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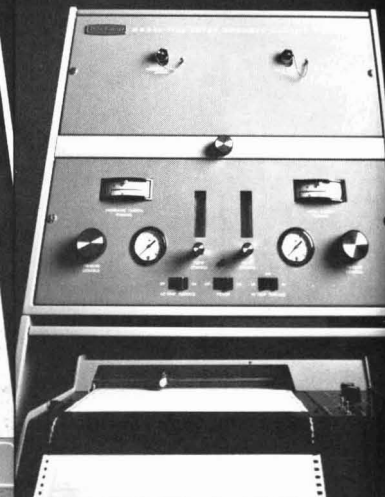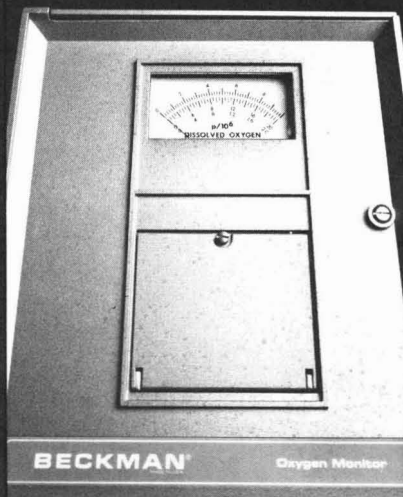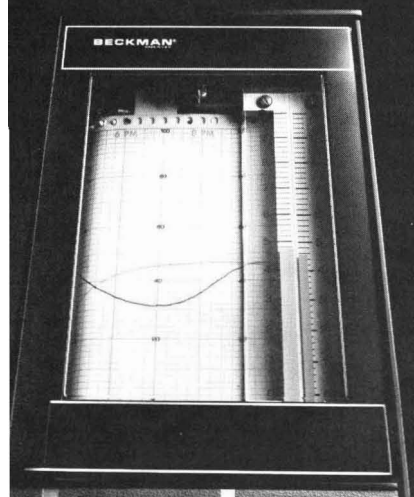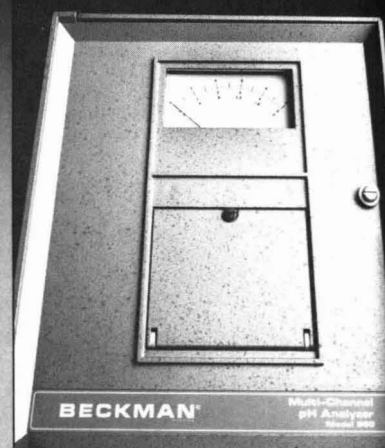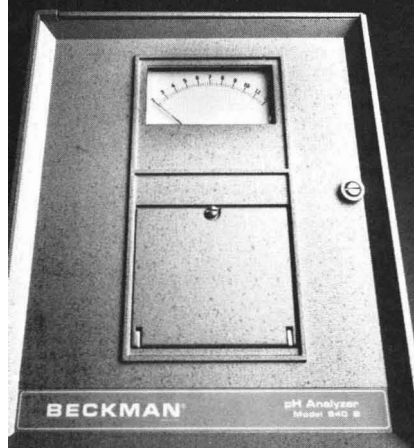
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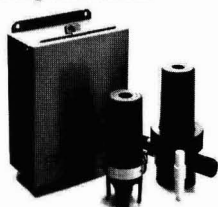**Model 940B pH Analyzer.** Most advanced analytical instrument for continuous measurement of process pH or ORP. NEMA-4 or fiberglass NEMA-4X watertight enclosure. Potentiometric output is standard. Options include alarm contacts and isolated current output.

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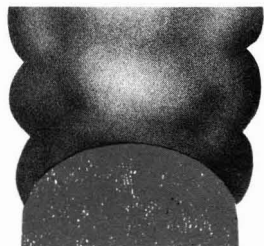
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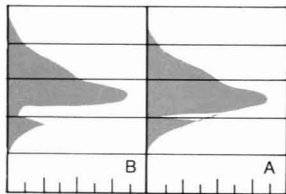

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GUEST EDITORIAL

Global chemical cycles and pollution

Pollution used to be a local or regional problem. But the side effects of technology and the consequences of energy dissipation are now being felt over increasingly larger distances—at times becoming global in character. Man in his social and cultural evolution continues to be successful in diverting energy for the advancement of his own civilization. In the northern hemisphere anthropogenic energy use already exceeds biotic energy flux (photosynthesis). Despite the ecosphere's remarkable buffering and feedback mechanisms, man has now become sufficiently powerful to influence some global chemical cycles.

Of serious concern are: (1) Man's alteration of the natural CO_2 cycle—resulting from fossil-fuel burning and perhaps from deforestation, which may lead to climate changes which in turn could trigger profound effects on human society; (2) enhanced N_2O production—being a by-product of man's nitrogen fixation (20–30% of that by natural processes)—which may interact with the stratosphere's ozone; (3) increased erosion rates resulting mainly from deforestation and modern agriculture; and (4) the release of oxides of N, H, and S, and of trace metals and ash into the atmosphere, which may cause production of acid rain and fallout (oxidation of S and N oxides to H_2SO_4 and HNO_3), nutrient enrichment of inland and coastal waters, and perturbations of natural biological cycles by heavy metals.

Scientists and engineers must assess more quantitatively the human influences on the earth's natural metabolism and on the various interlocking hydrogeochemical cycles. By evaluating the strengths of significant emission sources and by comparing natural and pollutant fluxes we will be able to better understand the present and future distribution of pollutants, their ecological consequences, and their effects on human health. The effects of damage to life support systems are, however, most elusive.

Environmental scientists and engineers are accustomed to cope with a broad range of mutually interacting systems; they are aware that it is dangerous to take a fragmental view. Some of the compartmentalization between atmospheric, earth, marine, and freshwater scientists and engineers must be reduced. Understandably, we are all concerned first with our immediate environmental surroundings but, while solving local problems, we should watch out that we do not overlook larger risks. Environmental chemists must have an interest in an a sense of responsibility for our global environment.

Dr. Werner Stumm *is currently Director and Professor at the Institute for Water Resources and Water Pollution (EAWAG), at the Swiss Federal Institute of Technology, Zurich, Switzerland.*

ES&T
LETTERS

Ocean thermal

Dear Sir: I was pleased to read the article about OTEC (*ES&T*, July 1977, p 651). It is time that this significant technology gets the attention it deserves. I especially loved the last sentence about the "glaring omission" in the President's budget.

I would like to point out one important thing that you missed. The best OTEC plant is not the one of TRW, APL or Lockheed. It is the design of Sea Solar Power, Inc.; 2422 S. Queen St., York, Pa. 17402.

This area subject is embroiled in controversy largely because the aerospace ripoff artists have been trying to force the acceptance of their inferior designs by the Department of Energy, and have been succeeding. Also, Alfa DeLaval has started their own privately funded OTEC project which is headed by William Heronemus. (Energy Systems Division; 730 West St., Amherst, Mass.).

David F. Mayer
University of New Orleans
New Orleans, La. 70122

Occupational health

Dear Sir: The National Institute for Occupational Safety and Health (NIOSH) invites research and demonstration grant applications designed to promote occupational safety and health. Innovative approaches designed to define occupational safety and health problems and recommend solutions, understand and prevent occupational disease and accidents, and eliminate or control hazards are welcome.

At this time, primary emphasis is placed on investigations related to cause and prevention of occupational skin, neurologic, respiratory, and musculoskeletal and back disorders; reproductive effects of occupational hazards; occupational safety; and control technology for occupational hazards.

In addition, other emphasis areas include, but are not restricted to, occupational safety- and health-related behavioral and motivational factors, epidemiology, ergonomics, physiology, toxicology, pathology, effects of physical agents, head and body protection, biological and environmental sampling and analysis, and the development of physical and chemical analytical methods.

Applications should be submitted on NIH Form 398 to the Division of Research Grants, National Institutes of Health, Westwood Building, Bethesda, MD 20014.

For further information please contact:

C. Ilana Howarth
Research Grants Program Officer
Grants Administrative and Review Branch, OECSP
National Institute for Occupational
Safety and Health, Parklawn Bldg., Room 8–63
5600 Fishers Lane,
Rockville, Md. 20857
Telephone: (301) 443-4493
C. Ilana Howarth
NIOSH
Rockville, Md. 20857

ES&T READERS' COMMENTS

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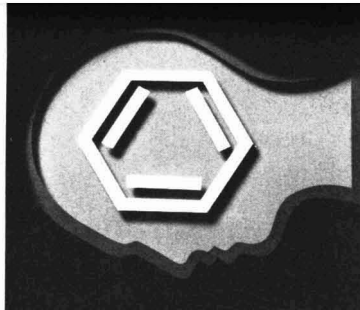
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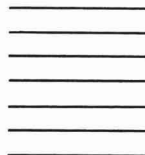
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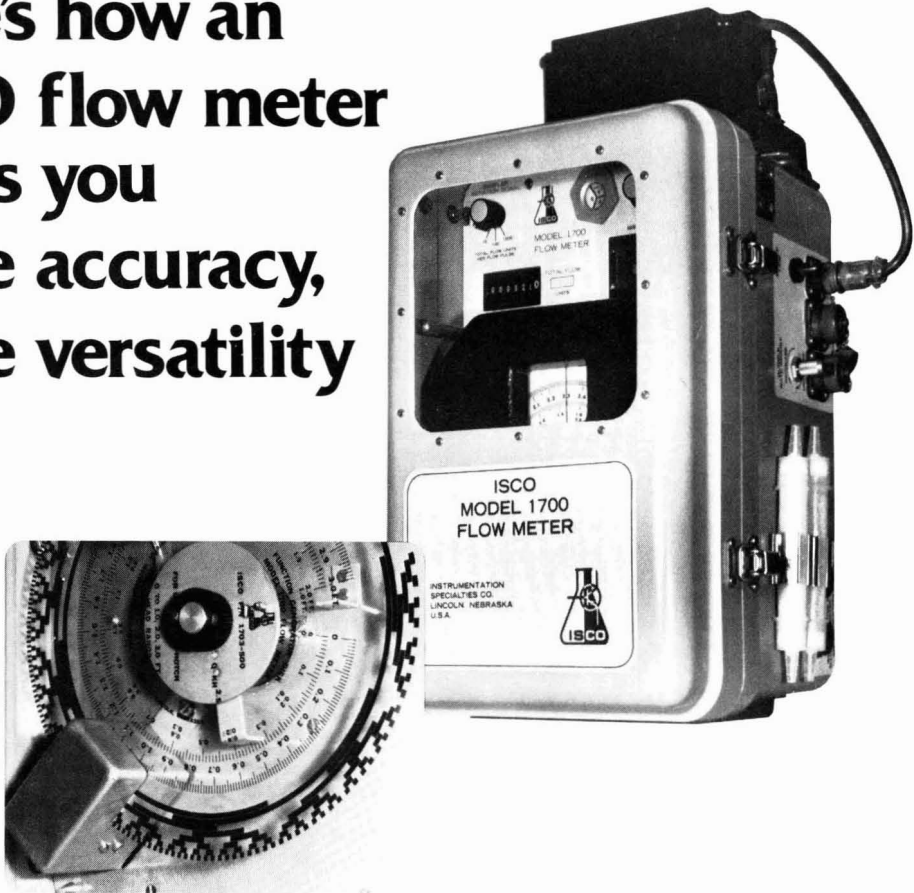
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CURRENTS

INTERNATIONAL

Seventeen Mediterranean coastal states, concerned about pollution of that sea, met under the auspices of the UN Environment Program. Emerging from that meeting were agreements to undertake a study of atmospheric transport of pollutants in the Mediterranean region, and to expand monitoring and research programs. A detailed study of river pollution will also be undertaken.

WASHINGTON

President Carter's first budget, for fiscal year 1979, increases EPA's budget to more than $1 billion, up from $890 million in fiscal 1978. The increase was the result of the zero-based budgeting, which showed how insufficient the agency's resources were. A large share of EPA's budget will go toward the control of toxic substances: $27.2 million in fiscal 1979, up 63% from

President Jimmy Carter

1978. Outlays for cleaning and maintaining the nation's waterways are slated at $334.7 million up from $275.1 million in 1978. Air programs will receive $199 million in fiscal 1979, up from $183.6 the previous year. Noise pollution programs remain funded at $7.9 million, no increase from 1978. The construction grant program will rise to $4.7 million in 1979, up from $4.1 million in 1978.

EPA's proposed regulation to limit organic chemicals in potable water supplies will involve capital expenditures of $350–450 million over a 3–5 y period, and annual operating

costs of about $60 million according to EPA head Douglas Costle. Costle estimated the annual cost to an average family of three at $6–10. The regulation will set the upper limit on trihalomethanes at 100 ppb for community water systems serving over 75 000 people, and require the installation of granular-activated carbon filters if these drinking water systems are contaminated with organic chemicals from industrial discharges or nonpoint sources. Costle said that the agency's recent regulations under the Safe Drinking Water Act was a "reasonable insurance policy" to protect the public against chronic, low levels of potential carcinogens.

The Army Corps of Engineers will help the EPA expedite the construction grant program under a new interagency agreement. Prior to bidding, the Corps will review plans and specifications of a proposed sewage treatment facility; once contracts have been enacted, the Corps will ensure that construction meets the highest standards; and for projects costing more than $50 million, the Corps will provide continuous on-site supervision.

EPA proposed an ambient air quality standard for lead of 1.5 $\mu g/m^3$, calculated on a monthly average. This "precautionary" standard is set at a level to protect children aged 1–5 y, the most sensitive population. EPA estimates that the total cost of installing the necessary controls will be about $600 million, and will primarily affect nonferrous smelters. EPA is continuing to study the economic impact of this standard on the affected facilities, but the agency notes that the Clean Air Act mandates only that it consider health factors in setting the standard. On another air matter, an internal guidance memo states that urban areas over 200 000 should be presumed to be in violation of the ambient air quality standard for photochemical oxidants in the absence of data showing attainment.

Last month, OSHA issued an emergency temporary standard for acrylonitrile. Under the ETS, permissible worker exposure is reduced to 2 ppm averaged over an 8-h period, and to 10 ppm for any 15 min period during the 8 h. Epidemiological evidence and laboratory tests on mice indicate that acrylonitrile "poses a potential carcinogenic risk to humans."

"A fresh examination of resource and environmental protection policies," was the way CEQ chairman Charles Warren described last year's environmental efforts. Among the new pieces of legislation, Warren cited amendments to the air and water acts, and a surface mining and reclamation act. The year 1977 also saw an Executive Order issued to protect wetlands and establish a wetlands acquisition program. Among CEQ's 1977 initiatives that are continuing into this year are the development of regulations to aid federal agencies implement the National Environmental Policy Act, and strategies for controlling toxic substances and for improving federal environmental monitoring and data collection programs.

A recent OTA report finds that coal-slurry pipelines, under some conditions, would be the cheapest way to transport coal. These pipelines, the Office of Technology Assessment admits, could pose a competitive threat to railroads. OTA said that there is water available for the slurry lines, which become competitive under conditions of high tonnage, long distances and a "secure market" of large customers located close to the pipeline. The House Interior Committee has held hearings on whether Congress should pass legislation granting federal "eminent domain" to the pipelines.

STATES

Some 728 sources, 88%, are in compliance with Indiana Air Pollution Control Board regulations; last year saw 69 sources achieving com-

pliance and 48 sources on strict timetables to meet these regulations. One new regulation was promulgated last year: APC 8, which requires continuous in-stack monitors for fossil fuel-fired steam generators, sulfuric acid plants, nitric acid plants and petroleum refineries. Three regulations were revised; one set air quality standards for particulates, sulfur dioxide, nitrogen dioxide, ozone, carbon monoxide and hydrocarbons. A continuous monitoring trailer was installed in New Albany, Ind., as part of the Continuous Aerometric Acquisition Program (CAAP). CAAP trailers exist in seven other Indiana cities.

Clayton, New Mexico's federally sponsored wind turbine generator recently began operating. Its 125-ft blades churn out 200-kW of electrical energy, enough to supply 15% of the town's electrical power needs. Clayton, a wind-swept ranching and farming community, is the first site for a DOE-sponsored/NASA-designed wind generator. A second, much larger wind machine will be installed near Boone, N.C. in late 1978.
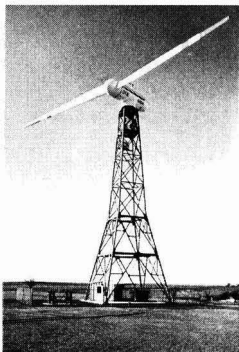
DOE/NASA's wind turbine generator

A unique 1-y-old California program to prevent job-related cancers may become a model for a similar nationwide project sponsored by OSHA this year. California's 1976 Occupational Carcinogens Control Act mandates that all employers throughout the state who handle 18 identified carcinogens be registered; the law further attempts to guarantee that unsafe exposure to substances such as asbestos, benzidine and vinyl chloride is eliminated. OSHA is funding the California effort at 50%. The budgeted $5 million program has registered

more than 2800 employers to date. The program went into effect on Jan. 1, 1977 and employers had until September to register or be fined. Companies exceeding health and safety standards were also fined.

A watershed in Lake County, S.D., was selected to demonstrate water quality management procedures under the Model Implementation Program sponsored by the USDA and the EPA. Six other watersheds in the U.S. will also participate in this program to develop control procedures to curb nonpoint source pollution within a three-year period. The watershed, Lake Herman, has been and will continue to be monitored for sediment and pollutants entering it. Funds for this monitoring come from an EPA grant under section 208 of P.L. 92-500; South Dakota's Dept. of Environmental Protection is now applying for a Clean Lakes grant under section 314 of P.L. 92-500.

An intensive effort to clean up Denver, Colorado's air will be made under a state-federal program. Stationary source pollution control op-

tions are not applicable in Denver's case as the main emissions polluting the air come from vehicular traffic. This clean-up effort will become a model for other cities. A cut back in vehicle miles traveled by federal employees will be the first steps taken, followed by efforts to encourage car pooling and increased public transit ridership. In the meantime, the Calif. Air Resources Board is shifting its clean-up efforts to oil refineries and other stationary sources of pollution in the Los Angeles and San Francisco Bay areas. Here, automobiles account for less than half the smog.

MONITORING

Sewage contamination can be pinpointed by detection of coprostanols, compounds derived from cholesterol, and present in mammalian fecal matter. Indeed, coprostanols are an "ideal" indicator, Pat Hatcher of NOAA (Miami, Fla.) says. NOAA has also found a way to quantify these compounds.

TECHNOLOGY

Hydrocarbon (HC)-contaminated aquifers can be economically re- stored to an acceptable quality through "Hydrocarbon Bioreclamation", a process that uses microorganisms indigenous to groundwater. The process was developed by Ground Water Associates, Inc. (Westerville, Ohio). First, the type of HC that contaminates the groundwater, and the kinds and numbers of microorganisms are determined. Next, nutrients needed for managed microorganism growth are ascertained. These factors are monitored during the bioreclamation process, which saves money when one considers the costs of alternative decontamination approaches involving pumping, barriers, or the groundwater resource loss.

A methyl fuel, rather than water, might slurry coal in a pipeline one day. Known as "methacoal", the slurry process was patented by Leonard Keller of the Methacoal Corp. (Dallas, Tex.). Finely pulverized coal is suspended in methyl fuel (predominantly methanol), instead of water. One advantage would be the very minimal need for water. Another is that methacoal appears "thixotropic"—forming a black, paste-like substance upon settling, rather than settling outright. This thixotropy allows for easy slurry reconstitution with very minimal chances for plugging. The Center for Energy Studies of the University of Texas at Austin is doing a complete methacoal study.

Plate cadmium and cut pollution— also, use no cyanide. Sounds like a tall order, but the "Cadvert" Sulfate Cadmium System developed by 3M Co. (St. Paul, Minn.) meets these requirements, according to Harold Berg, manager of 3M's Plating Systems Department. Berg says that the system provides a bright, ductile, lubricious finish on carbonitrited steel. It will also plate cadmium on other metals formerly plated with cyanide, such as certain stainless steels, cast iron, copper, brass, solders, and beryllium/copper. Metal precipitates out to 0.5 ppm or less, and metal distribution is better than that for cyanide, Berg notes.

What do 13 pollution control technologies cost the chemical industry? That is what Booz, Allen & Hamilton Inc. studied on a point source

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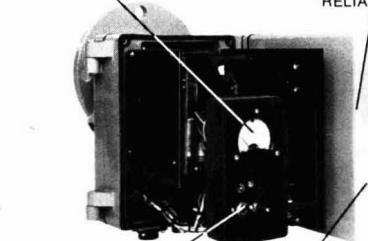
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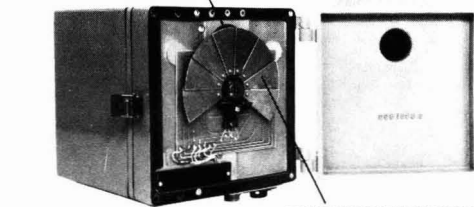
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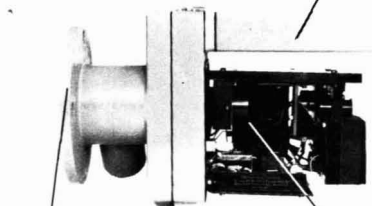
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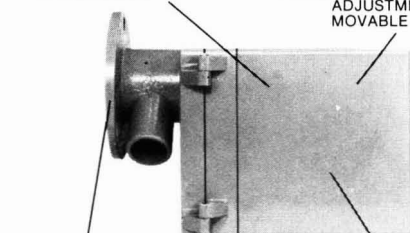
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Chemical industry's capital outlays for in-place HC controls

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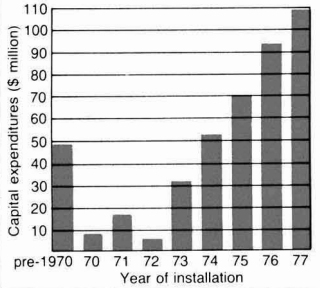
basis, with a computer program. Capital and operating cost factors were included, and types of abatement equipment applied to each emission source were taken into account. Among technologies were flare, incineration with and without scrubbers, active carbon with/ without recovery, catalytic oxidation, tie-in to existing devices, indirect condensation, and solvent scrubbing. The analysis used data from the Manufacturing Chemists Association. Hydrocarbon (HC) controls were emphasized.

Toxic hexavalent chromium (Cr^{+6}) shows reduction from 200 ppm to 0.05 ppm by means of an electrolytic ferrite formation system. Developed by Mitsubishi Petrochemical Engineering Co., Ltd. (MPEC), the first such system is in use at Marusan Metal Plating Co., Ltd.; both firms are in Japan. The MPEC device runs 12 tpd of metal wastewater through, and the effluent never contains more than 0.1 ppm of Cr^{+6}, according to MPEC. The system forms a ferrite sludge that prevents redissolving of the undesirable ions; also, operating costs are lowered. MPEC says that the ferrite sludge could have uses in the coatings and building industries.

Why not process pulp/paper effluent and village sewage together? That is just what Hoerner Waldorf Corp. is doing at Ontonagon, Mich., on Lake Superior. The combined treatment uses wet air oxidation by Zimpro, Inc., whose air compressor packages are made by Ingersoll-Rand (Woodcliff Lake, N.J.). Ontonagon's sewage goes to the mill, is mixed with effluent and spent liquor, fed to the wet air unit, and pressurized. BOD and COD are virtually eliminated, according to Ingersoll-Rand. Pulp/paper

chemicals survive, and go to the plant for reuse. Up to 80% of the energy used is also returned. Moreover, Ontonagon cancelled plans for a sewage plant, and saved taxpayers $1.5 million.

Reverse electrodialysis (RED) as a possible electricity source is being studied by the Southern Research Institute (SRI, Birmingham, Ala.). RED involves a series of compartments, with concentrated brine in alternating compartments, and fresh water in the others. Their flows form a "battery", with voltage generated across each membrane. Electrodes at each end of the system collect the charges and convert them into electrical current. Seawater, brines from oil fields and salt dome flooding, salt lakes, and solar-evaporated seawater are all good brine sources, according to SRI..

INDUSTRY

Membership rolls of the Institute of Scrap Iron and Steel (ISIS) grew, despite great difficulties during 1977. Among these difficulties was the scrap collection system, which almost fell apart because of scrap industry uncertainties, according to Joseph Schapiro, ISIS president. He notes that as demand rises, the collection system must be re-created—"similar to perpetually reinventing the wheel." Schapiro wanted to know, also, why consumers pleaded for scrap export controls "for this vital material" in 1973–1974 and then, over more than 36 months, have not been using more scrap. He called for cooperation and understanding by consumers and government.

"Totally unrelated to the real world" is how Prevention of Significant Deterioration (PSD) of the Clean Air Act Amendments of 1977 was characterized by Matthew Gould, Georgia-Pacific's director for energy and environment. Gould especially scored the EPA's definition of "potential emissions." He said that such PSD provisions would impede the use of renewable non-fossil fuels, such as wood waste. As examples, he gave the need for PSD reviews for even the smallest wood waste boilers, such as 5000-lb boilers, and called these reviews "more useless paperwork." Gould noted that in practice, a wood waste boiler would have to reach 200 000 lb of steam before reaching legal emissions limits.

UOP Inc. is supplying a new pelleted $HC/CO/NO_x$ catalyst for a system developed by Toyo Kogyo (Japan), which must meet that country's extremely stringent vehicle emissions standards. UOP says that this catalyst works for all of these emissions simultaneously. The company notes that Toyo Kogyo uses unique carburetion control and an advanced electronic ignition system, but does not require use of an oxygen sensor to meet Japan's new, very tough regulations that are in effect this year.

There will not be enough electric generating capacity to meet expected industrial and residential needs, unless power plants using coal and nuclear energy plants are built now. This is the warning by Robert Precious, president of the American Boiler Manufacturers Association (Arlington, Va.). He said that he is "encouraged" by an increase in coal-fired boiler orders this year,

ABM Association's Precious

but indicated that the market is not improving fast enough to meet future power needs. Precious cited the electric power shortage as "the most serious economic and social problem facing America today." He also described the lack of a clearcut energy policy consistent with environmental regulations.

How about smaller fluidized-bed combustion (FBC) systems for industry, as well as larger ones for power plants? It's coming. FluiDyne Engineering Corp. (Minneapolis, Minn.) is designing, fabricating, and managing such an FBC demonstration system for Owatonna Tool Co. (Owatonna, Minn.), under Dept. of Energy contract. The combustor would supply hot air and water for heating/process needs, and allow Owatonna to switch from gas to even high-sulfur coal (or waste). It will supply 28.5 million Btu/h, and be operational after October. FluiDyne notes that the State of Ohio has passed a law to give industry economic incentive to use FBC.

Industrial effluents yield to oxygen/activated sludge

Wastewaters with high organic levels and BOD values seem especially amenable to this type of treatment

The potential of pure oxygen for industrial wastewater applications was discussed at the 70th Annual Meeting of the American Institute of Chemical Engineers (AIChE), held in New York City last year. Introduced in 1968, pure oxygen systems are being used more and more with industrial wastewater. Such wastewater can be heavily laden with organic materials; consequently, they have high BOD values. Industrial users, including organic chemical manufacturing plants, pharmaceutical plants, and breweries often find pure oxygen attractive.

There are technical differences between conventional air and pure oxygen systems. Most experience to date substantiates the fact that the technical differences between the two are a result of the operating dissolved oxygen levels in the aeration basin. They do not result from the application of pure oxygen *per se,* according to AWARE (Associated Water and Air Resources Engineers, Inc.), a Nashville, Tenn., based consulting engineering firm.

Arriving at decisions

In their paper, Adams, Eckenfelder, and Koon noted that if, say, two systems are designed with minimum dissolved oxygen levels in the 2–5 mg/L range, the final decision as to what system to use will be based on capital and operating economics. Other factors, such as resistance to shock loading, the ability to handle inhibitory constituents in the waste effectively, and odor control sometimes present advantages that override minimum cost considerations.

Some considerations that should be looked at for industrial application of pure oxygen are cited by the AWARE
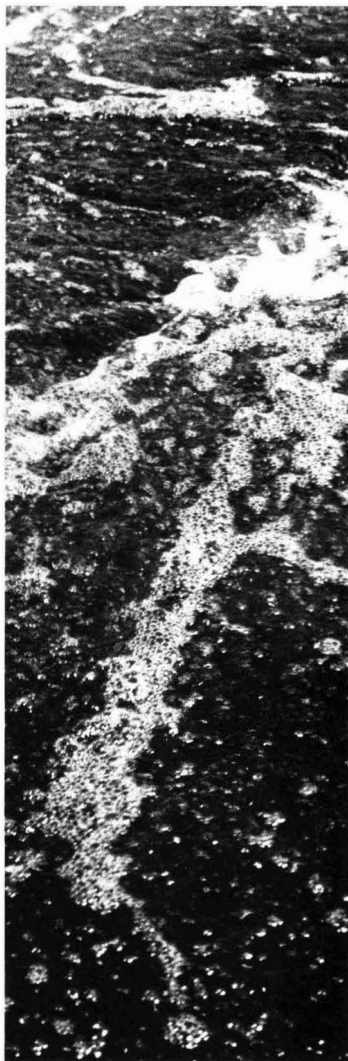
spokesmen. They noted that organic removal kinetics did not play an important role with municipal wastewaters. However, they said that for high-strength industrial wastewaters, organic removal kinetics may be an important consideration in the design of the overall system.

Another consideration is the equilibrium aeration basin temperature. Here, in a colder climate, a major advantage of the pure oxygen system over the conventional air system aerated by surface mechanical aerators is the maintenance of a higher aeration basin temperature.

Another consideration is the equilibrium aeration basin pH. the AWARE trio noted that it is well established that the pH in a pure oxygen system will be somewhat lower than that of a similar air system. This is caused by the accumulation of carbon dioxide.

For municipal wastewaters, the slightly lower pH is usually insignificant. However, for treatment of high-strength industrial wastes, the quanity of carbon dioxide produced can be great enough to affect the aeration basin pH significantly. So, in industrial applications, the addition of a basic material may be required to maintain the proper pH. Also, many high-strength industrial wastewaters contain organic acids, such as acetic acid and formic acid, in high concentrations. In addition, the BOD might be as high as 2000·mg/L.

Other considerations

With a conventional air system, certain volatile organics are stripped from solution. Thus, in the air system, stripping of organics may lead to better performance through either reduced

organic loading, or removal of potentially inhibitory compounds.

In other cases, however, the control of odors can be a significant consideration in the selection of a system. The authors noted that certain obnoxious odors may be degraded if their sources remain in the system over a period of time. Pure oxygen offers this capability. Moreover, in situations in which positive odor control is a necessary design consideration, an oxygen system may have certain advantages with respect to both capital and operating costs.

If sludge production and settling ability are the prime considerations, the oxygen system wins out. It is generally accepted that such a system produces 40–50% less sludge than does a comparable air system operating at a dissolved oxygen (DO) level less than 2 mg/L. However, it is well known that with air systems, sludge production decreases proportionately when the DO level is maintained at greater than 2 mg/L.

A quick look at costs

In general, a pure oxygen system will require higher capital expenditures than a comparable air system would. This higher cost of construction is generally based on the fact that oxygen systems must be enclosed in concrete or steel tanks, in order to support the tank cover, and provide positive containment of the oxygen-rich gas. Comparable air systems may be constructed of earthen basins with concrete riprap or basin liners. However, oxygen may offer substantial savings in operating costs.

The problems with industrial wastewaters are more difficult. With industrial wastewaters the relative transferability of oxygen into the water not only varies from industry to industry, but can also vary substantially within a single industry, because of

campaign scheduling of products or routine production changes.

Data presented by Eckenfelder and his associates indicated that the capital cost for the oxygen system was approximately $1 million greater than that for a system of comparable design, which uses static aerators. However, when the average power costs were added to the capital cost, it was seen that the oxygen system was approximately $1 million less costly than an air system was by using low-speed mechanical surface aerators.

Agricultural chemicals

Chemagro (Kansas City, Mo.) is the Agricultural Division of the Mobay Chemical Company. It manufactures primarily organophosphorus and organonitrogen insecticides and herbicides. With respect to pollution problems, as a class, Chemagro found herbicide wastes to be more resistant to biological degradation than insecticide wastes.

P. J. Pallanich told AIChE meeting attendees that the company is really a part of the organic chemicals industry. The common practice in this industry is to place the burden for pollution control on the individual production units. Thus, each individual production unit typically cleans its own wastewater discharge waste before sending it to the treatment plant. Each unit typically provides removal of solids and solvents, reduction of total organics, and control of toxicants.

In addition, this pesticide plant, as do others in the industry, provides emergency spill control. Also, all off-gases are controlled through thermal oxidation or ozone treatment, Pallanich told the AIChE meeting.

Chemagro installed biological treatment (UNOX) in 1975 (ES&T, October 1975, p 910). Pallanich explained that the Chemagro treatment plant design parameters are well

within conventional practice. These parameters were based upon pilot studies and waste characterization done in 1974, and are descriptive of the intended plant operating conditions.

The company's experience

The Chemagro treatment facility includes a 48-tpd cryogenic oxygen plant. In the company's experience, it was found that operators with a high-school-level education exhibited the capacity to learn the control of such an air separation plant, which is designed to produce much more oxygen than is currently consumed. The high purity oxygen aspect of the biological process requires little extra effort, or skill, Pallanich says. But one area that does require additional effort and skill is process control.

In his presentation, Pallanich noted that there is a significant increase in instrumentation for high purity oxygen systems. Increased maintenance requirements are inevitable, he reported. Hydrocarbon monitoring and oxygen purity measuring equipment must receive competent, routine attention. Thus, much of the instrumentation involved with oxygen systems is beyond the experience of the regular maintenance crew. But the vendor can supply manpower, training, or both to maintain specific equipment, and can upgrade the capabilities of the local maintenance staff.

A number of advantages have been realized through use of high-purity oxygen treatment at the plant. These include:

* reduced sludge yield
* high dissolved oxygen concentrations
* reduced land area.

These are the well-known advantages. Other less well-known advantages include:

* odor control
* overall control of air emissions.

Oxygenation, its use today and tomorrow for wastewater treatment

Company	Number of plants on stream	Municipal or industrial	Flow (mgd)	Dollar volume	Number of plants designed to go on stream	Municipal or industrial	Flow (mgd)	Dollar volume
(Union Carbide (Tonawanda, N.Y.)	90[a]	Industrial: 45 Municipal: 45	1544.2	N.A.	61[a]	Industrial: 5 Municipal: 56	2958.3	N.A.
AIRCO	1	Industrial	0.08	N.A.	1	Municipal	1.8	N.A.
Air Products	8	Municipal	112+	N.A.	13[a]	Federal: 1 Industrial: 1 Municipal: 11	1000+	N.A.
FMC Corp.	5	Industrial: 2 Municipal: 3	35[b]	N.A.	25	Municipal	636	$61.5 million

[a] Worldwide
[b] Municipal equivalent
Source: companies

All vapors from the treatment plant are treated by thermal oxidation, or by ozone. This odor and overall air emission control would be impractical with an air system.

Brewery waste

For a consulting engineering view on oxygenation in sludge, the firm of Flood & Associates, Inc. (Jacksonville, Fla.) reported a comparison of activated sludge and UNOX treatment.

There, at Jacksonville (Fla.), a 5-mgd plant was built in 1969 to handle the municipal wastes plus an industrial component from the brewery. It has been functioning for the past eight years. Full treatment at this plant has been carried out by the use of contact stabilization, complete mix, and pure (UNOX) oxygen-activated sludge modes of operation. The pure oxygen-activated sludge process became a standard wastewater treatment tool in only the last decade.

During the initial years of expansion of the brewery industry, new plants were generally located in large metropolitan areas, with waste discharged to large municipal treatment plants employing secondary biological treatment. In those early days, the brewery waste stream generally represented only a small percentage of the overall metropolitan waste load. Understandably, no major problems were experienced. As the industry continued to grow, however, breweries began moving into areas in which large municipal plants were not available to receive the waste stream.

A case in point is Anheuser-Busch. The company considered locating a major brewery in Jacksonville. The City of Jacksonville entered into a contract with Anheuser-Busch, whereby the city would construct and operate a treatment facility that would receive and treat all the brewery's wastewaters. Accordingly, in 1968, the City of Jacksonville retained Flood & Associates, Inc. to design the wastewater treatment facility.

The plant was originally designed as a contact stabilization plant, utilizing a trickling filter as a roughing filter prior to contact stabilization. When this plant went on line in the late summer of 1969, operational problems immediately became apparent.

First of all, the plant operation during this time was characterized by instability, according to the Flood Associates engineers. Also, the wastewater from the brewery bore little relation to the design parameters provided.

The plant was operated in the contact stabilization mode from June 1969 to November 1974. The almost doubling of waste strength as measured by BOD (design: 900–1100 mg/L; encountered: 933–3069 mg/L), combined with elevated temperatures (117 °F compared with a design value of 100 °F), immediately and severely overloaded all of the biological treatment units. Moreover, the plant was designed for 300–600 mg/L of suspended solids, but encountered 308–1000 mg/L.

The trickling filter became anaerobic, and caused severe odor problems. The mechanical aeration system was unable to transfer oxygen at the rate required, because of the organic overload. Dissolved oxygen concentrations of zero were not uncommon. The aerobic digester suffered from the same massive overload.

Enter UNOX

In 1972, a UNOX pilot plant study was undertaken, and assumed a retention time of approximately six hours. The study concluded that the pure oxygen-activated sludge system could be subjected to sustained periods of high, widely fluctuating loadings and still produce a good effluent quality. The actual UNOX plant was placed into operation in mid-1974.

In 1976, a 5-mgd expansion to the Jacksonville Sewer District 2 plant was bid. The expansion was designed for two alternate bids. Both alternatives were identical, except for the method of aeration. The base bid was for pure oxygen-activated sludge; the alternative was for diffused air-activated sludge. On the basis of both capital and projected operating cost, the pure oxygen system was selected.

Trickling filter BOD removals were in excess of 40%, while the UNOX system and overall plant removals arranged well over 90%. Thus, the pure oxygen-activated sludge system demonstrated a superior capability for removing BOD. To arrive at this conclusion, one has only to compare the BOD removals effected by the two systems.   SM/JJ

EPA looks at oxygen/activated sludge

The U.S. EPA has recently released a publication, "Status of Oxygen-Activated Sludge Wastewater Treatment, EPA 625 4-77-003a. It came out in October. For more information, contact: U.S. EPA/ERIC, Technology Transfer, Cincinnati, OH 45268.

Industrial water pollution program

Come to St. Louis, Mo., for the 6th WWEMA show.
You will see a display of water pollution control equipment
and instrumentation from WWEMA's 300-membered companies.
You will hear the following program. We will see you there.
The Water and Wastewater Manufacturers Association (WWEMA) show
will be held at the Stouffers' Riverfront Towers, April 11–13.

April 1978

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SESSION 1
Tuesday, April 11,
9:00–12:00

Topic: Environmental Law
Developer: Hershel Richman (Shralow, Newman, & Richman)
Panel Discussion:
9:00–12:00 GROUP PRESENTATION

Overview of the Resource Conservation and Recovery Act William L. Rosbe (Hunton and Williams)

Comprehensive Water Management Planning and Section 208 of the Clean Water Act Kelly O'Day (Betz, Converse, and Murdoch)

1977 Amendments to the Clean Water Law Hershel Richman (Shralow, Newman, & Richman)

Water Resources and Land Use Controls Daniel R. Mandelker (Washington University School of Law)

Safe Drinking Water Act and Its Proposed Regulations Victor J. Kimm (Environmental Protection Agency)

SESSION 2
Tuesday, April 11,
2:00–5:00

Topic: Mining and Metals Industries Case Histories
Developer: Art Fedrigon (Swift Environmental Systems)
Presentations:

2:00–3:00 **Treatment of Tailing Water in the Molybdenum Mining and Milling**
Industry Goplan Ramadarai (U.S. Borax and Chemical Co.)

3:00–4:00 **Alternate Methods of Treating Steel Mill Coke Plant Wastewaters** James Irwin (RETA)

4:00–5:00 **Phase Separation of Coke Plant Charging Liquors** Ali I. Aktay (Inland Steel Corp), S. R. Balajee (Inland Steel Corp)

SESSION 3
Tuesday, April 11,
2:00–5:00

Topic: Beverage and Brewing Industry Case Histories
Developer: Thomas Wilson (Greeley and Hansen, Engineers)
Presentations:

2:00–3:00 **Brewery Waste Treatment** Philip Hayden (Pollutior Control Science Inc)

3:00–3:30 **Activated Sludge Treatment of Brewery Waste Water** Ed Kominek (Envirotech Corp), Mark Beisinger (Envirotech Corp), Dave Stensel (Envirotech Corp)

3:30–4:00 **Application of the Deep Shaft Process to the Treatment of Brewing Industry Wastes** F. B. Knudsen (Molson Breweries, Ltd), Bernard Kuslikis (Eco-Research, Ltd), D. C. Pollock (Eco-Research, Ltd)

4:00–4:30 **Treatment of Brewery Waste Using an Oxygen Activated Sludge System** Fred Dailey (Union Carbide Corp), Irving Williams (Union Carbide Corp)

4:30–5:00 **Simplified Aeration System Treats Waste at Schlitz Brewery** George R. Fisette (Ralph B. Carter Co), Paul Burnett (Joseph Schlitz Brewing Co), John Riley (Joseph Schlitz Brewing Co)

SESSION 4
Tuesday, April 11,
2:00–5:00

Topic: Solving Operational Problems

Developer: Henry Mueller (Neptune Microfloc)
Presentations:

2:00–3:00 **Suspended Solids Monitoring at Chambers Works** D. C. White (E. I. du Pont, Inc), F. L. Williams (Leeds and Northrup Co)

3:00–4:00 **Steel Tank Coatings for Corrosion Control** Francis Grillot Jr. (Peabody TecTank, Inc)

4:00–4:30 **Bearings and Gears for Clarifiers, Thickeners, and Rotary Distributors** John C. Grinder (Rotek, Inc)

4:30–5:00 **Achieving Fast Payback with Heat Recovery** James Mueller (REECO)

SESSION 5
Tuesday, April 11,
2:00–5:00

Topic: Industry Solutions I
Developer: Richard Socolich (Kaiser Engineers)
Presentations:

2:00–3:00 **Ultraviolet Disinfection of Secondary and Tertiary Waste Effluents** Sidney Ellner (Ultraviolet Purification Systems, Inc)

3:00–4:00 **Reverse Osmosis to Achieve Water Quality Control and Recycling** Ray Heizer (Kaiser Engineers)

4:00–5:00 **Membrane Pond Liner Application** Ralph Woodley (Burke Industries)

SESSION 6
Wednesday, April 12,
9:00–12:00

Topic: BAT/BPT: Cost-effectiveness of Meeting Increased Effluent Limitations
Developer: Wesley Eckenfelder (Vanderbilt University)
Panel Discussion:
9:00–12:00 GROUP PRESENTATION

Refining Industry Viewpoints Lial F. Tischler (Engineering-Science, Inc.)

Federal Viewpoints W. Lamar Miller (Environmental Protection Agency)

Pulp and Paper Industry Viewpoints John Koon (AWARE, Inc)

Chemical Industry Viewpoints Richard Conway (Union Carbide Corp)

SESSION 7
Wednesday, April 12, 2:00–5:00

Topic: Pulp and Paper Industry Case Histories
Developer: George Strudgeon (Zurn Industries)
Presentations:

2:00–3:00 **Application of Activated Sludge Biological Treatment at a Typical Groundwood Pulp and Paper Mill** E. Breland (Weston Environmental Consulting Engineers), C. Vath (Weston Environmental Consulting Engineers)

3:00–4:00 **Treatment Plant Operation at Wausau Paper** Thomas Smith (Wausau Paper Co), E. O. Bergmann (Zurn Industries)

4:00–5:00 **High Solids Cake Discharge with a Continuous Feed Twin Roll Press** Marion Burn (Gilman Paper Co), J. R. Coughlin (Ingersoll-Rand Environmental Div), C. E. Gustafson (Ingersoll-Rand Impaco Div)

SESSION 8
Wednesday, April 12, 2:00–5:00

Topic: Food Industry Case Histories
Developer: Jack McVaugh (Envirex Inc)
Presentations:

2:00–3:00 **Recovery of Protein and Fats from Meatpacking Wastewater** Robert Sherman (AL Labs, Inc), Walter Adams (Sterling Packing Co)

3:00–4:00 **Winery Waste Treatment in the Northeast: A Case Study** A. C. Rice (Taylor wine Co)

4:00–4:30 **Evaluation of Biological Treatment Alternatives for Corn and Potato Wastes** Al Vickers (Frito-Lay, Inc)

4:30–5:00 **Design and Evaluation of a Corn Starch Wastewater Thickener** Robert Judson (Frito-Lay, Inc)

SESSION 9
Wednesday, April 12, 2:00–5:00

Topic: Industry Solutions II

Developer: Richard Prober (GMP Associates, Inc)
Presentations:

2:00–3:00 **Evaporative Possibilities with High Strength Biological Wastes** Thomas R. McWhorter (McWhorter & Associates), William A. Dedert (Dedert Corp)

3:00–4:00 **Economics of Granular Carbon Regeneration in the Electric Infrared Furnace** F. K. McGinnis III (Shirco, Inc), F. D. Richmond (Shirco, Inc)

4:00–4:30 **The Effect of Powdered Activated Carbon on Wastewaters of Babcock and Wilcox Stirling Avenue Plant** Paul Pflaum (Babcock and Wilcox)

4:30–5:00 **Stagewise Gasification in a Multiple Hearth Furnace** Robert Shelton (BSP/Envirotech)

SESSION 10
Wednesday, April 12, 2:00–5:00

Topic: Advanced Wastewater Treatment
Developer: Pat DeJohn (ICI United States, Inc)
Presentations:

2:00–3:00 **Evaluating Advanced Physical-Chemical Treatments for Dye Wastes** Aharon Netzer (University of Texas), S. Beszedits (B & L Information Services)

3:00–4:00 **Full-Scale Testing of an Alternate Powdered Activated Carbon** Brian Flynn (E. I. du Pont, Inc)

4:00–5:00 **Review of Federal and State Guidelines for Land Application of Sludges** R. Srinivasaraghawan (Greeley and Hansen), M. Stark (Greeley and Hansen)

SESSION 11
Thursday, April 13, 9:00–12:00

Topic: Chemical Industry Case Histories
Developer: Robert Hanson (ICI United States, Inc)
Presentations:

9:00–10:00 **Pesticide Laboratory Wastewater Treatment** Frank McNeice (ICI United States, Inc)

10:00–11:00 **Total Recycle in an Industrial Phosphate Plant** William B. McGregor (Olin Corp), Thomas R. Bernard (Olin Corp), Arnold L. Feldman (Olin Corp)

11:00–12:00 **Field-Scale Oxygen Transfer Testing: Problems and Results** Richard Bell (Monsanto Co)

SESSION 12
Thursday, April 13, 9:00–12:00

Topics: Power Industry Case Histories
Developer: Donald Kemp (Metcalf and Eddy)
Presentations:

9:00–10:00 **Compliance of Bottom Ash Sluice Systems to Federal EPA Regulations** Hassan M. El-Baroudi (Envirosphere Co)

10:00–11:00 **Removing Complex Iron and Copper from Power Plant Chemical Cleaning Wastes** William Throop (Envirex Inc)

11:00–12:00 **Waste Water Control Technology in Steam-Electric Power Plants** Tien-yung J. Chu (Tennessee Valley Authority), Richard J. Ruane (Tennessee Valley Authority)

SESSION 13
Thursday, April 13, 9:00–12:00

Topic: Sludge Handling
Developer: Andrew Pieper (The Permutit Co)
Presentations:

9:00–10:00 **Cost-Effectiveness of Thermal Sludge Conditioning** Michael R. Mayer (Zimpro, Inc)

10:00–11:00 **Applications of Coagulant Aids to Sludge Dewatering** Robert Bradley (The Permutit Co)

11:00–12:00 **Codisposal of Sludge with Solid Waste** Richard Eldridge (Waste Age Magazine)

SESSION 14
Thursday, April 13, 9:00–12:00

Topic: Powdered Activated Carbon Treatment
Developer: John Meidl (Zimpro, Inc)
Presentations:

9:00–10:00 **Process Kinetics of the Powdered Carbon-Activated Sludge System** Walter K. Johnson (Minneapolis Metropolitan Waste Control Commission), Jong S. Lee (University of Minnesota)

10:00–11:00 **Powdered Activated Carbon Treatment at Kalamazoo, MI** Felix Sampayo (Jones and Henry Engineers, Ltd), Donald Swets (City of Kalamazoo)

11:00–12:00 **Experience with Carbon Treatment at Du Pont** Francis L. Robertaccio (E. I. du Pont, Inc)

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This volume on the present ecological conditions of the Finger Lakes is the first of a unique series that will profile the physical, chemical, geological, and biological properties of freshwater lakes in New York State. Emphasis is placed on eutrophication, pollution, and other ecological factors changing the environment of these lakes. Much of the material is of a general nature and should be of interest to many ecologists working on temperate zone freshwater lakes. The volume documents existing knowledge, and represents a framework for future ecological studies and attempts at environmental management.

1978, 512 pp., $23.50/£15.25; subscription price: $19.50
ISBN: 0-12-107301-7

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A Volume in ENERGY SCIENCE AND ENGINEERING: RESOURCES, TECHNOLOGY, MANAGEMENT, An International Series

The book first characterizes waste as an energy resource and defines the quantities of material available by type of waste, i.e., municipal, crop, animal, industrial, and forestry. It then examines actual and potential energy recovery technologies. Primary and secondary processes for converting all types of residues into useful fuels are discussed. The contributors concentrate on thermal processes but also pay attention to biological systems. In focusing upon emerging technologies, they relate these systems to current waste management practices. Following the consideration of the technical issues, the text surveys the nontechnical problems of product marketing and system financing.

1977, 352 pp., $26.50/£18.80   ISBN: 0-12-056450-5

FUELS AND ENERGY FROM RENEWABLE RESOURCES

Edited by DAVID A. TILLMAN, KYOSTI V. SARKANEN and LARRY L. ANDERSON

Proceedings of the American Chemical Society Symposium on Fuels and Energy from Renewable Resources, held in Chicago, August 30-31, 1977

The purpose of this important volume is to establish an overall framework for the present and potential contribution of fuels from renewable resources. The contributors first examine total United States energy needs, offering a more complete analysis of the present energy contribution of nonfossil organic materials than is available elsewhere. Chapters next focus upon silvicultural materials, describing the potential amounts available, their fuel value, problems of collecting wood materials, and methods for utilizing wood and wood residues. The volume then turns to agricultural materials—crops and animal residues—and again deals with amounts available, collection, and utilization. Finally, current and potential systems for using urban residues are critically assessed.

1977, 352 pp., $17.50/£12.40   ISBN: 0-12-691250-5

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In fifteen carefully selected papers the editor portrays the development of the second law and, to a large extent, the development of classical thermodynamics in general from the rather uncertain beginnings in the nineteenth century to the more rigorous formulation due to Planck and Caratheodory. Stress is placed on the difficulties posed by irreversible processes.

1976, 352 pp., $30.00/£21.30   ISBN: 0-12-786839-9

VOLUME 4/COAL, PART II
SCIENTIFIC AND TECHNICAL ASPECTS

Edited by MONES E. HAWLEY

1976, 448 pp., $33.00/£23.45   ISBN: 0-12-786642-6*

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SOCIAL, ECONOMIC, AND ENVIRONMENTAL ASPECTS

Edited by MONES E. HAWLEY

1976, 400 pp., $33.00/£23.45   ISBN: 0-12-786641-8*

Set price for Volumes 3 and 4, Coal, Parts I and II, $58.00. Set prices are not valid in the United Kingdom, Australia, or New Zealand.

