550

June 30 deadline
Fifth National Conference on Energy and the Environment. American Institute of Chemical Engineers and others

Conference will be held November 1–3, 1977 at Cincinnati, Ohio. *Write:* Prof. Duane G. Nichols, West Virginia University, Dept. of Chemical Engineering, Morgantown, W.Va. 26506

June 30 deadline
7th North American Thermal Analysis Society Conference. North American Thermal Analysis Society

Conference will be held September 26–28 at St. Louis, Mo. *Write:* Dr. D. W. Brazier, Conference Chairman, NATAS, 1977, Dunlop Research Centre, Sheridan Park Research Community, Mississauga, Ont., L5K 1Z8, Canada

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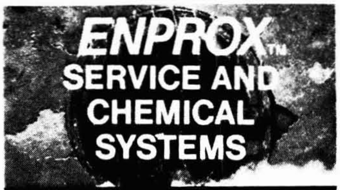

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