VOLUME 2/APPLICATIONS OF ENERGY
NINETEENTH CENTURY

Edited by R. BRUCE LINDSAY

1976, 432 pp., $34.00/£24.15   ISBN: 0-12-786961-1

VOLUME 1/ENERGY
HISTORICAL DEVELOPMENT OF THE CONCEPT

Edited by R. BRUCE LINDSAY

1975, 384 pp., $28.00/£19.90   ISBN: 0-12-786963-8

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SESSION 15
Thursday, April 13, 2:00–5:00

Topic: Metals Finishing Case Histories
Developer: John Koon (AWARE, Inc)
Presentations:

2:00–3:00 **Treatment of Wastewater Using the Baker Purification System Process** Stuart M. Raifman (Baker Bros, Inc)

3:00–4:00 **Treatment and Disposal of Anodizing Wastewater with Options for Re-Use** John W. Olver (Van Note—Harvey Assoc)

4:00–4:30 **Carbonate Precipitation for the Removal of Toxic Heavy Metals** James W. Patterson (Illinois Institute of Technology)

4:30–5:00 **Heavy Metals Removal at Philips Plating** Murray Scott (The Permutit Co)

SESSION 16
Thursday, April 13, 2:00–5:00

Topic: Petrochemical Industry Case Histories
Developer: Davis Ford (Engineering-Science, Inc)
Presentations:

2:00–3:00 **Using Polymers to Upgrade Plant Performance** Ralph Churchill (Petrolite Corp)

3:00–4:00 **Petrochemical Plant Waste Cleanup** Joseph Molina (University of Texas)

4:00–5:00 **Petrochemical Industry Wastewater Treatment** Larry Brackwell (Environmental Dynamics, Inc)

SESSION 17
Thursday, April 13, 2:00–5:00

Topic: Industrial-Municipal Treatment Solutions
Developer: Andrew Loven (Engineering-Science, Inc)
Presentations:

2:00–3:00 **Pretreatment: A Dilemma for Industry** Robert G. O'Dette (Tennessee Dept of Public Health)

3:00–4:00 **Payment of Sewer Service Charges, or Build Your Own Plant** Carl Ekuland (RETA)

4:00–5:00 **Plant-Community Solutions in a Food Processing Facility** James Hettenhaus (Anheuser Busch, Inc),

Tom Strehle (Anheuser Busch, Inc), Jon Hughey (Anheuser Busch, Inc)

SESSION 18
Thursday, April 13, 2:00–5:00

Topic: Biological Carbon Systems
Developer: Bill A. Carnes (Zurn Industries)
Presentations:

2:00–2:30 **Trinity River Authority Tertiary Carbon Absorption System** Ashok Varma (Forrest and Cotton)

2:30–3:00 **Enhancement of the Refinery Activated Sludge Process with Powdered Activated Carbon** George T. Thibault (Exxon Research and Engineering Co), Brian L. Steelman (Exxon Research and Engineering Co), Kenneth D. Tracey (Exxon Research and Engineering Co)

3:00–3:30 **Activated Carbon for Pretreatment of Industrial Wastewater** Ken Bradley (Uniroyal), Al Hiltgen (Zurn Industries)

3:30–4:00 **Combined Biological and Carbon Adsorption at the Duck Creek Plant, Garland TX** George Strudgeon (Zurn Industries), Maury Stiver (Zurn Industries)

4:00–4:30 **Application of Pact at Textile Mills** Mel Hockenbury (Engineering-Science, Inc)

4:30–5:00 **Use of Powdered Activated Carbon with Rotating Biological Discs for Refinery Wastewater Treatment** James Dehnert (Lion Oil Co)

Clean Water Act of 1977

The new amendments provide for the continuation of the construction grant program and more strict control of toxic pollutants and encourage innovative technology

A major legislative milestone in 1972 was passage of the omnibus Federal Water Pollution Control Act Amendments, P.L. 92-500. Among its many provisions was one for midcourse corrections. After three years of study, hearings, haggling and cajoling, these midcourse corrections were signed into law on December 27 as the Clean Water Act of 1977, P.L. 95-217.

Five more years

While the new law stresses innovative, alternate wastewater treatment technology (recycling and reuse of wastewater including sludge, land treatment and methods to decrease wastewater volume)—especially those methods and techniques that will reduce total energy requirements—certainly one of its more important provisions is the continuation of the municipal wastewater treatment construction grant program.

For those states that have already run out of construction grant money, the five-year extension of the grant program with total funds of nearly $25 billion is surely gratifying. The new water law authorizes construction grants totaling $4.5 billion for fiscal year 1978, and $5 billion for each fiscal year 1979, 1980, 1981 and 1982.

Deadlines

In signing the legislation into law, President Carter praised the Clean Water Act's emphasis on the "importance of controlling toxic pollutants" (*ES&T*, February 1978, p 154). The deadline for control using "best available technology economically achievable" is July 1, 1984 for toxic pollutants for which EPA is now formulat-

ing effluent standards (some 65 compounds).

EPA can add to or delete substances from its initial list. Industrial dischargers will have three years (from date listed) to comply with effluent standards for substances added to the list.

If an industrial discharger has shown "good faith" in attempting to comply with the original 1977 best practicable control technology deadline, and if treatment facilities are under construction, the new amendments extend the compliance deadline to April 1, 1979.

In addition to the deadlines for toxic and conventional pollutants, the new law establishes a third category for nontoxic, chemical or thermal pollution whose control deadline is July 1, 1987. Waivers from control standards can be issued to applicants who demonstrate that discharges of their "nonconventional" pollutants pose no danger to established fish populations or water quality.

For municipal compliance with secondary treatment standards, the EPA can authorize extensions to July 1, 1983.

Communities now discharging their primary treated sewage to deep-ocean outfalls may continue to do so if they can show that such disposal practices are not harmful to indigenous fish or to existing water quality standards.

And more assistance

The new law authorizes $200 million for fiscal year 1979 and $400 million for fiscal 1980 for programs, administered by the Secretary of Agriculture, incorporating "best management practices to control nonpoint source pollution." Contracts with land owners or operators to control nonpoint source pollution can be arranged through September 30, 1988.

The Department of the Interior also receives support under P.L. 95-217: $6 million to complete the National Wetlands Inventory of the U.S. by December 31, 1981.

The new law establishes an emergency contingency fund to be maintained at $10 million. This fund will permit the EPA administrator to assist in emergencies stemming from the release of pollutants into the environment that cause "imminent and substantial danger to public health and welfare."

To help small communities meet sewage treatment requirements, P.L. 95-217 provides for measures to fund decentralized treatment systems and areawide wastewater treatment management plans. For the first time, onlot or cluster sewage treatment systems, maintained by a municipal agency, become eligible for federal grants. Some 35 rural states are likely to benefit from this new provision.

Summing up

In signing the legislation into law, President Carter said that this new Clean Water Act "reaffirms our national commitment to protect the quality of our waters." But Carter is also concerned about getting energy legislation passed this session of Congress so he cautioned that some of the provisions of the water act may have to be relaxed in the future to accommodate a federal energy program. LRE

Chemical control of human fertility

A recent ACS study highlights the prominent role of **Chemistry in Medicine**

In the fifties and sixties the American public carried on a love affair with chemistry and "Better Living through Chemistry" was a popular slogan. But the seventies saw the love affair pale and "better" became "bitter." In some circles, chemistry became a blighted word synonymous with cancer. But chemistry has had some very positive effects, one of which is fertility control. Chemical contraception has freed women (and nations) from unwanted pregnancies, and chemically-induced ovulation has enabled infertile couples to produce progeny.

Some of the marvels that chemists have performed in the realm of medicine during the 20th century, and the responsibilities they have thus accrued are documented in *Chemistry in Medicine: The Legacy and the Responsibility,* a study by the Committee on Chemistry and Public Affairs, American Chemical Society. This publication is available from ACS Special Issues Sales.

Some positive effects

Gregory Pincus and John Rock may not be household names, but their basic discoveries have led to a product found in at least 10 million households in the U.S. and 50 million worldwide. The product: The Pill, the oral combination (steroidal) hormone tablet.

Although there have been some unfortunate side effects associated with use of these hormones, scientists, especially chemists, are searching for safer formulations, alternative delivery systems, and male contraceptives!

Nations plagued by unchecked population growth could turn to sterilization or chemical contraception as solutions to this worrisome problem. Nations that have introduced The Pill report varying degrees of success. But where The Pill has successfully checked population expansion, some ameliorating effects on the environment have also occurred.

For example, smaller populations result in less water usage and less attendant pollution; less water-related health problems; less pesticide usage and less deforestation with resultant climatic changes (desert creep).

Population control—decreases in growth—usually results in a slowdown in economic growth which, in turn, results in a tapering of energy demand. Less demand for fossil fuels results in less disruption of the environment.

Chemists have not only been busy concocting compounds that block pregnancies, they have also been busy developing compounds that enhance human fertility.

Chemists, for example, have for-

mulated hormonal concoctions that:
- induce ovulation to enhance the chance of pregnancy
- quiet uterine activity during pregnancy to inhibit premature labor
- initiate labor at term. They have also developed compounds that terminate pregnancies in the first and second trimesters.

Combined oral contraceptives

Pincus and Rock recognized that a combination of sex hormones with progestational and estrogenic activities could prevent conception by inhibiting ovulation and, when taken on a regular schedule, could mimic the natural menstrual cycle in women. But the

natural steroidal hormones were inactive when taken by mouth, and organic chemists set about synthesizing unique steroidal agents with high oral activity.

After years of manipulation, the first oral contraceptives became available in the mid-1950's. These active progestogenic compounds are generically called norethindrone or its isomer norethynodrel. They are analogs of a naturally occurring testosterone hormone with progestational activity. The estrogenic component is the methyl ether of ethynylestradiol.

A myriad of possibilities

Modifications of the naturally occurring 17α-hydroxyprogesterone, a steroid that lacks progestational activity, led to the development of compounds—medroxyprogesterone acetate, megestrol acetate and chlor-

madinone acetate—with enhanced oral progestational activity.

Chlormadinone acetate is in fact the first agent developed as a minipill: a pill containing no estrogenic component and one-third the concentration of progesterone found in the combination pill.

Unlike the combination pill, the minipill is taken daily throughout the menstrual cycle. It's inhibitory effects are not related to the ovulatory event as is the case with the combination pill. Although the exact inhibitory mechanism is not known, the minipill may act by making the uterus unreceptive to the ovum (egg) or by changing the composition of the uterine cervical mucus so that it no longer allows sperms to pass.

Unfortunately, women taking this pill often develop irregular bleeding patterns.

While the daily combination pill is still the most widely used contraceptive, other use-patterns and modes of introduction are being studied. For example, the separate but sequential ingestion of estrogen and progesterone; the one-time injection of a progestational agent that can block ovulation for up to six months; or the subcutaneous implantation of silastic capsules containing the hormonal formulations.

Some other possibilities include intrauterine devices that release microamounts of specific contraceptive agents (usually progesterone) to the uterine musosa; the "morning-after pill" (diethylstilbestrol taken in large

doses within 24–72 h after coitus); or, for the future, nasal aerosol sprays that deliver the hormones directly to the ultimate site of action—the brain.

Changing social attitudes have finally wended their way into the scientific laboratory. After decades of research on female contraceptives, scientists are now actively searching for a male contraceptive.

While a variety of approaches have been taken to control sperm formation, maturation and motility, no male contraceptive has been marketed to date. Progestational hormones have been tested that interrupt the sperm development cycle but these also interfere with libido and are unacceptable contraceptives. Clinical trials on combination progesterone/testosterone formulations are now being held.

Treatment for infertility

Sterility and infertility plague thousands of couples who desire children. Here, also, chemists have come to the rescue. One compound, acting positively on the hypothalamic-pituitary-ovarian axes, actually stimulates rather than inhibits ovulation. That compound: clomiphene citrate, a nonsteroidal weak estrogen introduced around 1960.

Still other compounds have been developed that quiet the uterus to prevent premature labor. Two such compounds with limited clinical use are isoxsuprine and ritodrine. Unfortunately these compounds may also effectively quiet other smooth-muscled organs such as the heart and blood vessels.

Ultimate control

The chemical wizardry previously used to block or stimulate ovulation has produced compounds that usually act on the pituitary-ovary link of the tripartite brain-pituitary-ovarian axes. The ultimate control, however, would be interference—either positively to induce ovulation or negatively to inhibit it—with the hypothalamic-pituitary chain. And even here, chemists are making headway.

After nearly 20 years of effort, chemists in the 1970's were able to isolate and elucidate the structure of a "master" hypothalamic hormone that controls the formation and release of gonadotropic hormones from the pituitary, which in turn govern the cyclic hormonal processes in the ovary. This master hormone plus its numerous first-cousins (analogs) are being biologically tested for their stimulatory or inhibitory effects on ovulation. Ultimate contraceptive control may be close at hand! LRE

Plant closes loop on its wastewater treatment

Mississippi Chemical turns out 6 million pounds of fertilizer products each day, and handles millions of gallons of water in making its various products

One of the world's most complete fertilizer facilities, the Pascagoula production facility of Mississippi Chemical, operates around the clock—24 hours a day, seven days a week, 365 days a year. During some of these 24-h days, the facility produces 3200 tons of 100% sulfuric acid, more than 3000 tons of granular fertilizers, 1200 tons of 100% phosphoric acid (equivalent to 850 tons of P_2O_5), and 560 tons of anhydrous ammonia. The facility is a large-volume producer of NPK (nitrogen, phosphorus, potassium) "mixed" fertilizers.

Since 1973, Mississippi Chemical has invested nearly $64 million at this facility—$28.4 million for expansion and modifications to production facilities and $35.6 million for environmental improvement programs. The facility employs about 600 non-union employees. In addition, the company's environmental protection activity requires a staff of 28 technical specialists. Mississippi Chemical General Manager, Jim Gambrell, says, "The wastewater treatment system at Pascagoula, Mississippi, is one of the most expensive, most comprehensive, and most advanced plants ever built in the U.S."

Mississippi Chemical President Tom Parry estimates that the new wastewater facilities, which alone cost $22 million and became operational last year, would increase the cost of the product by $6–$6.50 per ton. In addition, it would cost the company $500 000 annually to maintain and operate the environmental protection system.

To get an idea of this mammoth project, Area Supervisor, Luther Compton, says, "the project required 25 000 feet of pipe, 20 miles of electrical wire, and employed 22 sub-contractors". Nearly two years were involved in the engineering design and treatability studies and another two years lapsed in physically building the new system and putting it into operation.

Air-water team consultants

The wastewater treatment operation, involving ten separate systems, was engineered by Weston Environmental Consultants-Designers (Westchester, PA). The air emissions were engineered by Teller Environmental Systems, Inc. (Worcester, MA). These two engineering consulting firms worked in conjunction with one another. The air emissions were treated, scrubbed, and wound up in the wastewater, which was recycled and reused.

General manager Gambrell
". . .most advanced plant in U.S."

The objective of the Teller Company in its air improvement was to design scrubbing equipment that would remove the solid particulates, ammonia, fluorine and other objectionable matter contained in the various gas and vapor streams from the three NPK plants and the phosphoric acid plant so that the resultant emissions to the atmosphere would meet EPA requirements. The Teller Company designed facilities to meet all environmental air standards at increased rates of production and the recovery efficiencies of all three NPK plants were upgraded.

Mississippi Chemical's new wastewater treatment complex has 10 water treating units. It handles millions of gallons of water daily, primarily for cooling and scrubbing. With the Weston System, no water used in the manufacturing processes, or which falls on the plant area as rain, will enter nearby Bayou Casotte.

Now, with the Weston design, process water is treated and recycled and used over and over again. Only treated water that has had the pollutants removed is discharged into the bayou.

The control of fluorine and phosphate levels in this loop is essential. If the fluorine level in the water gets above a certain value, the fluorine escapes to the air and could become an air pollution problem. The fluorine is kept in the water by adding caustic to the circulating loop. Typically, process water at a pH of 3–3.5 and 110 °F leaves the phosphoric acid plant for the cooling tower and returns at a pH of 5.5 and 90 °F after caustic treatment. The fluorine is removed from the cooling tower water by adding lime to a slip stream of the loop. An essential

Water treatment systems

Gypsum slurry

Recycle water

| Phos acid plant | Hot water → Cold water ← | Cooling tower (2) | Contaminated water → Treated water ← | Gypsum pond system (4) |

Blowdown

| Triple super phosphate plant | Scrubber water ← Scrubber water → | Recycle pond (10) | | Neut. facility (6) | ← Blowdown |

| | | | | Liquid fert. plant | Hot water → Cold water ← | Cooling tower |

| NPK mixed fert. plants | Hot water → Cold water ← | Cooling tower (1) | Treated water ← Contaminated water → |

Raw sewage

| Sulfuric acid plants | Hot water → Cold water ← | Cooling tower | Rain. → Blowdown | Storm water collect. (3) | | Sewage treat. plant (8) |

Hot noncontact cooling water

| | | | | | | Cooling tower (9) | Cold water to Bayou → |

Treated water

| Ammonia plants | Hot water → Cold water ← | Cooling tower | Blowdown |

| Chromate removal (5) | Treated water |

| Oil collection (7) | Oil to sales → |

Treated water

Source: Mississippi Chemical Corp.

part of this loop is the use of some two miles of FRP (fiberglass reinforced plastic) piping ranging from 4–24 inches in diameter.

A closed-loop water system handles all the cooling requirements of the three NPK units. After providing these units with gas-scrubbing devices, the water picked up ammonia, dust, and fluorine. The water is now recirculated in a loop to eliminate water pollution. This loop minimizes water pollution, and at the same time creates a water balance, minimizes water usage, and conserves chemicals used to clean the water.

A slip stream of the cooling water is what is treated. The control of pH minimizes equipment corrosion and the caustic addition prevents the escape of fluorine vapors.

With this wastewater treatment system, Mississippi Chemical meets the requirements of its NPDES permit issued by the Mississippi Air and Water Pollution Control Commission. Weston engineers ensured that vapors from the wastewaters did not create an air pollution problem.

Additional air emissions corrected

The Pascagoula production facility has the world's first 1500 ton/day (tpd) double-contact sulfuric acid

plants. These plants each have seven major air emission control innovations; the first plant was completed in 1973, the second one in 1975. The EPA has found these sulfuric acid manufacturing plants, with a production capacity of 3000 tons, among the cleanest in the U. S.

One source of air emission that was corrected was ammonium phosphate emissions from the granulation operation. These emissions were eliminated by installing seven giant baghouses with fabric filters. These baghouses capture fertilizer dust before it has a chance to escape to the air. Another source of air emissions was the granulation plant, in which a liquid solution of the fertilizer is solidified and made into granules. Two-stage scrubber units were added here.

Designed by Teller Environmental, this system is a dual system. In a first co-axial Venturi scrubber, bases from the production processes of drying, granulating, and neutralizing are scrubbed with liquid phosphoric acid that is recirculated. In this recycle, solid particles of fertilizer, ammonia, and fluorine are extracted from the gases. After leaving the first section, the gases are carried through the cross-flow scrubber, which has two sections.

In a first half of this scrubber, the gases are scrubbed with a weak (5%) phosphoric acid solution. Here remaining ammonia and dust that might carry over from the Venturi scrubber are removed. About 80–90% of the fluorine in the off gases is removed at this point. In a second section of this scrubber, the scrubbing is performed with cooling tower water. Here the remaining fluorine is removed. Almost no ammonia or dust reaches this section. The cleaned gases, mostly air and water vapor, are exhausted up the stacks.

The 10 water systems

The NPK cooling tower supplies all scrubber water requirements for all the NPK plants (**System No. 1**). The main purpose of the cooling tower water is to supply scrubbing water to the second section of the cross-flow scrubber. Since the scrubbing in the water section is once through, the scrubbing water from the sprays and packed beds drain into a sump built into the bottom of the scrubber. From there it overflows to a lift station from which it is pumped back to the cooling tower neutralization unit.

In the neutralization well caustic is added to keep the pH above 6. In the recirculation, the cooling water picks

Controls. *In the aerial shot of the fertilizer plant at Pascagoula, Miss., the controls are not obvious. But close-up, the most important wastewater treatment system, the neutralization facility (center), and the scrubber on the phosphoric acid plant (bottom) are shown*

pollutants resulting from the operation of the phosphoric acid manufacturing plant and four phosphoric acid concentrators are absorbed in the water, which is treated to meet the federal standards.

Weston's closed-loop system eliminated the use of bayou water and minimized thermal enrichment of the bayou water. The system is pH controlled to minimize equipment corrosion problems. The escape of acidic vapors is prevented by treatment with caustic. The sodium compounds formed by reaction of the acidic pollutants with caustic are removed by treating a slip stream from the cooling tower with lime.

The Pascagoula facility also has an elaborate storm water collection system **(System No. 3)**. Every drop of water falling on the 13.5-acre manufacturing facility is collected in a series of concrete U-drains. In the manufacture of 1 million tons of mixed fertilizer product in the course of a year, the nature of the raw materials and products cause the deposition of solids and liquids containing nutrients in certain areas of the manufacturing facility.

These nutrients include, for example, phosphoric acid, sulfuric acid, potash, and all types and grades of NPK fertilizer products. The water collected by the series of U-drains is pumped to a holding pond capable of storing five million gallons of water. The impounded water is recycled back into the wastewater treatment system as NPK cooling tower makeup water.

In the production of phosphoric acid, byproduct gypsum is produced in the reaction stage. This gypsum is filtered out of the product acid, slurried with water, and pumped to a 280 acre landfill impoundment area. The slurry water is decanted through clear wells from the impoundment area to a 30-acre holding pond.

The water from the holding pond is recycled to the phosphoric acid plant for reuse as gypsum slurry water and process water **(System No. 4)**. The entire gypsum impoundment area and recycle water system is surrounded by a system of outer retainer dykes, reclaim ditches, and pumps to recover seepage and rainfall and return this water to the holding pond. The gypsum slurry water recycle system ensures zero discharge of water into the bayou.

In the ammonia plant at the Pascagoula facility, a chromate additive is fed to the cooling tower water; this additive serves as an anticorrosion agent. The chromate is removed **(Sys-**

up fluorine in the scrubbing action. The evolution of fluorine into the air at the cooling tower is prevented by keeping the fluorine concentration below 1800 ppm and by adding caustic to the circulation loop.

The scrubber-cooling tower system operates at essentially zero discharge. A key factor in maintaining this zero discharge condition is careful control of water usage in the NPK plant. The control of plant water balance is ab-

solutely essential to successful operation of the NPK plant environmental control system. Complete cooperation is required among plants and between plant operating personnel and the personnel responsible for cooling tower operation to maintain this control.

The Pennsylvania consulting firm of Weston designed a cooling system for the phosphoric acid plant **(System No. 2)** that offers an example of the air and water controls working together. The

tem No. 5) from the used water by a process of electrolytic precipitation. At Pascagoula, chromate is removed from the cooling tower blowdown water by the electrochemical process of the ANDCO Company (Buffalo, NY).

Chrome is removed to less than 0.05 ppm. No pH adjustment or chemical addition is needed in this process, which is continuous, once through, and automated. A prefabricated ANDCO unit requires a few square feet of space. The unit also reduces zinc and organic phosphates often used as anticorrosion agents in cooling towers. The ANDCO process can also be used to remove other metals including cadmium, copper, gold, iron, lead, mercury, nickel, silver and tin.

The nucleus and most important wastewater treatment system at the Pascagoula facility is a neutralization facility (System No. 6). The neutralization facility is a tertiary liming system consisting of three stages of neutralization; flocculation, clarification, and sludge removal.

This neutralization facility treats slip streams from system 1 through system 5 to remove acidic impurities and return treated water to the sys-

tems. The impurities are precipitated with lime. The water is returned to the systems for reuse; the precipitate is landfilled.

In the production of ammonia, oil and water are separated from the product streams in separators. The separators are piped to a centrally located collection tank (System No. 7) and are processed through oil separators and filters. The oil is removed and sold as waste oil for recycle. The clean water is discharged.

Before the plant improvements, the sanitary sewer system (System No. 8) at the facility consisted of septic tanks. These tanks were replaced with a complete system of lift stations at strategic locations in the manufacturing facility. A network of transfer piping, pumps and headers now pump all these wastes to an extended aeration treatment plant for complete treatment.

Thermal controls have also been included (System No. 9). The NPDES permit specifies that the maximum temperature of the effluent should not be greater than four degrees above the temperatures of the intake water during October to May, nor above 1.5

degrees above the temperature of the seawater intake, from the bayou, during June to September.

For example, 18 000 gallons per minute of bayou water is used in shell and tube heat exchangers as steam condensers on steam turbines. The only pollutant added in this process is heat. To remove the thermal pollutant from this once through non-contact cooling water, a cooling tower was installed to cool the water so that the effluent would be within the limits of the permit.

In the production of triple-super phosphate, acidic fumes are emitted. To prevent these fumes from being emitted to the air, scrubbers were installed to scrub the fumes from air pulled through the production and storage facilities (System No. 10). To prevent the scrubber water from being discharged to the bayou, a closed-loop pond system was installed. The recycle pond system is maintained at a 6 pH to prevent fluorine from escaping to the air. The contaminant concentration in the circulating loop is controlled by sending a side stream to the phosphoric acid plant where it is then used as process water.

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In the late 1960's there was a developing controversy in the U.S. over the environmental impact of most of our primary industrial processes. Concern was followed by proposals for radical changes, including changes in the siting, operation, and taxing of new and existing industrial facilities. Ambient air measurements in the major cities, as well as in the countryside, convinced us that the problems were real. The first step required for the implementation of a meaningful control strategy was the detailed analysis of the pollutant emissions from each specific stationary source.

Recognizing this need to provide real-time, accurate source-emissions data, a group of scientists and engineers from the Jet Propulsion Laboratory formed Environmental Data Corporation (EDC) in 1969. After researching monitoring requirements then in existence and planned for the near future, a survey was taken of the instrumentation presently being utilized to meet these requirements. Based upon this information an instrument development program was started.

Background

Los Angeles County was a leader in the development of an ambient air-monitoring network with stations across the Los Angeles basin. This ambient information was supplemented with periodic source tests by wet-chemical extractive techniques.

New Jersey had placed limits on SO_2 emissions from certain industrial sources and required that either a low-sulfur fuel be utilized or that the stacks be monitored to ensure compliance.

Many state and regional environmental control authorities had set existing regulations for the maximum allowable opacity emissions from the various industrial categories of stationary sources. Opacity monitors had been installed in compliance with these requirements.

Chemical analyses of stationary source emissions had been performed by means of an extractive wet-chemical determination. Very few instruments had been installed for continuous operation.

Discussions with the technical staffs of both the regulatory agencies and also those industries attempting to perform instrumental gas-stream analyses indicated that the analytical

ES&T

FEATURE

IN STACK MONITORING OF GASEOUS POLLUTANTS

The designed instrument package monitors source emissions and combustion control parameters

technology being utilized to make these measurements was more than adequate. However, in almost all cases, the analyzers were of a laboratory type, requiring sample preparation.

Typically the analyzer was mounted in a shed with a probe used to extract one or more samples from the gas stream. This gas was led through a sampling pump, flow and pressure regulators, a water trap, a particulate trap, and often through a chemical scrubber before being introduced into the analyzer. With periodic plugging of the traps and filters, possible water breakthrough and chemical attack on the sampling system, this sampling hardware increased maintenance requirements and reduced the representative nature of the sample finally being analyzed. The almost universal concern was the reliability of the sampling system.

After researching the complexities of sampling systems, and the variety of expected operating conditions, the solution selected was the elimination of the sampling system. The sample was to be measured in place as it flowed.

Having set up this operating constraint, an analytical technique had to be chosen. The minimum number of "absolute" requirements were:

• well-developed technology— no state-of-the-art breakthroughs required

• amenable to simple, rugged, reliable instrumentation

• specific, but useful for multicomponent analyses

• nonsampling, noncontacting methodology, no instrumentation to be mounted inside the gas stream

• relatively inexpensive, and easy to maintain and calibrate.

The analytical technique that seemed to best fit these requirements was absorption spectroscopy, with absorptions in the ultraviolet (UV), visible, and infrared (IR) portions of the optical spectrum.

A careful review of the literature indicated that all of the gases of interest could be uniquely measured in the concentration ranges desired in either the UV or the IR. Nitric oxide (NO) was selected as the first parameter to be measured.

Environmental applications

The first operating prototype in-situ absorption spectroscopic NO monitor was installed on a test basis in the Broadway Plant of the Pasadena (Calif.) Department of Water and Power in October 1970. The second prototype was installed on a similar test basis at the Alamitos Plant of

Southern California Edison in November 1970. The response by some plant operating personnel was very encouraging. For the first time, they commented, they were able to see every feature and detail of their operation as they made changes in load, fuel, and excess air. One year later, in February 1971, Southern California Edison placed an order for 26 NO monitors, all of which needed to be installed and operating by June 30, 1971.

Once the NO ultraviolet monitor was functional, the next instrument development was the addition of a second UV channel for SO_2. With the NO and SO_2 capability in a single instrument, EDC was able to offer an environmental monitoring package that would meet the then-developing EPA new source-monitoring requirements (include opacity in this package).

In August of 1971, the EPA proposed standards of performance for new stationary sources of specific categories (stea generators, Portland cement plants, incinerators, nitric acid and sulfuric acid plants), which set emission limits on certain pollutants (particulate matter, sulfur dioxide, nitrogen oxide, and sulfuric acid mist) and required testing, stack gas monitoring and data reporting. On December 23, 1971 these standards of performance of new stationary sources were promulgated.

Of these source categories, the one of most immediate interest was the fossil-fuel-fired steam generators. These regulations required that each new facility of more than 250 MBtu/h heat input must continuously monitor opacity, nitrogen oxide, and sulfur dioxide (except when gaseous fuel is burned or low-sulfur fuel was being burned to achieve compliance).

This requirement opened a new marketplace that would require some approximately 30 monitors per year as new sources were constructed. Since that time, emission limits have been placed on a large number of basic industries, with monitoring requirements on a significant fraction of those (see box).

On October 6, 1975, EPA promulgated additional important pieces of lawmaking. Part 60 of Title 40, Chapter 1, subchapter C-Air Programs, provides standards of performance for new stationary sources and instrumentation performance specifications for transmissometers, SO_2 and NO_x monitors, and CO_2 and O_2 monitors. In addition, at this time, the monitoring requirements were expanded to include the continuous

New sources: emissions limits, monitoring requirements[a]	
Steam generators (≥ 250 MBtu/h)	Opacity SO_2, NO_x, dilution
Nitric acid plants	NO_x
Sulfuric acid plants	SO_2
Petroleum refineries	Opacity, CO, SO_2
Primary copper smelters	Opacity, SO_2
Primary zinc smelters	Opacity, SO_2
Primary lead smelters	Opacity, SO_2
Ferroalloy production	Opacity
Iron & steel plants	Opacity

[a] In one or more parts of the operation

monitoring of dilution so as to be able to provide a dilution-free reporting base. Furthermore, the notification and recordkeeping requirements were expanded.

At the same time, EPA promulgated Part 51 of Title 40, Chapter 1, subchapter C, Requirements for the Preparation, Adoption, and Submittal of Implementations Plans. EPA promulgated requirements that the states must adopt and implement legally enforceable procedures requiring, as a minimum, monitoring of emissions from existing sources that fell into those source categories presently being controlled on a new source basis by EPA. The timetable of these requirements would result in a major installation of continuous monitoring hardware on existing stationary sources over the remaining years of this decade.

Certain states, such as California and Maryland, have not only required the monitors, but have had them installed and operational. The retrofit of continuous monitoring instrumentation to existing sources will be a short-term bubble, with the long-term marketplace being the testing, maintenance, and replacement market.

Stack monitoring

EDC's first in-situ continuous emissions monitors were installed in the Summer of 1971. These devices were tuned to respond to NO emissions only. While performing the preventive maintenance program, it quickly became evident that although the equipment was often not mounted in a centrally located position, the hardware was being utilized as one of the sensors for combustion control. When a load or fuel change was made in the

boiler, the first step would be to increase the air, and then make the appropriate change. Once the change had occurred, the excess air could be reduced to its normal operating point.

It seems that the O_2 analyzer, with its associated sampling system, had a response time of approximately 30 s. The in-situ NO stack monitor had a response time of approximately 3 s. As the operators gained experience with the instrumentation and their operations, they began to use the expected NO set point to re-adjust the excess air.

At approximately this same time, Anson and coworkers at the Central Electricity Generating Board (CEGB) in England published a paper entitled "Carbon Monoxide as a Combustion Control Parameter." Studies at CEGB's engineering laboratory, as well as field studies at power stations, had led them to the conclusion that the optimum combustion firing condition with minimum heat loss is achieved at that point at which a small incremental reduction in excess air first leads to a large incremental rise in combustible emissions (primarily carbon monoxide).

Since insufficient air will result in incomplete combustion—wasting fuel—one always wants to operate a boiler or heater with excess air and at a minimum heat loss position. For a well-balanced boiler, this is typically very close to stoichiometric.

Combustion emissions

The nitrogen oxide emissions are a function of several parameters including fuel-bound nitrogen (especially for coal-fired plants) and flame temperature. As the excess air is reduced, the flame volume increases, and the peak temperature decreases. The formation of nitrogen oxide is very temperature dependent. We have seen the reduction of excess oxygen from approximately 3.5% to 0.5%, resulting in a 15% decrease in NO_x emissions.

The fuel-bound sulfur to a large extent is all converted to SO_2 (some studies have shown that a portion of the sulfur may be retained in the fly ash). This oxidation of the sulfur to SO_2 is not readily controlled by changing firing conditions. However, the SO_2 may be oxidized to SO_3.

The measurement of carbon monoxide (CO) has been selected as the appropriate combustion-control parameter because instrumentation exists today that can measure its presence in very low concentrations, and also because the measurement of CO maintains its meaningfulness as the excess air is lowered toward stoichio-

metric. Instrumentation is available to measure CO in the few ppm region. Response time of the equipment is fast. Alternately, oxygen (O_2) can be measured with high sensitivity and rapid response, but there are two fundamental problems that result in ambiguous measurement.

As the excess air in the combustion process is reduced, the infiltration of air into the system begins to play a major role as the primary source of the measured oxygen. A 5% air leak resulting in 1% additional O_2 would reduce a CO monitor reading 200 ppm by only 10 ppm. Obviously, under these conditions, it becomes much easier to control with the CO analyzer.

Also, because of their rapid response time, the zirconium oxide-type O_2 sensors are being used more frequently today. These sensors have very high sensitivity and reliability, but unfortunately do not measure an absolute oxygen presence. The system measures the difference between the total available oxidized gas stream components minus the total available reduced-gas stream components. It is possible to reduce excess air to the point wherein considerably high levels of combustibles are being produced. The O_2 sensor would show a differential reading.

Sensor: sensitive and reliable

EDC recognized that it was able to enhance the benefits of online CO measurement for combustion control. By utilizing the EDC in-situ, longpath monitoring approach, we could provide a sensor that could:
- measure CO with very high sensitivity
- provide a fast response analysis (3 s)
- provide a longpath averaged flue-gas analysis
- be part of an instrument package monitoring both environmental emissions and also combustion control parameters.

As the excess air is reduced, the inbalance in air-to-fuel ratio at each burner begins to play a significant factor in the overall boiler emissions. Both the fuel flow and the air flow from some common supply to the individual burners is regulated primarily by pressure drop. Because of wear and tear, blockage, or poor selection of components, each burner operates as a local flame with its own air-fuel ratio. As load, fuel type, or excess air change, the relative air-fuel ratio from burner-to-burner will change slightly. At some point, as the excess air is lowered, a particular burner may become starved for air and may begin to create smoke, or very high levels of CO. A single-point extractive, or single-point in-situ monitor, thus becomes very position sensitive for low excess air control. The longpath averaging in-situ technique increases one's ability to control carefully.

EDC has supplied over 100 instruments in the last few years for the real-time in-situ monitoring of CO for combustion control. With this CO monitor installed, Canal Electric Company was able to reduce its flue-gas oxygen from approximately 2–3% down to approximately 0.6%. This resulted in a heat-loss reduction of 133 Btu/kWh or 107 920 bbl of oil per year (over a $1 million fuel savings).

However, as has been pointed out above, as the excess air is reduced to almost stoichiometric, burner balanced air-fuel ratios are very important for continued tight control. Present instrumentation and maintenance packages on utility and industrial boilers or heaters do not allow this. EDC has developed a new series of sensors, one of which will mount directly on the front of the boiler, one at each burner, collecting the radiation from the flame.

Spectral flame analyzers

This is an emission spectroscopic analysis, whereby the flame is the source, and the analyzer performs a chemical analysis. Two wavelengths are sequentially measured, and by the proper selection of these wavelengths, the ratio is related to the local flame stoichiometry. These analyzers are called spectral flame analyzers (SFA).

With the availability of these on-line combustion control sensors, EDC is proposing to augment the existing standard combustion control practice by means of careful burner-to-burner balancing. SFA will mount at each burner and its output will feed back to a central controller. This controller, to a first approximation, will operate to adjust the air-fuel ratio at each burner to be identical. This combustion control sub-loop will maintain the burners in a balanced operating condition independent of fuel type, load, or excess air. Now the standard overall combustion control system can be utilized with a CO sensor for the excess air control.

Such a system is presently being operated on a 300 000 lb/h industrial, four burner, front-wall fired, horizontal boiler. The system includes a stack monitor for CO (as well as opacity, NO, SO_2, and CO_2) and also a SFA, a fuel-flow-control valve, and a fuel-flow meter (for information purposes only) at each burner, and a central analog control unit.

With this system in place, the excess oxygen on gas firing has been reduced from an average of 2% to less than 0.1%, resulting in a calculated yearly fuel savings of approximately $100 000. On oil, the excess O_2 has been reduced from approximately 3.5% to less than 0.4%, resulting in a calculated fuel savings of $160 000/y. The total system hardware cost was approximately $100 000. This demonstration has been funded by the Department of Energy, with Exxon Research and Engineering as the prime contractor. A similar system will be installed shortly in a steel mill. In larger systems, it is anticipated that the individual spectral flame analyzers can be utilized for flame shaping, programmed off stoichiometric firing, as well as providing a secondary flame safeguard measurement.

The NO monitor

The fundamental instrument design is a light source mounted in a box external to the gas stream on one side, with a collimated beam of light passing through the gas stream into an analyzer box mounted external to the gas stream on the other side. The light beam passes through the diameter of the stack or duct. The light level would vary in the gas stream as a function of time. Over a long period of time, the intensity seen at the detector would vary as the light bulb decayed, the windows darken, and the opacity level of the gas stream varied.

To produce a result that was independent of varying light level, EDC utilized the best features of the two standard laboratory configurations—the single-beam and double-beam techniques. A single beam of light passes from the source, through

---

Beer's law

$$I = I_0 K e^{-\alpha cl}$$

where

I = signal strength after passage through the absorbing gas

I_o = signal strength before passage through the absorbing gas

K = constant

α = absorption coefficient of absorbing gas at the wavelength being observed

c = concentration of absorbing gas

l = optical pathlength (slot length in pipe)

the source box window, through the gas stream, through the next window, and into the analyzer. In the analyzer, the beam is separated into its component wavelengths. The wavelength of interest, where the gas absorbs, falls upon the detector. A very nearby nonabsorbing wavelength is also measured. The intensity of light transmitted to the detector at this wavelength is representative of the intensity of light at the absorbing wavelength with no gas absorption. This is true as long as the two wavelengths are so close together that there is no significant differential scattering by particulates between those two wavelengths.

Typically, in the UV, the two wavelengths are separated by approximately 10–20 angstroms, thereby guaranteeing that differential scattering will be minimal.

By measuring alternately the absorption (I) and the reference (I_o) wavelength falling upon a single detector, with a fixed optical path in the gas stream, I, one computes the gas stream concentration from Beer's Law. This dual-wavelength rationing system with high-spectral resolution, and both UV and IR sensitivity meets the operational criteria listed above.

Prototype installed

A prototype device was constructed in the Summer of 1970, and installed at a local power plant in October 1970. This was a single gas analyzer, measuring only nitric oxide. An UV, deuterium-arc source was used. The optical system is shown schematically in Figure 1.

The light from the source is collected by a $2\frac{1}{4}$-in. square, $\frac{1}{2}$-in.-thick quartz front surface mirror. This is overcoated with magnesium fluoride for maximum UV reflectivity. A $\frac{1}{2}$-in.-thick quartz blank is used to maintain optical stability with large variations in ambient temperature. The mirror is mounted kinematically on a $\frac{3}{8}$-in. thick aluminum mirror stand. This mirror stand is bolted firmly to the source box base by means of two bolts, and is positioned precisely with a dowel pin.

The source box is constructed of $\frac{1}{2}$-in.-thick aluminum that has been black anodized (to provide chemical inertness, and also to reduce the reflection of stray light). The box is welded at all the seams. The removable front cover of the box is "gasketed" and clamped in place so that the box is gas tight.

The light beam passes from the box into the gas stream through a $2\frac{1}{2}$-in. quartz window mounted in a slider, which can be raised for window cleaning. In this way there is direct access to the windows without ever affecting the optical alignment of the system (Figure 1). For the gas analy-

Blower air purge system

- defines optical pathlength, "1," measured in gas stream

- provides cooling air, reducing heat conduction from gas stream to instrument

- provides air purge across windows for cleanliness

- provides positive pressure air flow in shroud around instrument, reducing dust infiltration

sis, it is not essential that these windows remain clean, but only that they transmit enough light so as to allow the analyzer to function. An installation is shown in Figure 2.

The source box is mounted onto a spool piece that is a transition mounting between the source box and a pipe flange. This pipe flange is welded to an 8-in. pipe that is used as a cross member through the gas stream connecting the source and analyzer boxes. A blower fan is mounted on the spool piece, bringing in outside air and passing an air curtain across the slider windows to keep them clean.

The fan circulates outside cooling air, maintaining the analyzer at approximately ambient temperature even when the process gas stream temperature is significantly hotter. The air from the fan exhausts through the

FIGURE 1

In-situ flue-gas analyzer system
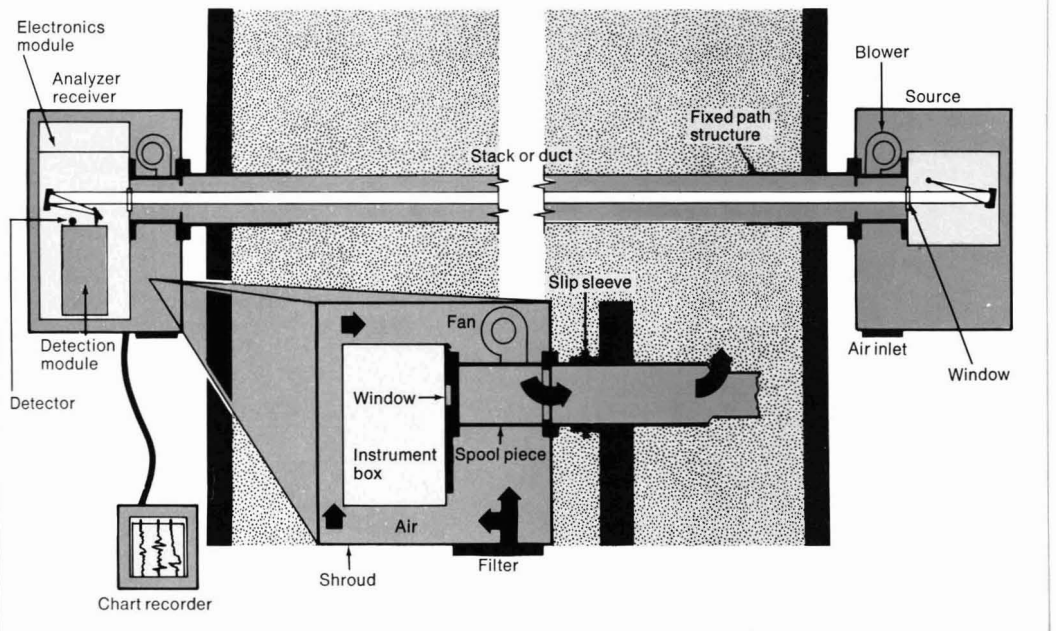
spool piece and down the pipe. There is a slot in the pipe running the width of the gas stream that allows the gas stream flow to pass uninterrupted. There is a shear at the edge of the slot, between the high-flow rate, lower pressure gas stream, and the higher pressure, lower flow rate air purge. This shear through the pipe defines the optical pathlength being analyzed by this system. The sample being analyzed is defined exactly by this slot length, as the ends of the pipe are purged by clean ambient air.

The source side and the analyzer side of the installation are essentially mirror images of each other. All of the mounting details described above apply to both sides. A protective shroud covers both the source box and the spool piece with the blower fan providing basic weather protection to the instrument. This shroud has an air inlet on the bottom with a filter to provide the first stage of air filtering.

More instrument details

The 8 in. cross-stack mounting pipe is fitted through a 10 in. slip sleeve that is directly attached to the stack or duct. In this way the pipe is able to ride free, maintaining the source and analyzer alignment, while the mounting platform (stack and duct) undergoes vibration, or thermal contortions. In metal stacks or ducts, the side of the stack toward the sun can become considerably warmer than the opposite side and undergo thermal expansion.

These gas analyzers, using the dual wavelength ratioing technique, are not dependent upon the amount of light received at the analyzer. It is not necessary that the entire 2-in. square beam pass through the gas stream and be entirely collected at the analyzer side. However, some significant portion of that beam must be collected to provide a signal for the analyzer to process. If the light beam is deflected to such a degree that it is not received at the analyzer, the system cannot work. This mounting configuration has proven highly successful in operations characterized by considerable vibration or thermal expansion.

The analyzer box, though larger, is of the same basic construction and design as the source box. This analyzer box is designed to contain up to five real-time analyzers, each with its own set of electronics locally mounted in the box. To provide maximum flexibility in the parameters being measured, EDC developed modules to measure specific absorbing species in the IR also. In addition, the basic instrument design accommodates a two-parameter UV module, an opacity module operating in the visible part of the spectrum, five sets of electronics, and a power supply tray. The gases measured in each spectral region are listed in a box.

The system primarily uses solid-state analog electronics. The signal from the detector is processed by a combination automatic gain control and preamp board. The second board is an integrator and analog divider

Spectral regions for parameters	
Ultra-violet	NO, SO$_2$, NH$_3$, H$_2$S[a]
Visible	Opacity
Infrared	CO, CO$_2$, H$_2$O(v), HCl, H-C[b]

[a] H$_2$S can only be measured in ≥ 100 ppm concentrations
[b] Use the 3.4 μ stretching frequency; response similar to n-hexane sensitized NDIR

board with zero and span adjustments. The front panel on each set of electronics contains several test points as well as the adjustable pots for the zero, span, and instrument gain.

As each of the signals are essentially nonlinear, an analog linearization circuit is available as an option. Also, special features such as temperature compensation are available.

For a five-parameter analyzer with two gases measured in the IR, two in the UV, and opacity measured in the visible, three light sources are used: UV, IR, and visible. The gas analyzer systems are single-path design (the source on one side of the gas stream and the analyzer on the other), and the opacity instrument is a double-pass system (source and detector on the same side. Because of limitations in energy in the IR source, when two infrared absorbing species are measured simultaneously, two infrared beams are used from a single source. Thus in this multiparameter analyzer, as many as four light beams, each approximately 2 in. square, will traverse the gas stream.

The UV and IR

Light from the source is collimated, sent through the gas stream, and is focused onto the UV analyzer. The UV analyzer is a monochromator. When two gases are being measured simultaneously in the UV, a second mirror picks off the appropriate wavelengths from the grating, focusing these upon a second phototube adjacent to the first. Each detector has its own set of signal processing electronics.

The IR source is a 1600 °K blackbody globar. The electronics are "synced" to an 800 Hz frequency, and the detector is able to discriminate among thermal emissions in the gas stream to see only the IR source. If two gases are being measured simultaneously in the IR, two mirrors are used in the source box, each picking up part of the light from the globar.

In the IR, because of the broader spectral features, lower gain detectors

FIGURE 2

NO monitor mounted on a typical installation
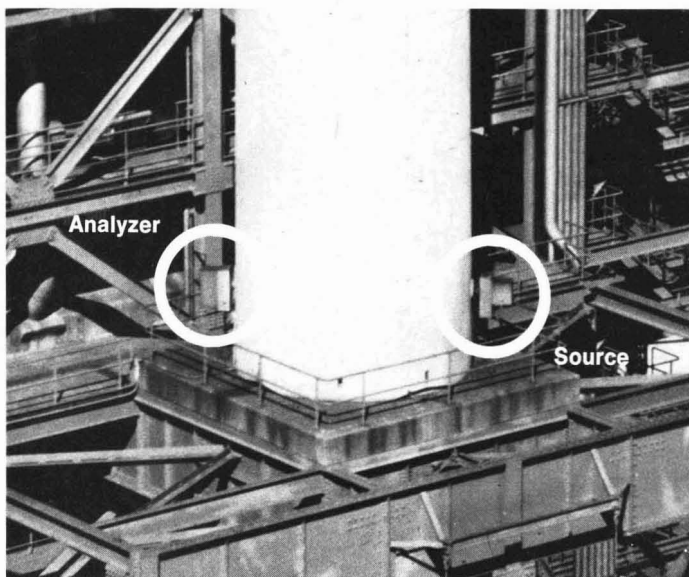
and weaker sources than the UV, a dispersive system is not used. The wavelength selection is performed by one of two methods: either by means of narrow bandpass filters, or by gas cell correlation.

The opacity module

The opacity module provides a measurement of the reduction in transmission of visible light through the gas stream. Since few if any gases with significant concentrations absorb light in the visible, this reduction is due almost exclusively to scattering of light by particulates, aerosols, or water drops. Because of calibration constraints, this is a double-pass system with the source and detector on the same side of the gas steam (in the analyzer box) and a retroreflector in the source box (Figure 3).

Since the instrument is a double-pass optical design, it is more sensitive to a given density of particulates than a single-pass design. However, the scattering of radiation by particulates can occur at all angles. so as to minimize the possibility that light would be scattered off of a particulate center and returned directly to the detector, thus being observed as if there were no scattering centers, the instrument is designed to have a very narrow angle of view (approximately 2.0°) and angle of projection (1.5°).

The light beam, which traverses the stack from the source, overfills the retroreflector. In this way absolute alignment is not required and the light beam is still returned back to the detector. With the retroreflector an incident beam is returned directly back upon itself. Therefore, precise perpendicularity between the opacity module and the retroreflector are not required. These two design features provide considerable flexibility in the alignment and long-term operation of this unit.

The opacity instrument is calibrated by means of an internal zeroing mirror. It is possible to check the zero calibration position of the instrument by inserting this mirror. This instrument has an automatic calibration check built into its operation which, by means of a timer, will insert the zero mirror and then the neutral density filter, providing a calibration readout on the strip-chart recorder, or other data-collecting device.

Gas monitor calibration

With no process gas in the gas stream, the instrument should be reading zero. Once the optics and electronics are aligned, the zero adjust pot on the front panel of the specific
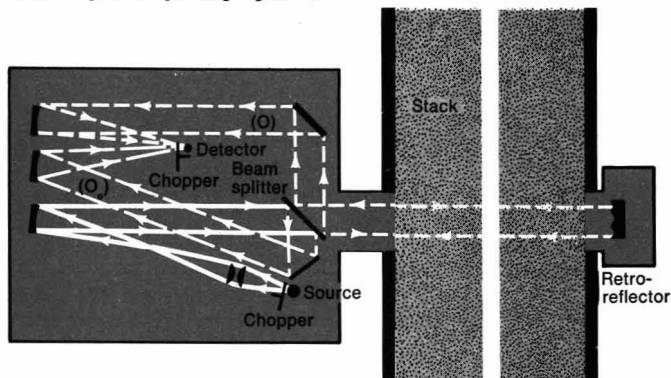
gas monitoring channel's electronic module is adjusted so that the instrument output is zero for this zero gas condition. With a cell in the light beam containing the appropriate concentration equivalent to the instrument full-scale span setting, the span pot on the electronic front panel is adjusted to one volt output, as read at the instrument by means of a digital multimeter. Since the instrument response curve is nonlinear, at least three additional cells are utilized to verify the instrument calibration curve.

When the process is in operation with gas in the stack, it is impossible to make a zero check by the above discussed procedure. Calibration can be checked by means of a secondary source in the analyzer box that bypasses the stack gas, similar to the opacity design. Since this source is not the one being utilized for the ongoing continuous gas measurement, the final calibration must be performed with the standard instrument source. This is done by the incremental addition of known concentrations of gas and curve fitting.

In conclusion

Stack-gas monitoring technology has evolved to the point where it can provide a long-term data base to meet EPA compliance requirements, and a real-time, fast, meaningful gas-stream analysis for more effective process control.

The sensor outputs are available for combustion control to reduce pollutant emissions, to enhance combustion efficiency, and to reduce system corrosion, as well as provide online sensors for the monitoring and control of abatement devices such as precipitators, flue-gas desulfurization units, and for process optimization.

With the increased interest in performance, advances in technology are expected to enable this equipment to perform on a level of reliability comparable to the rest of the plant hardware. Careful engineering to ensure high up-times and system longevity is occurring now. Future changes will continue to reduce the operator involvement, thereby increasing the usefulness of the instrumentation.

Additional reading

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Harry C. Lord, III, *is president and a director of Environmental Data Corp., a company he founded with others in 1969. Prior to 1969, Dr. Lord was a senior scientist at the Jet-Propulsion Laboratory. Dr. Lord holds patents in the fields of gas analysis and combustion control.*
Coordinated by LRE

FIGURE 3
Double-pass opacity system

Modeling man's influence on stratospheric ozone

*Complex mathematical constructs are being developed
to predict the ozone-depleting effect of a large fleet
of high-altitude flying supersonic aircraft*

Reynold Greenstone
*ORI, Inc.
Silver Spring, Md. 20910*

Man's activities might lead to a significant diminution of stratospheric ozone. For some years the principal concern was with the effects of emissions from aircraft flying in the upper atmosphere. When plans to build the U.S. Boeing SST, which was designed to cruise at 20 km, were dropped—at least partially for environmental reasons—concern shifted to the potential environmental hazards of the more imminent Anglo-French Concordes (17 km cruise altitude) and the U.S.S.R.'s Tupolev 144, and since then to any potential follow-on fleets of stratospheric aircraft.

More recently, worry over the effects of aviation on stratospheric ozone has abated considerably, and greater and more continuing concern has focused on the effects of the release into the atmosphere of CFMs (chlorofluoromethanes, also called halocarbons and fluorocarbons, and typified by the Freons) as the result of their use as refrigerants and as propellants in aerosol spray cans.

The postulated destructive effects of either aircraft or CFM emissions on stratospheric ozone are based essentially on the work of modelers.

The modelers use mathematical models of chemical kinetics and atmospheric transport to show that either the nitrogen oxides in the aircraft exhaust at stratospheric altitudes, or the chlorine atoms freed from the CFMs that survive ground-level release will interact with and destroy significant quantities of ozone molecules in the stratosphere.

No one has yet shown by direct measurement that stratospheric aircraft flight leads to ozone destruction. According to the modelers, the fleets of stratospheric aircraft would have to be considerably larger than the few Concordes flying today for a statistically significant ozone change to be produced and detected. The expected ozone changes would be small compared to the natural variability of stratospheric ozone.

In effect, the modelers have been prophesying possible calamities and urging remedial measures while, at the same time, saying there is no short-term hope of verifying their predictions short of allowing the calamities to occur.

This being the case, it is a matter of great interest to know the "track record" the modelers have established in predicting ozone destruction because of man's activities. I propose to trace through a sequence of predictions of the effects on the ozone region of exhaust emissions from stratospheric aircraft, ignoring the CFM problem with which I am less familiar.

The stratospheric ozone layer plays two physically related roles of direct concern to man: its climatic role and its ultraviolet shielding role.

Climatic role, uv shielding

The climatic pattern that results from ozone absorption of solar ultraviolet (uv) radiation at high altitudes is one of relative atmospheric instability in the lower, tropospheric regime where temperatures tend to decrease with height capped by relative stability in the upper, stratospheric regime where temperatures increase with height.

Stratospheric ozone chemistry

$$O_2 + h\nu \text{ (below 242 nm)} \rightarrow O + O$$
$$O + O_2 + M \rightarrow O_3 + M \text{ (twice)}$$

Net: $3O_2 + h\nu \rightarrow 2O_3$

$$O_3 + h\nu \ (\lambda \geq uv) \rightarrow O_2 + O$$
$$O_3 + O \rightarrow O_2 + O_2$$

Net: $2O_3 \rightarrow 3O_2$

$$NO + O_3 \rightarrow O_2 + NO_2$$
$$NO_2 + O \rightarrow NO + O_2$$
$$NO_2 + h\nu \ (<400 \text{ nm}) \rightarrow NO + O$$
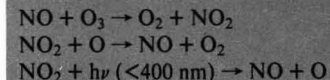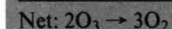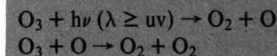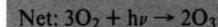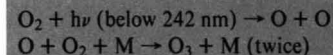
Of more immediate concern to mankind than possible climatic change, is the possible reduction in uv shielding by the ozone layer. It is widely believed that skin cancer in man—especially fair-skinned man—is caused by exposure to excessive uv radiation in the same wavelengths that produce sunburn (erythema).

According to the National Academy of Sciences (NAS) report (see additional reading), ". . . a reasonable estimate of the percentage increase in skin cancer . . . may be made by assuming that a 1% decrease of stratospheric ozone will cause roughly a 2% increase in skin cancer."

In recent years it has been pointed out, particularly by Harold Johnston, that earlier accepted reaction schemes are not adequate to balance out the ozone formation rate. Johnston and Paul Crutzen have both shown that catalytic ozone-destroying reactions involving the oxides of nitrogen (NO_x) could provide an adequate balance between worldwide ozone formation and destruction.

Once it is accepted that NO_x may be the key to determining the natural balance of stratospheric ozone, it is then natural to raise questions about the effect of NO_x from aircraft exhausts. This is what Johnston and Crutzen and, later, others did. They realized that aircraft exhausts, like automobile exhausts, contain NO_x and that aircraft flying in the stratosphere would inject the NO_x at altitudes near the natural ozone peak.

Johnston calculated the annual total amount of NO_x from a proposed fleet of 500 Boeing SSTs and found it to be about the same amount as might be expected to be present in the natural stratosphere. And then he sounded the alarm! If man's activities might double the natural amount of NO_x in the stratosphere, and NO_x is the key constituent in balancing global ozone production and destruction, what will be the new equilibrium level of ozone?

When Johnston did his initial cal-

culations he did find substantial ozone reductions. Crutzen found correspondingly large reductions for sufficiently large fleets of Concordes. Concerns like these were the stimulus that led to the initiation of DOT's Climatic Impact Assessment Program (CIAP).

U.S. findings

The DOT/CIAP *Report of Findings* was issued in December 1974, and was followed by the NAS' *Environmental Impact of Stratospheric Flight* in 1975. The two reports agreed qualitatively that stratospheric fleets of aircraft would cause ozone destruction, but quantitatively there was considerable difference.

Since only rarely do any two studies use the same input parameters for a problem, all results presented here have been linearly scaled to a standard level of 1.8×19^9 kg/y NO_2 injected into the stratosphere at 20 km, nominally representing the average global input of a projected fleet of 500 U.S. Boeing SSTs. On this basis, CIAP found approximately 12% ozone reduction globally and the NAS, 16%.

Since publication of the DOT/CIAP and NAS reports, work has continued and the estimated effects owing to aircraft have continued to change.

Evolution of calculations

The majority of the modeling studies that played a role in the DOT and NAS assessments of the aircraft threat

to ozone were presented in DOT's CIAP Monograph 3, *The Stratosphere Perturbed by Propulsion Effluents*. I will draw upon the work cited there plus two reports (SCEP and SMIC study) that antedated the CIAP study.

The 1970 *Study of Critical Environmental Problems* (SCEP) presented an assessment of the then-recognized global environmental problems attributable to man. It addressed, specifically, the impact of stratospheric

flight by supersonic transports and concluded that NO_x emissions were of no importance.

Still, hedging slightly, the authors did recommend a monitoring program for the lower stratosphere to include NO_x as well as water vapor, cloudiness, oxides of sulfur, hydrocarbons and particles.

According to SCEP (using prescribed emission parameters), the 500 SSTs would emit 2.63×10^9 kg/y of NO leading to a world average con-

FIGURE 1

Ozone-reduction predictions[a]
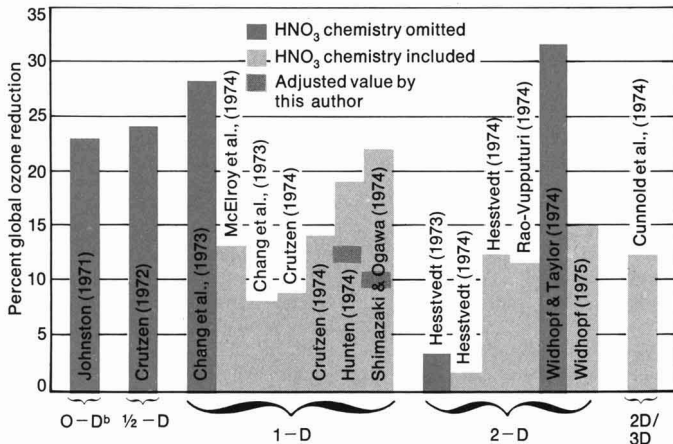
[a] 1.8×10^9 kg/y^{-1} NO_2 injected at 20 Km
[b] indicates type of transport model used

Author (Publication date)	Ozone reduction (%)	Nitric acid included yes/no	Model dimensions	Time dependent/steady state	Notes
Johnston (1971)	23	No	0-D	Steady state	No ozone diffusion, assumed uniform mixing of NO_x in specified band
Crutzen (1972)	23.6	No	½-D	Steady state	Ozone diffusion, NO quasidiffusion
Chang et al. (1973)	28	No	1-D	Steady state	Full diffusion, error in photolytic rate calculation procedure accounts for high value
McElroy et al. (1974) (Without temperature feedback)	13	Yes	1-D	Steady state	11% with temperature feedback
Chang et al. (1973)	8	Yes	1-D	Steady state	
Crutzen (1974)	8.5	Yes	1-D	Steady state	
Crutzen (1974)	14	Yes	1-D	Steady state	$10 \times K_z$
Hunten (1974)	19	Yes	1-D	Steady state	2-km adjustment
Shimazaki & Ogawa (1974)	22	Yes	1-D	Time dependent	Injection between 30–60 °N and 6000 km path N.Y. to Paris
Hesstvedt (1973)	3	No	2-D	Steady state	8 × Gudiksen et al. diffusion
Hesstvedt (1974)	2	Yes	2-D	Steady state	8 × Gudiksen et al. diffusion injection at 50°
Hesstvedt (1974)	12.3	Yes	2-D	Steady state	Luther diffusion, injection at 50°
Rao-Vupputuri (1974)	9.4	Yes	2-D	Steady state	Reed & German diffusion, temperature-dynamics—chemistry feedback
Widhopf & Taylor (1974)	32	No	2-D	Steady state	Luther diffusion, 50° injection
Widhopf (1975)	16	Yes	2-D	Steady state	Luther diffusion, 50° injection
Cunnold et al. (1974)	12	Yes (?)[c]	2D/3D	Time dependent	Gudiksen diffusion, 40–50° injection, HNO_3 in 2-D model, which set inputs to 3-D model.

[c] Indicates ambiguity in running "complete" chemistry in the auxiliary 2-D models, but incomplete chemistry in the 3-D model.

Johnston's calculations of the effect of injecting NO$_x$ at 20 km

Ozone concentration ($\times$ 10^{12} molecule/cm^3)
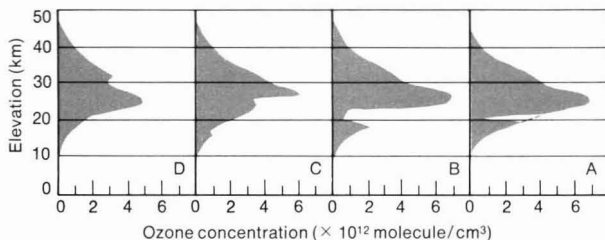
centration of 6.8 ppb, with a possible peak concentration ten times greater. Apparently unaware of the possible NO$_x$ catalytic cycle, the SCEP authors did not regard this NO buildup as significant.

The 1971 *Study of Man's Impact on Climate* (*SMIC*) was instituted "to review SCEP findings critically to point to global environmental problems that were slighted or overlooked, . . ." The SMIC authors returned to the question of the effects on ozone of the oxides of nitrogen emitted in the stratosphere.

They noted that NO$_x$ participates in the chemical process for stratospheric ozone and they described the now well-known catalytic cycle involving NO and NO$_2$ with the destruction of ozone, but did not draw any conclusions as to the amount of ozone destruction that would be caused by the injection of NO$_x$ in the stratosphere by the high-flying aircraft.

Figure 1 is the road map guiding the reader through the evolution of calculated ozone-reduction results. On the chart, the abscissa indicates the kind of model used: 0-D (D for dimension) means no explicit transport; $^1/_2$-D means *ozone* transport modeled in the vertical, but not other species; 1-D means vertical transport of all species; 2-D means 1-D plus north-south (meridional) transport; and 3-D means 2-D plus east-west (zonal) transport. Partial hatching on two of the bars indicates that I have adjusted the author's result to show comparability with other results except for a unique assumption made by the author. Full hatching shows the instances in which nitric acid chemistry was omitted from the models and indicates that possible ozone reduction tends to double because of the omission.

Simpler models

Harold Johnston at the University of California, Berkeley, in 1971 tested the effect of introducing the SCEP

amount of NO$_x$, reduced by the factor 0.35 (based on the engine manufacturer's recommendation).

He computed two general cases: case 1 where the NO$_x$ is distributed uniformly worldwide in the stratosphere in the horizontal sense but stratified vertically in a prescribed fashion; and case 2 where the NO$_x$ achieves a ten-times higher concentration corresponding to a latitudinal corridor enhancement effect, and is vertically stratified as in case 1. He assumed a two-year residence time for the injected material as had been done by SCEP.

Johnston's results for the uniform horizontal distribution throughout the world with four different patterns of vertical distribution are shown in Figure 2. In case A he assumed that all the NO$_x$ stayed in a 1-km band between 20–21 km, and found 3% ozone reduction. The greatest reduction occurred in case C where the injected NO$_x$ was assumed to spread over the band 17–25 km. It led to the often-quoted Johnston result of 23% ozone reduction.

In his worst-case calculations where he followed the SCEP lead and assumed a ten-time enhancement in the "corridor" where the SSTs would fly, Johnston computed 50% ozone reduction.

Paul Crutzen, now at NSF's National Center for Atmospheric Research (NCAR), introduced explicit time-dependent vertical diffusion calculations into the equations used to compute the ozone concentration.

Crutzen's results were reported in February 1972. Like Johnston, he made various assumptions about the vertical distribution of the injected NO$_x$, but treated the vertical diffusion of ozone explicitly. (Because ozone formation and diffusion were modeled but the NO$_x$ distribution was imposed, I denote Crutzen's modeling effort $^1/_2$-D).

Crutzen noted that nitric acid for-

mation could be an important process for removing NO$_x$ from the stratosphere but, like Johnson, did not take it into account in making his calculations.

Both Johnston and Crutzen had to make various assumptions about the background amount of NO$_x$ present in the "natural" stratosphere. For Crutzen's case closest to Johnston's, Crutzen found 23.6% ozone reduction, remarkably close to Johnston's 23%!

All the models described hereafter do explicitly include transport, in one, two, or three dimensions, of the reacting species.

One-dimensional models

Julius Chang and his colleagues at the Lawrence Livermore Laboratory published, in 1973, one of the earliest sets of results for ozone reduction, using full vertical diffusion of all species. Their adopted eddy diffusion profile had a minimum near 30 km.

The chemical reaction set was narrowly limited to the Chapman cycle for ozone formation and destruction plus the NO$_x$ catalytic cycle; nitric acid reactions were not considered. As can be seen in Figure 1, their result was among the highest shown in this review—28%.

In a later paper, also published in 1973, this time by Chang, Hindmarsh, and Madsen of Lawrence Livermore Laboratory (see the bar labeled Chang et al., 1973 in Figure 1) the authors calculated an approximate 8% ozone decrease with what appeared to be the same model. This large shift in effects was explained in a 1974 review by Chang and Johnston. They pointed out that not only was nitric acid's role ignored in the early paper, but also the photolysis coefficients used in the early paper were not properly recomputed as the calculated ozone was reduced.

Michael McElroy and colleagues at Harvard University used a simple one-dimensional eddy-diffusion model that included nitric acid chemistry. Their eddy diffusion profile differed from that of the Livermore group.

Since the stratospheric modelers have so often referred to different rationales leading to different choices of parameters, it is instructive to look at a sampling of the many profiles of eddy diffusion coefficients they have used.

For the works reviewed here (Figure 3), McElroy's minimum value of the eddy diffusion coefficient is apparently the lowest in value and occurs at the lowest altitude (about 16–18 km). Chang's minimum value is about twice McElroy's and occurs at near twice the altitude. Hunten's profile at the mini-

mum strongly resembles McElroy's.

The vertical diffusion profiles are indicators of how well ozone will diffuse downward from its formation region at higher altitudes; how well the injected NO_x will diffuse upward to mix with and destroy ozone; and how well the nitric acid will diffuse downward out of the stratosphere to serve as a sink for NO_x.

McElroy and coworkers obtained results for both a fixed-temperature case and one in which atmospheric temperatures were allowed to change as a result of computed changes in the amount of ozone and the consequent changes in energy absorption. The changed temperatures altered chemical reaction rates. By interpolation of the published results I found 13% ozone reduction as the "fixed-temperature" result to compare with the other studies in Figure 1 and 11% as the "radiative equilibrium temperature" result.

Crutzen, in 1974, published two new sets of results using 1-D models. By using some 60 reactions, now permitting vertical diffusion of all constituents, he found a decrease of 8.5% in ozone.

Later, in 1974, in *Ambio,* Crutzen revised his results, this time reporting approximately 14% ozone reduction. This newer answer comes from using larger vertical diffusion coefficients as shown in Figure 3.

In the key region between 20–30 km, the new Crutzen values of eddy diffusion coefficient are very close to the McElroy values and perhaps this accounts for their similar answers (14% and 13%, respectively).

Donald Hunten of Kitt Peak National Observatory used a composite model in which he computed the vertical mixing of NO_x, using his own choice of eddy diffusion profile, and then used the McElroy model to determine the relationship between ozone reduction and NO_x mixing ratio. Where McElroy had computed 13% ozone reduction, Hunten found 19%. The reason for the more drastic Hunten result was his assumption that aircraft altitudes ought to be adjusted to an effective altitude based on relative height above the tropopause. For instance, to determine the impact of SST flights at 20 km, Hunten used an effective altitude of 22 km.

Tatsuo Shimazaki and Toshihiro Ogawa, in 1974, reported on their 1-D results at the IAGA-IAMAP meeting in Melbourne, Australia. Unlike the steady-state models discussed above, this model is an example of the time-dependent solution to the ozone reduction caused by injection of NO_x.

FIGURE 3

Eddy diffusion coefficient profiles used to predict ozone depletion
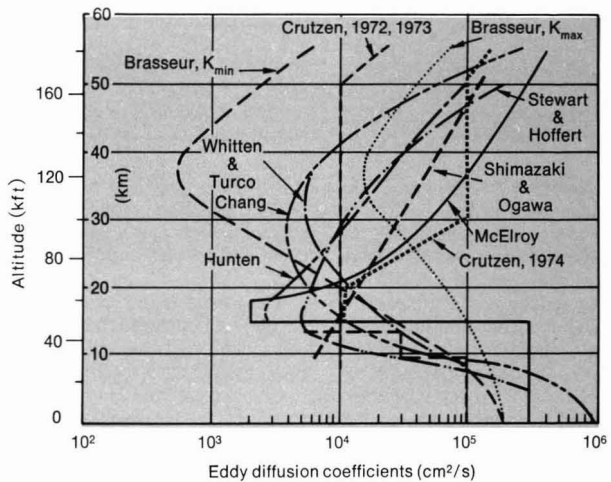
The model has a very complete set of chemical reactions.

The results appear to be equivalent to a 22% global reduction, unexpectedly high when compared to other 1-D results with comparable chemistry and transport. Figure 1 shows that this is the greatest ozone reduction obtained with any of the 1-D models that included nitric acid chemistry.

Was there something unique in the Shimazaki and Ogawa treatment? In fact there was. Unlike the other modelers, Shimazaki and Ogawa assumed that the injected NO_x would be confined to the typical SST flight corridor between New York and Paris (6000 km long), 30°–60° North latitude and 3 km thick.

In this way, they achieved an initial injection concentration of NO_x two-and-one-half times greater than that of Julius Chang, for instance, and this would go far to account for their more alarming prediction of ozone reduction.

Two-dimensional models

Eigil Hesstvedt of the University of Oslo was a pioneer among those who participated in the development of 2-D models portraying the interactions of stratospheric chemistry and transport. In order to introduce the meridional motions, he used two-dimensional eddy diffusion coefficients developed by Gudiksen and colleagues. But he found that the Gudiksen coefficients did not lead to a satisfactory representation of the natural ozone. Drastic changes were required. He ended by multiplying the Gudiksen coefficients by 8, and

doubling his original values of vertical wind speed.

Making calculations with the adjusted transport coefficients and omitting nitric acid chemistry, Hesstvedt, in a 1973 paper, found ozone reductions equivalent to 3%.

In a follow-up paper in 1974, Hesstvedt used much the same model as above but now added reactions related to the formation and destruction of nitric acid and permitted transport of the NO_x-related spcies. This time Hesstvedt reported a global average ozone reduction of about 2%.

Also in 1974 at the IAGA/IAMAP conference, Hesstvedt reported yet another set of calculations of ozone reduction, using diffusion coefficients developed by Fred Luther of Lawrence Livermore Laboratory. With the reduced rate of transport provided by the Luther coefficients, Hesstvedt now found 12.3% ozone reduction, which brought his results in line with the others.

Krishna Rao-Vupputuri of the Atmospheric Environment Service, Canada, reported calculations with a 2-D model in which the mean meridional circulation is generated from the meteorological equations of motion and there is thermal feedback involving both the transport and the chemical reaction rates. The model solves the equations for zonal momentum and heat balance as well as the continuity equations for the atmospheric trace species.

Rao-Vupputuri used 2-D eddy diffusion coefficients developed by Reed and German that are typically

large—often by as much as a factor of 2—than the Luther coefficients used by Hesstvedt. Rao-Vupputuri's calculated ozone reduction (9.4%) was somewhat less than Hesstvedt's 12.3%.

George Widhopf of the Aerospace Corporation presented 2-D results in 1974 in collaboration with Thomas Taylor, and other results by himself in 1975. In the earlier paper he omitted nitric acid chemistry but included it in the later paper. The model used the Luther diffusion coefficients.

Without nitric acid chemistry, the global ozone reduction was 32%. With nitric acid chemistry, the result was 16% ozone reduction, the typical factor-of-two dependence on nitric acid chemistry. This later result is reasonably close to the last result attributed to Hesstvedt (12.3%), as might be expected since they were using similar chemistry, and the Luther diffusion coefficients.

Three-dimensional model

Derek Cunnold and his coworkers at MIT, *Fred Alyea, Norman Phillips,* and *Ronald Prinn,* have published several papers concerning stratospheric modeling with the MIT

FIGURE 4

Results from the MIT 3-D model of the atmosphere

Total ozone distribution (Dobson units)

ᵃ Dashed line = natural background O_3 distribution
ᵇ Solid line = perturbed distribution

three-dimensional general circulation model (GCM) and ancillary two-dimensional models.

The MIT GCM was the only 3-D model of the atmosphere used during CIAP to calculate effects of chemical and photochemical interactions in the atmosphere. It has 26 levels from the ground to 70 km. The horizontal and vertical motions are generally derived from the governing meteorological equations, but there is an assumed vertical eddy diffusion profile. Only limited chemistry is modeled: the Chapman cycle plus the NO_x catalytic cycle. Nitric acid chemistry is omitted.

The model is run in a fully time-dependent manner so that a given run consists of many annual cycles, running through each season in turn.

Cunnold and his coworkers resorted to the use of Hesstvedt's 2-D model with "complete" chemistry to determine the proper natural background NO_x distribution and a consistent distribution for the natural ozone in the 3-D model. They then used a different 2-D model of their own with "complete" chemistry to determine the NO_x distribution caused by the addition of the standard NO_x injection from the 500-SST fleet. This new disturbed NO_x distribution was then introduced into the 3-D model to determine the change in ozone distribution.

Figure 4 shows the seasonal and latitudinal distribution (averaging over longitudes) of the total ozone in the course of a simulated year as redetermined by the MIT 3-D model. The net global ozone reduction was found to be 12%. This result is labeled 2D/3D in Figure 1 to acknowledge the device of running part of the problem with 2-D models and part with the 3-D model.

Assessment

Figure 1 summarizes the results presented in this article. The column labeled "time dependent/steady state" indicates a distinction among modeling techniques not emphasized in the preceding text. Briefly, steady-state modelers use some numerical "relaxation" technique to develop the equilibrium state of the atmosphere corresponding to a particular or average state of the atmosphere, whereas the time-dependent modelers seek a set of answers that evolve in time as the days, months, or seasons unfold.

Various reports in the literature have been reviewed. The object was to learn whether there was a reasoned path from the earliest conclusions of no effect, through a possible 50% reduction of ozone, to the consensus gener-

ally reached in the U.S. by the end of 1974 of 8–15% global ozone reduction that might be caused by the uniform global introduction of 1.8×10^9 kg/y NO_2 at 20 km from high-flying aircraft.

My conclusion is that out of the tangled jungle of special cases that were studied in this review, and the different assumptions that were made by the various authors, a reasoned path can be cleared. Discrepancies can generally be, and often have been, reconciled. The body of evidence does generally point in a consistent direction.

One-, two-, and three-dimensional modelers using different numerical methods, using time-dependent or steady-state calculations, using various assumptions about eddy diffusion coefficients, various boundary conditions, various choices of prescribed or predicted motions, various choices of inclusion or exclusion of feedback among temperature, dynamics, and chemistry, and various patterns of NO_x injection did manage to obtain results that, by and large, can be sensibly related to each other.

Additional reading

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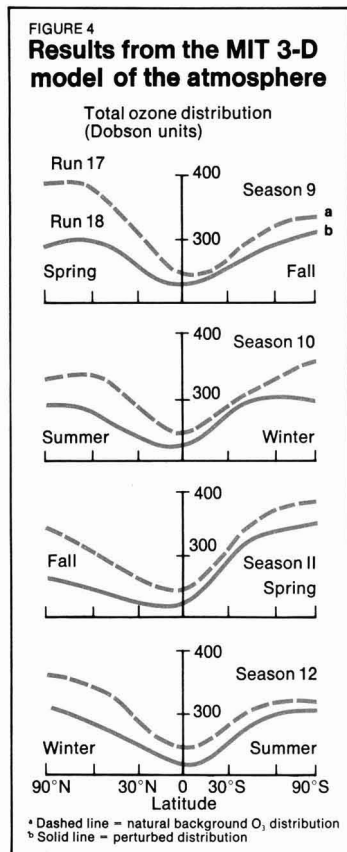
Reynold Greenstone *is a principal scientist at ORI, Inc. In May 1972, he led an ORI team that provided technical support services to DOT's Climatic Impact Assessment Program (CIAP). At the conclusion of CIAP, he provided similar technical support to the FAA's High-Altitude Pollution Program.*
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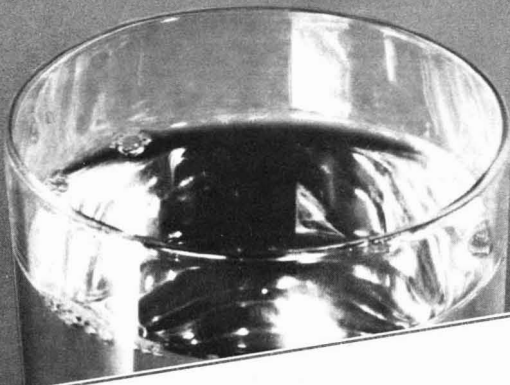
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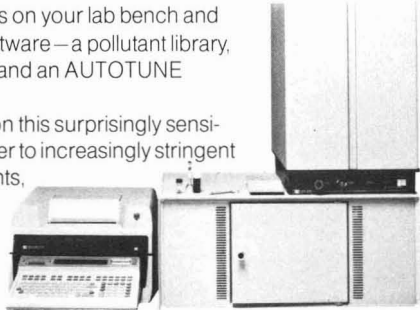
HEWLETT **hp** *PACKARD*

A majority of the public seems to be at loggerheads with the Legislature. Court battles continue. The doctrine of unrestricted rights to use one's lands and other resources as one pleases, and the ethic of improved quality of life clash. An industry faces heavy penalties assessed by the U.S. EPA. Despite all this, and slow and uneven though it may be, one can look forward to progress in the improvement of

Idaho's environment

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Idaho contains over 15 million acres of pristine wild lands and thousands of miles of wild rivers. But its point source pollution problems, although often isolated, are among the most complex in the nation. The diverse fish and wildlife resources, which most other regions have lost, remain, but depend on an increasingly threatened habitat base. Non-point air and water pollution from road construction, logging, grazing, agriculture, urbanization, and off-road vehicles occur at an aggregate rate that is often beyond the capacity of contemporary public policymaking to deal with. Indeed, Idaho's most important question may be whether or not one state in an industrialized society can arrest "environmental entropy", and retain high quality natural areas, when such areas possess exploitable resources.

A profile of the "old west": Unfettered exploitation rights vs. growing environmental consciousness

Idaho, one of the last of the "old west" states, is characterized by contrast: Physical contrast in its 53 million acres, social contrast, and the contrast in its natural and altered environments. Its quiet bucolic past and its 820 000 residents seem destined for rapid change to a less-than-idyllic future of industrialization and population growth.

The northern and central regions are characterized by mountains separated by narrow valleys and fast-moving streams. Northern Idaho, however, is more densely forested, and contains numerous lakes, including three large ones—Pend Oreille, Coeur d'Alene and Priest.

The forests of central Idaho are drained by the Salmon River system, and often broken by grasslands on the south-facing slopes or meadows. The Salmon is one of the nation's largest river systems outside Alaska, without a major dam impeding its free flow, or large industrial or municipal pollution sources.

The southern region contains forested mountains, high deserts, sage-covered rangeland, irrigated agricultural plains, and numerous precipitous canyons. The Snake River drains most of this area, and flows from east to west, before heading north to form the state's western border with Oregon. The Snake and its tributaries are affected by a complex mix of municipal, industrial, and nonpoint sources, and are often reduced to trickles by reservoir storage and irrigation diversions.

The state is traditionally conservative in its politics. Many Idahoans subscribe to the "cowboy ethic" of unfettered rights to exploit unlimited resources. According to this ethic, each man's destiny is, or should be, in his own hands. But others are intent on avoiding over-exploitation of resources, pollution and rapid growth.

New people are moving in. The state's growth rate has been approximately 2.5%/y in recent years, or about three times the national rate. Six counties are growing at five to seven times the national rate. The new residents have seen growth, pollution and environmental deterioration in other states. Many came to Idaho to "escape" those very same conditions. Thus, the various social characteristics combine to form an unusual pro-environment, anti-environmentalist, and anti-growth political potpourri.

IDAHO

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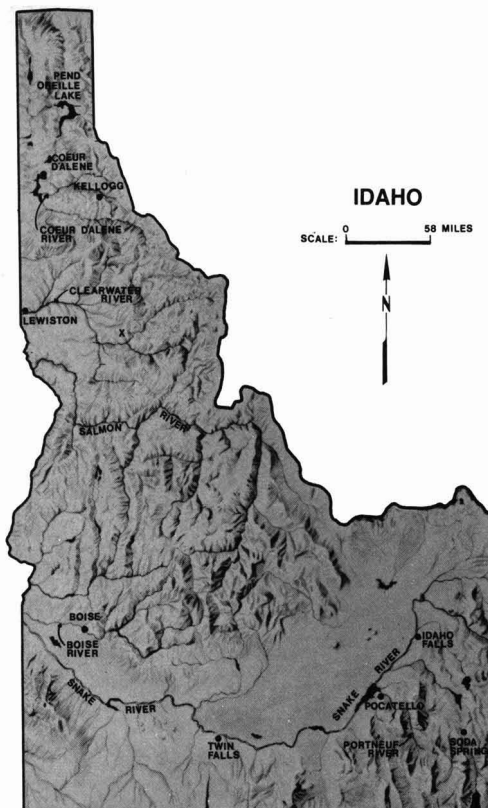
Public attitudes seem to be at odds with those of the Legislature

A 1977 statewide survey, the Idaho's Tomorrow Study, found that 59% favored environmental protection over economic growth in development of resources if a choice had to be made. Large majorities of 66–83% felt that more staff and funds should be allocated to water pollution (66%), soil erosion (66%), solid waste recycling (83%), and air pollution (76%). The survey also found that 82% opposed development of Idaho's relatively large amount of undeveloped "wilderness" lands.

By contrast, the Idaho Legislature has been consistently anti-environmental. A 1974 article in the *Idaho Falls Post-Register* stated, "A survey indicates there are no more than half a dozen Senators and less than a dozen House members of the 35 in the Senate and 70 in the House who would support any strong environmental measures at this time." The anti-environmental tilt has generally become more pronounced since 1974.

Only two major environmental protection bills that could be considered effective have been passed during the last six years. One provided for stream channel protection; the other mandated local land use planning. Both were subjected to spirited recision attempts during the sessions following passage.

Bills authorizing maintenance of minimum stream flows have died in the Legislature four times. However, an initiative drive has been started to place such legislation on the ballot. Also, other bills have passed, including a Surface Mining Act and a Forest Practices Act, but the effectiveness of these laws has been limited.

Agency programs

The Idaho Department of Health and Welfare (IDHW), through its Division of Environment, has primary responsibility for most of the pollution control programs in the state. But because the Legislature did not provide adequate penalties for violations, the important National Pollutant Discharge Elimination System (NPDES) is administered by the U. S. EPA.

The Division of Environment has three environmental program bureaus, plus a regional services bureau, structured as follows:

Water Quality
Source Control
Planning and Standards
Grants and Training
Surveillance and Analysis

Environmental Health
Public Water Supplies
Solid Waste
Vector Control
Milk and Food
Radiation Control

Air Quality

Regional Environmental Services
Coeur d'Alene
Lewiston
Boise
Twin Falls
Pocatello

The agency has 100 staff members—60 in the Boise headquarters, and 40 in five regional/sub-regional offices. The Division of Environment's administrator, Dr. Lee Stokes, a biologist, and 15-year veteran of the agency, feels that Idaho's environmental problems are among the most difficult to solve in the nation, because of the predominance of nonpoint pollution sources. Stokes says, "We will be dealing with activities, actually land-use practices, rather than discharges *per se,* and the technical, sociological, and political problems associated with controlling such activities will soon become obvious.
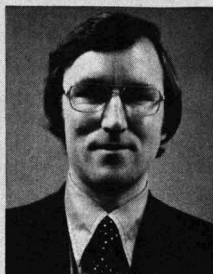
There is no question that the nonpoint sources of pollution are of great magnitude, and therefore must be controlled; but we must be patient, and not expect to accomplish too much too fast."

Lee Stokes
"nonpoint sources are the main problems"

Other state agencies and programs

Department of Fish and Game
Fish and wildlife management
Enforcement of fish and game laws
Research

Department of Water Resources
Administration of the Stream Channel Protection Act
Administration of the Disposal Well Act
Surface and groundwater monitoring
Water resources planning
Hydrologic studies
Geothermal resource investigations
Water rights administration

Department of Public Lands
Administration of the Surface Mining Act
Administration of the Dredge and Placer Mining Act
Administration of the Forest Practices Act
Management of beds of navigable rivers
Management of state endowment lands

Health Departments (seven semi-autonomous districts)
Individual subsurface wastewater disposal permits and studies
Solid waste studies and planning (by county)

Division of Budget, Policy Planning and Coordination
State comprehensive planning
State clearinghouse (A-95 local/state/federal coordination)
Idaho's Tomorrow citizen participation program
Local planning assistance

The federal connection: Some benefits, some detriments

Federal environmental programs and agencies play an important role. Two federal agencies, the Forest Service and the Bureau of Land Management, manage a total of approximately 60% of Idaho's land base, including most of its high-quality wild lands.

The three federal water development agencies, the Corps of Engineers, the Bureau of Reclamation and the Soil Conservation Service (SCS) are active in Idaho. The Corps has three completed major projects, numerous levees, park, and structural modification projects. It also administers the federal permit program for construction in navigable waters, as provided for in Section 404 of P.L. 92-500, and Section 10 of the Rivers and Harbors Act of 1899. The Bureau of Reclamation has ten operating projects in Idaho, with irrigation generally the primary aim. Two other bureau projects are authorized or under construction. The SCS has one major dam and reservoir project in Idaho, along with resource conservation and development projects in three areas. All three agencies have numerous studies in progress.

The Farmers Home Administration helped to create environmental problems in southwest Idaho by funding residential subdivisions from 1972 to 1974, that were outside planned community service areas. This contributed to extensive "urban sprawl" south of Boise, and was protested by state and local officials. Sprawling, dispersed development is considered one of the state's worst land-use problems.

Three "208" areawide planning agencies exist, including the five-county Panhandle Planning and Development Council in northern Idaho, the two-county Ada/Canyon Waste Water Management Committee for part of the southwest, and the seven-county Southeast Idaho Council of Governments. Three potential new designations are the Clearwater Economic Development Association in North

The state is involved in a "208" water quality planning effort involving 18 study elements: Erosion control in the Palouse area in northern Idaho; fish hatcheries; irrigation return flows; agricultural pollution abatement; irrigation incentives; on-site sewage disposal; wastewater facilities financing; municipal sludge disposal; land disposal of wastewater; municipal stormwater injection wells; forest practices; mine and mill waste disposal; Snake River nutrient analysis; groundwater protection; water quality standards and goals; effluent limits; computerized waste source inventory; and special water quality studies.

Idaho, the Ida-Ore Regional Planning and Development Association in the southwest, and the Shoshone-Bannock Tribal Business Council covering the Fort Hall Indian Reservation in the southeast.

Water quality
What, where, and how heavy the pollution problem is; and progress in, and some opposition to abatement

The EPA (1976) states: "A disproportionate share of the Pacific Northwest's water pollution is concentrated in the streams of the State of Idaho." Using an eleven-part Water Quality Index (WQI) that compares water quality conditions during a five-year period with federal criteria recommended by the National Academy of Sciences (1972), the EPA found that four of Idaho's nine major rivers were too polluted to meet federal water quality goals. A WQI rating greater than 6.0 indicated "unequivocal pollution". This rating was assigned to the Spokane/Coeur d'Alene (partially in Idaho), Portneuf, Lower Boise, and Upper Snake Rivers.

Four rivers, the Payette, St. Joe, Salmon, and Clearwater presently meet federal goals. The Bear River and two reaches of the Snake "provisionally" meet federal goals.

The state disagrees somewhat with the EPA assessment. Division of Environment administrator Lee Stokes points out that the Idaho total coliform standard, which the other northwest states do not have, biases the evaluation against Idaho streams. In addition, some of the data used are now outdated. However, the report is the most recent and

Water quality: an EPA view
"The picture of Idaho water quality that emerges from the index and from consideration of particular pollutants and stream reaches is not encouraging. The combination of intense use and management pressures in the semi-arid southern portion of the state with the effects of the mining operations' heavy metals on its northern waters provides a level of water quality stress that would appear to be far greater than that encountered by neighboring Pacific Northwest states."

This conclusion was published by the EPA in 1976, and was drawn from the 11-part Water Quality Index (WQI).
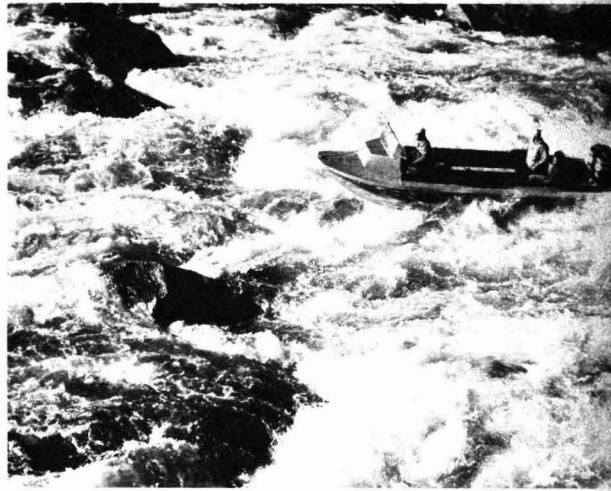
Salmon River. *One of the largest U.S. rivers, outside Alaska, with no major dams or pollution*

comprehensive attempt to profile Idaho's water quality status.

As of July 1976, approximately $50 million of federal and state wastewater facility grant money had been invested in 79 Idaho communities. However, municipalities are still a major pollution source for many rivers.

The Coeur d'Alene River system is the most seriously polluted in the state, but it has improved over the past 5-7 years. Most of the pollutants originate in the South Fork, and stem from mining and smelting operations, and municipal sources. They include copper, cadmium, zinc, BOD, bacteria, phosphate, and nitrate. Domestic sewage is also a contributing factor.

The lower ten miles of the Portneuf River are badly polluted. The main pollutants are bacteria, orthophosphates, and turbidity. The primary sources are phosphate processing, and municipal wastewater discharges.

The 60 miles of the lower Boise River from just above Boise to the confluence with the Snake River flows through Idaho's highest combined concentration of agricultural development, industrial activity and population. The river is primarily affected by large and small municipalities, urban runoff, septic tanks, soil erosion, cattle feedlots, sugar and potato processing, and irrigation return flows. Poor water quality conditions are sometimes aggravated by low river flows caused by irrigation, power, and flood control storage in three upstream dams.

Because of a combination of municipal and industrial wastewater cleanup efforts, and a relatively exhaustive local/regional water quality planning program over eight years, the Boise River may soon begin to show noticeable improvement. But a 1975 study by the Corps of Engineers and two local areawide planning agencies found that even after the municipal and industrial point source requirements are met, existing nonpoint sources will be sufficient to prevent the attainment of water quality goals in the Boise River.

The upper reach of the Snake suffers from low dissolved oxygen, bacteria, phosphorus, turbidity, and BOD. Contributing factors include inadequate river flows, food and minerals processing, irrigation return flows, fish hatcheries, phosphorus recycled from bottom sediments, agricultural runoff, municipalities, and mining.

In 1973, the state prepared, with EPA assistance, a draft water quality plan for the upper Snake region that contains two definitely polluted rivers—the upper Snake and Portneuf. The draft report, although rather mild, was greeted by outrage and indignation from the region's farmers because of its minimum streamflow and agricultural provisions. It was later modified and included as a regional section in the 1976 statewide plan.

Progress has been made with industrial sources on the Snake in the last ten years. In 1967, potato processing caused 24 000 tons of BOD_5 to be discharged to the Snake. Removal efficiency was approximately 65%. The loading was reduced to approximately 2000 tons by 1975, but would have been almost 140 000 tons without controls.

One approach to wastewater control that is being emphasized along the Snake is the use of effluent irrigation for treatment and disposal. This is a sound control method, and is particularly favored for food processing plants. It is also generally cost-effective, when compared to other alternatives.

However, its effectiveness relies heavily on the ability of the soil/plant complex to remove potential pollutants. Tight process control and extensive groundwater monitoring are needed to assure that the system operates consistently to remove nutrients (particularly nitrates) and trace constitutents. If not, out-of-sight solutions may turn into difficult-to-trace groundwater problems. This was recognized, and permit regulations to monitor and control the problem were adopted by IDHW in December, 1976. The Legislature rescinded them in January, 1977.

Air quality

It is still generally good, but particulate and SO$_2$ standards are often violated in specific areas

Air quality in Idaho is generally good, because of the low levels of development and population. However, some areas have air quality problems that range from moderate to severe. The EPA (1976) found, "During the three-year period ending in 1974, ten of Idaho's 44 counties experienced recorded concentration of pollutants that exceeded the allowable maxima specified by primary air quality standards." Two pollutants were involved—particulates in all 10 counties, and sulfur dioxide in one county.

Shoshone County, in north Idaho, failed to meet the national SO_2 standards for 45% of the days in 1974. Many of these violations were allowed by the EPA until July, 1977. The 217 violation days, including 69 above the "alert" level, for sulfur dioxide and particulates combined, constituted 77% of Idaho's violation days. The primary source of the SO_2 violations is the Bunker Hill smelter at Kellogg.

Idaho's most noticeable air quality problems originate with point sources, but "area" sources are predominant in Ada County, particularly because of automobile use around Boise. However, the full extent of Idaho air pollution is not known, because of the limited number of monitoring stations of the IDHW.

Air quality trends are uncertain. According to state sources, the general trend is toward improvement. However, the EPA forecast is for increasing standards violations in

FIGURE 1.

Days exceeding health standard, by pollutant
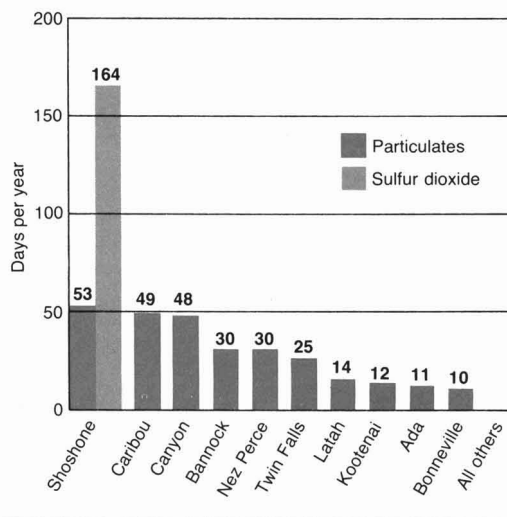
at least three counties: Canyon, Caribou and Kootenai. Violations of the carbon monoxide standard occur throughout Boise during the winter of 1976–77 were the highest ever recorded at 84, caused primarily by recent increases in numbers of automobiles, dispersed development, and poor meteorological conditions.

Idaho had the greatest number of violation days of the four northwest states during the three-year period of 1972–74, and ranked second only to Alaska in days above the "alert" level. This was caused primarily by area sources of particulates. Most of these problems, summarized in Figure 1, are technically and institutionally complex, with no solution in sight.

Wildlife: A principal pawn in the conservation-versus-development chess game

Idaho contains a large variety of North American wildlife species. In general, geologic, soil, meteorologic and vegetation conditions combine up form ecosystems that are diverse, but with low to moderate production. Consequently, many of the larger species have relatively low population densities, and require extensive habitat areas for survival. Certain species, for example, elk and mountain lion, generally have little tolerance for development intrusion. Even low-grade roads reduce the preferred habitat for those, and similar species.

The major "big game" species are elk, mule deer, whitetail deer, moose, mountain lion, mountain goat, Rocky Mountain bighorn sheep, pronghorn antelope and black bear. The major freshwater fish species include brook trout, brown trout, cutthroat trout, lake trout, and rainbow and whitefish trout. Anadromous fish of Idaho are the steelhead trout (a sea-run rainbow), and three species of Pacific salmon.

At one time, most of Idaho's streams provided salmon and steelhead trout. However, because of dams, the anadromous fishery has been reduced to the Salmon and Clearwater river drainages, and to a 100-mi portion of the Snake from Lewiston to Hells Canyon Dam.

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Mule deer. Under heavy hunting and habitat loss pressure

There are a number of important wildlands and wildlife areas in the state. But the most important single area for fish and wildlife is embodied in the Middle Fork Salmon River Basin. The various Idaho and national conservation organizations have jointly proposed that two "Primitive Areas" and 14 undeveloped contiguous areas be preserved by Congressional action in the National Wilderness Preservation System as a 2.3 million-acre "River of No Return Wilderness Area". "Primitive Area" was the pre-Wilderness Act administrative designation, by the Forest Service, of lands that were not subject to development. All such lands must now be either classified as wilderness, or used for general national forest development.

This area would be the largest wilderness area presently in the sytem, and only Alaska could eventually contain a larger one. By comparison, Yellowstone National Park is 2.2 million acres, but is divided into seven units by roads.

Former Idaho governor, and now Secretary of the Interior Cecil D. Andrus has proposed a 1.8 million-acre wilderness. However, this proposal, and the smaller proposals by the Forest Service, and the Ford administration, have generated almost no support in public hearings to date. The conservation group acreage appears to have public sympathy, but political, timber, and mining forces are moving for less. This wildlands-versus-development issue is typical of environmentally-related confrontation in Idaho over the last 10-15 years. It appears that such debate will continue for at least another decade, or until the remaining wildland parcels are allocated.

A special water and air pollution problem:

Severe enough to cause major court battles, its focus is on mining and smelting activities in Shoshone County

The state's foremost pollution problem is in the mineral-rich South Fork Coeur d'Alene River valley in Shoshone County. This valley is primarily known for lead, zinc and silver, but it has also produced cadmium, copper, antimony, and gold. The most important single pollution source is the Bunker Hill lead and zinc smelter complex at Kellogg.

For many years, raw sewerage, tailings from mining and minerals processing operations, and heavy metals made the South Fork and main stem of the Coeur d'Alene one of the nation's most severely degraded rivers. Then, approximately a decade ago, the mining companies installed settling ponds. The water quality improved somewhat, and the water looks much better. Now much of the raw sewage is being treated, and a healthy fish can swim through the main stem on its way from downstream Coeur d'Alene Lake to the North Fork. But even with an approximately two-thirds reduction in surface and subsurface heavy metal discharges over the last five years, problems, primarily from cadmium, copper, and zinc, remain. In late 1977, the EPA filed suit, alleging that the subsurface discharge from the central impoundment area violated the NPDES permit.

The metals problem originates from three source categories, according to the state. Approximately 10% appears to result from natural sources. The remaining 90% is about equally divided between small tailings deposits spread throughout the valley and the tailings ponds at the Bunker Hill smelter complex.

The air pollution problem at Bunker Hill is a complex environmental, economic, social, and political controversy. The issue has involved the EPA matched against Bunker Hill and, sometimes, the state. Strong criticism was directed at Bunker Hill, and at the state's handling of the issue, by environmentalists. There were also charges of political weakening of the EPA position; suits for over $20 million because of dangerous lead concentrations in children in the area; and a court challenge of the EPA position by Bunker Hill and the state.

In 1972, the EPA estimated that in order to meet national ambient SO_2 standards, 96% permanent control would be required. The EPA also concluded that the smelter could reach 85% removal through improved operation and maintenance of control equipment now in the smelter complex. In 1974, the state, with Bunker Hill support, proposed a supplementary control system (SCS), during periods of adverse meteorologic conditions, to meet ambient standards, assuming 72% removal through permanent control. Essentially, this means a reduction in plant production during those periods. The state strategy involved a complex sliding ambient scale based on production at the smelter. EPA agreed with the SCS strategy but disagreed with the 72%.

From August 1973, to July 1974, Bunker Hill reached an average of 72% removal. In the fall-winter of 1976, it became apparent that the smelter would violate the state's primary standards. However, the company refused to follow the SCS and reduce production sufficiently to meet the

An EPA view on air quality

"In conclusion, the capture of excess gases from the zinc roasters which are presently being bypassed, improvement in the heat exchanger capacity, a thorough cleaning of both zinc acid plants, a check of the No. 1 pass in the lead acid plant, and a greater emphasis to the improved lead sinter operation should enable Bunker Hill to meet the 85% requirement."

Reid Iverson, EPA's National Environmental Research Center, summarizing his agency's 85% SO_2 removal position.

Smelter at work. *One of the principal threats to the state's air quality*

standards. An out-of-court settlement resulted in Bunker Hill's paying $4000 in total fines for seven violations.

In 1975, EPA overruled the state position, but was taken to court by Bunker Hill, and later by the state. In July 1977, the Ninth District Federal Court remanded the decision back to EPA for a six-month reconsideration, and decided against Idaho's states rights argument. Since 1975, the EPA position on the potential effectiveness of scrubbers at Bunker Hill has apparently been strengthened by installation at similar facilities. Meanwhile, Bunker Hill is proceeding, in spite of lack of support by either EPA or the state, to install, at a cost of $11 million, two tall stacks for greater dispersal.

In January, the EPA filed suit, alleging that the smelter released high levels of particulates from the zinc fuming furnace, and charging area. It asked for a civil penalty of $25 000 for each day of violation after August 7, 1977.

In April, 1974, two Kellogg children were hospitalized for treatment of lead poisoning. A massive state/federal/Bunker Hill investigation found, based on blood samples from about 1000 children, that 98% of the children living within one mile of Bunker Hill had abnormal lead levels. Levels higher than 80 μg of lead per 100 mL of blood were found in 21% of the children. For children living between one and two miles of the smelter, the percentages were 75% and 2%, respectively. This is generally considered "unequivocal" lead poisoning.

If neurological effects are detected, "clinical" lead poisoning is deemed to have occurred. Differences of opinion still exist over whether clinical lead poisoning was found. Nevertheless, parents of nine children have filed a $20 million lawsuit against Bunker Hill.

Regardless of the pollution sources, or of the most appropriate control strategies, a few Shoshone County statistics stand out. Cancer death rates for white males during 1940–1959 were significantly higher for Shoshone County than for the rest of Idaho. The ratio varied according to the anatomic site, reaching a high of 2.65 for cancer of the esophagus. The annual rate (1964–1975) of end-stage renal disease, referred for dialysis treatment to the Spokane and Inland Empire Artificial Kidney Center, for Shoshone

County, was 1.5–8.7 times the rate for the other eight north Idaho counties. The county also has the highest death rate in Idaho for pulmonary tuberculosis, lung cancer, and suicide.

Mining: Pollution could increase markedly

Existing and potential mining operations present environmental pollution problems throughout Idaho. Potentially large open-pit mines at Cuprum for copper, and Delamar for silver in southwest Idaho, so far have not resulted in major environmental pollution. However, the size and nature of the mines create a high risk of water degradation.

The most serious potential for additional air and water pollution from mining exists in southeastern Idaho. The area contains extensive phosphate deposits that are presently being mined at six surface mines by a number of companies. Because of projected price increases for phosphate fertilizer, extensive mining expansion is proposed. Fifteen new surface mining proposals cover an area of 15 761 acres on 43 370 acres under federal lease plus one on non-federal lands.

In addition to the land presently under federal lease, 98 applications for prospecting permits covering 121 037 acres of federal land are pending. Many of the state's finest fisheries, such as the Blackfoot River, and outstanding wildlife populations will be reduced. Indeed, the fisheries could be eliminated.

Energy: Heated controversy about coal-fired, and nuclear power plant needs and siting

Idaho is not a coal resource area. However, proposals are being advanced for large increase in energy production through plants fired by coal from Wyoming. The largest additional energy consumption would probably be by new phosphate processing plants, and by pump irrigation projects.

In 1974, Idaho Power Company proposed to construct a 1000-MW coal-fired plant 20 mi southeast of Boise. Public reaction was, at first, limited to the expected support from business and industrial groups and the equally ex-

pected opposition from environmental organizations on the basis of potential air pollution. However, Governor Andrus stated that he, also, was opposed to the plant at its proposed location.

Then the issue turned to growth and the costs to pump-irrigation farmers of expanding energy production in this manner. The Idaho Power projections of energy need assumed continued high growth for southwest Idaho, and large increases in irrigated land through groundwater and surface water pumping. Idaho Power acknowledged that the rates would probably increase by approximately 150%, which many existing farmers believe to be beyond their ability to pay.

The issue was placed on the ballot for an advisory vote in May 1976, in Ada, Canyon, and Elmore Counties. The voters, to the surprise of many, voted against the plant. Later the Public Utilities Commission denied approval.

Idaho Power, and Utah Power and Light Company, which serves most of southeast Idaho, are now both exploring other locations for both coal-fired and nuclear plants. Opponents argue that the state does not need such a large expansion of energy generation, and can use alternative sources such as solar, geothermal, wind, and low-head hydro on canals and rivers.

Logging and livestock have had adverse effects on uniquely fragile soil and vegetation ecosystem

Two uses dominate the forests and grasslands of Idaho. These are logging and livestock grazing.

Approximately 21.6 million acres of Idaho's land base is forested, with 14.2 million acres classed as "commercial". The Forest Service manages 68% of this commercial forest land; private owners control 3 million acres; other governmental entities, such as the Bureau of Land Management and those of the State manage 1.5 million. Timber harvesting, as well as the construction of logging roads on these lands, has resulted in serious erosion, water pollution and aquatic habitat problems throughout Idaho.

Much of the forested area is on the 10 million-acre Idaho Batholith—a granitic formation that decomposes into soils that will rival any in susceptibility to water erosion. During the fifties and early sixties, the Forest Service allowed logging on less than 5% of the South Fork of the Salmon River Drainage. Even though the area logged was relatively small, from logging roads and logging on batholith soils in the drainage, enough coarse-grained granitic soil washed into the South Fork, essentially to destroy one of the state's most productive summer chinook salmon-spawning areas for almost two decades.

The South Fork has started a slow climb to recovery because of a moratorium on logging in the drainage area. However, the Forest Service is now preparing to log again. With a sophisticated research and monitoring program to evaluate any change, the agency has agreed to stop logging permanently, if it results in additional sedimentation problems, or if the stream's present rate of recovery is retarded.

The logging dilemma in Idaho revolves around in extremely fragile watershed system of soils, topography, vegetal cover and low timber volumes. The soils are highly mobile when disturbed, the slopes are steep, and the protective vegetation is thin and slow to recover once it is removed. To compound the problem, timber volumes are much lower than those estimated by the Forest Service 10-20 years ago.

Overcutting in Idaho is not limited to public lands. A 1976 study by the University of Idaho found the cutting rate on private "forest industry" lands in northern Idaho was 50% greater than the gross rate of growth. These lands contributed almost one-fourth of the state's 1975 harvest.

Grazing has created similar problems, which are less apparent to the layman. Livestock are grazed on 21 million acres in Idaho, or 40% of the state. This includes 1.6 million cattle and one-half million sheep. Approximately 60% of the grazing lands are public.

In 1973, a number of environmental groups, led by the Natural Resources Defense Council, challenged a decision by the U.S. Bureau of Land Management (BLM) not to prepare environmental impact statements on grazing allotments and range management practices. The test case involved the Challis Unit grazing program in south central Idaho. The U.S. Circuit Court ruled against the BLM in an important precedent-setting decision.

This decision has resulted in a much closer review of the millions of acres of overgrazed public range lands in the west. However, the complete examination of BLM and Forest Service lands through the EIS process will take many years, and range rehabilitation will take even longer.

Uneven progress is in the future of the State's environmental protection/improvement

To sum up, progress in water and air quality improvement, as well as in other environmental protection, may justify cautious optimism for the future. The same can be said for wildlands and wildlife protection.

But this optimism must be tempered by the knowledge that progress will be slow and uneven. The Idaho public seems to desire a large degree of environmental protection and improvement. But its members experience strong opposition from an agricultural, industrial, and political establishment that seems to subscribe to the ethic of unfettered rights to exploit resources perceived as unlimited. So a continuing high quality of life may be in the future of the majority of Idaho's citizens, but its attainment will be beset by many technical, economic, and political obstacles.

Additional reading

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ES&T RESEARCH

Sorption and Transformation of Mercury Vapor by Dry Soil

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■ Five Montana soils of different characteristics, five clay minerals, and several others exhibited various degrees of sorption for mercury vapor. Among the clay minerals, illite had the highest sorption capacity, and kaolinite the lowest. Different types of organic materials also showed a wide sorption capacity range that was highest for humic acid and lowest for cellulose powder. Both organic matter and the mineralogical makeup of the soil may play an important role in the wide range of mercury vapor sorption by the five Montana soils. The sorption phenomena were adequately described by the Freundlich-type equation. The data indicated that the sorption of mercury vapor did not reach its maxima when the mercury vapor concentration was increased to 209 $\mu g/m^3$ or the soils were continually exposed for 17 days. Only a small fraction of mercury sorbed, which was readily available for plant uptake, was transformed to mercuric form by these five soils. The major portion of the mercury sorbed by soils remained unidentified.

Because of abundant resources in the United States at relatively low cost, coal is being used as the primary fossil fuel for the production of energy. Although the mean mercury content in coal is small, more than 90% of mercury escapes into the atmosphere as vapors after burning (1). As mercury pollution of the entire ecosystem continues to increase through natural and man-made sources, a basic understanding of the cycling of mercury in the air–soil–vegetation system is urgently needed to complete the environmental picture. This paper describes a laboratory experiment designed to study soil parameters for the removal of mercury vapor from the air.

Materials and Methods

The radioactive mercury generator consists of a 30 × 150 mm test tube with a sidearm outlet and an inlet tube at the top which extends almost to the bottom of the test tube. After transfer of the liquid ^{203}Hg (172 mg, 29.5 mCi) into the test tube, the generator is placed into a lead jar of 1-in. thickness to provide shielding, and the jar is immersed in a thermoregulated water bath. Air is pumped into the generator from the inlet tube at a constant flow rate measured by a precision flow meter. The ^{203}Hg vapor is carried off from the generator and enters into a mixing flask in which mercury-free air can be added to give a desired concentration. ^{203}Hg vapor concentration of the atmosphere can be controlled by the temperature of the water bath, the air flow rate into the generator, and dilution with mercury-free air. The determination of ^{203}Hg vapor concentration was achieved by passing a known volume of air through a hopcalite trap)a mixture of manganese oxide and copper oxide, Hopkin and Williams Ltd., Chadwell Heath,

Essex, England), measuring the radioactivity in the trap, and calculating the vapor concentration from the known specific activity of the mercury. The temperature of the water bath used in these experiments varied from 25 to 40 °C.

In the experiments described here, a 2-g sample of air dry soil was placed in a test tube and exposed directly to a controlled atmosphere containing radioactive mercury vapor (^{203}Hg) for a given period of time, and the uptake of ^{203}Hg vapor was determined by direct measuring of the radioactivity in the soil with a γ-scintillation spectrometer equipped with a 3-in. NaI well detector (Packard Model 5260 or Technical Associate Model SM-10). The background was generally less than 20 cpm for Packard Model 5260 and 130 cpm for SM-10, respectively. The ^{203}Hg metal was purchased commercially with an initial specific activity of 169 mCi/g mercury. The dry soils were exposed either at various lengths of time or at different vapor concentrations. Five soil samples from southeastern Montana, and several clay minerals, sand, dry straw, humic acid, cellulose powder, peat, and charcoal were included in this study.

For the exposure of a large amount of soil, four 200-g samples of either Arvada, Heldt, Bainville, or Terry and 100 g of Campsspass were weighed and spread individually in petri dishes of 10 cm diameter, and the dishes were randomly placed and stacked in a bell jar. The bell jar was sealed. The top of the bell jar contained an inlet and outlet for passing the air containing ^{203}Hg vapor through the bell jar. The inlet tube was at the upper part of the bell jar with a small orifice and bent outward, so that the air flow from the inlet tube would create some mixing action. The outlet tube was extended almost to the bottom of the bell jar. A magnetic fan inside the bell jar operated continually to give additional mixing to avoid stratification of mercury vapor. The flow rate was maintained at 100 mL/min. The concentration of mercury vapor was measured before and after entering the bell jar. The difference between these two measurements was due to the uptake by soil.

These soil samples were exposed continually for 23 days. The vapor concentration was measured daily except on weekends. After exposure soil samples were removed from the bell jar, and the radioactivity of each was measured using a 2-g sample. The soils were then examined to learn the nature and characteristics of the radioactive mercury after being taken up by the soil. Soil samples were counted before and after each treatment. The treatments were: (1) 24 h under vacuum (5 mm pressure); (2) heated in a drying oven (110 °C) for 2 h; (3) suspended in a 10-mL tris buffer containing 50 mg of cysteine, air was bubbled through the suspension for 30 min, and the vapor was trapped and counted (volatile mercury); (4) air was bubbled through the soil suspension after addition

Table I. Sorption of [203]Mercury Vapor by Five Montana Soils, Clay Minerals, and Others

Soils, minerals, and others	pH	Organic matter, %	Clay content, %	[203]Hg vapor sorbed, μg^a
Arvada[b]	8.1	2.7	40	0.018
Campspass[b]	6.6	11.5	25	0.077
Heldt[b]	8.3	2.9	25	0.076
Bainville[b]	7.5	3.2	29	0.072
Terry[b]	8.3	1.6	12	0.015
Sand				0.002
Kaolinite[b]				0.004
Bentonite[b]				0.021
Illite #35[c]				0.308
Montmorillonite #25[c]				0.008
Metabentonite #38[c]				0.059
Cellulose powder				0.004
Dry straw				0.011
Humic acid, technical				0.170
Peat[b]				0.148
Charcoal				2.943

^{a} Sorption was carried out for 24 h in an atmosphere containing 75.9 μg [203]Hg vapor/m^3. [b] Kindly provided by the Soil Department, Oregon State University. Surface soil samples (0–20 cm depth) collected from uncultivated sites in southeastern Montana. [c] Purchased from Ward's Natural Science Establishment, Inc.

of stannous chloride solution, and the vapor was trapped and counted (mercuric mercury); (5) the radioactivity remained in the soil after treatment (4).

To determine whether or not the sorbed mercury is available for plant uptake, 50 wheat seeds were sown in each soil (200 g) and allowed to germinate under greenhouse conditions. The soils were maintained moist by adding water when needed. After 48 and 72 h, 10 seeds or seedlings were carefully removed from each soil, washed thoroughly to remove any soil particles, and their radioactivity was determined. On the 7th and 10th days the tops of 10 plants were cut off and counted. Because of the low level of radioactivity observed, each sample was counted for 60 min to ensure the accuracy of counting. After wheat cultivation the soils were allowed to dry at room temperature, and 2-g aliquots were taken from each sample for measurement of total and mercuric mercury as described previously.

Results and Discussion

Sorption of Mercury Vapor. Table I shows the results of mercury vapor sorption by five Montana soils, five clay minerals, peat, charcoal, sand, and three organic materials that were exposed to an atmosphere containing 75.9 μg metallic [203]Hg vapor/m^3 for 24 h at room temperature. Among the five soil samples, Campspass, which has the highest organic matter content, has the highest uptake, followed closely by Heldt and Bainville. The high clay content Arvada and sandy Terry soils sorbed approximately one-fourth of the amount sorbed by Campspass. A peat sample sorbed about twice the amount of [203]Hg as Campspass soil. Humic acid sorbed slightly more [203]Hg than the peat. Granular charcoal sorbed about 20 times of [203]Hg than the peat, whereas the dry straw and cellulose powder sorbed very little. Among the clay minerals, Illite #35 has the highest sorbing power (0.308 μg) for [203]Hg vapor, and kaolinite the lowest (0.004 μg). Higher sorption of mercury vapor by illite than those by montmorillonite and kaolinite was also reported by Trost and Bisque (2).

The nature of organic matter in the soil was also important since humic acid sorbed a great deal more mercury vapor than dry straw or cellulose powder. Trost and Bisque also indicated from their study that the organic-rich A soil horizons all sorbed more vaporous mercury than the clay-rich B soil horizons, and variation of mercury sorbed by the A horizons may reflect chemical variations in the type of humus matter forming under the three different vegetations. Such a wide range of sorption by these five clay minerals and different organic matters leads us to believe that the mineralogical nature of the soil particles and organic residues must play an important role in the sorption capacity for mercury vapor. Analysis of clay content, organic matter content, or pH of soil samples would not give much needed information for making predictions of mercury uptake as evidenced by these results.

In the bell jar experiment a total of 500 μg of [203]Hg vapor was passed through the bell jar with 353 μg absorbed by soils, 111 μg collected in Hopcalite traps, and 35 μg unaccounted for which could be adsorbed on the glass surfaces of bell jars, petri dishes, tubing, etc. The average [203]Hg vapor uptakes were 8.48 $\pm$ 0.82, 18.57 $\pm$ 0.62, 18.06 $\pm$ 1.51, 36.54 $\pm$ 2.74, and 6.57 $\pm$ 0.68 μg for Arvada, Campspass, Heldt, Bainville, and Terry, respectively. The variations of uptake among replicate samples were generally less than 10%. The concentration of [203]Hg vapor was reduced from 75.5 $\mu g/m^3$ at the inlet to 16.8 $\mu g/m^3$ at the outlet, showing an average of 78% reduction.

Three factors would influence the reduction of Hg vapor concentration in the air, namely, the sorbing power of soil, the surface area, and the duration of contact. Since the volume of the bell jar was 23 L and the air flow rate was 100 mL/min, a complete air change in the bell jar requires 230 min in which time 78% of the Hg vapor was sorbed. If the rate of sorption remains constant, then 99% of mercury vapor could be removed in a 12-h period, given a stagnant situation. In other

Table II. Uptake of [203]Hg Elemental Mercury Vapor by Dry Soils and Clay Minerals at Various Vapor Concentrations

Adsorbants	Hg^0 vapor concentration, $\mu g/m^3$ 85.16, $\mu g/2$ g^a	135.88, $\mu g/2$ g	185.19, $\mu g/2$ g	208.67, $\mu g/2$ g	Adsorption characteristics n	k
Arvada	0.016	0.026	0.057	0.080	1.79	4.89×10^{-6}
Campspass	0.045	0.084	0.152	0.191	1.60	3.52×10^{-5}
Heldt	0.037	0.065	0.126	0.147	1.56	3.40×10^{-5}
Bainville	0.052	0.094	0.183	0.217	1.63	3.54×10^{-5}
Terry	0.016	0.028	0.054	0.062	1.56	1.50×10^{-5}
Illite #35	0.383	0.607	0.692	0.948	0.91	6.71×10^{-3}
Kaolinite	0.005	0.011	0.028	0.020	1.74	2.28×10^{-6}
Bentonite	0.017	0.035	0.079	0.105	2.07	1.56×10^{-6}

^{a} Two-gram sample was exposed for 24 h in an atmosphere containing various [203]Hg vapor concentrations.
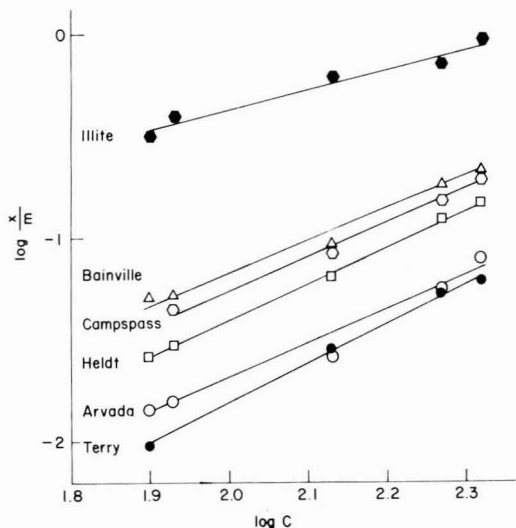
Figure 1. Freundlich's plots of metallic mercury vapor sorption by dry soils and illite

words, any mercury vapor in the air polluted by power plants can be removed by soil uptake within a day.

Mercury Vapor Concentration. Five Montana soils and three clay minerals were exposed to an atmosphere containing different concentrations of ^{203}Hg vapor, ranging from 85.16 μg to 208.67 μg/m^3, for 24 h. The results are summarized in Table II. The sorption of mercury vapor onto the soil and clay mineral surfaces increases with increasing mercury vapor concentrations. This sorption may be expressed by Freundlich's adsorption equation:

$$\frac{x}{m} = kC^n$$

where x is the amount of mercury vapor sorbed in μg, C is the concentration of mercury vapor in μg Hg/m^3, m is the mass of adsorbant (2 g soil), and n and k are constant. Expressed logarithmically, the equation for mercury vapor sorption takes the form

$$\log \frac{x}{m} = \log k + n \log C$$

By plotting $\log x/m$ against $\log C$, a straight line was observed. The fitness of the sorption data for illite, and five soils are shown in Figure 1. The empirical k and n values are estimated by the least-squares method from the experimental points. A higher k value is an indication of greater sorption.

Exposure Time. After establishing the sorptions of mercury vapor by the five Montana soils and clay minerals at various concentrations, we then proceeded to learn the sorption capacity of these soils for mercury vapor and to determine whether or not the capacity can be reached by continual exposure. The experiment was carried out for 17 days for the five soils and 16 days for three clay minerals and peat. The average mercury vapor concentration was maintained at 79.2 μg/m^3.

At first the sorption measurement was made daily and later every other day (Figure 2). During the exposure experiment, each sample was removed from the setup for a 10-min counting of radioactivity and then returned to the setup. Therefore, the value of sorption recorded per day was actually 15–20 min less, and the low radioactivity samples also had a

greater counting error. However, although the sorptions of mercury vapor were progressively decreased with time, their maximum was never reached after 17 days of exposure, and the experiment was discontinued. The average daily sorptions and ranges were 0.017 (0.012–0.025), 0.059 (0.039–0.077), 0.030 (0.015–0.080), 0.047 (0.018–0.072), and 0.010 (0.006–0.015) μg Hg per 2 g of Arvada, Campspass, Heldt, Bainville, and Terry soils, respectively. These values were slightly less than the single day values reported in Table I. The average Hg sorption by montmorillonite #25 was even lower than those of Arvada and Terry. There was very little increase of uptake after 12 days. Illite has the highest rate of Hg sorption; the Hg sorptions of illite and metabentonite per unit time were also progressively decreased with the time of exposure.

Nature of Mercury in Soil After Sorption. There was no loss of radioactivity in these soils after being placed in a vacuum desiccator for 24 h, being heated in an oven at 110 °C for 2 h, or bubbling a stream of air through the suspension to
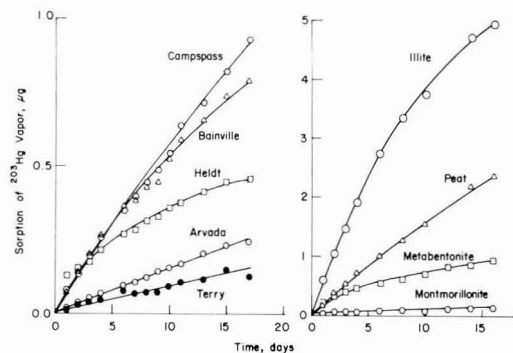
Figure 2. Accumulative sorption of metallic mercury vapor by dry soils and clay minerals
^{203}Hg^0 vapor concentration: 79.2 μg/m^3. Weight of soil or clay mineral sample: 2 g

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Table III. Total and Mercuric Mercury Content of Five Montana Soils Before and After Cultivation

Soils	Total ^{203}Hg content, μg		Mercuric mercury			
			Before		After	
	Before	After	μg	%	μg	%
Arvada	8.25	8.08	1.66	20.1	0.44	5.4
Campspass	20.03	22.21	0.42	2.1	0.99	4.5
Heldt	19.80	21.75	4.44	22.4	3.78	17.4
Bainville	40.05	36.70	4.04	10.1	3.78	10.3
Terry	7.20	4.56	1.97	27.4	0.41	8.9

Table IV. Uptake of ^{203}Hg by Germinating Wheat Seeds from Five Montana Soils After Exposure to ^{203}Mercury Vapor

Soils	Total ^{203}Hg, μg	Mercuric ^{203}Hg, μg	10 Seedlings, ng		Leaves from 10 plants, ng	
			2 days	3 days	7 days	10 days
Arvada	8.25	1.66	8.4	9.1	5.7	2.6
Campspass	20.03	0.42	6.5	9.7	2.3	1.5
Heldt	19.80	4.44	15.0	14.6	9.8	5.1
Bainville	40.05	4.04	15.0	18.1	4.6	6.2
Terry	7.20	1.97	7.6	6.5	2.6	1.6

Figure 3. Plant uptake of [203]mercury from five Montana soils previously exposed to metallic [203]mercury vapor for 23 days
Mercuric mercury content in dry soil in μg mercury per 200 g soil. [203]Mercury content in ng of mercury per 20 wheat seedlings or leaves from 20 plants

seedlings, the counting error remained high even though each sample was counted for 60 min. The decrease in leaf burden between 7 and 10 days is difficult to explain. Under a separate experiment we observed a small release of [203]Hg, recovered in the air, from wheat plants. The amount, 1.6 ng during a 7-day period, was too small to provide a satisfactory explanation for the large decrease shown in Table IV.

The combined [203]Hg uptake by the seedlings (2 and 3 days) and the [203]Hg content in the leaves (7 and 10 days) were analyzed against the total [203]Hg or mercuric mercury in the five soils. The seed uptake and leaf mercury content were highly correlated to the soil mercuric mercury content ($P = 0.05$) and were not correlated with the total soil mercury (Figure 3). This observation suggested that the mercuric mercury was readily available for plant uptake, while the other unidentified form may not be immediately available. John (4) studied mercury uptake from soil by various plant species and found that the mercury concentrations in root portions increased with the increase of soil mercury and were generally higher in the root than in the above-ground section. After wheat cultivation the Arvada and Terry soils showed about a 20% reduction in total [203]Hg content and a 15–18% reduction in mercuric mercury. This loss cannot be fully accounted for by the wheat uptake. In the other three soils, the reductions of total [203]Hg and mercuric mercury were negligible. Bache et al. (5) also indicated little loss of applied mercury in soils after the growing of agricultural crops.

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remove the mercury vapor (3). Failure to remove any radioactivity by these treatments suggested that the sorbed mercury vapor must be either very tightly bound or transformed into a nonvolatile form. A 5-g sample was then analyzed for mercuric mercury according to the method of Clarkson and Greenwood (3). The results are shown in Table III, indicating that only a small fraction of the sorbed mercury vapor was converted to mercuric form: between 20–27% in Arvada, Heldt, and Terry; 10% in Bainville; and 2% in Campspass. Other mercury forms remained unidentified.

Uptake of [203]Hg. The results of plant uptake experiment are shown in Table IV. The uptake was extremely small in comparison to the total amount of mercury present in the soils. Because of the extreme low radioactivity in the leaves and

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Determination of Trace Amounts of Butyltin Compounds in Aqueous Systems by Gas Chromatography/Mass Spectrometry

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During the last decade the industrial production of organotin compounds has markedly increased, mainly as a result of the versatility of these compounds (1–3). The very basis for the present wide range of applications is the profound influence of both the number and the nature of the organic groups R on the properties of these compounds. Tetraorganotin compounds, R_4Sn, have found only very limited practical application, but they are used as starting materials for the synthesis of other types of organotin compounds. Triorganotin compounds display biocidal activity. Tributyltin compounds are widely used as industrial biocides (antifouling paints, wood preservatives), whereas triphenyltin and tricyclohexyltin derivatives have found large-scale application as agricultural fungicides and miticides, respectively.

Diorganotin compounds, R_2SnX_2 (in particular, dibutyl- and dioctyltin compounds), find main application as stabilizers in PVC. At present the production volume of diorganotin derivatives is about twice that of triorganotin compounds. Applications for monoorganotin compounds, $RSnX_3$, so far are limited. They are used as stabilizers in PVC in combination with R_2SnX_2 compounds.

In recent years the subject of environmental aspects of man-made chemicals has met with increasing interest. The present study has been performed as a part of the ORTEP project, an acronym for *OR*gano*T*in *E*nvironmental *P*roject. ORTEP has been conceived and developed by the International Tin Research Institute, London, England, in conjunction with the Institute for Organic Chemistry TNO, Utrecht,

■ A sensitive, reproducible, and interference-free method is presented for simultaneous determination of tri-, di-, and monobutyltin species present in aqueous systems at tin concentrations of 0.01–5.0 ppm. The butyltin species are concentrated from HBr acidified aqueous solutions into an organic solvent by solvent extraction in the presence of a metal-coordinating ligand. Almost quantitative recoveries are achieved by solvent extraction using benzene, chloroform, or methylene chloride in the presence of 0.05% of tropolone. The butyltin species present in the organic extract are transformed into the corresponding butylmethyltin compounds, $Bu_nSnMe_{(4-n)}$, and analyzed as such by a GC/MS procedure. By this procedure the solubilities of $(Bu_3Sn)_2O$, Bu_2SnCl_2, and $BuSnCl_3$ in seawater at room temperature are determined to be 8–10, 6–8, and 9–10 ppm, respectively, and trace amounts of inorganic tin(IV) species in water are detected. The inorganic tin(IV) species present in the organic extract are butylated to tetrabutyltin, which is detected by GC/MS.

The Netherlands, and is supported by the major producers of primary organotin compounds from Western Europe, the United States of America, and Japan. The basic objective of ORTEP is to collect data on the behavior of organotin compounds in the environment.

As far as the environmental behavior of organotin compounds is concerned, compounds of the type R_3SnX that are used as biocides are the most interesting. Inherent to their mode of application, these compounds are intentionally introduced into the environment. The degradation of triphenyl- (4, 5) and tricyclohexyltin (6, 7) species under environmental conditions to R_2Sn and R_1Sn derivatives and ultimately to relatively nontoxic inorganic tin has been reported. Little is known about the degradation patterns of trialkyltin species. In this respect, in particular, tributyltin derivatives are of interest [(1–3) and references cited therein].

In recent years a variety of analytical techniques and procedures have been applied to the determination of organotin species in various media. Unfortunately, most of these procedures are nonspecific for individual organotin compounds and do not allow a conclusion to be drawn about the identity of the tin species detected. In general, these procedures consist of the extraction of organotin species into an organic solvent, the destruction of these tin species to inorganic tin(IV), and the determination of inorganic tin(IV) by analytical techniques such as colorimetry, polarography, and atomic adsorption spectroscopy.

At present there does exist a need for suitable analytical techniques applicable to the quantitative determination of various organotin species simultaneously present in environmental and biological materials. So far, only a few of these procedures have been reported. In their elaborate studies on phenyltin compounds, Freitag and Bock (8) have developed a series of selective extraction and detection techniques for phenyltin species (Ph_3Sn, Ph_2Sn, and Ph_1Sn) present in various media. Likewise, Getzendaner and Corbin (7) managed to detect the corresponding cyclohexyltin species by selective extraction from an aqueous solution. Recently, Woggon and Jehle (9, 10) reported on the quantitative detection of triphenyl and tri-, di-, and monobutyltin species in aqueous solution by a combination of liquid-liquid extraction, thin-layer chromatography, and anodic stripping voltametry.

Gas-liquid chromatographic procedures have been developed for the detection of cyclohexyl- and of butyltin compounds present at low concentrations in various samples. Gauer et al. (11) described a gas-liquid chromatographic procedure for determining residues of tricyclohexyltin hydroxide and its dicyclohexyltin metabolite on fruit samples. The cyclohexyltin species were detected as the bromide derivatives, Cy_3SnBr and Cy_2SnBr_2, which had been extracted from HBr-acidified crop samples into a benzene solution. Dressler et al. (12) developed a procedure for the detection of tributyltin species present in fungistatic plaster. The method is based on extraction of butyltin species into chloroform solution. Treatment with HCl results in the formation of tributyltin chloride that is detected as such by GLC. Neu-

bert and Wirth (13) reported on the quantitative determination of mono-, di-, tri-, and tetraalkyltin compounds, present in a mixture by GLC after alkylation to mixed tetraalkyltins. This technique was applied by Neubert and Andreas (14) to the quantitative detection of tributyl- and dibutyltin species present in dilute aqueous solution. Butyltin species were concentrated on a cation-exchange column, desorbed into diethylether–HCl, and determined by GLC after methylation.

In the course of our studies on the recovery of butyltin species from dilute aqueous solutions, we have developed a detection technique that makes use of a gas chromatograph/mass spectrometer combination. Butyltin species are extracted into an organic solvent and subsequently methylated to form butylmethyltin compounds $Bu_nSnMe_{(4-n)}$. In the gas chromatograph $BuSnMe_3$, Bu_2SnMe_2, and Bu_3SnMe and organic solvents such as diethylether, benzene, and cyclohexane are easily separated. The compounds are detected by mass fragmentography. The details of this method are reported in this paper.

Experimental Procedures

Apparatus. A Finnigan Model 9500 gas chromatograph, coupled with a Finnigan Model 3100 D quadrupole mass spectrometer, was used for the analysis. A glass jet separator forms the interface between the gas chromatograph and the mass spectrometer. The GC/MS combination is provided with a vent-off system between the end of the column and the separator to prevent large amounts of solvent from entering the mass spectrometer. Recently, the possibilities of this GC/MS combination have been extended by the addition of a Finnigan Model 6110 data system.

Reagents. Butyltin compounds (technical grade) were kindly supplied by M & T International BV, Vlissingen, The Netherlands, and by Schering AG, Bergkamen, BRD. Bis-(tri-n-butyltin)oxide (TBTO), $(Bu_3Sn)_2O$ (bp 118–124°/10^{-4} mm), and n-butyltin trichloride, $BuSnCl_3$ (bp 62–64°/$5\cdot10^{-2}$ mm), were purified by distillation in high vacuo. Di-n-butyltin dichloride, Bu_2SnCl_2 (mp 40–42°), was recrystallized from petroleum ether 60–80°. These compounds were used to prepare standard stock solutions in ethanol/water (96/4) containing 1000 μg Sn/mL.

Standard solutions of inorganic Sn(IV) (100 ppm Sn) were prepared according to refs. 15 and 16 by dissolution of metallic tin in a small amount of concentrated sulfuric acid that is subsequently diluted with water to a fixed volume. Aqueous solutions containing 1 ppm in Sn(IV) were obtained by dilution of 5 mL of the standard solution to 500 mL with tap water.

Complexing reagents such as dithizone and 8-hydroxyquinoline (HOx) were obtained from Merck. Tropolone (HTrop) was obtained from EGA-Chemie. Zinc bis(diethyldithiocarbamate) $[Zn(DDC)_2]$ was prepared according to ref. 17. Cyclohexane was purified by distillation after removal of contaminating unsaturated products by washing with concentrated H_2SO_4. Benzene thiophene-free was obtained from Baker Chemicals, and chloroform p.a. was obtained from

Merck. Standard solutions of MeMgBr and BuMgBr in diethyl ether (concentration 1.5–2.5 mol/L) were prepared in the normal manner by reaction of methyl bromide and n-butylbromide, respectively, with magnesium metal.

BuSnMe$_3$ (bp 41–42°/12 mm), Bu$_2$SnMe$_2$ (bp 70°/4.5 mm), and Bu$_3$SnMe (bp 122–124°/12 mm) were prepared by the methylation of BuSnCl$_3$, Bu$_2$SnCl$_2$, and Bu$_3$SnCl, respectively. HexBu$_2$SnMe (bp 96–97°/0.5 mm) was used as an internal standard in the quantitative GC/MS determination of Bu$_n$SnMe$_{(4-n)}$ (n = 1–3) compounds. This internal standard was prepared by the reaction of Bu$_2$MeSnBr (18) with n-hexylmagnesium bromide in diethylether. The purity of these tetraalkyltin compounds was estimated by gas chromatography to be 99.4% (BuSnMe$_3$), 99.6% (Bu$_2$SnMe$_2$), 94.1% (Bu$_3$SnMe), and 99.4% (HexBu$_2$MeSn).

Extraction and Methylation Procedure; Quantitative Detection of Butyltin Species Present in Dilute Aqueous Solutions by GC/MS. Dilute aqueous solutions of (Bu$_3$Sn)$_2$O, Bu$_2$SnCl$_2$, and BuSnCl$_3$ were prepared by addition of the appropriate amount of a standard stock solution of these compounds in ethanol/water (96/4) to 500 mL of water. Bu$_3$Sn, Bu$_2$Sn, and Bu$_1$Sn species, either individually or simultaneously present in such a solution (concentration range 0.01–5.0 ppm as Sn), were extracted twice with 25 mL of an extractant. Mixtures kept in a 1-L round bottom flask were shaken twice for 15 min on a mechanical shaker. Optimal results were obtained from aqueous solutions that were acidified with HBr 48% (5–20 mL) prior to extraction. After leaving such a solution for 15 min at room temperature, extraction with benzene or chloroform resulted in almost complete migration of Bu$_3$Sn and Bu$_2$Sn species into the organic solvent. With 0.05% of tropolone dissolved in the organic solvent, not only Bu$_3$Sn and Bu$_2$Sn but also Bu$_1$Sn and inorganic Sn(IV) species are extracted from the aqueous solution.

Benzene extracts can be submitted to a Grignard methylation procedure without any further precautions. The presence of traces of water in these extracts does not interfere with the methylation of butyltin species, Bu$_n$Sn, to butylmethyltin compounds, Bu$_n$SnMe$_{(4-n)}$ (n = 1–3), whenever an excess of MeMgBr is added (3 mL of a 2.5 N MeMgBr in diethylether). The reaction mixture is stirred for 0.5 h at room temperature and subsequently treated with 25 mL of a 1 N H$_2$SO$_4$ solution. Thereupon, the aqueous layer is separated from the organic layer and extracted with 25 mL of benzene. The combined organic layers are concentrated at reduced pressure to a volume of about 25 mL.

Toluene, less toxic than benzene, has not been applied as an extractant because it appeared that this solvent interferes with the detection of BuSnMe$_3$ by GC/MS, since both have about the same retention time in the gas chromatograph.

Chloroform and methylene chloride extracts are concentrated almost to dryness prior to the methylation procedure since these solvents react with the Grignard reagent. Diethylether (25 mL) or benzene (25 mL) is added to the residue prior to the methylation procedure. The amounts of Bu$_n$SnMe$_{(4-n)}$ (n = 1–3) species present in the methylated extracts were determined by mass fragmentography.

In a typical experiment, aqueous solutions (0.5 L) of (Bu$_3$Sn)$_2$O, Bu$_2$SnCl$_2$, and Bu$_1$SnCl$_3$ (Bu$_n$Sn concentration 1 ppm as Sn) acidified with HBr (10 mL, 48%) were extracted with benzene to give butyltin recoveries of 89% for (Bu$_3$Sn)$_2$O, 86% for Bu$_2$SnCl$_2$, and 0% for Bu$_1$SnCl$_3$. Upon extraction with benzene containing 0.05% of tropolone, these figures were 93, 90, and 84%, respectively.

The sensitivity of the latter procedure was demonstrated in the almost quantitative recovery of butyltin species, Bu$_n$Sn (n = 1–3) from aqueous solutions containing (Bu$_3$Sn)$_2$O, Bu$_2$SnCl$_2$, and Bu$_1$SnCl$_3$ at a concentration of 0.01 ppm as Sn.

One liter of this aqueous solution, acidified with 20 mL of HBr (48%), was extracted twice with 25 mL of benzene containing 0.05% tropolone. The methylated benzene extract concentrated to a volume of 10 mL was submitted to the GC/MS detection procedure. Butylmethyltin compounds were detected in 95% (Bu$_3$SnMe), 90% (Bu$_2$SnMe$_2$), and 84% (BuSnMe$_3$) yields calculated on the amounts of (Bu$_3$Sn)$_2$O, Bu$_2$SnCl$_2$, and BuSnCl$_3$ originally present.

Me$_4$Sn formed by the methylation of inorganic tin(IV) cannot be determined by GC/MS since it has the same retention time as the solvent. Butylation of an organic extract (50 mL) that contains inorganic Sn(IV) species by the addition of an excess of BuMgBr in diethylether (4 mL of a 2.0 N solution) results in the formation of Bu$_4$Sn. The reaction mixture is stirred for 0.5 h at room temperature and subsequently treated with 25 mL of a 1 N H$_2$SO$_4$ solution. The aqueous layer is separated and extracted with 25 mL of benzene, and the combined organic layers are concentrated at reduced pressure to a volume of about 25 mL. The Bu$_4$Sn content of this sample can be determined quantitatively by GC/MS.

Mass Fragmentography. A standard test solution of methylated butyltin compounds, BuSnMe$_3$, Bu$_2$SnMe$_2$, and Bu$_3$SnMe, and the internal standard HexBu$_2$SnMe is prepared by solution of these compounds in cyclohexane to a concentration of about 50 ppm each. It has been noticed that the composition of such a standard solution, kept in a volumetric flask, remains unchanged over a period of one year.

A standard solution of HexBu$_2$SnMe in cyclohexane is prepared by accurately weighing a sample of this compound in a volumetric flask to give a final solution with a precisely known concentration of about 2% (wt/vol). This solution may be used for several months, depending on the care with which evaporation of the solvent is prevented. (A volumetric flask with a specially ground-in stopper was used). To act as an internal standard, each time 50 μL of this standard solution of HexBu$_2$SnMe was added with a 50-μl Hamilton syringe to a sample to be analyzed.

Alternatively, 1 μL of the standard test solution of methylated butyltin compounds and 1 μL of an actual sample were injected into the GC/MS combination. The gas chromatographic separation was performed on a 1.2-m glass column (o.d. 6.2 mm; i.d. 2 mm) filled with 3% OV 17 on Supelcoport 80–100 mesh or filled with 3% OV 1 on Chromosorb WHP 100–120 mesh. The columns were not used for other samples. Column temperature: initial 70 °C; program rate: 15°/min, maximum 170 °C. Duration of the analyses: 11 min. Helium was used as carrier gas; inlet pressure, 50 psi; the flow rate was 20 mL/min, which resulted in an analyzer pressure of 10^{-5} torr. The temperatures of the injection port, separator, and transfer line were: 225, 200, and 225 °C, respectively. The vent-off system was opened during the first 54 s after injection to prevent the solvent from entering the MS. Mass spectrometer conditions were: electron energy, 70 eV; beam current, 14 μA, preamplifier, 10^{-8}. Mass fragments m/e = 135 and m/e = 193 were recorded as demonstrated in Figure 1.
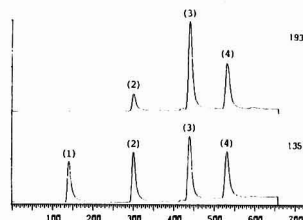

Figure 1. Mass fragmentogram of standard test solution of BuSnMe$_3$ (1), Bu$_2$SnMe$_2$ (2), Bu$_3$SnMe (3), and HexBu$_2$SnMe (4) at m/e = 135 and m/e = 193
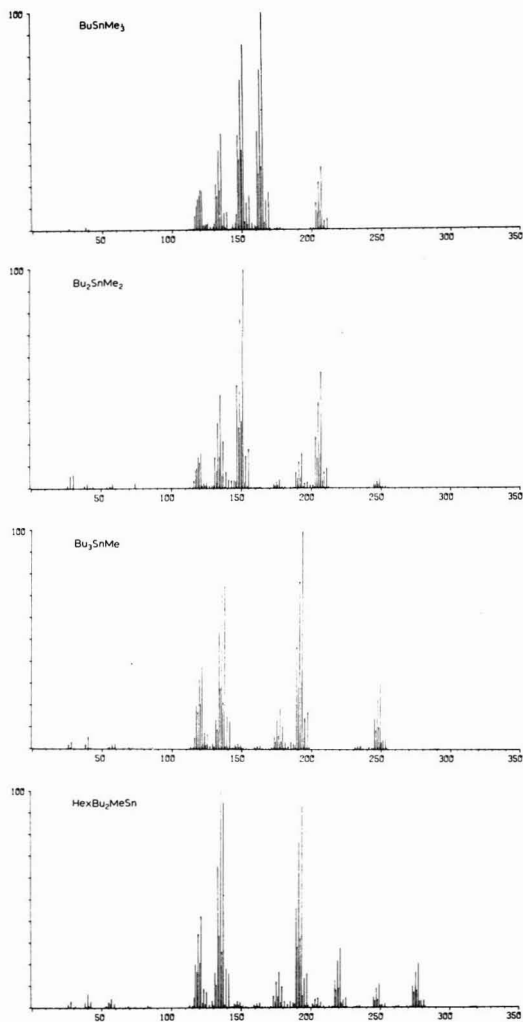
Figure 2. Mass spectra of BuSnMe₃, Bu₂SnMe₂, Bu₃SnMe, and Hex-Bu₂SnMe

Peak areas were initially calculated by multiplying peak height and peak width at half-height but are presently calculated by the data system. Amounts of butyltin species can be estimated by comparing peak areas in the samples of unknown concentration with the peak areas of the standard test solution.

HexBu₂SnMe cannot be used as an internal standard in the detection of Bu₄Sn formed by butylation of inorganic Sn(IV) species, because both have almost the same retention time. Moreover, Bu₄Sn has practically no fragment ions $m/e = 135$ and $m/e = 193$. Instead, the fragment ions $m/e = 121, 177, 178,$ and 179 are recorded, and no internal standard is used. Concentrations were estimated by comparison with a solution of a known concentration of Bu₄Sn.

Qualitative Detection of Bu₃Sn and Bu₂Sn Species by Thin-Layer Chromatography (TLC). The presence of Bu₃Sn and Bu₂Sn species in chloroform or benzene extracts from HBr-acidified aqueous solutions can be demonstrated qualitatively by TLC on Eastman chromatogram sheets using hexene/acetone/acetic acid 40/4/1 as an eluent. After spraying

with a 0.1% dithizone solution in chloroform, Bu₃Sn species are visualized as a yellow spot (R_f value 0.75) and Bu₂Sn species as a red spot (R_f value 0.50). The detection limit is improved by keeping the TLC strip for 10 s in bromine vapor after elution. Bromine breaks carbon–tin bonds, and both Bu₃Sn and Bu₂Sn species are now detected as red spots after spraying. The detection limit after bromination is about 0.5 μg tin per spot.

Determination of Solubility of (Bu₃Sn)₂O, Bu₂SnCl₂, and BuSnCl₃ in Seawater. Pure (Bu₃Sn)₂O (about 150 mg) was added to three 500-mL samples of seawater (taken from the North Sea at the shore near IJmuiden, The Netherlands) stored in 1-L conical flasks. After 4 days at room temperature with occasional shaking, 100-mL samples were taken from these solutions. Extraction of these samples twice with 25 mL of benzene/0.05% tropolone followed by GC/MS after methylation pointed to a (Bu₃Sn)₂O content in the saturated seawater solutions of 8–10 ppm.

By use of essentially the same procedure the solubilities of Bu₂SnCl₂ and BuSnCl₃ in seawater have been determined to be 6–8 and 9–10 ppm, respectively. Standard solutions of Bu₂SnCl₂ (11 mg in 10 mL of ethanol) and of BuSnCl₃ (9 mg in 10 mL of ethanol) were introduced in 500-mL seawater samples. After stirring for 2 h, tiny particles of a colorless solid were observed, indicating that part of the Bu₂Sn and Bu₁Sn species had precipitated from solution. After 4 days, 300-mL samples of clear aqueous solution were taken to determine their butyltin content by extraction twice with 25 mL of benzene/0.05% tropolone after acidification with 10 mL of HBr 48%, followed by GC/MS after methylation.

Results and Discussion

Analytical Procedure. Butyltin species Bu$_n$Sn ($n = 1$–3) present in low concentration in aqueous solutions have been detected quantitatively by an analytical procedure consisting of the following basic steps: acidification of the aqueous solution with HBr, extraction of the butyltin species into an organic solvent, methylation, and finally separation and detection by GC/MS of the butylmethyltin species, Bu$_n$SnMe$_{(4-n)}$ ($n = 1$–3), formed. Inorganic Sn(IV) species present in aqueous solutions have been determined by essentially the same procedure as Bu₄Sn formed after butylation of the organic extract.

Accuracy of GC/MS Detection Procedure. A comparison of the mass spectra of Bu$_n$SnMe$_{(4-n)}$ ($n = 1$–3) compounds reveals that they all show a common fragment ion $m/e = 135$ ([Me¹²⁰Sn]⁺). Moreover, the mass spectra of Bu₂SnMe₂ and Bu₃SnMe show a common fragment ion $m/e = 193$ ([MeBuH¹²⁰Sn]⁺) (see Figure 2). This implies that GC/MS analysis of these compounds can be performed by multiple peak scanning of these two fragments (mass fragmentography). This procedure has advantages over the procedure of detecting the total ion current in that it is considerably more sensitive, whereas no or substantially less disturbance by impurities with the same retention time as the Bu$_n$SnMe$_{(4-n)}$ species does occur. A contaminant with the same retention time as one of the Bu$_n$SnMe$_{(4-n)}$ compounds is not detected at all unless it presents the same mass fragments, $m/e = 135$ and also $m/e = 193$. The presence of such a contaminant is easily observed because the mutual ratio of these fragments will be disturbed. When this is the case, it is possible to monitor fragment ions containing one of the other isotopes of tin. However, this will affect the sensitivity as can be seen from the data presented in Table I and from the spectra presented in Figure 2.

Quantitative determinations are made possible by addition to the sample of an internal standard. Such an internal standard should have mass fragments at $m/e = 135$ and $m/e = 193$.

Table I. Natural Abundances of Main Isotopes of Tin [a]

Mass no.	Abundance (%)
116	14.30
117	7.61
118	24.03
119	8.58
120	32.85
122	4.72
124	5.94

[a] CNR "Handbook of Chemistry and Physics".

Moreover, it should display a retention time in the gas chromatograph different from those of the $Bu_nSnMe_{(4-n)}$ ($n = 1$–3) compounds. As shown in Figure 2, $HexBu_2SnMe$ prepared by the hexylation of $Bu_2SnMeBr$ (18) meets these requirements.

The standard deviations in the ratios of the peak areas of the butylmethyltin compounds to the peak areas of the internal standard, $HexBu_2SnMe$, have been determined. At seven injections on the same day, each time 1 μL of a test solution containing methylated butyltin species and internal standard, at a concentration of about 35 ppm in tin each, standard deviations appeared to be:

	$m/e = 135$	$m/e = 193$
$BuSnMe_3$	3.4%	. . .
Bu_2SnMe_2	2.6%	3.4%
Bu_3SnMe	1.6%	1.9%

Upon reducing the concentration of the butylmethyltin species present to 3.5 ppm in tin with the internal standard present at a concentration of 35 ppm in tin, the same accuracy has been achieved. Samples containing butylmethyltin species in the concentration range of 0.35 ppm in tin have to be analyzed by injecting 5 μL of sample solution.

As a general conclusion, for the quantitative analysis of butylmethyltin compounds, $Bu_nSnMe_{(4-n)}$ ($n = 1$–3) by GC/MS at least about 0.2 ng of each compound must be injected.

Recovery of Butyltin Species from Aqueous Solutions. Aqueous solutions of $(Bu_3Sn)_2O$, Bu_2SnCl_2, and $BuSnCl_3$ (concentration 1 ppm as Sn) have been extracted with a number of organic solvents under various conditions. The amount of butyltin species recovered has been determined by GC/MS after methylation. Results are presented in Table II.

Detection of Bu₃Sn and Bu₂Sn Species. Extraction of aqueous solutions of butyltin species (concn. Bu_nSn, 1 ppm as Sn) with benzene or chloroform results in the almost complete recovery of Bu_3Sn species in the organic extract. Under the same conditions Bu_2Sn and Bu_1Sn species, originating from Bu_2SnCl_2 and Bu_1SnCl_3, respectively, appear to be rather reluctant to extraction. Addition of HBr 48% prior to extraction markedly influences the recovery of butyltin species. Now both Bu_3Sn and Bu_2Sn species are extracted into the organic solvent in over 80% yield, whereas Bu_1Sn species reside in the aqueous solution. This procedure offers a reliable quantitative detection technique for Bu_3Sn and Bu_2Sn species either individually or simultaneously present in trace amounts in aqueous solutions. On a qualitative basis the presence of Bu_3Sn and Bu_2Sn species in these chloroform or benzene extracts can easily be demonstrated by thin-layer chromatography.

Detection of Bu₁Sn Species. The procedure outlined above, although valuable in itself, is incomplete in that any Bu_1Sn species present escape from detection. Recent studies

report on the use of metal-complexing reagents in the extraction of phenyltin species (8) and metal ions (17) from aqueous solutions into an organic solvent. We have modified these techniques to the detection of Bu_1Sn species present in aqueous solutions. In the absence of HBr the metal complexing reagents tropolone and 8-hydroxyquinoline appear to be effective in the recovery of Bu_1Sn species from aqueous solutions, whereas zinc bis(diethyldithiocarbamate) is ineffective under these conditions. Aqueous solutions acidified with HBr show a somewhat different behavior. Excellent recoveries of Bu_1Sn species are achieved with tropolone and with zinc bis(diethyldithiocarbamate). The use of 8-hydroxyquinoline appears to be less suitable under these conditions. Tropolone has been found to be the reagent of choice. The obnoxious smell spread by the methylated extract makes the use of zinc bis(diethyldithiocarbamate) far from attractive.

Simultaneous Detection of Bu₃Sn, Bu₂Sn, and Bu₁Sn Species. The use of tropolone as a complexing reagent in the extraction of butyltin species from aqueous solutions into organic solvents has been studied in greater detail. A series of experiments has been set up to establish recovery rates of mono-, di-, and tributyltin species, Bu_nSn ($n = 1$–3), either individually or simultaneously present in aqueous solutions. In combination with tropolone a number of solvents has been tested. Comparable results have been obtained with benzene, chloroform, and methylene chloride in the presence of 0.05% of tropolone.

The results obtained by GC/MS after methylation are presented in Table II. Bu_3Sn and Bu_2Sn recoveries appear to be almost quantitative both from neutral and from HBr-acidified aqueous solutions. Bu_1Sn recovery appears to be influenced by the presence of HBr in that, in general, recovery rates are higher from solutions acidified with HBr than from nonacidified solutions. Bu_3Sn and Bu_2Sn recoveries remain fairly constant with aging of an aqueous solution of these species over a period of several weeks. Bu_1Sn recoveries, however, do decrease with time to a notable extent (20–40%), most likely, in our opinion, as a result of adsorption/deposition of Bu_1Sn species to the glass wall of the vessel. Addition of

Table II. Recovery of Butyltin Species, Bu_nSn ($n = 1$–3), from Dilute Aqueous Solutions of $BuSnCl_3$, Bu_2SnCl_2, and $(Bu_3Sn)_2O$ (Bu_nSn Concentration 1 ppm as Sn) in Tap Water (0.5 L)

Extractant		HBr	Recovery [b] (%)		
Organic solvent/complexing agent [a] (2 × 25 mL)		(10 mL)	Bu_1Sn	Bu_2Sn	Bu_3Sn
C_6H_6		−	. . .	. . .	80–95
$CHCl_3$		−	. . .	20–25	80–95
C_6H_6		+	. . .	80–90	80–95
$CHCl_3$		+	. . .	80–90	80–95
C_6H_6/0.1% $Zn(DDC)_2$		+	80–90	c	c
C_6H_6/0.1% $Zn(DDC)_2$		−	0–5	c	c
C_6H_6/0.05% HOx		+	40–50	c	c
C_6H_6/0.05% HOx		−	80–90	c	c
C_6H_6/0.05% HTrop		+	70–90	80–90	80–95
C_6H_6/0.05% HTrop		−	50–90	80–90	80–95
$CHCl_3$/0.05% HTrop		+	70–90	80–90	80–95
$CHCl_3$/0.05% HTrop		−	40–80	60–70	70–90
CH_2Cl_2/0.05% HTrop		+	70–90	80–90	80–95
CH_2Cl_2/0.05% HTrop		−	60–70	80–90	80–95

[a] Complexing agents: $Zn(DDC)_2$, zinc bis(diethyldithiocarbamate); HOx, 8-hydroxyquinoline; HTrop, tropolone. [b] In each experiment at least three identical samples were extracted. The methylated extracts were analyzed in duplicate by GC/MS. [c] Not determined.

Table III. Solubility of Butyltin Compounds in Seawater at 22 °C

Compound	Solubility (ppm)
$(Bu_3Sn)_2O$	8–10
Bu_2SnCl_2	6–8
$BuSnCl_3$	9–10

Table IV. Recovery of Inorganic Tin(IV) from Dilute Aqueous Solutions (0.5 L) Containing 1 ppm Tin

Experiment[a]	Extractant Organic solvent/complexing agent (2 × 25 mL)	HBr 48% (10 mL)	Recovery[b] (%)
A	C_6H_6/0.05% HTrop	+	80–90
B	C_6H_6/0.05% HTrop	+	15–20
C	C_6H_6/0.05% HTrop	+	70–80
D	C_6H_6	+	0
E	$CHCl_3$/0.05% HTrop	+	80–90
F	$CHCl_3$/0.05% HTrop	–	80–90
G	$CHCl_3$	+	0
H	$CHCl_3$	–	0

[a] A, D, E, F, G, H: freshly prepared solutions of Sn(IV). B: stored for 3 days in a glass beaker prior to extraction. C: stored for 3 days in a polyethylene beaker prior to extraction. [b] In each experiment two identical samples were extracted. The methylated extracts were analyzed in duplicate by GC/MS.

HBr obviously effects the desorption of these species as recovery of Bu_1Sn species increases to almost the same values as obtained from HBr-acidified freshly prepared aqueous solutions of Bu_1Sn species.

Sensitivity of Detection Procedure. The sensitivity of the latter procedure has been demonstrated in the almost quantitative detection of $Bu_nSnMe_{(4-n)}$ ($n = 1–3$) compounds originating from 1-L samples of aqueous solutions of $(Bu_3Sn)_2O$, Bu_2SnCl_2, and Bu_1SnCl_3 containing Bu_nSn species at concentrations of 0.1 and 0.01 ppm as tin. Greater sensitivity may be achieved by changes in the analytical procedure. A sample greater than 1 L can be extracted, although the use of larger volumes becomes cumbersome.

Recovery of Butyltin Species from Natural Water. To test the practical utility of the present procedures, a series of experiments has been set up in which butyltin compounds, $(Bu_3Sn)_2O$, Bu_2SnCl_2, and Bu_1SnCl_3 were introduced into 1-L samples of canal water (taken from a Utrecht canal) and of seawater (collected from the North Sea shore near IJmuiden) to a butyltin concentration of about 1 ppm in tin. These samples were acidified with HBr prior to extraction to disrupt any interaction of butyltin species with inorganic or organic material present in natural water. Recovery data obtained upon extraction with benzene and benzene/0.05% tropolone solutions did not notably differ from those obtained in experiments with tap water solutions.

Determination of Solubility of $(Bu_3Sn)_2O(TBTO)$, Bu_2SnCl_2, and Bu_1SnCl_3 in Seawater. The analytical procedures described in this study have been applied to the determination of the solubility of $(Bu_3Sn)_2O(TBTO)$, Bu_2SnCl_2, and Bu_1SnCl_3 in seawater at 22 °C. The data obtained are presented in Table III.

Recovery of Inorganic Tin(IV) Species from Aqueous Solutions. A series of experiments was set up to establish whether under the conditions applied to the recovery of butyltin species from aqueous solution, inorganic species are also extracted into the organic solvent. To that purpose freshly prepared aqueous solutions of inorganic tin(IV) (1 ppm Sn) were extracted with chloroform/0.05% tropolone or benzene/0.05% tropolone. The tin content of these extracts was determined both by AAS after destruction and by GC/MS after butylation to tetrabutyltin Bu_4Sn. Both detection procedures revealed the presence of over 80% of the inorganic tin species originally present in water in the organic extract irrespective of whether the aqueous solution had been acidified with HBr prior to extraction. The presence of tropolone as a metal complexing reagent was found to be essential. In the absence of tropolone, by use of pure benzene or chloroform as an extractant, not even a trace of tin-containing species was found present in the organic solvent.

A strong tendency of tin(IV) ions to adsorb to glass surfaces was demonstrated. Aqueous solutions of Sn(IV) ions (1 ppm Sn) kept in glass beakers for a period of 3 days showed only 15–20% recovery of tin(IV) species upon extraction with benzene/0.05% tropolone, whereas duplicate experiments in polyethylene beakers showed recovery rates of 70–80%.

The results obtained in the recovery of inorganic tin(IV) species from aqueous solutions are compiled in Table IV.

Conclusions

With the analytical methods described in this paper, the presence of trace amounts of butyltin species of the types Bu_1Sn, Bu_2Sn, and Bu_3Sn, either individually or simultaneously present in dilute aqueous solutions, can be determined quantitatively. Inorganic tin(IV) species are extractable into organic solvents in the presence of tropolone.

We foresee that the present procedure may be modified and elaborated to a method of choice for the quantitative determination of a large variety of organotin species present in trace amounts in various media.

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Collaborative Testing of a Manual Sodium Arsenite Method for Measurement of Nitrogen Dioxide in Ambient Air

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■ The sodium arsenite method for 24-h integrated measurement of NO_2 in ambient air was subjected to a collaborative test. Ten collaborators sampled ambient air and simultaneously the same ambient air spiked with a reliable source of NO_2 for 4 days at a common site in Kansas City, Mo. NO_2 concentrations of 50–370 $\mu g/m^3$ were sampled. Within and between laboratory standard deviations were 8 and 11 $\mu g/m^3$, respectively, over the range 84–312 μg NO_2/m^3. The method had a bias of −3% of the concentration over the above range. The lower detectable limit (LDL) of the method was 8 $\mu g/m^3$. The test results indicated that the method will produce accurate, precise measurements of ambient NO_2 concentrations.

On July 14, 1972, the U.S. Environmental Protection Agency (EPA) withdrew the EPA promulgated (1) reference method for measuring atmospheric concentrations of nitrogen dioxide (NO_2) because of demonstrated inadequacies in the procedure (2, 3). After withdrawal, EPA embarked on an extensive program to develop a replacement for the original reference NO_2 method and selected five candidate procedures: a manual arsenite procedure, a manual triethanolamine-quiacol-sulfite procedure, a manual triethanolamine procedure, a continuous chemiluminescence procedure, and a continuous colorimetric procedure.

This paper reports work on evaluation of the manual arsenite procedure. The first phase of the work, a laboratory investigation to develop specifications and procedures for the use of the method and the incorporation of the results in a detailed method write-up describing the proper use of the method, has been reported (4). The second phase of the work involved subjecting the method to a collaborative test to determine its bias and precision in the hands of a group of typical users and is the subject of this paper.

Experimental Procedure

Sampling System for Collaborative Test. A diagram of the sampling system is shown in Figure 1. Incoming ambient air is split into a spiked and unspiked line with a sampling manifold near the end of each line. The spike was generated by adding known amounts of NO_2 at a constant rate over a 24-h period from permeation devices maintained at 25.1 ± 0.1 °C. These devices were obtained from the National Bureau of Standards (prototype of Standard Reference Material 1629). Since the spike concentration of NO_2 was used as the standard against which bias was determined, its integrity had to be established. Teflon parts were used downstream from the injection of the spike to minimize loss of NO_2 to the walls, and a high constant flow rate of 60 L/min of ambient air was maintained through the spiked line. The high flow rate and consequent short NO_2 residence time minimize loss of NO_2 by reaction with water vapor and allow an ample excess of sample over that being taken by the collaborators.

The integrity of the spike was checked before and during the test by monitoring the NO_2 concentration in the spiked and unspiked manifold with a Bendix NO_2-chemiluminescent monitor, as shown in Figure 1. The difference in NO_2 concentration between the spiked and unspiked manifolds was within 5 $\mu g/m^3$ (limit of instrument sensitivity) of that predicted by the gravimetric permeation rate and the air volume; therefore, the latter data were used to determine the spike values. Additional details on design of the sampling system can be found in the referenced report (5).

Discussion

Collaborative Test. Collaborative testing has long been recognized as an effective way of determining the statistical limits of error inherent in an analytical method (6). To provide useful information on the performance of a method, an adequate number of test participants, that are representative of the average user community using the method, should be selected. Ten volunteer collaborators were selected to participate in the test. The selection was based primarily on past experience in use of the method, ability to furnish equipment necessary to perform the test in accordance with the method, and type of organization. Seven of the collaborators selected were from state and local organizations, two from industrial laboratories, and one from a government laboratory. The collaborators and their affiliations are given in ref. 5 and are referred to subsequently as collaborators A–J to maintain anonymity.

The test involved sampling ambient air and the simultaneous sampling of the same air spiked with NO_2 for 4 days at a common site in rural Kansas City, Mo. The sampling system is shown in Figure 1. Spikes, nominally 50, 100, 200, and 300 μg NO_2/m^3, were added (one level per day) over a 24-h period to obtain typical ambient NO_2 concentrations. The ambient NO_2 concentration varied from 10 to 50 $\mu g/m^3$ over a 24-h
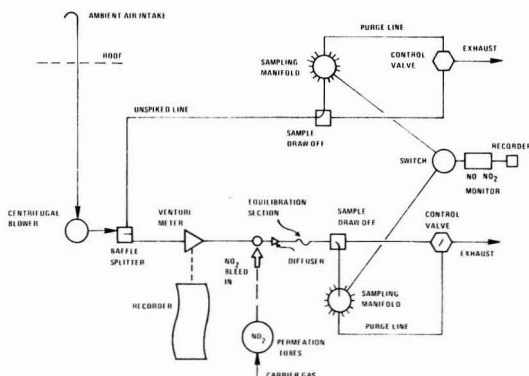

Figure 1. NO_2 sampling system

Table I. Collaborators' Data; Spike Value 90.9 $\mu g/m^3$

	Collaborator									
Sample	A	B	C	D	E	F	G	H	I	J
Spiked line	92.4	99.0	112.77	104.08	107.72	103.93	114	121.0	92.9	115.2
	94.2	100.0	106.02	102.36	109.54	84.37	90	114.0	87.2	115.3
	81.0	101.0	102.37	125.62	112.12	103.54	116	113.0	92.9	113.4
	77.4	100.0	107.89	106.37	118.44	103.54	115	118.0	94.2	115.7
Unspiked line	19.3	20.0	21.14	30.49	25.49	23.30	26	28.8	16.6	24.6
	21.4	14.0	22.06	25.31	25.01	23.30	13	28.0	15.0	23.7
Samples supplied to collaborators										
Control = 1.00 $\mu g \ NO_2/mL$	1.092	1.007	1.03	0.51	1.00	1.03	1.01	1.033	1.01	0.994
Blank = 0.0 $\mu g \ NO_2/mL$	0.017	0.0	0.006	0.01	0.0	0.02	0.01	0.012	0.01	0.005

period. Although these values were somewhat low, compared to typical ambient NO_2 levels, the concentration did exhibit the normal variability typical of ambient conditions. Thus, the collaborators were sampling an atmosphere that contained a known recoverable amount of NO_2, and the concentration was changing with time.

The collaborators were provided with a copy of the method and instructed to follow it in detail. Each collaborator prepared absorbing solution at his home laboratory and brought an adequate supply to the test site along with the equipment called for in the method. Collected samples, 24 per collaborator, plus one blank and one control sample (the latter samples were supplied to the collaborators) were returned to the collaborators' home laboratory for analysis. These procedures were used to minimize any biasing of the test results that may have resulted from the collaborators having to work together to collect samples.

Experimental Design. It was desired to determine estimates of both precision and bias. Precision was determined by having all 10 collaborators collect samples from the spiked line at each NO_2 level. Bias was determined at each level by having all collaborators simultaneously collect samples from the ambient and spiked lines (each collaborator had two sampling trains); both samplings were carried out over exactly the same 24-h time period. All data were reported as 24-h average concentrations.

One way to obtain estimates of precision and bias is to express the observed NO_2 concentration as a linear combination of certain variables. Each individual 24-h average, X_{ikj}, is described by the following linear model for the purpose of determining precision:

$$X_{ijk} = \mu + C_i + L_j + CL_{ij} + e_{k(ij)}$$

The model assumes initially that a constant value, μ, is being measured that does not change during the experiment. However, there are a number of reasons that the two values X_{ijk} and μ will not be exactly the same. There will be a day-to-day fluctuation in ambient NO_2 concentration that can raise or lower the concentration by an amount L_j depending on the day, j. A slight raising or lowering, C_i, of the concentration may be due to the collaborator, i, that made the measurement. This difference due to collaborators may not be the same for all collaborators on all days; this effect is called the collaborator-level interaction and is denoted by CL_{ij}. These effects are about all the experimental design allows us to examine. In addition to the above effects, there is usually some

unexplained variation that fluctuates randomly each time a measurement is made. This effect is denoted by $e_{k(ij)}$ and is called experimental error. All of these effects are included in the linear model.

Since the collaborators were chosen at random and the days during which the experiments were conducted had no particular significance, we can assume that the model is completely random. The random properties of the model imply that the overall average for each of the effects C_i, L_j, CL_{ij}, and $e_{k(ij)}$ is zero with variances of $\sigma_C{}^2$, $\sigma_L{}^2$, $\sigma_{CL}{}^2$ and $\sigma_e{}^2$, respectively. Statistical theory then tells us that the total variance of an observation is made up of the sum of these components. These components are used to estimate the precision of the method. The components of variance of principal interest were $\sigma_e{}^2$ (variance of repeated observations within a collaborator) and $\sigma_c{}^2$ (variance between collaborator means).

Bias is determined from the collaborators' simultaneous measurements on the spiked and unspiked lines. An individual bias, Z_{ijk}, is determined by first subtracting from a collaborator's response on the spiked line, X_{ijk}, the average of all collaborators' ambient observations over the same time period, $\overline{A}.j$. The spiked level, N_{js}, is then subtracted from this quantity to obtain the deviation from the true value, i.e., a bias. The relationship is expressed as follows:

$$Z_{ijk} = (X_{ijk} - \overline{A}.j) - N_{js}$$

The design for determining bias is subject to error mainly to the extent that $\overline{A}.j$ differs from the "true" ambient level. Additional information on these models can be obtained from ref. 5.

Collaborators' Data. Table I shows one of the four data sets obtained in the test. Each collaborator collected four samples from the spiked line and two samples from the ambient line per 24-h run. The control and blank samples were supplied to the collaborators to provide a separate check on the analytical portion of the method.

Outlying Values. An inspection of all the data submitted revealed that collaborators A and I had much larger negative biases than the other eight collaborators and that these two collaborators made systematic computational errors. An analysis of variance was carried out with data from all 10 collaborators and with collaborators A and I excluded to determine the effect of these computational errors on the components of variance. Including collaborators A and I results had no effect on the standard deviation within a laboratory (collaborator), but significantly affected the standard devia-

Table II. Components of Variance, All NO₂ Levels

| Components | Value, $\mu g/m^3$ | Relative standard deviation, % | |
		84 $\mu g/m^3$	311 $\mu g/m^3$
σ_e	8.2	10	3
σ_c	7.9	. . .	. . .
$(\sigma_e^2 + \sigma_c^2)^{1/2}$	11.3	13	4

Table III. Average Bias

| True NO₂, concn, $\mu g/m^3$ | Bias | |
	$\mu g/m^3$	%
84.1	−5.1	−6
113.2	−4.7	−4
228.3	−5.7	−2
311.7	−9.7	−3
Av 184.3	−6.3	−3

tion between laboratories, σ_c. The values of σ_c were 7.9 $\mu g/m^3$ with 8 and 14.6 $\mu g/m^3$ with 10 collaborators' results, respectively. Data from collaborators A and I were therefore deleted to maintain a data set that represented the capabilities of the method when followed. These computational errors prompted the authors to reexamine the method for clarity of directions on computations. It was concluded that the directions were clear, and no changes in the method description were made. In the remaining data there was one individual outlying value (via the Dixon test (7) at $\alpha = 0.05$) and one missing value. Both of these values were replaced with artificial values (8).

Precision. The assumption of homoscedasticity (equal variance at all NO₂ concentrations) in the analysis of variance model was checked by carrying out an analysis of variance at each of the four NO₂ concentrations and computing the standard deviation within a laboratory, σ_e. With increasing NO₂ concentration these values were 5.4, 7.3, 9.8, and 9.3 $\mu g/m^3$. Thus, the variance is not uniform. It depends on concentration but not in a simple way (5). Since σ_e does not monatonically change with concentration or μ, it is unlikely that any standard data transformation would improve the homoscedasticity. Therefore, no data transformation was applied. Details of the statistical analysis concerning the homoscedasticity of the data have been published (5).

The four data sets were pooled, and the analysis of variance was carried out. F-tests were performed to determine the significance of collaborator and collaborator-level interaction variances. The F-values for collaborator and collaborator-level were significant; however, the degree of significance may be inflated by nonhomogeneity of the variances. This means that different collaborators had different average NO₂ values and that there was a collaborator-level interaction. However, the interaction is due almost entirely to one collaborator, D (5).

The individual components of variance are shown in Table II. The standard deviation within a laboratory is given by σ_e, and the standard deviation between laboratories is given by $(\sigma_e^2 + \sigma_c^2)^{1/2}$. These values represent the best *average* estimate of the precision that will be obtained with the method over the range 84–311 $\mu g/m^3$. That one value, in $\mu g/m^3$, is given for the complete range should not be interpreted as meaning that the precision is completely independent of concentration. The precision does depend on NO₂ concentration, but not in an easily defined manner, as was discussed earlier.

Using the average value for σ_e and σ_c, the relative standard deviation within a laboratory varies from 10% at 84 $\mu g/m^3$ to 3% at 311 $\mu g/m^3$. Over the same range the relative standard deviation between laboratories varies from 13 to 4%.

Bias. In the model for determining bias, the true value is the NO₂-spiked level plus the average of the collaborators' ambient values. A bias is the difference between a collaborator's reading on the spiked line and the true value. For example, the true value for the spike value of 90.9 $\mu g/m^3$ (Table I) was 113.2 $\mu g/m^3$. The bias for the first reading of collaborator F in Table I would then be $103.9 - 113.2 = -9.3$ $\mu g/m^3$.

The bias data are presented in Figure 2, wherein percent bias is plotted against the true values for all eight collaborators. Five collaborators produced negative biases, and three had positive values. Collaborator-level interaction, shown to be significant in the analysis of variance, is indicated by nonparallel lines. Most of this interaction is due to the variable bias exhibited by collaborator D. In other words, although there is a significant collaborator-level interaction, seven of the eight collaborators produced a relatively uniform percent bias irrespective of the NO₂ level. Therefore, the percent bias values for all four levels were averaged. The average value, shown in Table III, was −3%.

Lower Detectable Limit. The lower detectable limit was estimated in two ways. The between collaborator standard deviation from the ambient readings and the standard error of estimate from the collaborators' calibration curves were doubled (5). The two values were 7 and 8 $\mu g/m^3$, respectively. Thus, the smallest NO₂ concentration that can be detected as significantly different from zero when comparing results from different laboratories is approximately 8 $\mu g/m^3$ (0.004 ppm).

Conclusions

The sodium arsenite method exhibits excellent precision, a small negative bias, and an acceptable lower detectable limit for monitoring ambient levels of nitrogen dioxide. The method is a reliable procedure for making 24-h integrated measurements of nitrogen dioxide in ambient air.
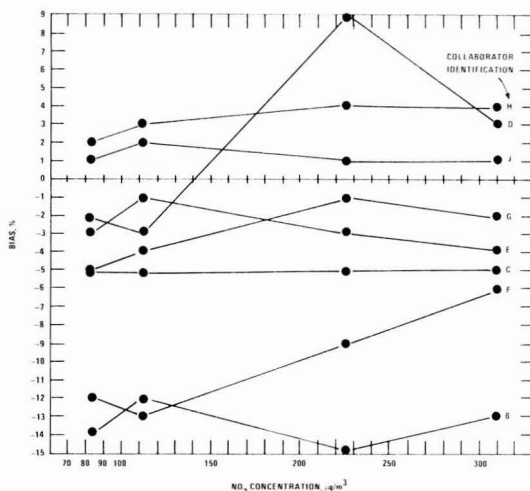
Acknowledgment

Figure 2. Collaborator bias as a function of NO₂ concentration

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Analytical Methodology for Kepone in Water and Sediment

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■ An analytical procedure for the determination of Kepone in water and sediment is described. The method adapts the regular, multiresidue procedure for the common chlorinated hydrocarbon pesticides and PCB's for the determination of Kepone. After elution of the common chlorinated hydrocarbon pesticides and PCB's from the Florisil column, Kepone is eluted using 200 mL of a solvent mixture consisting of 10% methanol and 5% benzene in hexane. This solvent mixture also produces consistent response of the electron capture detector to Kepone. The lower detection limit in water is 20 ng/L, and in sediment is 10 μg/kg. Average recovery of Kepone in sediments spiked with 4 mg/kg is 103%.

The chlorinated hydrocarbon pesticide Kepone, also known as chlordecone, is used for control of banana and potato bugs in foreign (non-USA) countries and was formerly used as part of a roach and ant poison sold in the U.S. (*1*). It was manufactured by Life Sciences Products until 1975, and the wastewater discharges from this firm have contaminated the James River from just below Richmond, Va., to the mouth of Chesapeake Bay.

This has caused the initiation of several studies on the occurrence and fate of Kepone in the environment. A study of the behavior of Kepone in association with dredging of the James River sediments revealed that the regular EC–GC multiresidue procedures for chlorinated hydrocarbon pesticides (*2*) were not adequate for analysis of Kepone in water and sediment samples. Two problems were encountered. The first was the increase of the electron capture response to standard Kepone solution as the percentage of methanol in the injection solvent increased. The second problem was the poor recovery of Kepone from the Florisil column normally used to separate organic pesticides from other coextracted organics. Both problems may result in erratic data on Kepone levels in environmental samples.

This paper describes an analytical methodology for the determination of Kepone in water and sediment. The approach taken in this procedure was to adapt the regular, multichlorinated hydrocarbon pesticide residue procedure for determination of Kepone, thus allowing the simultaneous study of a large number of chlorinated hydrocarbon pesticides and PCB's without repeating the extraction and cleanup procedures.

Kepone is the trade name of decachloro-octahydro-1,3,4-metheno-2H-cyclobuta[cd] = pentalen-2-one. Figure 1 shows the empirical formula and structure of Kepone and its hydrate. The pure compound is a white powder that decomposes

at 350 °C. It is reported to be slightly soluble in water and hydrocarbon solvents but soluble in alcohol, ketones, and acetic acid (*3*). A literature review indicated that very little information is available on the properties and behavior of Kepone in natural waters. The presence of the carbonyl group in the molecule would indicate the ease of formation of the hydrate in aqueous solutions. Oswald and Moseman (*4*) reported that Kepone exists in the diol form in aqueous and also in nonpolar organic solvents such as hexane and benzene. They also reported that in the presence of methanol, Kepone forms hemiacetal, the structure of which was confirmed by NMR, IR, and MS.

Different procedures have been developed for the analysis of Kepone in environmental samples (*5–9*). Most of these procedures recommend the addition of 1–2% methanol to the final sample extract or standard solution before injection into the GC, to provide optimum response to the EC detector. Several alternatives were used to overcome the low recovery of Kepone during the Florisil column cleanup procedure. In some procedures (*5, 7, 8*) a micro-Florisil column containing from 1.6 to 3 g of activated Florisil and from 1.6 to 2.5 g anhydrous sodium sulfate was used. Eluting solvents of varying composition were used with the micro-Florisil column to produce high recovery (more than 80%) of Kepone.

Base partitioning was another alternative used to separate Kepone from other chlorinated hydrocarbon pesticides (*5*). In another procedure (*9*) most coextracted organics were destroyed with fuming sulfuric acid. In one procedure (*6*) the use of Florisil column cleanup was completely avoided, and the

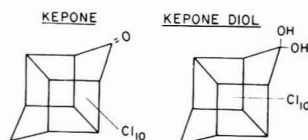| EMPIRICAL FORM	CHEMICAL NAME
$C_{10}Cl_{10}O$	Decachloro-octahydro-1,3,4-metheno-2H-cyclobuta [cd] = pentalen-2-one

Figure 1. Empirical formula, chemical name, and structure of Kepone and its hydrate

EC detector temperature was increased to 337 °C. Most of the above-mentioned procedures focused primarily on the analysis of Kepone. For some studies, it may be required to investigate other chlorinated hydrocarbon pesticides and PCB's in addition to Kepone. In such situations the development of analytical methodology suitable for determination of all these compounds with only minor modifications is highly desirable. This paper reports on a modification of the regular chlorinated hydrocarbon analytical procedures for analysis of Kepone in natural waters and sediments.

Experimental

The instrument was a Varian Model 2100 gas chromatograph equipped with an Sc³H electron capture detector. Columns were glass U shaped of 4 mm i.d. × 6 ft L. One column was packed with 80–100 mesh Chromasorb WHP coated with 4% SE-30/6% OV-210. Another column was packed with 80–100 mesh Chromasorb WHP coated with 1.5% OV-17/1.95% QF-1.

The GC operating conditions were: carrier gas, purified nitrogen; flow rate, 60–70 cc/min; temperatures—detector 275 °C, injector 225 °C, column 200 °C; input range, $10^{-10} \times 10$ or $10^{-10} \times 8$ A; linearity range of standard Kepone, 10 000 to 50 pg.

Apparatus and Reagents. For extraction an empty 1-gal solvent bottle with Teflon-lined cap was used. A 2-L separatory funnel with a Teflon stopcock was used. The Soxhlet extractor was an all-glass unit consisting of a condenser, 250-mL extractor flask, and large-size extractor glass thimbles with extra coarse fritted disc. The Chromaflex column was 19 mm i.d. × 300 mm L with a 250-mL reservoir and stopcock. A Kuderna Danish concentrating apparatus with a 500-mL capacity and 3-ball Snyder column and graduated concentrating tubes of 10 and 4 mL was used. Solvents were benzene, hexane, methanol, ethyl-ether and acetone, all pesticide quality. Anhydrous, granular sodium sulfate was extracted for 20 h with hexane in an all-glass Soxhlet extractor, air dried, and stored in an oven at 130 °C. Silanized glass wool was extracted and stored the same as the sodium sulfate.

Florisil, activated at 1200 °C, 60–80 mesh, should be purchased in one lot. One pound was placed in a glass jar and stored in an oven at 130 °C for immediate use. Elution patterns for each lot were evaluated for the proper strength of the eluting solvent. Standard Kepone was purified solid of 87.3% purity. A stock solution of 20 ng/μL was prepared in benzene. Diluted standards were prepared as required using hexane, methanol, and benzene. Standards of other chlorinated hydrocarbon pesticides were high purity; concentrated stock solutions of 20 ng/μL were dissolved in 2,2,4-trimethyl pentane or benzene and stored in the refrigerator. Fresh standards were prepared as required by dilution of the stock solution.

Procedure. All glassware was washed with detergent and hot water, chromic acid, tap water, distilled water and acetone in that order. When using an ultrasonic cleaner and detergent, there was no need to use the chromic acid. The cleaned glassware was put in an oven at 130 °C for at least 2 h; then the ends of each piece were wrapped in aluminum foil and stored. Just prior to use, all glassware used for pesticide residue concentrations was rinsed with a few milliliters of hexane.

Extraction of Water and Sediment. Three liters of water were extracted twice with 75 mL of 35% ethyl-ether hexane mixture (solvent "A"). (The percentage of ethyl-ether in hexane was established for each lot of Florisil.)

Sediment samples were air dried and homogenized to pass through 25 mesh sieves. The moisture content in the sediment was determined by drying a known weight of the sediment at 103 °C to a constant weight. For pesticide residue analysis, two aliquots of 10 g dry sediment were placed in a glass thimble

padded with a layer of glass wool. A 100-ng heptachlor epoxide in 1 mL hexane was added as an internal standard to one of the aliquots. Each sample was extracted with 75 mL of solvent "A" in the Soxhlet extractor for 4 h. The cycling rate was adjusted to 30 cycles/h.

Florisil Column Cleanup. The column was prepared by placing 20 g of activated Florisil over a layer of glass wool and 0.5 in. Na₂SO₄. The column was pre-eluted with 50 mL hexane, the pre-eluate was discarded, and just prior to exposure of the sulfate layer, the extract was quantitatively transferred to the column. The first eluate was received in a 500-mL Kuderna Danish (KD) concentrator. The elution rate was adjusted to 5 mL/min, and an extra 50 mL of solvent "A" was added to complete the elution of the chlorinated hydrocarbon pesticides and PCB's. In the case of sediment extract (total volume of 75 mL), an additional 125 mL of solvent "A" was used. A final 25 mL of hexane was added, and before exposure of the sulfate layer, the stopcock was closed and another KD unit was placed. Kepone was then eluted with 200 mL of solvent consisting of 10% methanol and 5% benzene in hexane (solvent "B") at the rate of 5 mL/min.

Both eluates were concentrated down to 10 mL or less, using a water bath at 90 °C. Care was taken to avoid complete drying of the extract or mechanical loss of the solvent during the concentration step, especially for concentration to less than 10 mL. The first eluate I from solvent "A" contained the common chlorinated hydrocarbon pesticides and PCB's that could be analyzed according to the EPA (2) procedures. The second eluate II contained Kepone and its decomposition products that could be analyzed by EC–GC under the regular operating conditions. The final volume of the second eluate II was always adjusted to contain 10% methanol and 5% benzene in hexane before injection into the GC. The LDL in water was 20 ng/L and in sediment 10 μg/kg. These values were based on extraction of 3 L of water or 10 g of sediment and concentrating the extract to 1 mL.

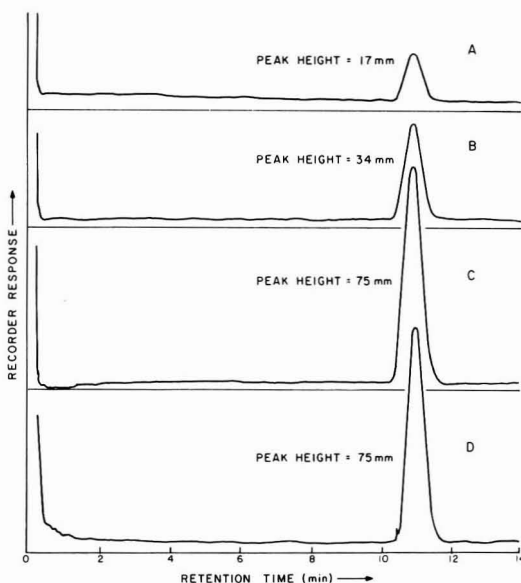**Figure 2.** Increase of EC response to standard Kepone solution in presence of increasing percentage of methanol

A) EC chromatograms of 5 μL of standard Kepone (400 pg/μL) in hexane on GC column 4% SE-30/6% OV-210. B) 5 μL of the same standard in 1% CH₃OH–5% C₆H₆ in hexane. C) 5 μL of the same standard in 5% CH₃OH–5% C₆H₆ in hexane. D) 5 μL of the same standard in 10% CH₃OH–5% C₆H₆ in hexane

Table I. Recoveries of Kepone [a] from Florisil Column

	Replicate			
% Recovery	1	2	3	4
First aliquot of solvent "B" [b] (100 mL)	60.7	64.7	57.1	85.1
Second aliquot of solvent "B" [b] (100 mL)	48.6	35.6	42.1	14.9
Total % recovery	109.3	100.3	99.2	100

[a] 100 μg of Kepone in 5 mL of benzene. [b] Solvent "B" consists of 10% CH_3OH–5% C_6H_6 in hexane.
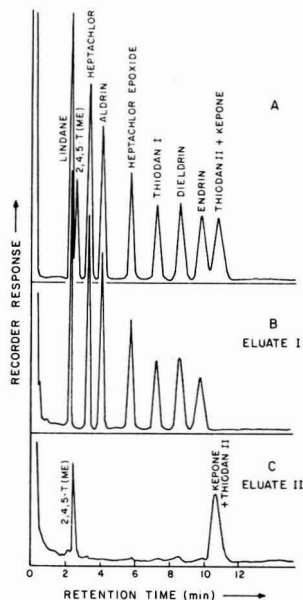

Figure 3. Separation of Kepone from nine chlorinated pesticides
A) EC chromatograms of 10 μL of mixture of nine chlorinated pesticides and Kepone in solvent "B", total volume 10 mL, GC column 4% SE-30/6% OV-210. B) EC chromatogram of 10 μL eluate I of total volume 10 mL in solvent "A". C) EC chromatogram of 10 μL eluate II of total volume 10 mL in solvent "B"

Results

The above-mentioned procedure was tested for its reliability and precision. The approach used to solve the problems associated with the Kepone analysis was to produce a stable signal for Kepone on the EC detector and to recover Kepone from the regular Florisil column. The EC response to standard Kepone in solvents such as benzene or hexane gradually increased as the percentage of methanol in the solvent increased up to 5%. Above this percentage the EC signal was constant. Figure 2 shows the increase of the EC response to 5 μL standard Kepone solution (400 pg/μL) with an increase of the percentage of methanol in the solvent. The 5% benzene was added to effect the complete miscibility of methanol in hexane.

To test the efficiency of Kepone elution from the Florisil column using solvent "B", two experiments were run. In the first experiment four Florisil columns were prepared. To each column 100 μg of Kepone in 5 mL of benzene was added and eluted with two aliquots of 100 mL of solvent "B". Each aliquot was separately collected in a 100-mL volumetric flask. Table I shows the recoveries obtained from each aliquot. The first aliquot of solvent "B" eluted from 57.1 to 85.1% of the
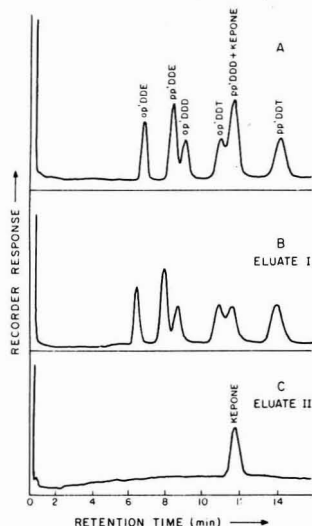

Figure 4. Separation of Kepone from DDT and its analogs
A) EC chromatogram of 10 μL of mixture of DDT and its analogs and Kepone in solvent "B", total volume 10 mL, GC column 4% SE-30/6% OV-210. B) EC chromatogram of 10 μL eluate I of total volume 10 mL in solvent "A". C) EC chromatogram of 10 μL eluate II of total volume 10 mL in solvent "B"

Kepone. Total recoveries using 200 mL of solvent "B" were 109.3, 100.3, 99.9, and 100.0%, respectively.

In the second experiment, Kepone was mixed with some of the common chlorinated pesticides. In one test 1 μg Kepone was mixed with 0.5 μg of each of the following chlorinated pesticides: lindane, 2,4,5-T(ME), heptachlor, aldrin, heptachlor epoxide, thiodan I, dieldrin, endrin, and thiodan II, using solvent "B". The total volume of the mixture was 10 mL. Thus, the concentration of each of the chlorinated pesticides was 50 pg/μL, and that of Kepone was 100 pg/μL. Figure 3A shows the EC chromatograms of 10 μL of the standard mixture on the GC column packed with 4% SE-30/6% OV-210. The figure shows that the retention time of Kepone (136 mm) overlaps with that of thiodan II (139 mm). This standard mixture was subjected to the Florisil column fractionation using solvents "A" and "B" as described in the procedure. Figure 3B shows the EC chromatogram of 10 μL eluate I, and Figure 3C the EC chromatogram of 10 μL eluate II. Apparently, solvent "A" eluted all the chlorinated pesticides except 2,4,5-T(ME), thiodan II, and Kepone. The last three compounds were effectively eluted with solvent "B".

In another test the same amount of Kepone (1 μg) was mixed with 0.5 μg of the following DDT compounds: op'DDE, pp'DDE, op'DDD, op'DDT, pp'DDD, and pp'DDT. The rest of the test was similar to the previous one. Figure 4A shows the EC chromatogram of 10 μL of standard mixture. Note that here the retention time of Kepone (136 mm) overlaps with that of pp'DDD (138 mm). Figure 4B shows the EC chromatograms of 10 μL eluate I, which includes all the DDT compounds. Figure 4C shows the EC chromatogram of eluate II, which includes Kepone. Table II shows the relative retention time (Rr) and the percent recovery of each compound from either the first or second eluate. Solvent "A" effected more than 90% recovery of all the compounds investigated except endrin, for which the recovery was 81.3%. No endrin was recovered in the second eluate. Also, solvent "B" effected complete recovery (100%) of Kepone, thiodan II, and 2,4,5-T(ME). The results of these two experiments indicated that both solvents "A" and "B" could be used for the complete separation of Kepone from mixtures containing 16 organic

Table II. Fractionation of Kepone from Other Chlorinated Pesticides (Results Derived from Figures 3 and 4)

Compound	X_{mm}[a]	Rr[b]	% Recovery Eluate I,[c] solvent "A"	% Recovery Eluate II,[d] solvent "B"
Lindane	29	0.57	97.3	0
2,4,5-T	31	0.61	0	100
Heptachlor	41	0.80	97.3	0
Aldrin	51	1.0	100	0
Heptachlor epoxide	72	1.41	96.2	0
Thiodan I	91	1.78	92.9	3.6
Dieldrin	108	2.12	92.9	8.8
Endrin	124	2.43	81.3	0
Kepone	136	2.67	0	100
Thiodan II	139	2.72	0	100
op'DDE	77	1.51	95.1	0
pp'DDE	97	1.90	96.3	0
op'DDD	105	1.98	100	0
op'DDT	129	2.53	96.4	0
pp'DDD	138	2.71	100	0
pp'DDT	171	3.35	93.1	0

[a] X_{mm} = distance between injection and midpeak in mm. [b] Rr = relative retention time with respect to aldrin, column 4% SE-30/6% OV-210. [c] Solvent "A" = 35% ethyl-ether in hexane. [d] Solvent "B" = 10% CH_3OH–5% C_6H_6 in hexane.

Figure 5. Effect of concentration on standard Kepone
A) EC chromatogram of 5 μL of standard Kepone solution (1000 pg/μL) in solvent "B". B) EC chromatogram of the standard Kepone after dilution and concentration, recovering 97%. C) EC chromatogram after dilution and concentration, recovering 77.6%, secondary peak apparent at Rr = 0.98

Table III. Relative Retention Time (Rr) of Kepone and Its Decomposition Product on Two Chromatographic Columns

EC–GC Operating Conditions—See Text

Column	Rr[a] Kepone	Rr[a] Kepone decomposition product
4% SE-30/6% OV-210	2.63	0.98
1.5% OV-17/1.95% QF-1	2.87	0.82

[a] Rr = Relative retention time with respect to aldrin.

Table IV. Recoveries of Kepone[a] from Spiked Sediments

Type of sediment	% Recovery Duplicate A	% Recovery Duplicate B
Silt and sand	77.4[b]	96.8
Clay	101.6	97.5
Sand	106.4	114.5

[a] 40 μg Kepone in 2 mL of benzene added to 10 g sediment, i.e., concentration of Kepone is 4 mg/kg. [b] Secondary peak of Rr 0.98 on SE-30 column was observed.

pesticides. The herbicide 2,4,5-T(ME) and thiodan II were two of the compounds eluted with Kepone using solvent "B".

The effect of the KD concentration on Kepone was investigated. In triplicate tests 10 μg of Kepone in 10 mL of solvent "B" was diluted to 200 mL and concentrated to 8 mL using the KD concentrator. The final volume was adjusted to 10 mL maintaining the 10% methanol and 5% benzene in hexane. Percent recoveries of Kepone were 89, 97, and 77.6, respectively. The 77.6% recovery was associated with the appearance of a secondary peak of Rr = 0.98 on the SE 30 column. Figure 5A shows the EC chromatograms of 5 μL of standard Kepone (1 ng/μL). Figure 5B shows the EC chromatogram of 5 μL of one of the replicates after dilution and concentration, recovering 97%. Figure 5C shows the EC chromatogram of 5 μL of another replicate recovering 77.6% of Kepone and showing the secondary decomposition peak at Rr = 0.98. Table III shows the Rr values of standard Kepone and the secondary peak noted upon concentration on the two chromatographic columns used.

The recovery of Kepone from spiked sediments was investigated. Three types of sediments were used. One type was a mixture of silt and sand, the other was mostly clay, and the third was almost all sand. All three sediments were initially extracted with 50% ethyl-ether in hexane, in the Soxhlet extractor for 8 h to remove organic residues. Each type of sedi-
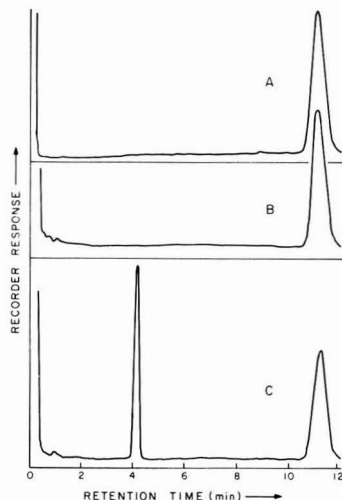
ment was run in triplicate. Three aliquots, each weighing 10 g, were added to a glass thimble padded with a layer of glass wool. Two of the aliquots were spiked with 40 μg of Kepone in 2 mL of solvent "B". Caution was taken to introduce the standard through the sediment particles. The spiked sediments were left for 2 h to equilibrate. The third aliquot was used as a sediment blank to check the background residue left in the sediment.

All the sediments were then subjected to the outlined analytical procedures. Table IV presents the recovery data. In the clay and sandy sediments, average recoveries were 99.6 and 110.5%, respectively. In the silty and sandy sediment, percent recovery for one of the duplicates was 96.8 and for the other, 77.4%. The latter low recovery was associated with the appearance of the secondary peak of Rr = 0.98 on the SE 30 column.

In association with the dredging operations of the James River, several water and sediment samples were collected from the area in mid-July 1976. All samples were analyzed for 15 chlorinated hydrocarbon pesticides, total PCB's, and Kepone. The results of these studies are presented by Saleh and Lee (10). Kepone was analyzed using the above-mentioned procedure. Figure 6 shows EC chromatograms of eluates I and II for a water sample. Figure 7 shows the EC chromatogram of both eluates in a sediment sample collected from Bailey Creek, which is close to the Hopewell sewage plant. Duplicate anal-
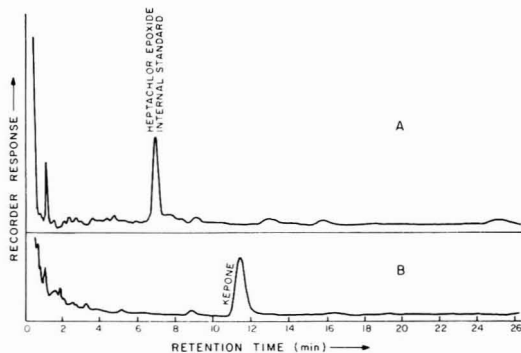
Figure 6. EC chromatograms of water sample collected from the James River

A) 5 μL eluate I containing chlorinated hydrocarbon pesticides and PCB's, total volume 1 mL ≡ 3 L sample, GC column 4% SE-30/6% OV-210. B) 5 μL eluate II containing Kepone, total volume 1 mL ≡ 3 L sample
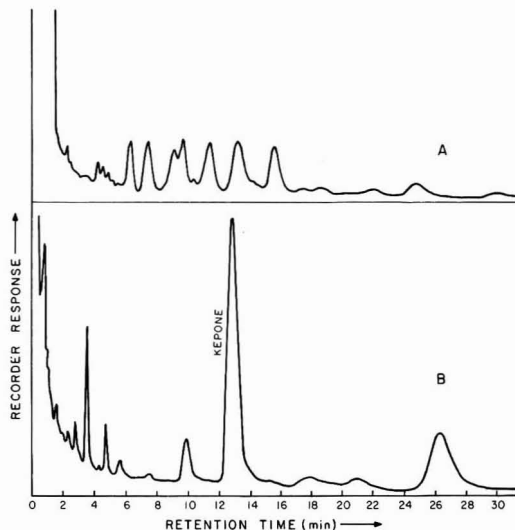

Figure 7. EC chromatograms of sediment sample collected from Bailey Creek

A) 5 μL eluate I containing chlorinated hydrocarbon pesticides and PCB's, total volume 10 mL ≡ 10 g sediment, GC column 4% SE-30/6% OV-210. B) 5 μL eluate II containing Kepone total volume 100 mL ≡ 10 g sediment

yses were run on selected water and sediment samples. Table V shows the results and the standard deviation.

Discussion

The problems associated with Kepone analysis can be attributed to its molecular structure and the presence of the carbonyl group. Though the exact explanation of the increase of the EC response to Kepone in the presence of methanol is unknown, it is possible to attribute the phenomenon to the increase of electron affinity upon elutriation of Kepone through the EC detector. It is recognized that whether Kepone is present as a hydrate in nonpolar solvents or as a hemiacetal in the presence of methanol, it is decomposed to the anhydrous form upon injection on the GC with the injector port at 225 °C. The low recovery of Kepone from the regular Florisil column can be attributed to the strong binding forces that hold Kepone molecules on the Florisil particles. Apparently, the polarity of the ethyl-ether hexane is not enough to counteract these binding forces. Initial experiments performed using an increasing percentage of ethyl-ether in hexane up to 80% did not yield satisfactory recovery results. Probably, the formation of Kepone hemiacetal in the presence of methanol plays an important role in releasing Kepone from the Florisil particles.

The stability of Kepone is another area that needs to be investigated. The occasional decomposition of Kepone upon concentration or during the Soxhlet extraction procedure was also noted upon storing the standard Kepone solution for a period of one month.

The outlined procedure allows for the analysis of Kepone in addition to several other chlorinated hydrocarbon pesti-

cides and PCB's using a single extraction and single Florisil column. Also, the procedure allows the separation of Kepone from other chlorinated hydrocarbon pesticides that have retention times close to that of Kepone, such as *pp'*DDD on the SE-30 column and endrin on the OV-17 column.

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Table V. Evaluation of Precision of Kepone Procedure Results of Duplicate Analyses of Water and Sediment Collected from the James River and Bailey Creek

Kepone concn	Duplicate A	Duplicate B	Av	SD[a]
Water (in ng/L)	44.4	46.6	45.5	1.6
Sediment (in mg/kg)[b]	1.45	1.34	1.40	0.08

[a] SD = standard deviation. [b] Results are based on dry weight.

Statistical Correlation Between Ambient Sulfate Concentration and Sulfur Dioxide Concentration, Total Suspended Particulates, and Relative Humidity for 13 Eastern States

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■ Daily ambient sulfate concentration, C_2, data monitored for 13 eastern states (USA) were related to sulfur dioxide concentration, C_1; particulate concentration, C_p; % relative humidity, H; temperature, T; and solar radiation, S. The range of basic variables studied was $3.8 < C_2 < 44.1$ $\mu g/m^3$, $0.0 < C_1 < 167.0$ μg m^3, $22.0 < C_p < 377.0$ $\mu g/m^3$, $35.4 < H < 100\%$, $13 < T < 96$ °F, and $0 < S < 12$ h. A semiempirical Lagrangian box model and nonlinear generation kinetics were used to develop simple relationships for sulfate with meteorological and chemical quantities. Laboratory results concerning the mechanism of sulfate information were reviewed and discussed in relation to atmospheric variables. At low temperature, $T < 50$ °F, C_2 was correlated with C_1, C_p, and H. At higher temperature, $T > 50$ °F, higher correlation coefficients resulted when C_2 was related to C_p alone than when related to any other combination of variables tested.

Particulates compounded with SO_2 and sulfate aerosol have been implicated as lung irritants and have been linked with pulmonary emphysema and lung cancer (1, 2). Aerosols containing sulfur are likely to be more toxic than comparable concentrations of sulfur dioxide. As a result, discussions for setting ambient standards for sulfate concentrations are now under way.

One may predict regional ambient concentrations by developing the equations of component mass transport (diffusion equation) for typical meteorological and source situations. For linear reaction generation rates, the solutions are well known. A few empirical approaches have also been reported for finding the dependence of ambient sulfate on other atmospheric and pollutant variables. Prior to 1970, relatively little sulfate data were available at stations that monitored other pollutant and meteorological variables.

Studying 8 hourly data at four USA locations (period Aug.–Oct. 1965), Wagman et al. (3) found that sulfate mean particle size generally increased with increased relative humidity and that sulfate concentration was weakly dependent on the absolute humidity. Altshuller (4) correlated nationwide urban site *annual* average sulfate values with SO_2 data and found that $[SO_4^{2-}]$ followed the relationship

$$[SO_4^{2-}] = 0.144 \, [SO_2] + 4.92 \, \mu g/m^3 \qquad (A)$$

when $[SO_2] < 80$ $\mu g/m^3$ and was independent of $[SO_2]$ above that concentration. Correlations of averaged sulfate and SO_2 concentrations were for both urban and nonurban sites in the United States. The mean concentrations for the urban sites (period 1964–68) were $C_1 = 53$ $\mu g/m^3$ and $C_2 = 11.4$ $\mu g/m^3$ for SO_2 and SO_4^{2-}, respectively. Sites in the East had generally higher concentration averages than did those in the West. Charleston, W.Va., $\bar{C}_1 = 26$ $\mu g/m^3$ was omitted from the cor-

relation, however. In the range $100 < C_1 < 204$ $\mu g/m^3$ the value of SO_4^{2-} remained essentially constant (mean $C_2 = 17$ $\mu g/m^{3-}$). New York City yearly average values did not associate well with this range having mean $C_1 = 383$ $\mu g/m^3$ and $C_2 = 28.2$ $\mu g/m^3$ over the years studied. The intercept found from Equation A indicates a residue level of about 5 $\mu g/m^3$. Sanberg et al. (5) confirmed a linear dependence on SO_2 for the San Francisco Bay area.

Tong and coworkers (6) analyzed data at 12 stations (40–45°L) between Collins, Ill., and Albany, N.Y., and concluded the following:

Means of *daily* averaged $[SO_4^{2-}]$ values, taken over 5 °C ΔT intervals, increase with increase in ambient temperature.

Means of *daily* averaged $[SO_4^{2-}]$ values, taken over 5 °C Δ dew point intervals, increase with increase in dew point.

$[SO_4^{2-}]/[SO_2]$ ratios taken within 2 mb ΔP_{H_2O} intervals, increase sharply with increased ambient partial pressure of moisture.

In a more recent study, Altshuller (7) reported the $[SO_4^{2-}]$ varied much less from urban to nonurban areas (i.e., 2:1) than did $[SO_2]$ values (i.e., 5+:1). The mass median diameter ranged between 0.2 and 1 μm, with 80–90% of the aerosol below 2 μm.

Smith and Jeffrey (8) flight sampled air along the eastern coast of England and off the western coast of Denmark under westerly meteorological conditions. They observed a strong influence of relative humidity on sulfate concentration with the interaction decreasing sharply at values below 70% RH.

If the overall oxidation reaction is assumed to be a nonlinear function of concentration, the computational difficulties of the diffusion equations are magnified. Also, the kind and quantity of data available for verification are insufficient to test the model parameters. Hence, the goal of the current work is to correlate daily averaged sulfate concentration values and key meteorological and pollutant measurements based on a semiempirical box-type flow model.

Mechanism of Aerosol Formation

The precise multistep mechanism of the formation of sulfur-containing aerosols is still uncertain although many laboratory investigations have been attempted to determine the sequence. (See refs. 9 and 10 for a review of this literature.) Although these investigations do not exactly simulate the atmospheric situation, much has been learned and some of the noteworthy results will be summarized below. Obviously, the overall reaction path must include the oxidation of sulfur dioxide with ultimate production of sulfate. It is convenient to classify competing mechanisms for this change as being of the homogeneous photochemical, the heterogeneous catalyzed by solid particles, and the absorption in liquid aerosol reaction types. The latter may also include catalytic steps in the presence of dissolved metallic ions. Brosset et al. (11) found that sulfate-bearing aerosol particles off the coast of Sweden have a substantial quantity of NH_4^+ ions. Tomasi et al. (12) implied that NH_3 and SO_2 concentrations will affect the SO_4^{2-} concentrations in Milan, Italy. They concluded that an ob-

served increase in acidity and therefore a decrease in the SO_4^{2-}/SO_2 ratio can be attributed to a reduction of airborne NH_3.

The *homogeneous photochemical* route involves a sunlight-catalyzed reaction that takes place via the formation and further reaction of active intermediates such as SO_2^* (i.e., activated SO_2), OH^-, HO_2^- as well as various branched chain hydrocarbon radicals (13). The overall photochemical reaction rate in air is first order with respect to SO_2 and does not increase with increase in humidity above 50% (14-16).

The *heterogeneous catalyzed by solid particles* route is accompanied by great activity increases in the presence of particles such as hydrous ferric oxide, alkaline alumina, and calcium oxide (15, 17). Sodium chloride, calcium carbonate, and oxides of vanadium and chromium had little effect on rate. The weight ratio of particles/SO_2 was much larger in their laboratory studies than would appear in the atmosphere. The rate constant reported as first order with respect to catalyst concentration was unaffected by either relative humidity (50-94%) or sulfur dioxide concentration (4-19 ppm).

The *absorption and aerosol reaction* mechanism might be the rate-controlling process in atmospheric sulfate production. It involves the formation of condensation nuclei and the diffusion, absorption, dissociation, and ultimate oxidation of an ionized sulfur-containing species. The aerosol thus formed contains dissolved SO_2 and H_2SO_4 that ionize to form SO_3^{2-}, HSO_3^-, HSO_4^-, and SO_4^{2-}. The aerosols undergo dynamics that include an expansion (growth) dependent on the relative humidity in the atmosphere and their degree of ionization. Ammonia can produce primary solid products with SO_2 in the stratosphere (i.e., temp. < -70 °C) (18). Also at 25 °C, formation rates of sulfate nuclei from SO_2 in the presence of NH_3 and moisture increase from 540 particles/s-cm^3 @ 27% humidity to 892 particles/s-cm^3 @ 100% humidity (19). A number of investigators noted dependence of their oxidation rates on sulfur dioxide concentration (zero to second order), on relative humidity, usually only above 60-70%, and on both catalyst composition and concentration (20-27). Tang (28), using a phase equilibrium analysis, suggests that the formation of aerosol in the ammonia–sulfuric acid system may be affected by a critical relative humidity value.

Freiberg (29, 30) analyzed the laboratory data of Neytzell, de Wilde, and Taverner (29), and developed a rate expression for iron-catalyzed sulfate formation, which suggests a cubic dependence on $[NH_3]/(1 - RH)$. Although his assumption that NH_4^+ and SO_4^{2-} ions are the only significant contributors to the vapor pressure lowering effect is unsubstantiated, the directional effect of RH is probably correct (i.e., very significant rate increases as fractional RH $\rightarrow$ 1).

Freiberg (30) also concluded that conversion should decrease with increasing temperature, since absorption equilibrium constants of NH_3, and SO_2 and dissociation equilibrium constants for H_2SO_3 and H_2O all decrease with increasing temperature. He predicts a rate decrease of one order of magnitude for each 5 °C increase. McKay (31) (1971) predicts a factor of 1.5-5 reduction in rate over the range 15-25 °C using the approach of Scott and Hobbs (32). In his estimate, the liquid-phase reduction activation energy range was based on previously measured values of 18.3-22.8 kcal/mol in the presence of copper catalyst. It should be pointed out in summary that in the absence of a base such as ammonia to reduce $[H^+]$ concentration or without a catalyst such as $[Fe^{3+}]$ to enhance the liquid-phase oxidation rate, the overall reaction rate by this process would be exceedingly slow, compared with the other mechanisms described.

In addition to the stationary models just discussed, a considerable body of literature exists that describes the nucleation and growth processes involved in droplet dynamics, including effects of drop diameter, concentration, and size distribution (33, 34).

Modeling Effort

Depending on local and long-range meteorological conditions, the formation of sulfate may occur via all three mechanisms described. The key atmospheric variables involved in the conversion processes have been neither totally identified nor monitored. It is beyond the scope of this study to specify the partial differential equations of the atmospheric processes including both chemistry and meteorology. The intent here is rather to use simplified models that empirically establish the major variables involved in each mechanism and to relate them as closely as possible to data bases that include daily air pollution and meteorological information from the same locale. The parameters are lumped, and the interactions derived from the equations are used as first approximations for the correlation and *are not intended to be interpreted as a valid description of the physics and chemistry of the formation process.*

For our model system we shall examine a rectangular-shaped box of height h, length l, and width w, meters moving with the magnitude and direction of the mean wind vector. We shall assume the material within the system to be well mixed so that properties are uniform throughout. Lateral and axial transport to (from) the system is neglected (i.e., $w \gg h$ and $l \gg h$). Vertical exchange inputs are taken as source emissions averaged on a per volume basis. Dry and wet depositions are considered the major outputs. The time changes in concentration C_1 and C_2, of $[SO_2]$ and $[SO_4^{2-}]$, respectively, may be expressed as a two-column vector equation,

$$\frac{d\bar{c}_i}{dt} = -\frac{\bar{c}_i}{v}\frac{dv}{dt} + \bar{q}_i - \frac{\nu_{di}\bar{c}_i}{h} + \sum_{j=1}^{4} r_{ij} \qquad (1)$$

The first two terms represent the accumulation of ith species allowing for expansion of volume, $v = lhw$. The $\bar{q}_i$ terms are the volumetric source terms, ν_{di} is the dry deposition velocity, and j is the mechanism identification number. The first three rates, r_{i1}, r_{i2}, r_{i3} are the functions described by the three formation mechanisms described previously. They are assumed to act in parallel and hence are additive. The expression for r_{i4} estimates rain (wet deposition) removal rates.

The *homogeneous photochemical* rate per unit volume, r_{i1}, may be expressed in terms of a direct dependence on both photon source strength and absolute humidity below a cutoff value inferred from Katz and Gale's (16) results. The activation energy for the slow reaction step is likely to be moderately high, and the value of Timmons et al. (35) (1971) may be considered representative; $\Delta E_1 = 3.43$ kcal/gmol. This would correspond to a rate in summer (ex. @ 30 °C) that is approximately double that of winter (ex. @ 0 °C).

The generation rate per unit volume ith species by *gas-solid heterogeneous reaction*, r_{i2}, is assumed to occur by reaction with an Arrhenius dependence on temperature and with a Langmuir-Hinshelwood dependence on concentration. Here an activation energy value, $\Delta E_2 = 12$ kcal/gmol (for unpromoted vanadium pentoxide), is taken as representative of solid phase catalysis, with SO_2 assumed to be the predominating adsorbed species.

The *adsorption and aerosol formation* rate, r_{i3}, is expected to depend directly on SO_2 concentration. Diffusion to small (<1 μm) aerosol particles is very rapid, since the transport coefficient is inversely dependent on drop size. Sulfur dioxide adsorption is extremely rapid, and the equilibrium coefficients may be used to relate liquid-phase concentrations to SO_2 concentrations (32, 36). A dependence on relative humidity above that of a critical value is expected. Thus, $H_m =$

Table I. Suffolk County Winter Data 1975

Run	SO_4^{2-} $(\mu g/m^3)$ C_2	SO_2 $(\mu g/m^3)$ C_1	TSP $(\mu g/m^3)$ [a] C_p	T, °F	% RH	PPt (in.)	Year/ month/day
1	3.26	24.4	13.03	48.	40.	. . .	750130
2	1.92	15.5	13.61	31.	42.	. . .	750203
3	2.77	15.2	12.91	32.	96.	0.37	750205
4	8.22	45.1	36.29	36.	61.	. . .	750207
5	5.51	45.6	31.02	29.	68.	. . .	750209
6	7.78	57.1	35.44	31.	70.	. . .	750211
7	6.53	51.9	35.12	26.	58.	. . .	750213
8	5.43	60.0	23.73	33.	71.	. . .	750215
9	9.58	57.6	19.79	38.	84.	0.06	750217
10	7.52	42.4	35.29	44.	72.	0.10	750219
11	4.69	18.6	19.11	28.	45.	. . .	750303
12	6.28	35.1	24.37	34.	48.	. . .	750305
13	10.31	31.6	42.47	43.	66.	0.18	750307
14	2.79	22.0	17.81	26.	27.	. . .	750309

[a] These nephelometer redgs. are "equivalent" to data available from the Environmental Protection Agency monitoring system. However, TSP values at the air monitoring stations are typically obtained from deposition on filters of a high-volume sampler.

$max|RH, RH_m| \times 100\%$, is used as a convenient variable with RH_m value expected to lie in the range 0.60–0.80. The rate also depends on particulate concentration where particulate is assumed to supply such soluble ions as Fe^{2+} and Mn^{2+}. Presumably, these ions can nucleate or be dissolved in an aerosol drop.

The rain removal term, r_{i4}, would have dependencies very similar to those of adsorption and aerosol formation with long-term averages being corrected for the rain frequency and intensity.

A more complete development for each rate expression may be found elsewhere (9). The computation of fractional relative humidity, RH and absolute water vapor concentration from temperature T, °F, and dew point, T_{dp}, °F data was accomplished using the Hurwitz relationship—see Murray (37).

One approach to establishing relationships between key variables is to assume that the concentration of SO_4^{2-} approaches a pseudo-steady state value for the majority of measurements (that Lagrangian accumulation is zero). Although this situation probably is not attained, the simplification is convenient for establishing correlation parameters. Thus, the SO_4^{2-} concentration is described as a linear function of the rate of formation terms by eliminating the accumulation in Equation 1.

$$C_2 \approx \frac{hq_2}{\nu_{d_2}} + \frac{h}{\nu_{d_2}} \sum_{j=1}^{4} r_{2j} \qquad (2)$$

If, for example, the heterogeneous absorption process were to predominate, then

$$C_2 \approx \frac{hq_2}{\nu_{d_2}} + \frac{h}{\nu_{d_2}} k_3' e^{-\Delta E_3/RT} H_m^\sigma C_p^\eta C_1^\epsilon \qquad (2a)$$

Here, as often in kinetic analysis, a power function of the key variable concentrations (law of mass action) is used to empirically describe the generation rate. Various special cases of Equation 2 had their coefficients linearly best fit to the data as will be described in the next section. Higher correlation coefficients might be expected from a rate expression that more nearly represents the true atmospheric mechanism, but any conclusions drawn from these gross results should be considered at most suggestive. Also, it was hoped that a correlation of statistical significance would be found for use in calculating sulfate concentration where all but $[SO_4^{2-}]$ data are available.

Data Base Establishment

a. Suffolk County Winter Data (Early 1975). Semiempirical correlations of daily ambient data were first applied to winter measurements supplied by Brown (38) of Brookhaven National Laboratory (BNL) and by Long Island Lighting Co. (LILCO) both in Suffolk County, New York. Referring to Table I, these include concentrations of SO_2 (Phillips monitor, LILCO), of SO_4^{2-} (methylthymal blue method, Technicon Analyzer, LILCO) and of temperature and relative humidity (MacArthur Airport Weather Observatory, via LILCO), and total suspended particulate (Integrating Nephelometer, BNL). The temperatures of these winter cases were all below 48 °F.

b. Data from Various Eastern Locations (1972). Daily averaged data were obtained for different locations east of the Mississippi River. The availability of sulfate data supplied by the EPA largely controlled the locations chosen. The propinquity of weather stations limited the number of cases to be investigated. The sites chosen for this study are presented in Table II, including the number of data extracted for each location. For those days in which sulfate, SO_2, and TSP data were all known for the year 1972, daily averaged temperatures, humidities, precipitations, and solar radiation hours have been added from nearby weather stations, usually at the same nominal latitude and longitude. This "dedicated" data base now resides in BNL's Computer Center, Evans and Benkovitz (39), containing 319 individual cases. No accuracy figures were given, and some differences in analytical techniques among sites might be anticipated. Tanner and Newman (40) review existing and innovative methods and their accuracy.

Results and Interpretation

a. Suffolk County, New York. When linear regressions of C_2 (sulfate) vs. either C_1, C_p, T °F, or % RH are performed (see Table III), the strongest interaction is found with C_p (particulate), relatively low correlation with either T or % RH, and moderate correlation with C_1 (sulfur dioxide). A sample correlation coefficient, r, of at least 0.54 is necessary to hypothesize that a "true" or population correlation coefficient, ρ, is nonzero. It might be expected that sulfate being a constituent of particulate matter would correlate with particulates. Reviewing the data of Table I (Cases 1 and 14, for example), we note that increasing nephelometer C_p alone will

Table II. Location and Data Available for 13-State Study 1972

State (or district)	Site	Latitude (°N)	Longitude (°W)	No. of data pts
Alabama	Birmingham	33.5	86.8	29
Connecticut	Bridgeport	41.2	73.2	30
D.C.	Washington	38.9	77.0	22
Georgia	Atlanta	33.8	84.4	30
Illinois	Springfield	39.8	89.7	25
Kentucky	Louisville	38.2	85.8	14
Louisiana	Shreveport	32.4	91.2	24
Maryland	Baltimore	39.3	76.6	26
Massachusetts	Worcester	42.3	71.8	27
Michigan	Dearborn-Detroit	42.3	83.2	26
New Jersey	Newark	40.7	70.2	26
New York	Albany	42.6	73.8	24
North Carolina	Durham-Raleigh	35.9	78.9	16

Table III. Sample Correlation Coefficients, r, for Suffolk County Data—Winter of Early 1975 [a]

Y/X	C_pH_{70}	$C_1^{1/2}C_pH_{70}$	$C_1C_pH_{70}$	$(1/T, °R)$	C_1	C_p	T, °F (or °R)	H	H_{70}
C_2/C_1	...	−0.067	0.093	−0.451	−0.313	−0.331	0.459	0.105	0.062
C_pH_{70}	...	...	...	−0.347	0.587	...	0.351	...	...
C_2	0.827	0.827	0.781	−0.547	0.664	0.786	0.548	0.431	−0.105
C_2/C_p	...	0.207	0.167	−0.480	0.387	−0.001	0.476	0.435	0.353
$\ln(C_2/C_1C_pH_{70})$	...	...	...	0.308	...	...	−0.311	...	...
$\ln(C_2/C_1^{1/2}C_pH_{70})$	...	...	...	0.308	...	...	−0.311	...	...
$\ln C_2$	0.834	...	...	0.467	...	...	0.469	...	...

[a] C_1: [SO_2] $\mu g/m^3$, C_2: [SO_4^{2-}] $\mu g/m^3$, C_p: nephelometer rdg. [TSP] $\mu g/m^3$.

not automatically result in increased sulfate concentration. Reactions dominated by rates r_{i_1} and r_{i_2} would be expected to follow Arrhenius temperature behavior using their reasonably high estimated activation energies (i.e., $\Delta E_1 = 3.43$ and $\Delta E_2 = 12.0$ kcal/gmol, respectively). Hence, regression analyses were performed on various logarithmic functions vs. $1/T$ °R, where °R is degrees Rankine (absolute).

The function $C_2/C_1^nC_pH_{70}$ was relatively invariant with temperature for divers n values. Assuming various mechanisms postulated in the literature, the value of n might be expected to fall within $0 < n < 2.0$. When variables of type, $C_pC_1^nH_{70}$ with $n = 0, 1$ and $1/2$, respectively, are correlated with sulfate, Y_c, the regression appears to reach a maximum $r > 0.827$, $n > 1.0$, with a 95% confidence interval on the population coefficient of $0.47 < \rho < 0.93$. As this was a preliminary analysis, no attempt was made to find still more precise values either of n or of powers for C_p and H_{70} for these data. Using $n = 1/2$ for convenience, the correlation equation may be expressed as

$$C_2 = 3.87 \times 10^{-4} C_1^{1/2}C_pH_{70} + 1.41 \ (\mu g/m^3)$$

$$\text{with } \sigma_{YC} = 1.4 @ \overline{YC} = 5.9 \qquad (C)$$

One may interpret the intercept [SO_4^{2-}] level of 1.41 $\mu g/m^3$ as a background (or residual) concentration. The logarithmic function was primarily considered for testing Arrhenius behavior between sulfate functions and temperature, for which incidentally no significant correlation functions containing H_{70} always resulted in the highest coefficients when compared with similar independent variables having the humidity functions H_0, H_{60}, or H_{80}, in its place. Note that SO_4^{2-} correlation with nephelometer reading alone had ($r = 0.786$) with

$0.38 < \rho < 0.92$ @ 95% confidence interval. The results of this analysis encouraged us to continue the investigation using a larger data base.

b. Data from 13 Eastern USA Locations. A more intensive functional analysis was performed for the data of the 13 locations, guided by the findings of the Suffolk correlation. Table IV presents the regression coefficients found for the better sulfate functions, Y, vs. representative functions, X. The sulfate data for *all states combined* and for temperatures between 13 and 96 °F (319 points) correlate in a positive linear fashion with TSP ($r = 0.549$, with $0.52 < \rho < 0.68$ @ 95%) as per Table IV (a). The correlation coefficient was not nearly as high as that for the Suffolk data, which is not surprising considering the widely divergent locations, source strengths, and background levels in 13 states vs. single-state data. Also, the Suffolk data were a purely winter sample.

In an attempt to further investigate these relationships, the data set was arbitrarily divided into "low" temperature, $T < 50$ °F, and "high" temperature, $T > 50$ °F, regimes. The lowest temperature of the data set was 13 °F (6 points were below 20 °F), and the highest was 96 °F (with only one point above 90 °F). Each state was also analyzed individually within these two temperature regions.

Of the Y functions initially studied, sulfate concentration alone, C_2, produced the highest correlation coefficient values; see Table IV for a number of instances that demonstrate this result. Such a finding has the semiempirical support of Equation 2, provided that a single mechanism r_{2j} limits the overall rate. An array of X functions of type $C_1^{a_1}C_p^{a_2}H_{70}^{a_3}$ were investigated for all permutations of the variables with a_i taken between zero and two in steps of $1/2$ ($a_1 = 0, 1/2, \ldots, 2; a_2 = 0, 1/2, \ldots$, etc.). Note a single variable, for example, particulate,

Table IV. Sample Correlation Coefficients of 13 States Combined Data Analysis for X Values Shown

	C_p H_70	C_1 C_p H_70	C_1^{1/2} C_p H_70	(1/T, °R)	C_1	C_p	T, °F	H_6	H_70	S	C_p H_70^2	(C_p − C_2) H_70^2	C_1^{1/2} C_p^{1/2} H_70
(a) Coefficients, r for all temperatures (13–96 °F) (319 points) Y↓													
C_2	...	0.388 ↑	0.457	−0.239 ↓	0.280	0.549	0.138	0.062	0.046		0.630	0.559	0.546
$\ln(C_2/C_1 C_p H_{70})$											...	...	...
(b) Coefficients, r for $T < 50$ °F (136 points) Y↓													
C_2/C_1	−0.288	...	−0.283	−0.043	−0.401	−0.052	0.042	−0.049	−0.071				
C_2	0.614	...	0.567	0.193	0.388	0.602	−0.194	0.098	0.066				
C_2/C_p	−0.514	...	−0.478	−0.030	−0.004	−0.561	0.029	0.349	0.288				
$\ln(C_2/C_1 C_p H_{70})$	−0.272			−0.272			0.271			−0.033			
$\ln(C_2/C_1 C_1^{1/2} C_p H_{70})$	−0.272			−0.272			0.271			−0.085			
$\ln C_2$	0.190			0.190			−0.191						
(c) Coefficients, r for $T > 50$ °F (183 points) Y↓													
C_2/C_1	−0.272	...	−0.293	−0.291	−0.366	0.118	0.290	−0.005	−0.066				
C_2	0.449	...	0.439	−0.268	0.313	0.517	0.267	0.033	−0.105				
C_2/C_p	−0.292	...	−0.160	−0.150	0.120	−0.301	0.151	0.305	0.140				
$\ln(C_2/C_1 C_p H_{70})$	−0.058			−0.138			0.138			−0.04			
$\ln(C_2/C_1^{1/2} C_p H_{70})$				−0.138			0.138			−0.23			
$\ln C_2$				−0.251			0.249						

C_p, could be correlated with sulfate by setting $a_1 = a_3 = 0$. In addition to the above X functions, new ones were formed by replacing C_p with, $C_p - C_2$, the nonsulfate portion of the TSP, and by replacing H_{70} with $(100\% \text{ RH})^{-1}$ after Freiberg (29). All possible combinations were again correlated with sulfate over the same range of a_i values. A detailed discussion of the various functions may be found elsewhere (9). Only the major conclusions are presented later in the "Conclusions and Discussion" section.

Local sources and prevailing wind velocity variables might change results from one location to another. Another series of correlations was therefore attempted for individual states having a reasonably large sample date (sufficient to have statistical significance at an r value of about 0.7) for the two temperature regimes. Only the better correlating functions are displayed in Table V. Correlation coefficients for all five states were significant when relating sulfate with $C_1^{1/2}C_p^{1/2}H_{70}$ as the independent variable. This was true of only two other functions tested, and of these the above variable had the highest r value in the 13-state test discussed previously.

One may argue that TSP sulfates are effects of the same cause. However, higher correlation coefficients do result when relative humidity above 70% and SO_2 concentration are added in a positive way to the independent variable. The low correlation between sulfate and TSP alone for the states of Massachusetts and Michigan might have to be further rationalized. [For the five individual states, sulfate was correlated with the nonsulfate portion of TSP in the function, $C_1^{1/2}(C_p - C_2)^{1/2}H_{70}$, but with slightly lower unweighted mean values, $\bar{r}$, than for the same function using C_p in place of $C_p - C_2$ [$\bar{r} = 0.624$ as compared with 0.675, from Table V (a)]. The difference in significance between these $\bar{r}$ values is inconclusive. Lower and higher correlation coefficient lines for two functions used with Michigan's 15 cases @ $T < 50$ °F are plotted in Figure 1. The visual reduction in scatter when sulfate concentration, C_2, is plotted against $C_1^{1/2}C_p^{1/2}H_{70}$ as compared with C_2 vs. C_1 is evidence of the beneficial effect of the multivariable function. Again the reader is referred to the report of Meyers and Ziegler (9) for further discussion of the variable statistical comparison. The correlations are plotted for the five states in Figure 2 corresponding to the equation

$$C_2(\pm 3.6, 1\,\sigma) = m C_1^{1/2}C_p^{1/2}H_{70} + b \quad (\bar{r} = 0.675)$$

with "residual" sulfate levels (ordinate intercept) falling between 5–7 μg m³.

The data in the warmer regime, $T > 50$ °F, has highest correlation for the eight states displayed in Table V(b) when
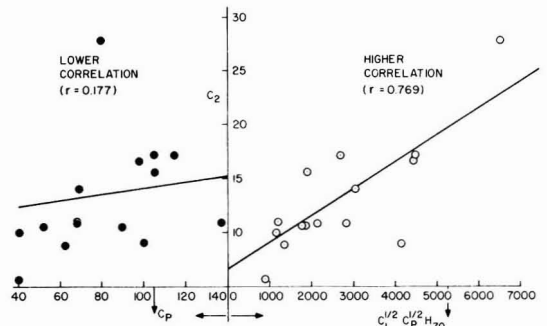
Figure 1. High and low correlation for trial functions—state of Michigan data $T < 50$ °F, 1972

Table V. Individual States Sample Correlation Coefficients

(a) Coefficients, r, for selected correlating variables, $T < 50\,°F$ (Number of data points in parentheses)

X variable	Conn. (15)	Md. (10)	Mass. (14)	Mich. (15)	N.Y. (15)	Mean unwtd.
			State			
			Sulfate concentration vs. X			
C_pH_{70}	0.638	0.681	0.373	0.304	0.722	0.544
$C_1C_pH_{70}$	0.712	0.587	0.506	0.788	0.602	0.639
$C_1^{1/2}C_pH_{70}$	0.713	0.666	0.480	0.715	0.700	0.654
C_p	0.688	0.659	0.383	0.177	0.737	0.529
$(C_p - C_2)H_{70}^p$	0.515	0.592	0.302	0.129	0.520	0.412
$C_1^{1/2}C_p^{1/2}H_{70}$	0.750	0.679	0.511	0.769	0.664	0.675
$C_1^{1/2}(C_p - C_2)^{1/2}H_{70}$	0.714	0.647	0.459	0.703	0.616	0.624
			Sulfate to TSP concentration ratio vs. X			
C_pH_{70}	−0.629	−0.483	−0.853	−0.500	−0.111	
$C_1C_pH_{70}$	−0.490	−0.400	−0.603	−0.364	−0.102	
$C_1^{1/2}C_pH_{70}$	0.103	0.021	0.055	−0.523	−0.140	
C_p	−0.614	−0.584	−0.853	−0.611	−0.190	
			Logarithm of sulfate concentration vs. $(1/T\,°R)$			
	0.167	0.027	0.570	−0.049	0.352	0.213

(b) Coefficients for $T > 50\,°F$

X variable	Ala. (24)	Conn. (13)	Ga. (24)	Md. (16)	Mass. (12)	Mich. (13)	N.J. (17)	N.C. (12)
				Sulfate concentration vs. X				
C_pH_{70}	0.494	0.824	0.258	0.673	0.783	0.422	0.720	0.135
$C_1C_pH_{70}$	0.228	0.280	0.119	0.406	0.298	0.033	0.106	−0.309
$C_1^{1/2}C_pH_{70}$	0.319	0.620	0.151	0.434	0.480	0.194	0.225	−0.277
C_p	0.482	0.814	0.355	0.850	0.805	0.423	0.709	0.185
				Sulfate to TSP concentration ratio vs. X				
C_pH_{70}	−0.567	−0.048	−0.681	−0.010	0.083	−0.563	0.184	−0.560
$C_1C_pH_{70}$	−0.494	−0.315	−0.592	0.100	−0.187	−0.648	−0.098	−0.112
$C_1^{1/2}C_pH_{70}$	0.527	−0.207	−0.620	−0.020	−0.156	−0.629	0.159	−0.350
C_p	−0.579	−0.127	−0.679	−0.040	−0.078	−0.575	0.123	0.044
				Logarithm of sulfate concentration vs. $(1/T\,°R)$				
	−0.135	−0.669	−0.020	−0.843	−0.436	−0.547	−0.570	−0.049

sulfate is linearly related to TSP, the unweighted mean $\bar{r}$ being 0.578. Inclusion of relative humidity and SO_2 usually reduced the correlation coefficient values for these cases. With even less justification a mild positive effect of temperature on sulfate might be inferred from the negative correlation coefficient observed for every state for the relation between $\ln C_2$ and $(1/T\,°R)$, with unweighted mean $r = -0.41$. Interestingly, Georgia and North Carolina, which are roughly in the same geographic region, have values that fell considerably below the mean r value.

Conclusions and Discussion

A number of conclusions can be drawn concerning the interrelationships of daily ambient pollutant weather variables. Any interpretation of the data regarding mechanism, however, is from a consistency rather than a sufficiency point of view.

- Daily sulfate values for Suffolk County winter data were preliminarily correlated. Sulfate concentration C_2, increased with increase in SO_2 concentration, C_1, nephelometer TSP value, C_p and relative humidity when humidity is greater than 70%, H_{70}. The highest correlation coefficients of the functions tested were $r = 0.827$, with a standard deviation to mean ratio for predicted to experimental sulfate values of $\sigma_{C_2}/\overline{C}_2 = 0.24$. We accept hypothesis, $\rho \neq 0$ @ 95% confidence level.

The range of variables was $1.9 < C_2 < 10.3$, $15.2 < C_1 < 60.0$, $12.9 < C_p < 42.5$, and $70 < H_{70} < 96$. No temperature dependence for Suffolk winter data over range $26\,°F < T < 48\,°F$ was observed, except via its influence on relative humidity at a given absolute water content.

- The data of 13 states analyzed in combination gave the following results:

No simple linear relationships of C_2 with functions of C_1, C_p, H, T, and S correlate well. The highest, r, of these (i.e., vs. C_p) had a correlation coefficient of 0.55 for 319 points, which has significance at the 95% confidence level.

The correlation coefficients improve considerably by partitioning the data into low temperature, $T < 50\,°F$, and high temperature $T > 50\,°F$, regimes.
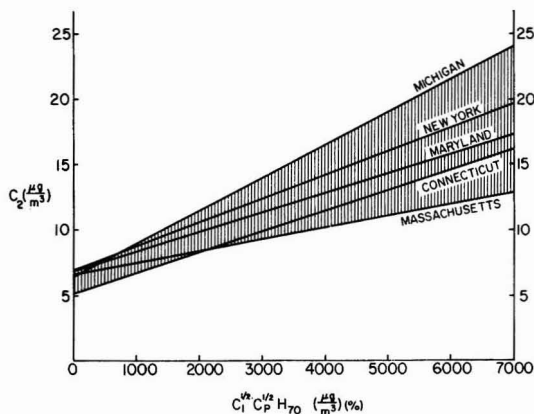
Figure 2. Sulfate concentration vs. $C_1^{1/2}C_p^{1/2}H_{70}$ regression lines for various locations

The mean daily sulfate concentration value for the $T < 50$ °F data was $\bar{C}_2 = 13.2$, the mean SO_2 was $\bar{C}_1 = 44.6$, and the mean TSP was $\bar{C}_p = 51.3$.

The equation for the $T < 50$ °F data with highest correlation was

$$C_2(\pm 4.7, 1\,\sigma) = 0.12 \times 10^{-4}\, C_p H_{70}^2 + 7.5 \ (r = 0.63)$$

• The regression coefficients might be functions of background, source strength, and flow profile which differ from one location to another. Therefore, sulfate relationships were tested for a number of regions on an individual site basis for the two temperature regimes. A homogeneous gas phase mechanism is *not* supported by correlations with temperature, solar intensity, and relative humidity functions at low RH.

A weak influence of SO_2 on the daily average sulfate levels was found for $T < 50$ °F. The form having the highest r of those investigated was $C_2 (\pm 3.6, 1\,\sigma) = mC_1^{1/2}C_p^{1/2}H_{70} + \bar{b}\,(\bar{r} = 0.675)$ where $0.91 < m < 2.52$, and $5.1 < b < 6.9$. Each of these was significant at the 95% confidence level.

For $T > 50$ °F daily sulfate concentration was correlated significantly at the 95% confidence level with TSP concentration. No significant trend was found with SO_2 concentration or relative humidity. Sulfate concentration might increase with increase in temperature, but the mean $r = 0.4$ is not conclusive.

Although the C_2 (sulfate) values of this study follow similar patterns with regard to temperature, dew point and C_1 as those described by Tong and coworkers (6), the equations expressed above deal with actual daily values rather than means grouped within intervals. As such, the relationships are more valuable for estimation purposes. Variance in C_2 values within a 5 °C temperature interval can be considerable (almost equal to the mean itself in some cases). The notable increase in mean sulfate (over an interval of 5 °C) with temperature that they observe is more likely to occur for daily sulfate in the regime, $T > 50$ °F, whereas the increase of mean (over an interval of 5 °C) sulfate with dew point and with SO_2 level is likely to be most pronounced for daily sulfate in the regime, $T < 50$ °F.

• Some additional observations may be made on the results.

The simple model (Equation 2) has been helpful in generating candidate variables for correlation tests. It is anticipated that further correlations incorporating regional source strengths, diffusion, and advection can be made using a refined version of the model. Nonlinear regression may be used to increase the accuracy.

If an absorption aerosol mechanism were involved, one would require an interaction of SO_2, sulfate, and humidity. Such an interaction was found for $T < 50$ °F. Results were consistent with possible cutoff humidity (60–80%) anticipated by Tong (28) and others. Other possible explanations for the results are filter artifact formation, and increased collection efficiency with RH. The higher value of correlation coefficient found when a nephelometer reading was used rather than a "high-vol" TSP value should be further investigated.

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Preservation of Phenolic Compounds in Wastewaters

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■ Copper sulfate and phosphoric acid with sample storage at 4 °C is a common preservative technique used for phenolic compounds in wastewaters. However, there are no data showing its effectiveness. A study was conducted to compare the preservation method with the addition of strong base or acid and sample storage at 25 and 4 °C. The addition of 2 mL conc H_2SO_4/L with sample storage at 4 °C was most consistently effective in preserving stability for 3–4 weeks. However, the other chemical preservatives were effective for at least 8 days. Substantial loss of phenolic compounds rapidly occurred in all samples unless the chemical preservative was added immediately after sample collection. A positive correlation was found between loss of phenolic compounds and microbiological activity, suggesting the latter is the dominant factor in determining sample stability.

The 1972 Amendments to the Clean Water Act have resulted in limitations on the concentration and loading of pollutants that can be discharged by industries and municipalities (*1*). The need to monitor these discharges has substantially increased the number of environmental samples requiring analysis, especially for toxic substances such as phenolic compounds.

Kelly has reviewed the literature for methods of analyses of phenolic compounds in wastewaters (*2*). The most common methods are the 4-aminoantipyrine (4-AAP) (*3–6*) and 3-methyl-2-benzothiazolinone hydrazone (MBTH) (*7, 8*) colorimetric procedures and the ultraviolet bathochromic shift method (*9*). The difficulty and equipment requirements for these methods often result in samples being shipped to a large centralized laboratory for analysis. The shipping process can lead to substantial delays between sample collection and analysis. As a result, the effectiveness of the sample preservation technique will substantially affect the accuracy of the data. It is also necessary to consider sample stability during the collection process, especially if the 24-h composite method is used (*10*).

Very little data exist in the literature to give guidance about the best method to stabilize phenolic compounds in wastewaters. The current recommended technique (*11*) is a modification of work performed over 30 years ago (*12*). Ettinger et al. found that copper sulfate effectively preserved river water and river water seeded with sewage for 2–4 days when

the samples were stored at 25 °C. Subsequent to the work of Ettinger et al., phosphoric acid was added to the copper sulfate preservative to keep the metal ions in solution when added to alkaline samples (*11*). In addition, it was recommended that all samples be stored at 4 °C until analysis.

No data were presented until 1974 about the effectiveness of the combined phosphoric acid, copper sulfate, 4 °C storage technique for preserving phenolic compounds in water samples. Afghan et al. showed that either strong acid or base was more effective in retarding bacterial activity and stabilizing phenol in Great Lakes' waters than the combined copper sulfate preservative (*4*).

The observation of Afghan et al. raises doubt that the copper sulfate–phosphoric acid preservation method is best for stabilizing phenolic compounds in wastewaters. Therefore, a study was undertaken to determine the most effective and practical preservation method and maximum allowable holding time for phenolic compounds in wastewaters.

Methods

Preparation of Samples. Fresh samples were collected in 5-gal high-density polyethylene jugs and immediately brought to the laboratory. The water samples were homogenized with a Tekmar Super Dispax system, preserved and split into 250-mL high-density polyethylene bottles. Some samples were spiked with phenol to raise the starting concentration to a level that could be accurately measured. The samples were preserved and stored as described in Figures 1–4.

Chemical Analysis of Samples. The first analysis of each sample was completed within 2 h of sample collection. All samples, standards, and blanks were distilled from acidic solution to separate phenolic compounds from potential interferences (*13*). The distillates were analyzed by an automated version of the 4-aminoantipyrine method shown in Figure 5.

The buffered potassium ferricyanide reagent was prepared by adding 2.0 g potassium ferricyanide, 2.1 g boric acid, 3.75 g potassium chloride, 44 mL of 1 N sodium hydroxide, and 0.5 mL Brij-35 (Technicon Corp. No. T21-0110) to a volumetric flask and diluting to 1 L. The 4-aminoantipyrine reagent was prepared by diluting 0.65 g of the chemical to 1 L. Both reagents were filtered through a 0.45-μm membrane filter before use.

Two control standards were prepared and preserved with copper sulfate and phosphoric acid by an independent analyst at the beginning of each study to check on the consistency of the day-to-day standard preparation and instrument calibration. These samples were preserved with copper sulfate–phosphoric acid and stored at 4 °C.

Standard Plate Count. Plate count agar was prepared fresh just before use, added to petri dishes, and 1, 0.1, and 0.01 mL of each sample were plated in triplicate (*13*). All samples were incubated at 35 °C for 24 h. Only those plates having 30–300 colonies were considered valid, and the values reported in Table I are an average of the three replicate dilutions.

Results and Discussion

The stability of phenolic compounds in nonwastewater aqueous solutions has been studied by several investigators. Phenolic compounds are good preservatives themselves at high concentrations (>0.5%) but are readily biodegraded at lower concentrations (*14–17*). Chambers and Kabler found no detectable nonbiological degradation (*15*). Extremes in pH (*18–22*), temperature (*23–26*), and the use of toxic chemicals (*27–29*) have been used to reduce microbiological activity in aqueous solution. Strong base (*4, 30, 31*), acid (*4*), and copper sulfate–phosphoric acid (*11, 12*) in combination with temperature control have been used to stabilize phenolic compounds in surface waters.

The stability of phenolics in three different wastewaters preserved with copper sulfate–phosphoric acid and stored at 4 °C was studied first. The results are shown in Figure 1. The raw sewage was fairly weak with a biochemical oxygen demand (BOD) of only 95 mg/L, and the treated sewage sample was collected after secondary biological treatment but before

Figure 2. Plot of stability of phenolic compounds in several wastewaters with time; Study 2

All samples preserved with 1.0 g CuSO₄·5H₂O/L, pH adjusted to 4.0 with phosphoric acid, and stored at 4 °C. Industrial waste, raw and treated sewage samples spiked with phenol to bring their initial concentrations to 110, 165, and 110 µg/L, respectively

Figure 1. Plot of stability of phenolic compounds in several wastewaters with time; Study 1

All samples with points plotted as "B" preserved with 1.0 g CuSO₄·5H₂O/L, pH brought to 4.0 with phosphoric acid, and then stored at 4 °C. Samples plotted as "A" stored at 4 °C with no chemical preservatives. Both industrial waste, raw and treated sewage samples spiked with phenol to bring their initial concentrations to 50, 100, and 60 µg/L, respectively

Figure 3. Plot of stability of phenolic compounds in raw sewage sample preserved with several chemicals; Study 3

Aliquots 1 and 2 preserved with copper sulfate and phosphoric acid and stored at 25 and 4 °C, respectively. Aliquots 3 and 4 preserved with 2 mL conc H₂SO₄/L and stored at 25 and 4 °C, respectively. Aliquot 5 preserved with 2 mL 10 N NaOH/L and stored at 4 °C. Aliquots 1–4 spiked with phenol to bring their initial concentrations to 125 µg/L. Aliquot 5 spiked with phenol to bring its initial concentration to 130 µg/L

chlorination. The industrial wastewater was collected from the Grand Calumet River, which is essentially a composite from the South Chicago industrial area.

Since the samples chosen for study often had low background concentrations of phenolics, each was spiked with phenol as needed so that changes in phenolic concentration would be easier to determine. Phenol was chosen for the spike because Kaplin et al. found phenol to be the least stable of all the phenolic compounds in natural waters (32-35).

The most important result of study 1 was the rapid loss of phenolics from the samples at 4 °C with no addition of any

Figure 4. Plot of stability of phenolic compounds in raw sewage sample preserved with several concentrations of sulfuric acid

Aliquots 3 and 5 preserved with 2 mL conc H_2SO_4/L and stored at 25 and 4 °C, respectively. Aliquot 4 preserved with 4 mL conc H_2SO_4/L and stored at 25 °C. All samples spiked with phenol to bring their initial concentration to 130 μg/L
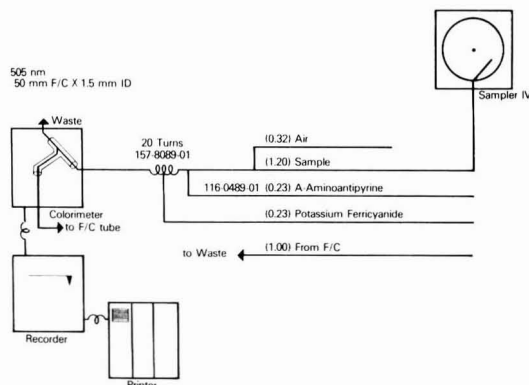
chemical preservative. The percentage loss of phenolics within 24 h for the industrial waste, raw, and treated sewage samples was 85, 80, and 40%, respectively. Ettinger et al. reported that an unpreserved river water sample stored at 2 °C lost only 15% of the original phenolic content after 4 days (12). However, the same sample stored at 25 °C lost all of its phenolic compounds within 2 days. The results from these two studies show that the loss of phenolics from unpreserved samples is variable depending upon sample type, but significant in all cases. The expected precision of sample analysis was determined from daily analysis of the control A and B samples to be ±12 μg/L (2 σ). There was no statistically significant change in phenolic concentration over the 22-day study for the samples preserved with copper sulfate–phosphoric acid and stored at 4 °C. However, there were large day-to-day changes in the concentration of phenolics measured. This poor precision was determined to be caused by the problem in taking a representative sample for analysis due to the presence of particulate matter. The problem was solved in later studies by homogenizing all samples before analysis.

In the second study (Figure 2), the effectiveness of the combined copper sulfate–phosphoric acid preservative was studied vs. sample type. Activated sludge was added to raw sewage to create a sample organically rich and biologically active. This sample was stable for 12 days, but degraded to 85% of the original phenol concentration after 33 days. The other samples were stable for the duration of the study. The dip in all values on day 1 of the study was attributed to improper calibration.

Baylis reported the use of 1.2 mL 1 N NaOH/L of sample to preserve phenolic compounds in potable water samples (30). However, Ettinger et al. found Baylis' procedure to be ineffective for sewage-seeded stream samples (12). Kaplin and Frenko found that a hundredfold increase in base concentration was effective for preserving stream waters (31). Afghan et al. verified the effectiveness of the higher concentration of base for preserving lake waters (4). Afghan et al. also showed that 0.1 M HCl was an effective preservative.

The effectiveness of strong base or acid in preserving phenolic compounds was compared with copper sulfate in the third study (Figure 3). The concentration of phenolic compounds was stable in the raw sewage sample studied when stored at 4 °C regardless of the preservative used. However, the sulfuric acid and copper sulfate preserved samples dete-

Figure 5. Automated phenol manifold diagram

Numbers in parentheses correspond to flow rate of pumptubes in mL/min. Numbers adjacent to glass coils and fittings are Technicon Corp. part numbers

Table I. Effectiveness of Preservatives in Sterilizing Sewage as Indicated by Total Plate Counts

Preservation method,[a] raw sewage	Total plate count, colonies/mL		
	Day 0[b]	Day 8	Day 20
4 °C	≫>30 000	≫>30 000	≫>30 000
2 mL conc H_2SO_4, 25 °C	730	3 500	2 200
2 mL conc H_2SO_4, 4 °C	...	70	200
4 mL conc H_2SO_4, 25 °C	560	40	[c]
$CuSO_4$, H_3PO_4, 4 °C	6 300	800	600
2 mL 10 N NaOH, 4 °C	28 000	110	270
10 mL 10 N NaOH, 4 °C	230	90	100
Secondary treated sewage before chlorination			
4 °C	23 000	20 000	5 400
2 mL conc H_2SO_4, 25 °C	<30	<30	<30
2 mL conc H_2SO_4, 4 °C	...	<30	<30
4 mL conc H_2SO_4, 25 °C	<30	<30	<30
$CuSO_4$, H_3PO_4, 4 °C	<30	<30	<30
2 mL 10 N NaOH, 4 °C	40	<30	<30
10 mL 10 N NaOH, 4 °C	<30	<30	<30

[a] Volume of acid or base added per liter of sample. Copper sulfate, phosphoric acid preservative prepared as described in ref. 13. Temperatures refer to storage conditions. [b] Plated within 1 h of preservation. [c] Confluent colonies.

riorated rapidly after 8 and 2 days, respectively, when stored at 25 °C.

Doetsch and Cook reported that a common feature of acidophilic bacteria was a resistance to copper ions (28). Growth of acidophilic bacteria occurs at pH 2–5, the pH range for the copper sulfate preservative. These facts make the use of copper sulfate at pH 4 suspect as a good preservative, especially if the samples are not stored at 4 °C. The same sample with 2 mL conc H_2SO_4/L, which produces a pH of about 1.5, at 25 °C was stable for eight days. Kushner has reported that far fewer microorganisms can tolerate pH 1.5 than 4 (22). Note that even at pH 1.5 but at 25 °C that the phenolic concentration decreased substantially. This observation indicates that while neither acidification or cold storage stabilizes phenolic compounds in a wastewater, the combination does.

To evaluate the biological-induced degradation of phenolic compounds, microbiogical activity was measured on a raw and secondary treated sewage. Samples were preserved as indicated in Table I, and total plate counts taken after 1 h (day 0), 8, and 20 days. The only secondary sewage aliquot that showed any significant activity was the chemically unpreserved sample stored at 4 °C. The microbiological activity noted corresponds very closely with the chemical stability of phenolics in treated sewage found in studies 1 and 2.

The unpreserved raw sewage sample stored at 4 °C showed very great microbiological activity that corresponds to the phenolic instability noted in study 1. The addition of 2 mL conc H_2SO_4/L initially reduced the microbiological activity significantly. However, by day 8, the activity increased fivefold and then decreased slightly again by day 20. This trend corresponds closely with the rapid loss of phenolics in study 3, after day 8 and then a moderate but continued loss thereafter. The same sample stored at 4 °C with 2 mL conc H_2SO_4/L showed at least a tenfold lower microbiological activity and a corresponding increase in chemical stability shown in study 3.

The raw sewage sample with copper sulfate–phosphoric acid and stored at 4 °C exhibited greater microbiological activity than the aliquot with sulfuric acid. This observation corresponds to the moderate effectiveness of this preservative—stability in studies 1 and 3 and instability of the raw sewage in study 2. Addition of strong caustic also lowered the microbiological activity of the raw sewage sample. However, the higher concentration of caustic, 10 mL 10 N NaOH/L, was required for a quick initial kill. The high initial microbiological activity of the 2 mL 10 N NaOH/L aliquot did not affect the chemical stability found in study 3. However, to overcome the buffering capacity of many samples, the higher concentration of sodium hydroxide should be used.

Increasing the concentration of H_2SO_4 twofold with storage at 25 °C reduced the microbiological activity to the same level as the aliquot stored at 4 °C with 2 mL conc H_2SO_4/L. A fourth study was conducted to determine if a greater acid concentration could preserve phenolic stability without cold storage. The results in Figure 4 show good stability for the aliquots preserved with 2 mL H_2SO_4/L at 4 °C and 4 mL H_2SO_4/L at 25 °C. The aliquot with 2 mL H_2SO_4/L at 25 °C showed a substantial loss of phenolic compounds after the eighth day.

The enhanced stability of the samples preserved with the higher acid concentration is excellent evidence that the greatest cause of sample instability is microbiological activity, not chemical activity. Gordon claimed that phenolic compounds in many refinery effluent waters can be oxidized in acid solution (36). However, he did not state the temperature conditions for storage or provide any data to support the claim. Emerson noted that phenol was less reactive under oxidizing acidic than basic conditions (37). Stewart (38) and Waters (39) also noted that phenolic compounds were more reactive in basic solution. However, in practice basic preservation does not cause instability of phenolic compounds especially if stored at 4 °C (4, 30, 31, 36).

Conclusions and Recommendations

All samples quickly lost phenolic compounds in the absence of a chemical preservative, even if stored at 4 °C. Therefore, all samples must be chemically preserved at the time of collection. The chemical preservative must be added to the first aliquot of a composite sample.

The desired time period for holding samples determines the choice of chemical preservatives. All preservatives studied, NaOH, H_2SO_4, and $CuSO_4$–H_3PO_4, were effective—no more than 5% phenolic compound loss—for at least 12 days when the samples were stored at 4 °C. Strong base or acid was effective for 26 and 28 days, respectively, when the samples were stored at 4 °C.

The use of acid or base preservation has the advantage of eliminating the use of one separately preserved bottle specifically for phenolic analysis (11, 13). The choice of acid or base preservation will depend on whether cyanide (base preserved) or nutrient (acid preserved) analyses will be performed. The advantage of acid preservation is that sulfides, a common interference in the colorimetric methods, will be driven out of the sample (36). The basic preservation will be advantageous if any organic extraction is required in the analysis method to remove organic interferences (13).

Use of 2 mL conc H_2SO_4/L with sample storage at 4 °C is recommended over the use of 4 mL conc H_2SO_4/L at 25 °C. The former conditions combine the preservative qualities of low temperature and pH and are milder conditions chemically, which should reduce the possibility of undesirable chemical reactions.

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Identification of C₃–C₁₀ Aliphatic Dicarboxylic Acids in Airborne Particulate Matter

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■ Airborne particulate samples collected during photochemical smog episodes were subjected to solvent extraction and fractionation, and the derivatized acid fractions were analyzed by combined gas chromatography–mass spectrometry using capillary columns and methane chemical ionization. Fifteen aliphatic dicarboxylic acids ranging from malonic acid (C_3) to sebacic acid (C_{10}) were identified, nine of which (including all seven branched-chain acids) are reported for the first time. Possible hydrocarbon precursors of these acids in urban photochemical smog are discussed.

Secondary organic particulates formed in the polluted atmosphere by photochemical reactions involving hydrocarbons (HC), nitrogen oxides (NO_x), ozone, and free radicals (*1, 2*) constitute a significant fraction of urban aerosols (*3*). Despite the obvious health implications associated with human exposure to high levels of secondary organic aerosols, which accumulate almost exclusively in submicron particles (*3*), few studies have been directed to elucidate the nature of the components of the complex organic mix (*4–8*).

Recent smog chamber studies of the chemical composition of "model" organic aerosols resulting from the irradiation of single HC–NO_x mixtures in air have shown that secondary organic aerosols contain many oxygenated species including several mono- and dicarboxylic acids, nitrate esters, and a variety of polyfunctional compounds (*3, 9–11*). Although these studies suggest that these compounds are formed in photochemical smog (*12*), only a small fraction of the secondary organic products identified in smog chamber experiments has been detected to date in ambient air (*4–8*).

As part of a comprehensive investigation of the modes of formation of secondary pollutants in the California South Coast Air Basin (*13*), we recently initiated a detailed inventory of compounds present in organic aerosols. We report in this paper results concerning the identification of a series of aliphatic dicarboxylic acids in airborne particulate matter collected in Riverside, Calif., a smog receptor site located downwind from the Los Angeles urban area.

Experimental Section

Ambient particulate samples were collected over 24-h periods on the Riverside campus of the University of California during multiday photochemical smog episodes. The samples were selected for further analysis on the basis of their high total organic carbon content measured with a Dohrman-Envirotech Model DC-50 organic carbon analyzer (*14*). Important parameters indicative of the occurrence of photochemical smog [ozone, peroxyacetyl nitrate (PAN), and the aerosol light-scattering coefficient b_{scat}] were also measured during the sampling periods and are listed in Table I.

The particulate samples were collected on washed Gelman AE glass fiber filters using high-volume samplers equipped with constant flow controllers (40 cfm), and were extracted for 5 min using a Tekmar Model SD-45 Tissumizer with 200 mL of an equal parts per volume mixture of benzene, dichloromethane, and methanol (Burdick and Jackson, distilled in glass). After filtration and evaporation of most of the solvents, the residues were distributed between a two-phase solvent system consisting of dichloromethane and a 2 N aqueous sodium hydroxide solution. After centrifugation and removal of some emulsified material, the aqueous fraction was acidified to pH = 1 with hydrochloric acid and subjected to continuous extraction with dichloromethane for 24 h. After concentration and removal of traces of water by drying over molecular sieve 4 Å, the dichloromethane extract containing the acid material was derivatized with a freshly prepared solution of diazomethane in ether, thus yielding the methyl esters of the acid components. No attempt was made to estimate the possible loss of some of the diacids on molecular sieve.

The derivatized acid fractions were analyzed by combined gas chromatography–mass spectrometry (Finnigan Model 3200 with a Model 6100 data system) using both electron impact (EI) and chemical ionization (CI), the latter with methane (CH_4) and isobutane (i-C_4H_{10}) as reagent gases. Gas chromatographic separation of the methyl esters was performed using a Ucon 50-HB-5100 glass capillary column (30 m × 0.29 mm) prepared according to the method of Grob and Grob (*15*). The column temperature was programmed from 30 to 230 °C at a rate of 6 °C/min. A platinum capillary in-

Table I. Selected Air Quality Parameters During Photochemical Smog Episodes Studied

Sampling period	Ozone (pphm)[a]		PAN (ppb)		b_{scat} $(10^{-4} m^{-1})$		TSP[c] $(\mu g\ m^{-3})$	POC[d] $(\mu g\ m^{-3})$
	Max	Av[b]	Max	Av	Max	Av		
10/1/75	35.4	10.1	24.1	10.3	15.2	10.9	250.8	24.7
10/2/75	24.6	8.8	14.7	10.3	16.5	9.2	269.6	26.7
8/25/76	21.5	5.2	13.3	3.8	9.1	3.3	133.5	13.4
8/26/76	18.7	5.5	9.0	4.8	8.9	4.7	152.4	15.0
2/19/77	23.5	5.8	27.2	14.5	28.4	14.9	246.6	31.5
2/20/77	20.0	6.7	21.3	9.4	>35	14.0	229.9	26.8

[a] California Air Resources Board UV photometer method (27). [b] Av = 24-h average. [c] TSP = total suspended particulates, 24-h average. [d] POC = particulate organic carbon, 24-h average.

terface was used as a direct coupling device between the column and the ion source. The interface was conditioned prior to analysis by the glas flow from the column at 200 °C, and its adsorption characteristics were tested with a mixture of naphthalene, n-octanol, and 5-nonanone (16).

Retention times could be reproduced with a precision of 0.3%, thus allowing the direct comparison of EI and CI mass spectra obtained in different runs. Mass spectral scans were conducted every 1.5 s, yielding a total of over 1000 spectra per run. Reference samples of the linear dicarboxylic acid methylesters were available from Polyscience Corp. Branched-chain esters were prepared by derivatization of the corresponding acids with diazomethane. Acids No. 2, 4, 6, 7, 9, 10, and 11 in Table II were obtained from Aldrich Chemicals Co. and Pfaltz and Bauer, Inc.

The possibility of sampling artifact (adsorption of gaseous dicarboxylic acid on filters and/or oxidation of difunctional oxygenates on the filter surface to form the corresponding diacids) has not been investigated experimentally. Various aspects of this problem have been discussed in detail in the literature (3–12) and are briefly summarized here. Gas adsorption seems unlikely in view of the very low vapor pressures of dicarboyxlic acids, which indicate that only the most "volatile" diacid, oxalic acid ($Vp \simeq 2\ 10^{-4}$ torr), might exist at trace levels in the gas phase. Moreover, dicarboxylic acids have been found in samples collected from 2 to 24 h at flow rates ranging from a few L/min to 60 ft³/min, on gold and brass impactor plates as well as on various types of glass fiber filters. This again is not indicative of any significant artifact formation due to gas adsorption, which is expected to depend strongly upon filter media, sampling time, and sampling flow rate.

In addition, all smog chamber studies of cyclic olefin–NO_x mixtures in air have presented conclusive evidence of aerosol formation (by measuring physical properties such as light scattering) irrespective of filter sampling for chemical analysis (which showed dicarboxylic acids to be among the major aerosol products). Finally, further oxidation of difunctional oxygenated products to the corresponding diacids, if it occurs on the filter surface, is even more likely to occur in and/or on the surface of ambient aerosol droplets irrespective of sampling.

Therefore, although the general problem of artifact formation when sampling organic aerosols should be further investigated, all available data indicate that artifact is negligible in the specific case of dicarboxylic acids.

Results

The dicarboxylic acids found in all ambient aerosol samples are listed in Table II. They were unambiguously identified by comparison of the EI, methane–CI, and isobutane–CI mass spectra of their dimethyl esters with reference samples. Also

Table II. Dicarboxylic Acids Identified in Ambient Particulate Samples

No.	Dicarboxylic acids	Rel retention time[a]	Dimethyl esters	
			Typical fragments	
			$[M^{+\cdot}-OCH_3]$ (EI) or $[MH-CH_3OH]$ (methane–CI)	[MH] (isobutane–CI)
1	Malonic acid	0.578	101	133
2	Methylmalonic acid	0.563[b]	115	147
3	Succinic acid	0.707	115	147
4	Methylsuccinic acid	0.705[b]	129	161
5	Glutaric acid	0.852	129	161
6, 7	2- and 3-Methylglutaric acid	0.866[b]	143	175
8	Adipic acid	1.000	143	175
9	Dimethyl glutaric acid[c]	1.013[b]	157	189
10, 11	2- and 3-Methyladipic acid	1.036[b]	157	189
12	Pimelic acid	1.129	157	189
13	Suberic acid	1.252	171	203
14	Azelaic acid	1.370	185	217
15	Sebacic acid	1.481	199	231

[a] Relative to dimethyladipate on Ucon-HB column. [b] Branched-chain isomers are eluted before the corresponding linear dimethyl ester on the polar column used. [c] Isomer not specified (see text).

listed in Table II are the retention times and most typical fragment ions of the dimethyl esters.

The two couples of C_6 and C_7 branched-chain isomers (compounds 6, 7 and 10, 11 in Table II) could not be resolved on the Ucon HB column but were separated using a 30-m SE-52 glass capillary column. The exact structure of the dimethylglutaric acid isomer is uncertain because of lack of reference samples. Comparison with the only isomer available in our laboratory, 3,3-dimethylglutaric acid, indicated that this isomer was not the one found in the ambient air samples. Moreover, the presence of an ethyl glutaric acid isomer, rather than dimethyl glutaric acid, cannot be ruled out from the mass spectra.

The need for using chemical ionization mass spectrometry for the selective detection of dicarboxylic acids in complex pollutant mixtures is illustrated in Figure 1, which shows the EI and methane–CI and isobutane–CI spectra of the dimethyl ester of suberic acid found in the air samples.

In the EI mode the mass spectra of dicarboxylic acid methyl esters do not give any measurable molecular ion $M^{+\cdot}$. Moreover, the major high mass fragment, the $[M^{+\cdot}-OCH_3]$ ion (m/e = 101, 115, 129, etc., see Table II) is isobaric with the fragment ions of methyl esters of fatty acids, another class of pollutants always present in airborne particulates. Therefore, the gen-

eration of mass chromatograms in the EI mode is not an adequate method for selective detection of dicarboxylic acids in ambient aerosol samples.

In the methane–CI mode, a distinct quasi-molecular ion [MH] and a [M+C₂H₅] adduct are present, and the base peak of dicarboxylic acid methyl esters is the [MH–CH₃OH] fragment (17). Fatty acids also give [MH–CH₃OH] fragments but at higher m/e values. Furthermore, no fragments from fatty acid methylesters appear at m/e = 101, 115, 129, etc., in the CI mode. Thus, there is no interference due to fatty acids in the methane–CI mode, and the [MH–CH₃OH] fragment can be used for selective detection of the dicarboxylic acid methyl esters.

In the isobutane–CI mass spectra of dicarboxylic acid methyl esters, the base peak is always the quasi-molecular ion [MH] which is accompanied by a minor [MH–CH₃OH] fragment (17). Therefore, isobutane–CI, although less sensitive than methane–CI, allows the monitoring of these compounds using directly the quasi-molecular ion. The combined use of methane and isobutane chemical ionization mass spectrometry permits unambiguous determination of the molecular weight as well as sensitive monitoring of dicarboxylic acids present at trace levels in urban aerosols.

Discussion

Six aliphatic dicarboxylic acids, glutaric, adipic (4, 5, 7, 8), malonic, succinic (4), methyl adipic [isomer not specified (8)], and azelaic (18) have been identified before in ambient air samples. No branched-chain isomers have been reported prior to our work.

The relative abundance of the dicarboxylic acids in the airborne particulate samples was calculated from the intensity of the [MH–CH₃OH] ion in the methane–CI mode assuming the same response factor for all acids (Table III). Although no quantitative analysis of the samples was attempted, the known sensitivity of the mass spectrometer in the methane–CI mode indicates that the least abundant acids were present in ambient air at concentrations of about 0.02 μg m⁻³. Combining this value with relative abundance data in Table III, we can estimate concentrations of 0.2–0.5 μg m⁻³ for the most abundant components (glutaric, succinic, and adipic acids). Since the samples were collected over 24-h periods during photochemical smog episodes, it is likely that the ambient levels of these acids were substantially higher when ozone reached its maximum in the midafternoon. Ambient levels of up to 1.2 and 1.6 μg m⁻³ for glutaric and adipic acid, respectively, have been previously reported in particulate samples collected during a smog episode in the Los Angeles area (4).

The presence of dicarboxylic acids in urban aerosols may result from primary emissions and/or secondary photochemical reactions. Although the primary origin of these acids cannot be ruled out, there are no known anthropogenic sources of dicarboxylic acids in the Los Angeles area. Diurnal profiles of glutaric and adipic acid established from 2-h samples have been found to parallel the diurnal variations of ozone (8), thus indicating the possible secondary origin of these compounds. More conclusive of the secondary nature of dicarboxylic acids is the fact that adipic and glutaric acids have been identified as major aerosol products in smog chamber experiments conducted with irradiated mixtures of cyclohexene–NO$_x$ and cyclopentene–NO$_x$ in air (3, 9).

On the basis of these experiments as well as kinetic and mechanistic considerations, it has been suggested that cyclic olefins may be an important class of hydrocarbon precursors leading to the formation of dicarboxylic acids and other organic aerosols (9, 12). Cyclic olefins have been identified in gasolines, automobile exhaust (19–23), and ambient air (24–26), and the most abundant acids identified in this work

can be accounted for in terms of photooxidation of a cyclic olefin precursor. Thus, succinic acid and the five acids having 5 and 6 carbon atoms, which account for about 80% of all diacids found in our samples (see Table III), may result from the photooxidation of cyclohexene, cyclopentene, and the methyl cyclopentene isomers (Table IV). In the same way, the branched-chain isomers, which account for a significant fraction of the C₅, C₆, and C₇ acids (Figure 2), may originate from the methyl cyclopentene and methyl cyclohexene isomers listed in Table IV.
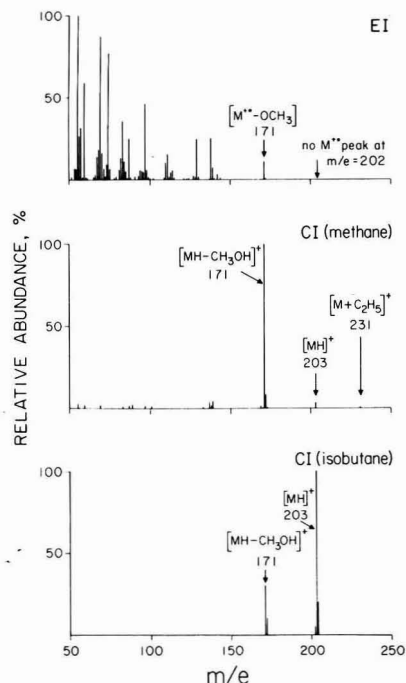
Figure 1. Electron impact (top), methane–chemical ionization (middle), and isobutane–chemical ionization (bottom) mass spectrum of dimethylsuberate

Table III. Relative Abundance of Aliphatic Dicarboxylic Acids in Airborne Particulate Samples [a]

	10/1–2/75	8/25–26/76
Malonic	3.6	3.9
Methylmalonic	8.3	1.0
Succinic	21.8	24.9
Methylsuccinic	13.7	12.0
Glutaric	17.2	23.2
Methyl glutaric [b]	10.5	8.3
Adipic	13.2	11.6
Dimethyl glutaric	0.8	0.6
Methyl adipic [b]	2.0	1.9
Pimelic	1.7	2.4
Suberic	2.2	2.8
Azelaic	4.5	5.8
Sebacic	0.4	1.5
Total	100%	100%

[a] Expressed as percent of the sum of the dicarboxylic acids identified. [b] Sum of the 2-methyl and the 3-methyl isomers.

Table IV. Possible Hydrocarbon Precursors of Dicarboxylic Acids

HYDROCARBON PRECURSOR	DICARBOXYLIC ACID
Smog chamber experiments [a]	**Aerosol products**
Cyclohexene	Adipic, glutaric
Cyclopentene	Glutaric
Cyclic olefins identified in gasolines, auto exhaust, and/or ambient air [c]	**Possible products** [b]
Cyclopentene	Glutaric, succinic [d]
3-Methyl cyclopentene	3-Methylglutaric, methyl succinic
Cyclohexene	Adipic, glutaric
2-Methyl cyclohexene	2-Methyl adipic, 2-methyl glutaric
3-Methyl cyclohexene	3-Methyl adipic, 3-methyl glutaric

[a] From ref. 3, p 73. [b] By analogy with aerosol products from cyclohexene in smog chamber experiments (3, 9). [c] From ref. 3, p 99. [d] Another possible precursor of succinic acid, the unstable cyclobutene, has not been found in exhaust or ambient air (3).
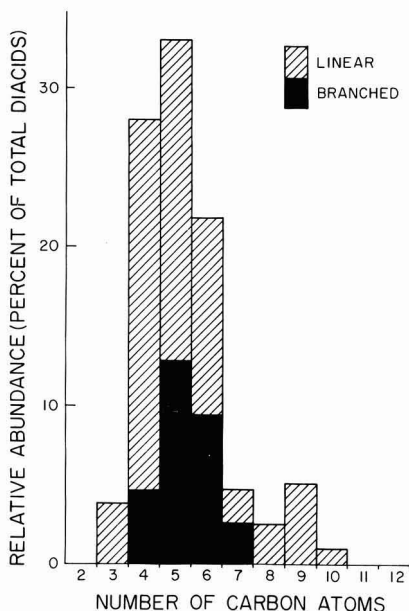
Figure 2. Relative abundance of linear and branched-chain dicarboxylic acids in ambient particulate samples collected during photochemical smog episodes (average of four 24-h samples collected on 10/1–2/75 and 8/25–26/76)

Because of their high gas-phase reactivity and their ability to form products of low volatility (3), cyclic olefins, although minor components of gasolines and automobile exhaust, yield significant amounts of organic aerosols. For example, smog chamber data indicate that about 30% of the initial cyclopentene (or cyclohexene) is converted to organic aerosol after a few hours of irradiation (9). Thus, assuming 100% gas-phase reaction and 30% of conversion to aerosol, ambient concentrations of 0.2–0.5 μg m^{-3} of glutaric (or adipic) acid would require only $\simeq$0.5 ppb of cyclopentene (or cyclohexene) precursor. Ambient concentrations of up to 9 ppb have been re-

ported for cyclopentene in the Los Angeles area (24–26). Therefore, the dicarboxylic acid concentrations reported in this work are consistent with those estimated from smog chamber, gasoline, and exhaust data for cyclic olefins.

Dicarboxylic acids are also formed as a result of the photooxidation of diolefins. For example, smog chamber studies have shown that adipic acid is a major aerosol product of the photooxidation of 1,7-octadiene (3, 9). Thus, 1,4-pentadiene and 3-methyl 1,4-pentadiene are possible precursors of malonic acid and methylmalonic acid, respectively. Possible hydrocarbon precursors of the C_8 to C_{10} dicarboxylic acids found in our samples, for example, long-chain diolefins, have not to our knowledge been identified in gasolines, automobile exhaust, or ambient air. Photooxidation mechanisms involving other hydrocarbon classes (paraffins, monolefins) may also account for the presence of these diacids in urban aerosols.

Conclusions

Analysis by combined gas chromatography–mass spectrometry of aerosol samples collected during photochemical smog episodes revealed the presence of eight linear and seven branched-chain dicarboxylic acids, nine of which (including all branched acids) are reported for the first time. Available data seem to indicate that cyclic olefins are likely precursors of these diacids in photochemical smog. Work is in progress in our laboratory to further elucidate the complex molecular composition of photochemical aerosols and the relationships between particulate organic compounds and their hydrocarbon precursors.

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Estimation of Time-Averaged Hydroxyl Radical Concentration in the Troposphere

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■ With the global emission figures for methylchloroform, the atmospheric monitoring data, and the experimental bimolecular rate constant for hydroxyl attack, a calculation of the time-averaged hydroxyl radical concentration was made. Values of 4.8×10^5 and 1.8×10^6 molecules/cm^3 ($\pm 20\%$) for the northern and southern troposphere were necessary to satisfy the mass balance equations. These numbers agree favorably with other estimations of the hydroxyl radical concentration in the troposphere. Based on these calculations, the residence time for methylchloroform in the troposphere was in the range 2.6–4.0 years with an average value of 3.3 years.

In recent years a great deal of atmospheric monitoring data have shown that in addition to the chlorofluoromethanes, a wide variety of simple organochlorine compounds have been found in relatively unpolluted air (*1, 2*). These include such species as $CHCl_3$, CH_3Cl, CH_3CCl_3, and $CHCl_2CH_2Cl$. To assess the future impact of these and other halocarbons in the atmosphere, it is necessary to balance the rate of production against the rate of dissipation. An important step in this problem is the discovery of sinks for the chlorocarbons in the lower atmosphere. In this connection the critical role of the hydroxyl radical as the rate-limiting step in the photodissociation reaction of the hydrogen-containing halocarbons has been receiving great attention (*3–5*). The general reaction is shown in Equation 1:

$$RCl_xH + OH \cdot \rightarrow RCl_x^- + H_2O \tag{1}$$
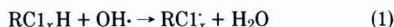
This type of bimolecular reaction has been studied by many investigators, and it is unlikely that the experimentally derived rate constants will be in serious error (*7, 8*). The value that becomes very critical, however, is the time-averaged concentration of hydroxyl radical assumed to be present in the troposphere. The actual hydroxyl radical concentration varies diurnally, seasonally, as well as vertically and horizontally. What is required for modeling purposes is a number that will average out these differences over a long time frame.

Again this has been studied quite intensively, and values ranging from 10^5 molecules/cm^3 to 10^7 molecules/cm^3 have been reported (*5–11*). The main source of OH· in the troposphere is the reaction shown in 2. The electronically excited

oxygen for this reaction is produced by the photolysis of ozone.

$$O + H_2O \rightarrow 2OH \cdot \tag{2}$$

The destruction of OH· occurs through Reactions 3 and 4 (*6*).

$$OH \cdot + CO \rightarrow H + CO_2 \tag{3}$$

$$OH \cdot + CH_4 \rightarrow H_2O + CH_3^- \tag{4}$$
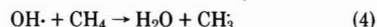
The work in this paper represents a different approach from previous studies in deriving a time-weighted average value for the OH· concentration. The study is based on the use of the production history of methylchloroform (1,1,1-trichloroethane) and matching it against the monitoring data collected over the past few years, summarized recently by Lovelock (*12*), and shown in Figure 1. In this figure the low tropospheric values for the halocarbon in the early 1970's with the subsequent rise to the present values would argue that no significant natural source for this volatile gas exists. Hence, the assumption that what is present in the atmosphere is due to man-made emission is probably valid. Accepting this assumption it is possible to carry out a mass balance study of the production data in a manner similar to our previously reported studies on trichlorofluoromethane and carbon tetrachloride (*13*). The problem then reduces to estimating what hydroxyl radical concentration in the troposphere is required to satisfy the mass balance equations. Note that both Lovelock (*12*) and Singh (*14*) have used a simplified compartmental analysis study, and their results will be discussed in a later section.

The Model

We have recently worked out a mass budget model for the distribution of volatile gases in the various compartments of the biosphere (*13*). The model shown in Figure 2 was developed for trichlorofluoromethane and partially validated using carbon tetrachloride data. This model requires an estimate of worldwide emission as input plus a knowledge of the chemical and physical properties of the agent under question.

Production Data. The global production and emission figures for methylchloroform were estimated by the Corporate Product Department of the Dow Chemical Co. and are shown in Table I.

Chemical and Physical Properties. The key properties are shown in Table II. Henry's constant and the transfer constants between air and water were calculated (*15*) using the method originally described by Liss and Slater (*16*). Since

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the parameters used by Liss and Slater were based on observations made in the North Atlantic, the derived rate constants for methylchloroform will be suitable for estimating the flux in an ocean environment.

Material Balance Equation. The equations relating to the four main compartments of Figure 2 are given below:

Northern troposphere:

$$dN/dt = k_0/V_1 - k_5N - k_3N$$
$$- k_6N - k_1N + k_4S + k_2(V_3/V_1)A$$

Southern troposphere:

$$dS/dt = k_3N + k_2(V_4/V_2)B - k_5S - k_4S - k_7S - k_1S$$

Northern ocean:

$$dA/dt = k_1(V_1/V_3)N - k_2A$$

Southern ocean:

$$dB/dt = k_1(V_2/V_4)S - k_2B$$

where N, S, A, and B represent concentrations of the chemical in the respective compartments.

The various symbols and rate constants are shown in Table III. The two unknowns are the values for k_6 and k_7, the rate constants for photodegradation in the northern and the southern troposphere, respectively. The above equations were programmed to run on the Continuous System Modeling Program of the IBM 370 computer. Values for k_6 and k_7 in reciprocal years were adjusted to obtain the best fit to the experimental data of Lovelock shown in Figure 1.

Results

Figure 1 shows the actual monitoring data collected over the years and summarized by Lovelock (12). In addition, the recent measurements of Rasmussen are also included. The Rasmussen data were collected between March 5 and March 20, 1976, on a trip down the coast of California and into the Southern Hemisphere (20). The continuous curves in Figure
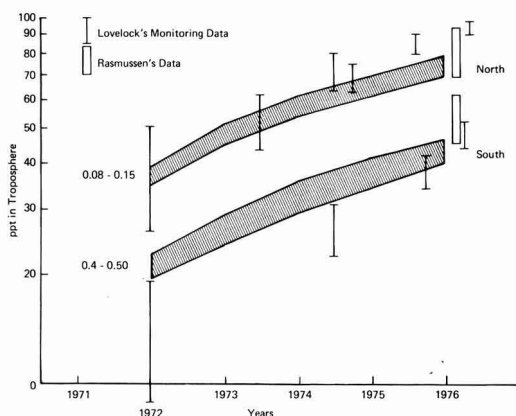
Figure 1. Computer simulation of tropospheric concentrations of methylchloroform
Bars: uncertainty associated with monitoring data. Range in photodegradation rate constant shown at left of simulation curves

Where
- rate constants have been described in text.
- V_1, V_2, V_3 and V_4 are the volumes of the respective compartments.
- N, S, A and B represent concentrations.
- k_0 annual production vented into northern troposphere.

Figure 2. Schematic representations of distribution of methylchloroform in major compartments of environment
k_6 in south troposphere should be k_7

Table I. Worldwide Global Production of Methylchloroform in Millions of Pounds

Year	Released to atmosphere	Produced	Cumulative release
1951	0.3	0.3	
1952	0.5	0.5	0.8
1953	2.1	2.2	2.9
1954	6.0	6.4	8.9
1955	17.6	18.5	26.5
1956	27.4	30.4	53.9
1957	43.2	45.5	97.1
1958	45.7	48.1	142.8
1959	66.8	70.3	209.8
1960	79.6	83.8	289.2
1961	83.8	88.1	373
1962	124	131	497
1963	112	128	609
1964	125	142	734
1965	161	182	895
1966	240	256	1135
1967	288	321	1423
1968	320	349	1743
1969	327	370	2070
1970	341	400	2411
1971	368	422	2779
1972	508	589	3287
1973	750	772	4037
1974	800	859	4837
1975	804	825	5641
1976	917	965	6558
Total	6558	7105	

Table II. Chemical and Physical Properties of Methylchloroform

Vapor pressure	96 mm Hg at 20 °C
Water solubility	480 ppm at 20 °C
Henry's constant	1.41[a] 1.51 (calcd)[b]
Transfer air to water	7.54 cm/h[b]
Transfer water to air	11.4 cm/h[b]

[a] Ref. 17. [b] Calculated according to ref. 15.

2 are the result of the computer simulation where k_6 was varied from 0.08 to 0.15 yr^{-1} and k_7 was varied from 0.4 to 0.5 yr^{-1}. This represents the best fit generated by the model to the actual measurements of methylchloroform in the troposphere.

Watson et al. (7) reported a value of 3.72×10^{-12} exp $(-1627/T)$ for the bimolecular rate constant between methylchloroform and the hydroxyl radical. This constant is very similar to the value of 3.50×10^{-12} exp $(-1562/T)$ determined by NASA (8); hence, an average value of 3.61×10^{-12} exp $(-1600/T)$ was estimated. Since the rate constant is temperature dependent, it becomes important to select a value that will reflect average tropospheric conditions. Temperature in the troposphere ranges from 15 °C at sea level to −45 °C at 10 km (18). This yields an average value of ~−12 °C, which will be used in the calculation. It could be argued that a value closer to 15 °C would be a better choice since this is the region where the bulk of the reaction takes place. However, our main interest is in deriving a tropospheric average value for the hydroxyl radical concentration; consequently, a temperature of −12 °C is more suitable for our objective. With these considerations in mind, the hydroxyl radical concentration can then be estimated from Equation 5:

$$[OH\cdot] = k/2.48 \times 10^{-7} \text{ (molecules/cm}^3) \quad (5)$$

where k is the estimated rate constant in reciprocal years derived from the simulation (k_6 for the northern and k_7 for the southern compartment).

Using average values for k_6 and k_7 of 0.12 and 0.45 yr^{-1} in Equation 5, the average hydroxyl radical concentration in the north is estimated to be 4.84×10^5 and 1.82×10^6 molecules/cm³ in the south within ±20%. From the temperature dependence of the bimolecular rate constant as shown in the Arrhenius expression, it was determined that for every increase of 1 °C there would be a 2% decrease in the estimated hydroxyl radical concentration.

A summary of the simulation results using the values for k_6 and k_7 of 0.12 and 0.45 yr^{-1} is shown in Table IV for the last five years. The only validation possible was comparing the calculated concentration of methylchloroform in water in the North Atlantic with experimental observations by Lovelock. In a personal communication Professor Lovelock provided a range of sea concentrations taken in the North Atlantic in November 1973 (48N 01W to 21N 06W). The results of eight determinations gave a 95% confidence range of 3.01×10^{-13} to 5.05×10^{-13} g/mL (21). Our calculation yielded a value of 2.0×10^{-13} g/mL. If we consider the assumption used in deriving the calculated number, the agreement with the experimental numbers is most reassuring.

Figure 3 illustrates the rate of disappearance of methylchloroform from the troposphere with time, assuming no further input after 1976. From this graph a residence time for the halocarbon of 3.3 years (±20%) was estimated. Note that 3.3 years is a high value since it is based on the reported emissions of the chlorinated hydrocarbon. If the actual worldwide emissions were greater, a shorter residence time would be necessary to keep the model in balance.

Discussion

Time-averaged hydroxyl radical concentrations have been estimated by other investigators. A brief summary of these results will be presented, and the values compared with those derived from the study. Crutzen and Isaken (6) calculated average OH· concentration based on CO/CH₄ tropospheric profile data. Their results start with values of 1.3×10^6 molecules/cm³ at ground level and reach a minimum of 2×10^5 molecules/cm³ at the tropopause for an average value of 3.5 $\times 10^5$ molecules/cm³. Chang and Wuebbles (11) produced a theoretical model of global tropospheric OH· distribution and

estimated the latitudinal and vertical distribution, which varied seasonally and diurnally. They determined that approximately 71% of the OH· is contained in the band 30°S–30°N, and 97% is contained between 60°S and 60°N with 1.5 times as much in the south as in the north. Their values ranged from 5×10^6 molecules/cm³ at the equator to 10^5 molecules/cm³ above 60°N. Davis et al. (10) experimentally found 1–3 $\times 10^6$ molecules/cm³ at 34°N at 7 km and projected a 24-h average of 5×10^5 molecules/cm³. Levy (22, 23) calculated values of 1.5×10^6 to 4.1×10^6 molecules/cm³. Warneck (9) calculated the hydroxyl production rates in the northern troposphere and estimated a yearly average of 7.5×10^5 molecules/cm³.

More recently, Crutzen and Fishman (25) presented data to support their earlier observation of an average OH· in the Northern Hemisphere in the range of $3–5 \times 10^5$ molecules cm⁻³. Furthermore, they estimated a ratio of 2.7 between the Northern and Southern Hemisphere, with the higher value

Table III. Parameters for Model Shown in Figure 1

Parameter	Description	Value	Ref
V_1, V_2	Weight of air in ½ of troposphere assuming height of 10 km	2×10^{21} g	18
	Area of water north of equator	1.54×10^{18} cm²	19
	Area of water south of equator	2.09×10^{18} cm²	19
k_5	Transfer from troposphere to stratosphere	0.03 yr^{-1}	13
k_3, k_4	Transfer between northern and southern troposphere	0.9 yr^{-1}	13
	Mixing depth of ocean	100 m	13
	Mixing depth of troposphere	10 km	13
V_3	Weight of water in north (depth × area)	1.54×10^{22} g	
V_4	Weight of water in south	2.09×10^{22} g	
k_1	Flux between ocean and air	9.98^a yr^{-1}	
k_2	Flux between air and ocean	0.066^b yr^{-1}	

^{a} 9.98 = 11.4 cm/h (24 × 365/depth of ocean) yr^{-1}. ^{b} 0.066 = 7.54 cm/h (24 × 365/depth of troposphere) yr^{-1}.

Table IV. Summary Printout of Computer Simulation of Methylchloroform in Various Compartments of Figure 1

Year	Concn in troposphere (ppt)		Concn in ocean (10^{-13} g/mL)		Annual release to stratosphere ($\times 10^{10}$ g)
	North	South	North	South	
1970	28	17	1.15	0.52	
1971	31	22	1.25	0.57	1.3
1972	37	22	1.5	0.65	1.5
1973	49	27	2.0	0.81	2.0
1974	58	34	2.3	0.99	2.4
1975	64	39	2.6	1.1	2.8
1976	73	44	3.0	1.3	3.1
Production assumed to be terminated in 1976					
1977	49	39	2.1	1.2	2.9
1978	36	29	1.6	0.96	2.2
1979	26	22	1.11	0.68	1.7
1980	19	16	0.82	0.51	1.2
1981	15	12	0.52	0.38	0.9

being in the south. Singh (26) has used the methylchloroform data to make an estimate of average hydroxyl radical concentrations, and their results yield values of 2.6×10^5 molecules/cm^3 in the north and 7.8×10^5 molecules/cm^3 in the south with a ratio of 3.0. These results along with the estimation from this study are given in Table V. Our value for the northern troposphere is in good agreement with some of the other calculations, particularly, Warneck (9), Davis et al. (10), Crutzen and coworkers (6, 24, 25), and Singh (26). We project a higher differential between the north and the south than was estimated by other investigators (11, 25, 26). It appears obvious that whatever the absolute number may be, there must be a higher concentration of OH· in the south. This is probably due to a combination of higher water vapor and a lower CO level in the south as compared to the north. Both of these factors would contribute to the lower value of OH· in the north.

The model predicts a flux of 2.8×10^{10} g of methylchloroform into the stratosphere in 1975 (see Table IV). This converts to a flux of 2.32×10^6 atoms of Cl cm^{-2} s^{-1}. Crutzen and Isaken (6) in their calculation estimated a flux of about twice this value. The difference is probably attributed to the higher hydroxyl radical concentration in the southern troposphere that was used in this study as compared with the constant value of 3.5×10^5 molecules/cm^3 used by Crutzen and Isaken (6). By way of comparison the estimated flux of chlorofluoromethane is in the range of 12×10^6 atoms Cl cm^{-2} s^{-1} (6). As Crutzen and Isaken (6) state, methylchloroform is not nearly as serious as the alleged chlorofluoromethane problem; however, the future growth of this chlorocarbon should be watched carefully. An examination of the simulation results in Table IV and Figure 3 illustrates another reason for not being overly concerned with methylchloroform in the stratosphere. As the data demonstrate, if at some future time a problem is perceived, the troposphere will cleanse itself much more rapidly than in the case of the chlorofluoromethanes. The residence time for methylchloroform is in the range of 2–4 years as compared with trichlorofluoromethane where the time is measured in decades (13). It is reassuring to note that our residence time is in agreement with the value of 3 years estimated by Yung et al. (1).

Using a budget analysis on methylchloroform production, Singh (14, 26) predicts a residence time of about eight years. In addition to the many uncertainties in the data base, one of the reasons for the discrepancy between our results and Singh's must be related to the average global concentrations of methylchloroform that were used in the two calculations. Singh uses a value of 90 ppt (26), whereas our estimation is 76 ppt. The lower estimate results from using all the past monitoring data and fitting the best curve through the points by means of adjusting the dissipating reaction constants k_6 and k_7. Another problem between the two studies is that Singh uses a continuous exponential growth function to represent input of methylchloroform into the troposphere. This function is fitted with an annual growth rate of 16% in the halocarbon (14). Our model uses the actual production history that has been assembled for methylchloroform over the years. Examination of this data (Table I) indicates a fast growth in the early years followed by a steady growth of about 16–18%. To fit an exponential curve to the production data starting in 1951 and ending in 1976 with an accumulated total of 6.5×10^9 lb, a growth constant of 0.36 would be required instead of 0.16 used by Singh.

Finally, the suggestion was made by one of the reviewers that the discrepancy in the residence time might be due to the uncertainties in the interhemispheric exchange rates (k_3 and k_4). A sensitivity analysis on these parameters indicated that a ±10% change in k_3 and k_4 caused only a 1–2% change in the predicted methylchloroform concentration. In addition, the value of 0.9 used for this exchange rate is in agreement with what other investigators are using (26).

Regardless of the discrepancies in the absolute number, it is apparent that the hydroxyl radical concentration in the Northern Hemisphere is in the range of $3–5 \times 10^5$ molecules cm^{-3} and that there is about three times this amount in the south. It now becomes important to determine if this ratio is becoming larger with the passage of time as suggested by Wofsy (27) and Singh (26).

Figure 3. Simulation of disappearance of methylchloroform in troposphere, assuming no further input after 1976

Table V. Summary of OH· Concentrations in Northern Troposphere

Author	Ref	Av [OH·] concn (molecules/cm^3)
Crutzen & Isaken	6	3.5×10^5
Crutzen	24	5.0×10^5
Davis et al.	10	5.0×10^5
Warneck	9	7.5×10^5
Levy	22	4.1×10^6
Levy	23	3.3×10^6
Levy	23	1.5×10^6
Chang & Wuebbles	11	2.0×10^6 Ratio south/north ~1.5
Crutzen & Fishman	25	$3.0–5.0 \times 10^5$ Ratio south/north 2.7
Singh	26	2.6×10^5 Ratio south/north 3.0
This work		4.8×10^5 Ratio south/north 3.75

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Phosphorus Loading and Response in Lake Vänern Nearshore Areas

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■ Phosphorus retention in five archipelagic areas of Lake Vänern, Sweden, was estimated, and the observed local impact on trophic state was compared with that predicted from steady state considerations. Only theoretical residence times for water were used to define changes, but other more precise methods are discussed. Five archipelagic areas of Värmlandssjön retained about 38% of the P load, and the open lake retained a similar fraction. Thus, one-half of the incoming P was retained in nearshore areas. Predicted P content agreed reasonably well with observed, and even estimates of chlorophyll a content from predicted P fell largely within the confidence intervals of chlorophyll a previously predicted from observed P concentrations for whole lake systems. Thus, with reasonably good data on P loading, retention coefficient, and flushing rate, at least crude predictions of trophic state changes and retention capacity are possible in archipelagic areas of large lakes.

Lake Vänern, Sweden, may as a whole be considered an oligotrophic lake. However, some of the archipelagic nearshore areas have reached a mesotrophic or even eutrophic state in terms of chlorophyll and phosphorus content. Five nearshore areas of the lake were studied during 1973–75 to determine present trophic state, their effect on whole lake P retention, and effects of changed nutrient loading. The five nearshore areas shown in Figure 1 were designated largely according to earlier work (*1*), but with some modification of physical measurements according to Lindell (*2*). In addition to measurements of nutrient input to and the concentration of algae and nutrient within the areas, considerable emphasis was placed on the movement of water within and through the areas (*2*).

The approach to this problem was similar to that proposed by Vollenweider and Dillon (*3*), Dillon and Rigler (*4*), and Dillon (*5*), but applied to the lake subbasins. That is, phosphorus concentration was predicted from known P loading,

flushing rate, water distribution, and estimated retention coefficients in the different parts of five nearshore areas. The conventional concept of theoretical residence time or flushing rate (reciprocal of residence time) was used. While reasonably good agreement was obtained between predicted and observed P content, agreement would improve with more precise estimates of flushing rate. Predicted P content was compared to observed values and estimated values for chlorophyll a were calculated from predicted P according to Dillon and Rigler (*4*) and compared to the observed values. The procedure was the same for the open lake in addition to partitioning the quantity of P retained in the nearshore areas and the amount retained and sedimented in the open lake.

Such an approach not only allows one to explain the present P loading-trophic state relation in the different areas of Vänern, but also represents a procedure to judge the effect of future loading on the trophic state of the open lake as well as its nearshore areas. The Vollenweider-Dillon approach allows one to judge the trophic state of a lake by tying the predicted concentration of P, the factor that determines the plankton algae biomass, to the loading rate. Thus, a loading can have a real meaning transferable to concentration and ultimately to the lake response in terms of algal biomass, water transparency, and possibly other variables such as zooplankton biomass. The approach works rather well in Vänern's nearshore environments. The problem, of course, is the wide variability in the results when rather simple relationships are used. The counteracting advantage, however, is its simplicity, general applicability, and straightforward usefulness to management.

In summary, the purposes of the research described here were threefold:

• Determine the predictability of P concentration and in turn chl a in nearshore areas of a large lake using retention and loading rate of P

• Compare the relative retention of P in five nearshore areas of a large lake with that in the open water

• Evaluate methods for determining retention coefficient in nearshore archipelagic regions.

Sampling and Analytical Methods

Lake Data. Sampling for physical variables was performed by an automatic in situ instrument (*6*), whereas nutrients and

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chlorophyll were determined by collecting water samples for laboratory analysis. Water samples were collected from the five areas and their designated subareas in two ways. A rather complete coverage for nutrient content was obtained on at least two occasions for each area through week-long synoptic cruises in 1973 and 1974. Area 5 was similarly sampled intensively in 1975.

In addition to the synoptic survey, regular stations were sampled on a monthly basis between 1973 and 1974 in all but area 1. In all cases, the mean values for P for an area or subarea were averaged in with the other monthly single-station or multiple-station means to obtain a seasonal (April–October) mean value. In subareas where regular stations did not exist, the mean from the synoptic surveys necessarily sufficed for the subarea mean. This is considered reasonable for these nearshore areas because of the rather low seasonal variation in P content. The one exception was area 2A, the area receiving the input from the river Tidan at Mariestad, where observations were few and variability was great. Physical data were also most scarce and variable in area 2A.

The number of regular stations sampled for P content in the nearshore areas and the subareas during 1973–1974 are as follows: area 1, none; 2A, none; 2B, one; 2C, none; 3A, one; 3B, two; 4, two; 5A, one; 5B, two; and 5C, one. The mean values and associated standard deviations for both P and chl a reflect, as near as existing data permit, the seasonal conditions. P concentrations reflect the water column content since the mean value for each observation was determined by averaging all values through the water column. In general, area 5 has the best coverage for both physical data and phosphorus and chl a content, whereas results from area 2 are not too reliable.

Estimates of Residence Times. To estimate the effects of nutrient input to lakes, it is obvious from Vollenweider (7) and Vollenweider and Dillon (3) that knowing the water res-

Figure 1. Lake Vänern showing nearshore areas and area sections
Areas are (1–5) Kinneviken, Mariestadsfjärden, Åsfjorden, Kattfjorden, and Sätersholmsfjärden, respectively

idence time is of great importance. However, the concept of residence time can vary. The theoretical residence time is most commonly used. This is usually defined as

$$T_t = \frac{V}{Q_I} \quad (1)$$

where V is the volume of the lake (or part of the lake), and Q_I is the inflow rate of water to the lake. For simplification it is often assumed that precipitation on the lake equals the evaporation from the lake, thus, $Q_I = Q_O$ (discharge from the lake). In some lakes the theoretical residence time of the input water will not be sufficiently accurate to be able to precisely determine the time available for physical, chemical, and biological agents to operate on the input of, for instance, nutrients. However, a more accurate measure is complicated to obtain even in the seemingly most uncomplicated lakes.

When dealing with archipelagos, instead of the entire lake, the inflow of water from the open lake must also be considered as the other main source of water and material to the nearshore areas. Assuming that the mixing in the archipelagos is complete, it is possible to use the steady state continuity equation as suggested by Palmer (8) to calculate the inflow from the open lake. With this technique the theoretical residence times of archipelago water, for example, can be calculated for each of the five nearshore areas according to the following equation:

$$T_A = \frac{V_A(C_A - C_L)}{Q_I(C_I - C_L)} \quad (2)$$

where C_A, C_I, and C_L are the concentrations of some conservative substance in the archipelago, input water, and lake water, respectively. (In the calculations we have used spec. conductance as a conservative substance.) Finally, the inflow of lake water to the archipelago will, under the same assumptions, be

$$Q_L = Q_I \frac{C_I - C_A}{C_A - C_L} \quad (3)$$

The comparisons between the residence times could then give some useful information for understanding the behavior of the archipelagic water and at the same time indicate why estimated effects of nutrients on the archipelago are different from observed.

P Loading. The mean annual loading rates of P into the five nearshore areas were estimated for the period 1972–1974. River input was estimated by multiplying monthly flows by monthly measured concentrations. Loadings from municipal sewage and from industrial wastes were included according to published values (9). The loading of P into subsequent subareas was estimated by multiplying the mean P content in the preceding subarea by the annual discharge either from the river, or in the case of area 2, the river combined with lake water flow through the area using a net lake flow estimate (2).

Prediction of P Content. For the purpose of predicting mean P content in the various subareas, the equation of Vollenweider and Dillon (3) was used. That equation was derived from a steady state solution of Vollenweider's (7) model for lake P content and is

$$\frac{L(1 - R)}{\bar{z}\rho} \quad (4)$$

where L is areal P loading in mg P m^{-2} yr^{-1}, R is the retention coefficient, $\bar{z}$ is the mean depth (m), and ρ is the flushing rate (yr^{-1}). P was also predicted from Vollenweider's (7) original steady state equation:

$$\frac{L}{\bar{z}(\rho + \sigma)} \quad (5)$$
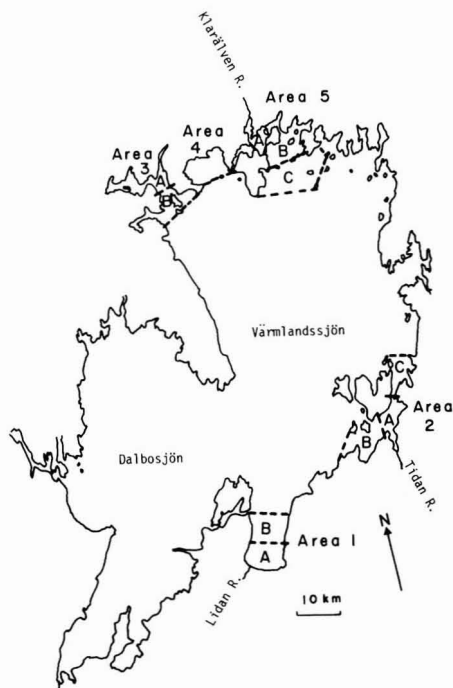
where the net sedimentation coefficient σ is used (yr^{-1}). Mean sedimentation coefficients were obtained for this equation from the ratio of observed mean sedimentation rates for the five areas [L. Håkanson (Dept. of Physical Geography, Univ. of Uppsala, Uppsala, Sweden), written communication] in g P m^{-2} yr^{-1} to the observed amount of P in the various areas in g P m^{-2}.

The most difficult parameter in the first equation to obtain is R, the retention coefficient. R was estimated in two ways: R_o, the observed coefficient, was estimated in the various areas and subareas from

$$\frac{\text{P load in} - \text{P load out}}{\text{P load in}} \qquad (6)$$

and R_c was calculated from an equation by Kirchner and Dillon (10):

$$R = 0.426 \exp(-0.271\ qs) + 0.574 \exp(-0.00949\ qs) \quad (7)$$

where qs is determined from Q/A-inflow over area.

Prediction of Chlorophyll Content. Chl a was predicted from the P content with the aid of the empirical equation of Dillon and Rigler (4):

$$\log_{10} \text{chl } a = 1.449 \log_{10} P_{tot} - 1.136 \qquad (8)$$

Dillon and Rigler developed this equation from observations on a number of North American lakes—46 data points in all. The equation defines the relationship between pregrowth period total phosphorus concentration and mean summer chl a content. The correlation coefficient was 0.95, although the confidence interval for a given estimate is quite large because the relationship is log-log.

Although Dillon and Rigler used the pregrowth period P content, the spring-summer mean was used from the Lake Vänern nearshore areas because of the relatively small seasonal variability in the values. Also, Dillon and Rigler stated that their equation was valid only if P could be considered the most limiting nutrient as indicated by an N:P ratio greater than 12. This was always the case in Lake Vänern.

Results and Discussion

Water Movement. Residence times and the transport of water from the lake to the archipelago (Q_L), calculated with Equations 1–3, are listed in Table I for the archipelagic areas. Comparison between the residence times shows that in all areas the theoretical residence times for surface water input alone are much longer than those that also take into account the inflow of lake water.

A general feature of the values for Q_L is that they almost always indicate smaller amounts of transported water compared with the actual volume transported when physically measured, due to the fact that complete mixing never occurs. This has been shown for area 5 where several direct current measurements were performed (2). Here, the mean water transport was estimated to be at least three times the value shown in Table I. The same phenomenon has been observed for the exchange of water between the two main basins of Lake Vänern and in Åsfjorden (area 3) where extremely high values of water transport were shown by others (11). Also, a number of instantaneous observations in areas 1 and 2 indicate that very large volumes of water are transported from the lake to the archipelago. In Kattfjorden (area 4), however, the estimated transport (Q_L) should be fairly close to a physically measured transport of water.

Thus, note that the physically transported volumes of water through a cross-sectional area, representing the outer limits of the archipelago, do not always represent the exchanged water volumes that are needed to estimate a water quality condition. Furthermore, even if the open lake water is well

mixed in the archipelago, the river input may not be; e.g., if the surface water entering the archipelago has the character of a jet, it will not mix significantly. This condition exists to some extent in all areas except area 2. In area 5 the river Klarälven (main input) behaves like a jet thorugh the archipelago for part of the year. The inflow (Q_I) may then be too high a value if one wants to use water residence time to estimate the movement of a substance. The result of the incomplete mixing of the input river water will often tend to offset the effects from excessive lake water inflow, which means that the theoretical residence times (T_{tI}) are more realistic for purposes of estimating substance residence times.

From our experiences (2), it is rather obvious that in Vänern neither the estimated volumes of water entering from the open lake nor the theoretical residence times (T_{tA}) are entirely adequate. Because data on water movement are insufficient, the conventional estimate of theoretical residence time was used as a first approximation in the following calculations, although calculations including lake water inflow and other more sophisticated residence time concepts based on the salt budget would no doubt improve agreement between observed and predicted values.

Phosphorus. Phosphorus loading and the physical characteristics in the five nearshore areas are shown in Table II. Industry contributes a sizable amount of P to areas 2–4, most of this coming from pulp mills. These are mean values for the three-year period 1972–1974. Interestingly enough, the input to area 5 during that period dropped by 87% because of the initiation of secondary treatment in 1973 and tertiary treatment in 1974. Thus, the present input of P to area 5 is only 21% of the 1972–1974 mean value shown in Table II.

Note that areal P loading appears rather high in all the nearshore areas, ranging from over 1 g P m^{-2} yr^{-1} to 0.7. The loading to the total area of Värmlandssjön is only 0.14 g P m^{-2} yr^{-1}. While the areal loading is rather high in the nearshore

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Table I. Calculated Residence Times in Days in Five Nearshore Areas of Lake Vänern [a]

Area	1	2 (A + B)	2 (A + B + C)	3	4	5 (A + B)	5 (A + B + C)
T_{tI}	605	181	510	157	715	74.8	241
T_{tA}	2	6.7		[b]	38	38	
Q_L	5800	555		[b]	305	147	

[a] t = theoretical, I = surface water inflow, A = archipelago water, Q_L = input of lake water in m^3/s. [b] Not possible to calculate.

Table II. Phosphorus Loading and Physical Characteristics in Five Nearshore Areas in Lake Vänern, Sweden, During 1972–1974

Physical characteristics from Lindell (2)

	Areas				
	1	2	3	4	5
P load in tons					
River	78.3	51.8	37.5	9.9	76.0
Sewage	25.5	44.4	4.2	11.0	47.6
Industry	. . .	18.7	39.2	25.0	. . .
Total	103.8	114.9	80.9	45.9	123.6
P load in g m^{-2} yr^{-1}	0.92	0.80	1.09	0.85	0.70
Mean river inflow m^3 s^{-1}	19	25	75	17	147
Mean detention time in days	605	510	157	715	241
Mean depth ($\bar{z}$) in m	8.6	7.7	20.6	19.5	11.3
Area in km^2	112.9	143.2	74.1	54.0	177.3

areas, Tables III–VII show that the predicted and observed concentrations are not proportionately as high. That is due to the relatively high flushing rates in the nearshore areas (mean of 7.0 yr^{-1}). The amount of P measurable at any one time and available for algal uptake is relatively low in highly flushed areas (5).

The agreement between predicted and observed P is quite good if the observed retention coefficient (R_o) from Equation

6 is used. This is clearly represented by the solid circles in Figure 2. The striking anomaly is the highest predicted value in area 1 (Table III), which is relatively easy to explain. The flushing rate is greatly underestimated (residence time overestimated) if only theoretical residence time for the surface water input is used. A pattern of rapid inflow of water from the open lake into area 1, described earlier, effectively carries the external supply of nutrients into the open lake; therefore, they are not observed in the nearshore area. If this is taken into account, then the predicted P level is much closer to the observed value of 11 $\mu g/L$.

There is also a slight difference between predicted and observed values in areas 3B and 5A. The cause of the higher observed values in 3B could be an influence from the open lake, due to inflow of lake water, but data are not available

Table III. Physical Characteristics, P Loading, and Predicted and Observed P and Chlorophyll Content in Kinneviken, Area 1

P loading from 1972–1974, and observed values from 1973–1974 for P and 1973 for Chl a except where indicated[a]

	Whole area	Lake
Area, km^2	112.9	
$\bar{z}$, m	8.6	
Volume, km^3	0.997	
ρ, yr^{-1}	0.60	
L, g P m^{-2} yr^{-1}	0.92	
R_o	0.47	
R_c	0.65	
σ, yr^{-1}	0.0	
$P_p(R_o)$, $\mu g/L$	94.5	
$P_p(R_c)$, $\mu g/L$	62.4	
$P_p(\sigma)$, $\mu g/L$	178.3	
P_o, $\mu g/L \pm$ SD	11.0 ± 2.1 (n = 10)	8.4 ± 1.6 (n = 11)
Chl a_p, $\mu g/L$	54.0	
Chl a_o, $\mu g/L$	4.9[b] (n = 3)	1.5 ± 0.37 (n = 6)

[a] ρ = flushing rate, L = loading rate of P, R_o = retention coefficient observed, R_c = retention coefficient calculated (10), σ = sedimentation rate, P_p = predicted phosphorus content using respective correction for sedimentation, P_o = observed mean ± standard deviation (seasonal), Chl a_o = observed mean ± standard deviation (seasonal), Chl a_p = predicted mean. [b] Data from 1970, 1971, and 1973 (1).

Table IV. Physical Characteristics, P Loading, and Predicted and Observed P and Chlorophyll Content in Designated Sections of Mariestadsfjärden, Area 2

P loading from 1972–1974, and observed values from 1973–1974 except where indicated. See legend from Table III

	Section A	Section B	Section C	Lake
Area, km^2	28.0	46.6	68.6	
$\bar{z}$, m	4.3	4.6	11.2	
Volume, km^3	0.119	0.214	0.767	
ρ, yr^{-1}	8.64	3.55	1.68	
L, g P m^{-2} yr^{-1}	2.95	0.911	0.23	
R_o	0.61	0.77	0.07	
R_c	0.41	0.50	0.48	
σ, yr^{-1}	3.86	9.35	3.92	
$P_p(R_o)$, $\mu g/L$	31.0	12.8	11.4	
$P_p(R_c)$, $\mu g/L$	46.8	27.9	6.4	
$P_p(\sigma)$, $\mu g/L$	55.1	15.4	3.7	
P_o, $\mu g/L \pm$ SD	29.5 ± 12 (n = 4)	11.4 ± 3.5 (n = 9)	11.2 ± 2.9 (n = 7)	8.8 ± 1.3
Chl a_p, $\mu g/L$	10.5	3.0	2.5	
Chl a_o, $\mu g/L \pm$ SD	10.5 ± 2.4[a]	1.9[b]	2.5[b]	2.2 ± 0.7[c] (n = 6)

[a] Data from 1970, 1971, and 1973 (1). [b] Data from 1973 in vivo (1). [c] Data from 1973 (1).

Table V. Physical Characteristics, P Loading, and Predicted and Observed P and Chlorophyll Content in Designated Sections of Asfjorden, Area 3

P loading from 1972–1974, and observed values from 1973–1974 for P and 1974 for Chl a. See legend from Table III

	Section A	Section B	Lake
Area, km^2	28.4	20.4	
$\bar{z}$, m	20.6	20.6	
Volume, km^3	0.586	0.420	
ρ, yr^{-1}	4.04	5.63	
L, g P m^{-2} yr^{-1}	2.85	1.23	
R_o	0.46	0.43	
R_c	0.26	0.19	
σ, yr^{-1}	1.44	2.52	
$P_p(R_o)$, $\mu g/L$	18.5	6.1	
$P_p(R_c)$, $\mu g/L$	25.3	8.6	
$P_p(\sigma)$, $\mu g/L$	25.1	7.3	
P_o, $\mu g/L \pm$ SD	18.6 ± 8.6 (n = 8)	10.6 ± 2.2 (n = 9)	10.0 ± 2.2 (n = 11)
Chl a_p, $\mu g/L$	5.1	1.0	
Chl a_o, $\mu g/L \pm$ SD	2.2 ± 0.5 (n = 3)	2.8 ± 0.7 (n = 3)	2.2 ± 2.2[a] (n = 5)

[a] Data from 1973.

Table VI. Physical Characteristics, P Loading, and Predicted and Observed P and Chlorophyll Content in Kattfjorden, Area 4

P loading from 1972–1974, and observed values from 1973–1974 for P and 1974 for Chl a. See legend from Table III

	Whole fjorden	Lake
Area, km^2	54.0	
$\bar{z}$, m	19.5	
Volume, km^3	1.05	
ρ, yr^{-1}	0.51	
L, g P m^{-2} yr^{-1}	0.85	
R_o	0.88	
R_c	0.55	
σ, yr^{-1}	3.87	
$P_p(R_o)$, $\mu g/L$	10.3	
$P_p(R_c)$, $\mu g/L$	38.5	
$P_p(\sigma)$, $\mu g/L$	10.0	
P_o, $\mu g/L \pm$ SD	10.2 ± 1.2 (n = 13)	10.9 ± 3.7 (n = 11)
Chl a_p, $\mu g/L$	2.1	
Chl a_o, $\mu g/L \pm$ SD	21 ± 0.6 (n = 9	10.9 ± 3.7 (n = 6)

from 3B. If 1974 loading values are used for 5A, instead of the 1972–1974 mean, loading is reduced from 5.6 to 3.9 g P m^{-2} yr^1, and the predicted value comes out equal to the observed: 16 μg/L. Clearly, if the loading and flushing rates are reasonably accurate, the expected concentration will be very close to the observed when R_o is used.

The use of retention coefficients (R_c) from Equation 7 gave a much poorer fit between observed and predicted P, as expected, than the observed values (R_o) (Figure 2). In most cases the R_o values were greater than the R_c values, which were a function of surface hydraulic loading (10). R_c values would be independent of the lake water movement into the nearshore areas and tend to predict the fractional retention if the river inflow were the only water inputs to each system. For those lake inflows that have lower concentrations of P than within the areas, the area P content would be diluted and cause the R_o values to appear greater than they would be without any lake inflow. The relatively good agreement between observed and expected P may be due in part to that phenomenon. The comparison of the two methods of estimating retention coefficient is shown in Figure 3.

The method of predicting P using the sedimentation coefficients and Vollenweider's original model (Equation 5) was less accurate in most cases than by the R_c method (Tables III–VII). That also was more or less expected since the sedimentation rates reported by L. Håkanson (written communication) were means for the entire nearshore area in question. The one case (area 4, Table VI) where the entire fjord was used and not subdivided, the predicted P using the sedimentation coefficient was very close to the observed, 10 vs. 10.2 μg/L.

Chlorophyll a. The data on chl a were not as numerous as that for P. Many of the observed values (chl a) are based on as few as two or three calculated area means. Of course, each area mean determined at one time was often a result of more than one observation throughout the area. Because of the sparse data, the relative agreement between observed and predicted chl a can only indicate a general trend.

Chl a predicted by Equation 8 agreed reasonably well with observed values, even when predicted instead of measured P was used (Figure 4). The 95 and 50% confidence intervals reported by Dillon and Rigler's results were included in Figure 4 to indicate how well the prediction in Vänern agreed with

observed values within a variability expected from the equation. Interestingly enough, six of the values fall within the 50% limits, and all except the value from area 1 are close to or within the 95% limits. The extreme width of Dillon and Rigler's confidence intervals is a result of plotting the data on an arithmetic scale while their relationship is log-log. Although it is very useful as a management tool to predict chl a to within 50% probability, the log-log relationship gives too much error at the 95% level to be very useful within a narrow range of chl a like that in Lake Vänern.

Open Lake. The loading of P to the open water in Värmlandssjön was considered from the standpoint of determining the role of the nearshore areas in retaining P and the response in terms of algal biomass in the open lake. Because the cal-
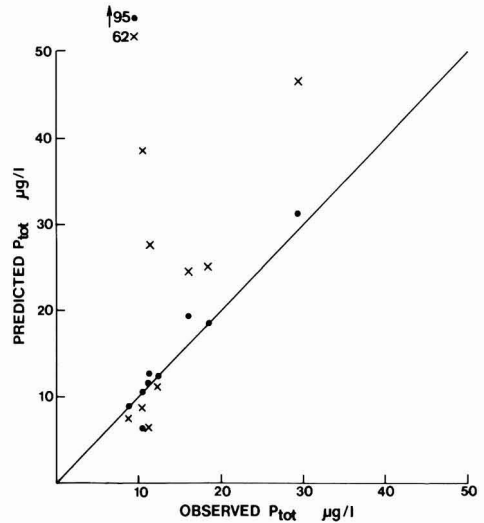
Figure 2. Observed vs. predicted total phosphorus content in five nearshore areas of Lake Vänern
Predicted values using R_o and R_c indicated by solid circles and crosses, respectively

Figure 3. Comparison of retention coefficients R_o and R_c for five nearshore areas in Lake Vänern

Table VII. Physical Characteristics, P Loading, and Predicted and Observed P and Chlorophyll Content in Designated Sections of Sätersholmsfjärden, Area 5

P loading from 1972–1974 and 1973–1975 for observed values. See legend from Table III

	Section A	Section B	Section C	Lake
Area, km^2	21.9	63.2	92.2	
$\bar{z}$, m	6.8	12.8	23.0	
Volume, km^3	0.149	0.81	2.12	
σ, yr^{-1}	31.1	5.72	2.17	
L, g P m^{-2} yr^{-1}	5.64	1.17	0.61	
R_o	0.27	0.24	0.28	
R_c	0.077	0.29	0.36	
σ, yr^{-1}	13.6	9.49	7.33	
$P_p(R_o)$, μg/L	19.5	12.1	8.8	
$P_p(R_c)$, μg/L	24.6	11.3	7.8	
$P_p(\sigma)$, μg/L	22.9	9.9	5.4	
P_o μg/L ± SD	16.0 ± 2.1 (n = 6)	12.2 ± 1.6 (n = 16)	8.8 ± 2.0 (n = 7)	9.5 ± 1.9 (n = 17)
Chl a_p, μg/L	4.3	2.7	1.7	
Chl a_o, μg/L ± SD	6.0 ± 2.0 (n = 2)	3.7 ± 1.2 (n = 12)	2.2 ± 0.9 (n = 12)	1.8 ± 0.7 (n = 11)

culated retention coefficient, R_c, is more independent, it was used to estimate the quantity of P retained in the nearshore areas. Also, R_c is the only value obtainable for the entire lake. Thus, a weighted retention coefficient for the nearshore area was obtained (0.38). R_c values were used for each area, except no retention was assumed to occur in area 1. Therefore, all P

Figure 4. Observed chl a content vs. chl a predicted from calculated P using Dillon and Rigler's 1974 equation
Confidence intervals are those from Dillon and Rigler (4)

Figure 5. Phosphorus loading, corrected for retention and flushing, vs. mean depth (5), showing limits for eutrophy and mesotrophy and distribution of 10 subareas in Lake Vänern

from the river Lidan was considered to enter the lake. Otherwise, the mean nearshore R_c values were weighted to the P load into each area.

The R_c value for the total area of Värmlandssjön was 0.75. The difference, 0.37, is the retention coefficient that can logically be applied to the open water area, whereas 0.38 can be applied to the nearshore areas. The predicted P content for the open water is

$$\frac{139 \text{ mg P m}^{-2} \text{ yr}^{-1} (1 - 0.75)}{0.115 \text{ yr}^{-1} \cdot 30 \text{ m}} = 10.0 \text{ } \mu\text{g/L P}$$

The observed mean value for the open lake is 9.5 μg/L. A chl a content of 2.1 μg/L can be predicted from the P value of 10 μg/L, and the observed mean chl a is 2.0 μg/L. The similarity of observed and predicted values to some extent validates the use of an R_c value for the whole lake.

It would appear that the nearshore areas have about an equal role in removing P as the open water area. The role of the nearshore areas would be relatively greater than the open water if R_o values had been used, but this was not done for this purpose as indicated before, because dilution effects from inflowing lake water probably caused an unrealistic raising of the R_o values. The equally high retention of P in the open lake compared to the nearshore areas is largely a result of a much smaller surface hydraulic loading (also longer retention time) in the open lake.

Loading Concept and Management. As pointed out by Dillon (5), the use of loading rates to predict the trophic state of lakes is more meaningful if the parameters of flushing rate and retention coefficient are considered. A given relationship between $L(1 - R)/\rho$ and $\bar{z}$ should indicate a steady state P concentration. In addition, Vollenweider and Dillon (3) argue that the resulting concentration is the important variable that determines the lake response.

As shown in Figure 5, if the two above-mentioned parameters ($L(1 - R)/\rho$ and $\bar{z}$) are plotted, given straight lines indicate potential steady state concentrations. If a P concentration greater than 30 μg/L indicates eutrophy and less than 15 μg/L is oligotrophy, then three areas in Vänern could be considered mesotrophic, none is eutrophic (2A is on the line), and the remainder are oligotrophic. Placement of area 1 in the eutrophic range is, of course, in error because flushing from the lake water was not considered. The use of T_{tA} instead of T_{tl} would place area 1 in the oligotrophic range. Note also, as would be expected, the A's or more shoreward subareas are mesotrophic.

If we use Dillon and Rigler's equation, the predicted chl a concentrations from those steady state P concentrations in Figure 5 are 10 and 3.7 μg/L chl a. Those values agree very well with earlier suggested limits for chl a (12), 10 and 4 μg/L, respectively. Furthermore, the value of 30 μg/L total P is not too different from Sawyer's "critical" value of 15 μg/L for soluble P in Wisconsin lakes (13), if one assumes that soluble P is about one half of total.

If we included Secchi disk depth, that along with chl a and phosphorus do not provide all the needed information for management nor the precision desired. Obviously, even if the process itself is very simple, the physical behavior of the lake is very difficult to include in an elementary model of the type discussed above. Prediction of a lake response from changes in loading of about 10–30% are not predictable with much confidence even with modifications of the methods discussed here. For that, a much better understanding of the specific lake in question is required.

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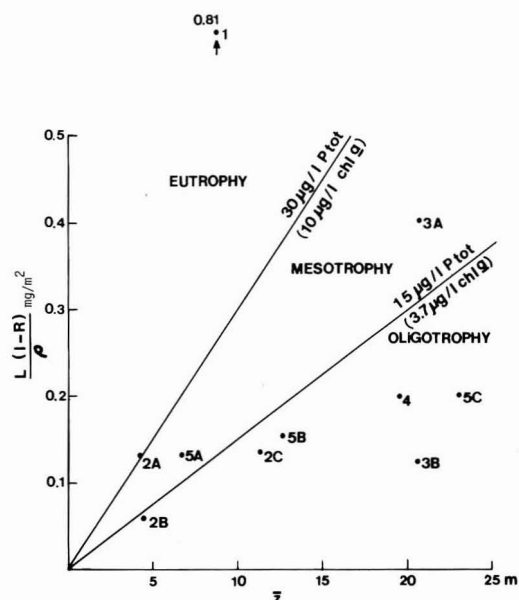
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NOTES

Quantum Yields for Reaction of Pollutants in Dilute Aqueous Solution

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■ Procedures are reported for determining quantum yields for direct photolysis of pollutants at low concentrations in water. Quantum yields are used to compute half-lives for direct photolysis of aquatic pollutants under sunlight.

In a recent report, Zepp and Cline (1) described equations and parameters required to compute direct photolysis rates of pollutants in the aquatic environment. Photolysis rates $(-dC/dt)$ can be computed by Equation 1 where k_a is the specific rate of light absorption, ϕ is the quantum yield for reaction, and C is the pollutant concentration.

$$-\frac{dC}{dt} = k_a \phi C \qquad (1)$$

Usually, the quantum yield for a reaction is determined under conditions in which all the incident light or a directly measurable fraction is absorbed by the system (2). The concentrations of substrate employed in these experiments typically range from 10^{-3} to greater than 0.1 M. The extremely low solubilities of most organic pollutants in water preclude measurement of quantum yields under conditions of complete light absorption. In this communication a technique that can be used to determine quantum yields in very dilute solution is described. An explicit description of the use of quantum yields to compute sunlight photolysis half-lives is also included.

The general rate expression for photolysis in a cell containing volume V of solution and having exposed area A is:

$$\text{Rate} = -\left(\frac{dC}{dt}\right)_\lambda = \phi I_{o\lambda} \left(\frac{A}{V}\right) F_{s\lambda} F_{c\lambda} \qquad (2)$$

where $I_{o\lambda}$ is the incident light intensity at wavelength, λ; $F_{s\lambda}$ is the fraction of light absorbed by the system; and $F_{c\lambda}$ is the fraction of absorbed light that is absorbed by the photoreactive substance (3). The terms $F_{s\lambda}$ and $F_{c\lambda}$ are expressed by:

$$F_{s\lambda} = 1 - 10^{-(\alpha_\lambda + \epsilon_\lambda C)l} \qquad (3)$$

$$F_{c\lambda} = \frac{\epsilon_\lambda C}{\alpha_\lambda + \epsilon_\lambda C} \qquad (4)$$

where α_λ is the absorption coefficient of the solvent, ϵ_λ is the molar extinction coefficient of the photoreactive substance,

and l is the light pathlength. When light is weakly absorbed by the system ($F_{s\lambda} < 0.1$), $F_{s\lambda}$ very nearly equals 2.303 ($\alpha_\lambda + \epsilon_\lambda C)l$, and Equation 2 simplifies to a first-order rate expression:

$$\text{Rate} = 2.303 I_{o\lambda} \left(\frac{A}{V}\right) \epsilon_\lambda l \phi C \qquad (5)$$

Thus, when the light intensity, extinction coefficient, and pathlength are known, the quantum yield may be computed from the slope of a first-order plot of ln C vs. exposure time:

$$\phi = \frac{-\text{Slope}}{2.303 I_{o\lambda}(A/V)\epsilon_\lambda l} \qquad (6)$$

Procedures that can be used to determine these parameters are outlined below. Monochromatic light isolated by filters (2) is usually employed in these experiments.

The intensity term, $I_{o\lambda}(A/V)$, can be directly determined by exposing a solution of an appropriate reference compound, i.e., a chemical actinometer, to light in exactly the same fashion as the pollutant. The same or an identical reaction cell should be used, and the cell should be filled with the same volume. The chemical actinometer should photoreact with a well-defined quantum yield at wavelength λ. When all of the incident light is absorbed by the actinometer, i.e., $F_{s\lambda}$ is unity, the intensity term, $I_{o\lambda}(A/V)$, equals the rate of photoreaction of the actinometer divided by its quantum yield. The potassium ferrioxalate actinometer is reliable and easy to analyze (4).

The average pathlength of the photolysis cell can be determined experimentally by the following procedure. If the concentration of the light absorbing substance, C, in a photoreactive system is sufficiently high that $F_{c\lambda}$ (Equation 4) is close to unity, then Equation 2 reduces to:

$$(\text{Rate})_C = \phi I_{o\lambda} \left(\frac{A}{V}\right) (1 - 10^{-\epsilon_\lambda l C}) \qquad (7)$$

In the special case in which $\epsilon_\lambda l C$ exceeds 2, essentially all of the light is absorbed, and Equation 7 further simplifies to Equation 8.

$$(\text{Rate})_\text{max} = \phi I_{o\lambda} \left(\frac{A}{V}\right) \qquad (8)$$

The ratio, X, of the rate at concentration C to the maximum rate is then given by:

$$\frac{(\text{Rate})_C}{(\text{Rate})_{max}} = X = 1 - 10^{-\epsilon_\lambda l C} \tag{9}$$

Thus, a plot of $-\log(1-X)$ vs. $\epsilon_\lambda C$ gives a straight line with a slope equal to the pathlength, l. Such a plot is shown in Figure 1 for the benzophenone-sensitized *cis-* to *trans*-isomerization of 1,3-pentadiene (5) in our photochemical apparatus. In Figure 1, X is the ratio of *trans*-isomer formed at benzophenone concentration C to *trans*-isomer formed at a benzophenone concentration in which all the light was absorbed (0.050 M); ϵ is the extinction coefficient of benzophenone at 313 nm, the wavelength employed in the cell pathlength determination.

If possible, the molar extinction coefficient of the pollutant (ϵ_λ, Equation 3) should be determined in water. This task is sometimes difficult, if not impossible, because the solubility limits of DDT, benzo(a)pyrene, and some other pollutants are lower than 10^{-8} M. As an alternative, we have determined extinction coefficients in mixtures of water and acetonitrile or methanol (6), two polar organic solvents whose refractive indices are very close to that of water (7). Our choice of organic solvents was dictated mainly by the theoretical prediction that, at least for strong absorption bands of nonpolar compounds, absorption coefficients should be the same for solvents with the same refractive indices (8).

In agreement with theory, Schwarz and Wasik (9) reported that the absorption spectra of several polycyclic aromatic hydrocarbons are the same in water and ethanol, another organic solvent whose refractive index is nearly the same as that of water. Polar substances are very sensitive to changes in solvent, especially if the substance forms hydrogen bonds with solvent. Because of hydrogen-bonding effects, for example, the spectra of ketones like acetone and of nitrosamines such as N-nitrosodimethylamine differ significantly in water and ethanol (10). Fortunately, polar substances are usually sufficiently water-soluble that their spectra can be obtained in pure water or in water mixed with only a small amount of organic solvent.

Pure chemicals, not technical grade substances, should be used in the measurement of extinction coefficients. Overestimates of extinction coefficients usually occur when technical substances are employed, because the impurities frequently absorb in the same spectral region as the pure chemical.

Quantum yields may also be determined by comparing the photolysis rates of the pollutant with a reference compound under conditions in which the light is weakly absorbed by both compounds. Such comparisons are conveniently made in the "merry-go-round" photochemical apparatus originally designed by Moses et al. (11). The quantum yield for reaction of the pollutant, ϕ, can be calculated:

$$\phi = \frac{(SLOPE)_P}{(SLOPE)_R} \cdot \frac{\epsilon_R \phi_R}{\epsilon_P} \tag{10}$$

where $(SLOPE)_P$ and $(SLOPE)_R$ are the slopes of log plots of concentration vs. exposure time for pollutant and reference compound, respectively; ϵ_R and ϵ_P are molar extinction coefficients of reference compound and pollutant; and ϕ_R is the quantum yield for reaction of the reference compound. Values of $\epsilon_R\phi_R$ at 313 nm for a few pesticides are: DDE in water, 12 (6, 12); DDE in hexane, 15 (6, 12); DMDE in water, 120 (6, 12); DMDE in hexane, 72 (6, 12); carbaryl in water (pH 5.5), 2.3 (13); parathion in water, 0.39 (14); methyl parathion in water, 0.43 (15). Unfortunately, most well-established chemical actinometers cannot be analyzed at the low concentrations required for this technique.
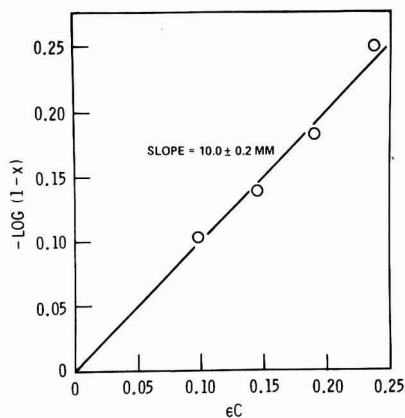
Figure 1. Determination of average cell pathlength for quantum yield studies by use of benzophenone-sensitized photoisomerization of *cis*-1,3-pentadiene

Once determined, the quantum yield for reaction can be used to compute the half-life for photolysis of the pollutant under a variety of environmental conditions (1). The photolysis half-life is independent of the optical properties of a water body near its surface (1). Estimates of the effects of light attenuation in water bodies appear elsewhere (1). Near surface half-lives can be computed by Equation 11 where Z_λ is underwater solar irradiance (1) at a wavelength interval centered at λ, and $\bar\epsilon_\lambda$ is the average extinction coefficient at this wavelength interval. The value of j is 6.02×10^{20} photon mole^{-1}.

$$t_{1/2} = \frac{0.693}{k_a\phi} = \frac{0.693\, j}{2.303\, \phi \sum \bar\epsilon_\lambda Z_\lambda} \tag{11}$$

A sample computation of the half-life of the pesticide carbaryl is presented in Table I. In computing sunlight half-lives, we have generally assumed that the quantum yield is wavelength independent in the region of sunlight absorption (1). This assumption is valid for most complex molecules in solution because photoreaction from second or higher electronic states usually cannot compete with the rapid radiationless decay of excited molecules to their first excited state. If photoreaction often occurred from higher excited states, excitation spectroscopy would not have general applicability (16). Exceptions to the general rule include certain coordination compounds. For example, the photolysis of iron (II) cyanide complexes is clearly wavelength dependent (3). For such cases, sunlight half-lives equal $0.693\,(\Sigma\phi_\lambda\epsilon_\lambda Z_\lambda)^{-1}$ where ϕ_λ is the average quantum yield in the wavelength interval centered at λ.

Finally, it should be emphasized that direct photolysis is but one of several potential mechanisms for photochemical transformation of pollutants. Natural substances in the aquatic environment are known to sometimes accelerate photolysis by mechanisms that are presently not defined (6, 17). Nonetheless, several studies (6, 13, 15) indicate that photolysis half-lives determined in natural waters are often nearly the same as half-lives computed by the procedures described above.

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Table I. Sample Calculations of Direct Photolysis Half-Life of Carbaryl in Water Midday, Midsummer, Latitude 40°N

Wavelength, nm	ϵ_λ	$Z_\lambda \times 10^{-14}$	$\epsilon_\lambda Z_\lambda \times 10^{-15}$
297.5	1480	0.00716	1.06
300	918	0.0240	2.20
302.5	741	0.0723	5.36
305	532	0.181	9.63
307.5	427	0.305	13.0
310	356	0.495	17.6
312.5	388	0.717	27.8
315	261	0.933	24.3
317.5	235	1.15	27.0
320	101	1.35	13.6
323	45	2.52	11.3
330	11	8.46	9.31

$$\sum \bar{\epsilon}_\lambda Z_\lambda = 162$$

$$k_a = \frac{2.303}{6.02 \times 10^{20}} \times 1.62 \times 10^{17} = 6.20 \times 10^{-4} \text{ s}^{-1}$$

$$\phi_{313} = 0.0060$$

$$t_{1/2} = \frac{0.693}{(0.0060 \times 6.20 \times 10^{-4})} = 1.86 \times 10^5 \text{ s} = 51.7 \text{ h}$$

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Simple Apparatus for Monitoring Land Disposal Systems by Sampling Percolating Soil Waters

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■ The treatment efficiency achieved by land disposal of effluents may conveniently be assessed by collection and analysis of waters percolating through unsaturated soil zones underlying treatment plots. A simple and inexpensive suction sampler constructed from "Swinnex"-type filter holders, membrane filters, and glass fiber filter discs is described. Air entry and vacuum loss occur only at high soil-moisture tensions; therefore, the system will sample soil waters over relatively long periods after a single evacuation. Loss of sample under high soil-moisture tensions is avoided by collecting the sample in a container separate from the sampling probe. The sampler materials cause minimal (if any) changes in sample composition.

The efficiency of conventional treatment processes is usually assessed by comparing the composition of wastewater before and after passing through the treatment process. Use of this approach for irrigation or infiltration/percolation modes of land disposal treatment requires the collection of a "treated" sample that may be compared directly with the applied effluent. This can usually be achieved by collecting waters percolating through unsaturated soil zones underlying the treatment plot, where predominantly vertical water movement can be assumed.

Collection of samples from the saturated zone (e.g., by wells) is often unsuitable for assessing treatment efficiencies, because this zone will usually contain water originating both from the applied effluent and from rain or irrigation waters infiltrating in other areas and moving laterally under the treatment plot. The proportions of mixing of waters from the different possible sources are seldom known. Installation of drains for the purpose of monitoring a land disposal site is not recommended, because "short circuiting" of relatively poor quality effluent into the drains is likely (1, 2).

Porous ceramic cups have been used to sample waters percolating through unsaturated soil zones for a variety of investigations including assessment of the effectiveness of systems for land application of effluents (3) and movement of nitrates through soils (4, 5). In a typical application the sampler is inserted into a tightly fitting hole bored in the soil profile and then evacuated to a pressure that will withdraw water present in the soil profile under soil-moisture tensions in the range of interest. The water sample collects in the ceramic cup and is withdrawn after removing the bung sealing the tube to which the porous cup is connected.

Porous ceramic cup samplers are often unsuitable for determination of phosphorus concentrations in soil solution because of adsorption/desorption reactions that can cause significant changes in concentrations of this element in sampled solutions. For example, one ceramic cup examined at this laboratory released phosphorus to distilled water passed through it, giving concentrations of ca. 0.025 g/m³ P. A similar but smaller problem may exist for ammonium ion and other cations.

A further disadvantage of some porous cup samplers is associated with the storage of sample in the porous cup, in that

when soil-moisture tensions exceed the applied vacuum, the sample is withdrawn from the sampler into the soil.

An all-plastic suction sampler not subject to significant phosphorus adsorption/desorption problems has been described (6). However, this sampler is subject to entry of air at relatively low soil-moisture tensions and can therefore only be used under conditions of high soil moisture and with constant pumping.

This communication describes a suction sampler constructed from readily available plastic and glass fiber components. Soil waters may be sampled over relatively long periods after a single evacuation of the sampler, and little sample water collected is lost at high soil-moisture tension.

Construction of Sampler

The suction sampler is based on "Swinnex"-type (Millipore Corp.) filter holders, often used for filtration of fluids delivered by syringe. To prepare the filter holder for use in the sampler, the cap is cut so as to remove much of the dome, but leave the sealing shoulder (or O-ring groove in some types) and threaded portion intact (Figure 1a). A polycarbonate (0.4–0.8-μm pore size) or cellulose acetate membrane filter (0.45–5-μm pore size) and a glass fiber prefilter (e.g., Whatman GF/C or GF/F) are fitted to the holder, and a fine-bore sampling tube is attached to the filter support/base. Filter holders for 25-mm membranes are convenient, but other sizes (preferably larger) may be used.

To install the suction sampler, a hole (typically 10 cm diameter) is dug to an appropriate depth in the soil, using an auger or coring tube. Three or four sheets of 9- or 11-cm-diameter Whatman GF/C glass fiber filter are placed in the bottom of the hole, and two or three smaller glass fiber "wick" discs that fit within the hole in the filter holder cap are placed centrally on the sheets (Figure 1b). The filter holder is placed so that the smaller glass fiber "wick" discs contact the prefilter; while the filter holder is held down against the collector sheets, some of the finer material removed from the hole is replaced and tamped lightly to retain the filter holder in place. During back-filling of the hole, it is desirable to include some layers of decreased permeability to encourage the movement of percolating waters out of the disturbed core above the suction sampler and into the surrounding undisturbed profile. Depending on circumstances, this may be achieved by tamping the backfill at intervals or by inserting polythene discs at various depths in the backfill.

The sampling tube passes to the surface and is connected to a sample receiver as illustrated in Figure 2. A Buchner flask (250 or 500 mL) is a convenient sample receiver. A 2-L glass bottle covered with glass fiber-reinforced tape is used as a vacuum reservoir.

The vacuum indicator consists of a small bore (3 mm) glass tube into which a segment of water colored with copper sulfate is introduced. The volume (length) of the air trapped by the water segment is inversely proportional to the pressure in the sampler, and the device provides adequate indication of the sampling vacuum at pressures down to approximately 0.5 bar. In operation the pressure in the sampling system is usually reduced to approximately 0.6 bar, corresponding to soil-moisture tensions above which many soils drain only slowly. This is achieved by evacuating the vacuum reservoir to approximately 0.5 bar in the laboratory, connecting it to the sample receiver in the field, and then releasing the vacuum reservoir clamp.

In practice, collected waters will often stand in the sample receiver for several days, and sample preservation is necessary. Mercuric chloride solution is added to the receiver to give a concentration of 40 g/m^3 HgCl$_2$ when the receiver is full. A number of studies have demonstrated the effectiveness of
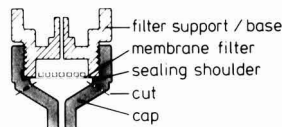
Figure 1a. Preparation of "Swinnex"-type filter holder for suction sampler
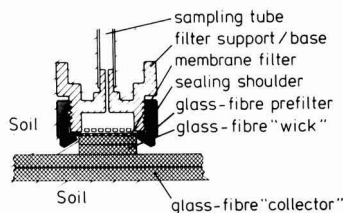
Figure 1b. Installation of suction sampler showing glass-fiber "wick" and "collector" arrangement
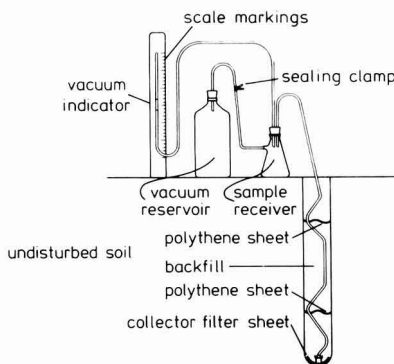
Figure 2. Suction sampler installation, sample receiver, and vacuum indicator

mercuric chloride as a preservative for samples to be analyzed for nitrogen and phosphorus constituents (7–9).

Discussion

Once installed, the sampler withdraws water from the soil profile at a slow rate (ca. 1–15 mL/h) when the soil moisture tension is below the applied vacuum in the sampler. The rate of sample collection appears to be controlled predominantly by the hydraulic conductivity of the soil at the time of sampling. Relatively high sampling rates are obtained under moderately moist soil conditions, when relatively high permeability and low soil moisture tensions would be expected. Low sampling rates occur under drier conditions when permeabilities would decrease and soil moisture tensions increase. When the soil-moisture tension rises above the applied vacuum, only the small sample volume in the sampling tube and filter holder is withdrawn into the soil. So long as the membrane filter is moist, the small pore size and hydrophilic character of the membrane prevent passage of air through the membrane; therefore, no entry of air, and consequent vacuum loss, occurs. When the soil is wetted again, further water is collected.

Under very dry soil conditions the membrane dries out, and rapid vacuum loss occurs. In practice, these suction samplers have been found to retain their vacua for a period of about two weeks after a single thorough soaking of a very freely drained

pumice soil, when fitted with 5-μm pore membranes. Membranes having smaller pores would presumably extend this period.

In early tests the "Swinnex" holders, fitted with a membrane and prefilter, were installed without the glass fiber "wick" and "collector". Under these conditions, rapid blockage of the membrane occurred, and the sampling rate became unacceptably low (ca. 0.2 mL/h). The "wick and collector" system gives capillary contact with a relatively large area of soil; even where the "collector" becomes blocked by fine soil particles, a satisfactory sampling rate is maintained. Obviously, the sampling area and rate can be increased by using a larger "collector" sheet. In general, it is preferable to use a membrane filter having a larger pore size than the effective pore size of the glass fiber "collector", to restrict blockage to the large area of the "collector".

It is possible that microbiological growths could be established on the membrane filters (particularly on cellulose acetate membranes) and limit the useful life of the samplers by filter blockage or breakdown, or sample contamination. Since the polycarbonate membranes are made of a relatively nonbiodegradable material, they are generally preferred.

Wagemann and Graham (10) have shown that cellulose acetate membranes and glass fiber filters cause little, if any, changes in concentration of dissolved constituents during filtration. Tests at this laboratory have shown that polycarbonate membranes (Johns-Manville "Membra-fil") did not add detectable amounts of ammonia, nitrate, organic nitrogen, or total phosphorus to 300 mL of distilled water that passed through the unwashed membranes. When two synthetic samples containing concentrations of NH_3–N, NO_3–N, and organic–N each in the range 0.05–0.33 g/m^3 and total phosphorus in the range 0.005–0.01 g/m^3 were passed through the distilled water-washed membranes, the observed concentration changes did not exceed the experimental errors of the analyses (5% or ±0.005 g/m^3 N for ammonia, 1% or ±0.001 g/m^3 N for nitrate, 10% or ±0.02 g/m^3 for organic–N and ±0.001 g/m^3 for total phosphorus).

In the cellulose acetate membrane samplers used by the author, possible microbiological problems have been minimized by precipitating silver chloride in the prefilters. Two drops of silver nitrate solution (1–5% w/v) were placed on each prefilter, followed by two drops of sodium chloride solution (1–5% w/v). After precipitation of the silver chloride, the filter was washed thoroughly with distilled water. The equilibrium solubility of silver chloride maintains silver concentrations of approximately 0.01–0.1 g/m^3 in solutions, and these concentrations are bactericidal and fungicidal (11). The silver chloride precipitate should be sufficient to be effective during the collection of 10–300 L of sample water, depending on the quantity of the precipitate and the chloride concentrations in the soil. Under conditions of low chloride concentrations in soil water, the use of silver bromide may be preferable. Samplers treated with silver chloride have operated successfully for a period of 11 months at the time of writing.

Laboratory checks have shown that the silver chloride precipitates removed approximately 25% of the ammonia and 75% of the organic nitrogen from a solution containing 0.24 g/m^3 NH_3–N and 1.1 g/m^3 organic–N. However, concentrations of nitrate (0.43 g/m^3 NO_3–N) and reactive phosphorus (0.012 g/m^3) were unchanged by the precipitate. These results suggest that silver chloride is a suitable membrane preservative in nutrient removal studies where nitrate is the predominant nitrogen constituent in soil solution, as often occurs in aerobic soils.

Silver halide precipitates may not be suitable for use under anaerobic soil conditions. A deoxygenated solution containing 50 g/m^3 ferrous ion and 20 g/m^3 manganous ion was passed through a silver chloride-treated filter in the dark, at a rate of 2 mL/h. The chloride concentration in solution increased from 18.5 to 23.5 g/m^3, and the ferrous ion concentration decreased by approximately 10 g/m^3 relative to the same solution that had passed through an identical filtration system in the absence of silver chloride. This suggests that the reaction

$$Fe^{+2} + AgCl \rightarrow Fe^{+3} + Ag + Cl^-$$
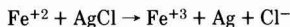
may have occurred. Ferric oxide was observed on the silver chloride precipitate after the experiment, and this would adsorb phosphate and possibly a variety of cations from solution.

The sampling system described has been used successfully at depths of up to 1 m. In principle, it should be suitable for sampling at depths up to about 4 m, but at greater depths a modified sample receiver would need to be buried to overcome the head resulting from drawing up a water column in the sampling tube. A valve system, as described by Wood (12), would be required to withdraw sample from the receiver. For most land disposal systems, monitoring at depths greater than 1 m offers little advantage, since the predominant effluent renovation effect is usually obtained in the upper 0.3 m or so of soil.

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Distribution of Trace Metals During Oil Shale Retorting

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■ Three samples of raw oil shale from the Green River formation of Western Colorado were retorted under conditions simulating a potentially commercial process. The raw shales and all resulting retort products were analyzed for various trace metals in an attempt to ascertain migratory patterns and resulting distributions through the retort system. Some evidence of low-level fluoride, boron, and copper partitioning to the water fraction was found. Similar behavior of arsenic and zinc partitioning to the shale oil product was observed with the remainder of the metals investigated predominantly retained in the spent shale fraction.

Environmental regulatory agencies are concerned with the mobility of trace metals in coal during its burning for electrical power generation and for coal gasification processes (1–3). Therefore, we in the oil shale industry were anxious to investigate the behavior of trace metals during retorting of oil shale, so that effective control measures could be implemented if necessary. Previous studies have been conducted to determine individual elemental concentrations and some group concentrations on various samples of either raw shale or the pyrolyzed solid residue (4–8). None, however, has been concerned with the possible migration of the trace metals from an initial raw shale sample through a simulation of a potentially commercial process. This investigation was initiated to quantify the distribution of trace metals during retorting of oil shale using the Fischer assay method (9). Fischer assay is a laboratory method for retorting oil shale, and it produces a product slate similar to the TOSCO II process (9, 10).

The Fischer assay of oil shale produces four products: spent shale, oil, water, and gas. The raw shale to be retorted and Fischer assay products were examined for trace metals of interest. Analytical data were tabulated for 15 elements as percent recovery of each element and percent distribution in the various Fischer assay products.

Experimental

Fischer Assay Procedure. Fischer assay is a laboratory method that has been used to estimate oil yields for economic evaluation of oil shale reserves for nearly the last three decades (11). At Tosco Corp. this method has been routinely utilized to produce total material balances (9).

In the standard Fischer assay, a known sample weight ($\approx$100 g) of minus 65 mesh oil shale is placed into a 7-oz aluminum can, together with three aluminum heat transfer disks placed at regular intervals in the sample. The container is then placed in a steel retort, and thermocouples are inserted both in the sample and on the periphery of the retort. The sealed retort is placed in a retort heater connecting a tared adapter and centrifuge tube along with a condenser. The system is purged three times with nitrogen to ensure an inert atmosphere. The condenser system is maintained at 32 °F. The retort is heated following a predetermined temperature-time profile and then held at 932 °F for 20 min. Subsequently, the retort is allowed to cool, and the apparatus is disassembled. The volume of water in the receiver is recorded, and a sample of the oil is

removed for specific gravity determination. The spent shale is removed from the retort and weighed. The weight of product oil is obtained by subtracting the weight of water (assuming unit specific gravity) from the total weight of liquid product. The measurement of specific gravity permits calculations of oil yields in gallons per ton of raw shale retorted. In these experiments the product gas was also collected for analysis. The weight of gas produced was calculated from gas chromatographic (GC) analysis.

Sample Description. Three samples of raw shale were tested: Tosco-1-164, Tosco-2-164, and Tosco-3-164. The raw shale samples were composites of representative Mahogany zone oil shale core taken from the Colony mine site in the Piceance Creek Basin of Western Colorado.

Weight percent distributions of Fischer assay products for the composite samples are given in Table I. The water fraction

Table I. Percent Distribution of Oil Shale Samples in Terms of Various Fischer Assay Products

	Sample number		
Product (wt %)	Tosco-1-164	Tosco-2-164	Tosco-3-164
Spent shale	82.98	82.62	83.20
Oil	12.62	13.18	12.82
Water	1.38	1.20	1.10
Gas	3.02	3.00	2.88
	100.00	100.00	100.00

Table II. Sample Preparation Methods

Element	Sample preparation method[a]
Antimony	Combustion and total absorption of all products into acid
Arsenic	Sample digestion in mixture on nitric acid and sulfuric acid (18)
Beryllium	Low-temperature ashing (LTA)
Boron	Samples fused at 900–950 °C with carbonate salts of sodium and potassium, fusion method
Cadmium	Low-temperature ashing (LTA)
Chromium	High-temperature ashing (HTA)
Cobalt	Low-temperature ashing (LTA)
Copper	Low-temperature ashing (LTA)
Fluoride	Samples fused at 900–950 °C with carbonate salts of sodium and potassium, fusion method
Lead	Low-temperature ashing (LTA)
Manganese	Low-temperature ashing (LTA)
Mercury	Nitric:sulfuric acid sample digestion (15)
Molybdenum	Low-temperature ashing (LTA)
Nickel	High-temperature ashing (HTA)
Selenium	Low-temperature ashing (LTA)
Vanadium	Low-temperature ashing (LTA)
Zinc	Low-temperature ashing (LTA)

[a] The numbers in parentheses indicate reference numbers.

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from this retorting process was only about 1.2 wt % of the total products. The small sample size restricted quantitative analysis to only a few elements in the water product. Data for trace metals in retort water have been incorporated from previous analyses (12). The gas fraction of the Fischer assay product slate accounted for about 3 wt % of the products. Analysis of the gas for trace metals was limited to arsenic and mercury.

Sample Preparation. A variety of sample preparation approaches were attempted. Special efforts were directed to analyze as many elements as possible with a single sample preparation technique. Table II summarizes the techniques finally selected for each of the elements included in this study. Water samples were analyzed without additional treatment.

Gases from a typical Fischer assay were absorbed in 100 mL of 1:1 nitric acid:water mixture that was subsequently boiled down, cooled, and diluted to a known volume. Trace metal determinations in gas fractions were carried out using this resulting solution. Only arsenic and mercury could be determined in this fraction. The concentrations of the other elements were below detection limits.

Analytical Approach. Acidic sample solutions of all Fischer assay products and raw shale were used for the determination of antimony, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, nickel, vanadium, and zinc by using an atomic absorption technique (13) (Perkin-Elmer Model 305B). Mercury determinations used a flameless atomic absorption method (14, 15). Boron (16) and molybdenum (17) contents were determined by well-established colorimetric methods. Fluoride analyses were by specific ion-electrode. The Gutzeit method (18) was used for arsenic analyses. Quantitative catalytic reduction of methylene blue (19) by selenium sulfide was utilized for determination of selenium.

Verification of analytical methods was made with a National Bureau of Standards sample No. 1632, "Trace Elements in Coal", which was analyzed concurrently. A comparison showed that the methodology used in these experiments gave acceptable determinations.

Results and Discussion

The antimony concentrations in all the three samples of raw shale, spent shale, oil, and water were less than 4 ppm. These low concentrations did not allow a material balance for this element to be made.

Atomic absorption techniques for arsenic determinations could not be made without interference. Variable results were obtained when evolved arsine gas from a sample solution was trapped in a silver diethyldithiocarbamate (20) solution. The Gutzeit method (18) gave good, reproducible results and was used in this study. Tables III–V show the material balances for all elements examined, including arsenic. Only about 90% of the arsenic could be accounted for. One explanation for arsenic losses could be the formation of gaseous arsine, since retorting is done under reducing conditions. Attempts were made to identify arsenic in the retort gas, resulting in arsenic concentrations of 0.5 ppm by weight of product gas. This low concentration could not account for the missing 10%.

The distribution of beryllium and boron after oil shale retorting is also shown. Two of the three samples analyzed gave a good boron material balance. Only 70% of the boron could be accounted for in the third sample.

A specific ion-electrode was used for fluoride determinations of the samples of raw shale, spent shale, oil, and water. All sample digests were diluted 1:10 with total ionic strength activity buffer solution (available from Orion Research, Stock No. 94-09-09) and measured against standards.

The mercury material balances were variable, ranging from 58 to 196% recovery of the mercury present in raw shale. For this reason mercury data will not be reported in this paper.

Good elemental balances for chromium, cobalt, copper, lead, manganese, nickel, vanadium, and zinc were obtained. The major portion of these trace metals was retained in the spent shale. Sample solutions prepared for chromium and nickel determinations by low-temperature ashing (LTA) gave nonreproducible results. Sample solutions prepared by high-temperature ashing (HTA) were used to obtain the material balances reported.

Conclusions

This program examined the trace metal distribution during retorting of oil shale using the Fischer assay process. The majority of the trace metals are retained by the spent shale. Fluoride (3–4 ppm), boron, and copper (0.2–0.5 ppm) were detected in the water fraction. Chromium, cobalt, manganese, molybdenum, nickel, selenium, and zinc were also found in the retort water fraction at concentrations <0.1 ppm. The shale oil fraction contained arsenic (20–23 ppm) and zinc (1–2 ppm), and beryllium, chromium, cobalt, copper, fluoride, lead, manganese, molybdenum, nickel, and vanadium at less than 1 ppm.

Table III. Trace Metal Balances—Oil Shale Sample No. TOSCO-1-164

Element	Weight (ppm)				% Recovery	% Distribution		
	Raw shale	Spent shale	Oil	Water		Spent shale	Oil	Water
Arsenic	60.0	60.0	21.0	0.0	87.4	95.0	5.0	0.0
Beryllium	1.0	1.2	0.0	0.0	99.6	100.0	0.0	0.0
Boron	63.3	54.0	0.48	0.55	70.9	99.8	0.1	0.0
Cadmium	1.25	1.50	0.00	0.00	99.6	100.0	0.0	0.0
Chromium	41.7	53.8	0.8	0.004	107.3	99.8	0.2	0.0
Cobalt	6.5	8.0	0.26	0.005	102.7	99.5	0.5	0.0
Copper	47.5	55.0	0.25	0.16	96.2	99.9	0.1	0.0
Fluoride	1162.	1352.	<1.0	2.6	96.6	99.9	0.0	0.0
Lead	29.3	34.5	0.14	0.0	97.8	99.9	0.1	0.0
Manganese	230.	275.	0.05	0.02	99.2	99.9	0.0	0.0
Molybdenum	30.0	37.7	0.50	0.006	104.5	99.8	0.2	0.0
Nickel	23.9	27.5	1.4	0.034	96.2	99.2	0.8	0.0
Selenium	14.6	16.7	0.0	0.1	94.9	99.9	0.0	0.0
Vanadium	57.1	70.6	0.48	0.0	102.7	99.9	0.1	0.0
Zinc	65.0	76.0	1.4	0.045	97.3	99.7	0.3	0.0

Table IV. Trace Metal Balances—Oil Shale Sample No. TOSCO-2-164

Element	Weight (ppm)				% Recovery	% Distribution		
	Raw shale	Spent shale	Oil	Water		Spent shale	Oil	Water
Arsenic	60.0	62.0	19.6	0.0	89.6	95.2	4.8	0.0
Beryllium	0.85	1.0	0.0	0.0	97.2	100.0	0.0	0.0
Boron	61.	72.	0.70	0.55	97.6	99.8	0.1	0.0
Cadmium	1.4	1.8	0.0	0.0	106.2	100.0	0.0	0.0
Chromium	45.5	55.0	0.6	0.004	100.0	99.8	0.2	0.0
Cobalt	5.2	7.0	0.2	0.005	111.7	99.5	0.4	0.0
Copper	41.0	48.0	0.0	0.16	96.7	99.9	0.0	0.0
Fluoride	976.	1239.	<1.0	3.0	104.8	99.9	0.0	0.0
Lead	30.3	37.0	0.2	0.0	100.9	99.9	0.1	0.0
Manganese	210.	257.	0.05	0.02	101.1	99.9	0.0	0.0
Molybdenum	37.0	44.5	0.75	0.006	99.6	99.7	0.3	0.0
Nickel	23.9	28.5	1.5	0.034	99.3	99.2	0.8	0.0
Selenium	12.0	13.2	0.0	0.1	90.9	99.9	0.0	0.0
Vanadium	48.9	63.9	0.32	0.0	108.0	99.9	0.1	0.0
Zinc	62.5	80.0	1.7	0.045	106.1	99.7	0.3	0.0

Table V. Trace Metal Balances—Oil Shale Sample No. TOSCO-3-164

Element	Weight (ppm)				% Recovery	% Distribution		
	Raw shale	Spent shale	Oil	Water		Spent shale	Oil	Water
Arsenic	65.0	65.0	23.0	0.0	87.7	94.8	5.2	0.0
Beryllium	0.75	0.95	0.0	0.0	105.4	100.0	0.0	0.0
Boron	97.8	109.9	0.63	0.55	93.6	99.9	0.1	0.0
Cadmium	1.4	1.7	0.0	0.0	101.0	100.0	0.0	0.0
Chromium	42.6	48.9	0.75	0.004	95.7	99.8	0.2	0.0
Cobalt	6.0	7.2	0.2	0.002	100.3	99.6	0.4	0.0
Copper	40.0	46.0	0.2	0.16	95.7	99.9	0.1	0.0
Fluoride	915.	1254.	<1.0	3.5	114.0	99.9	0.0	0.0
Lead	27.6	34.5	0.18	0.0	104.1	99.9	0.1	0.0
Manganese	201.	259.	0.05	0.02	107.2	99.9	0.0	0.0
Molybdenum	32.8	40.0	0.65	0.006	103.5	99.7	0.2	0.0
Nickel	22.4	27.5	2.0	0.034	103.3	98.9	1.1	0.0
Selenium	10.0	11.4	0.0	0.1	94.8	99.9	0.0	0.0
Vanadium	43.5	51.8	0.35	0.0	99.2	99.9	0.1	0.0
Zinc	65.0	80.0	2.3	0.045	102.8	99.5	0.4	0.0

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TCDD Solubilization and Photodecomposition in Aqueous Solutions

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■ The solubilization and photodecomposition of 2,3,7,8-tetrachlorodibenzoparadioxin (TCDD) in aqueous solutions of cationic, anionic, and nonionic surfactants are described. A cationic surfactant, 1-hexadecylpyridinium chloride, acts as an energy transfer agent in the photodecomposition process, thus increasing the TCDD decomposition rate. Samples of material from Seveso's contaminated area are treated according to the proposed decontamination method, and results are discussed.

On July 10, 1976, a wide area near Seveso, Italy, was contaminated by an extremely toxic fallout consisting of 2,3,7,8-tetrachlorodibenzoparadioxin (TCDD) in a chemical mixture of other chloroorganic substances (1, 2).

The decontamination of soil, buildings, personal belongings, and other different materials from TCDD is difficult, not only because of the extremely high toxicity of such a substance, but also because of the peculiarities of this product, which is chemically refractory and insoluble in water. Although much work has been done in this particular field, only three different techniques for decontamination from this kind of pollutant have been proposed: incineration, chlorinolysis, and soil biodegradation (3). Although the first method is undoubtedly the safest as far as complete TCDD destruction is concerned, the use of very high temperatures (~1000 °C) does not allow any recovery of contaminated materials. Chlorinolysis is also a destructive method involving high chlorine pressures and temperatures for conversion of organic compounds to carbon tetrachloride. The third option appears to be the most promising technique; however, it is now feasible only for cultivable soils.

Therefore, we are seeking an alternative decontamination method that is simple, inexpensive, and effective. Our method would allow the recovery of contaminated materials treated with aqueous solutions, and the photodecomposition of both TCDD and the solubilizing agent. To date, photodecomposition is the most rapid method of TCDD degradation. This is achieved by an energy transfer mechanism. Micellar solubilization of TCDD in the water medium has been studied, and significant results have been obtained. Among the different surfactants used for these experiments, 1-hexadecylpyridinium chloride (CPC) appears to be the most effective because of enhanced solubilizing properties and faster photochemical degradation of TCDD in this micellar solution.

Materials and Methods

A pure sample of TCDD was supplied by Rochester University, New York, to Istituto Superiore di Sanità, Rome, Italy. All surfactants and reagents were of analytical grade. UV measurements were carried out with a Beckman DU-2 spectrophotometer, using quartz cells having a path length of 10 mm. A Desaga Uvis UV lamp (254–356 nm) was used for photodecomposition experiments. (Since the relative effect of the solubilizing solution was the aim of photochemical degradation studies, no absolute value of light intensity was determined). Isolation and identification of TCDD were performed according to the method proposed by Camoni's research team of the Istituto Superiore di Sanità, Rome (4); and quantitative determinations were carried out by gas chromatography–mass spectrometry techniques using a Hewlett-Packard 5980 A instrument (GC operating condi-

tions: 4-ft column 3% OV-17 on 100/120 chromosorb W-HP; inlet temperature, 300 °C; column temperature, 240 °C; separator temperature, 240 °C).

For TCDD solubilization from soil, experiments were performed with 90-g homogeneous samples from Seveso's contaminated area. Samples were treated twice with 300 mL of solubilizing solution and then three times with the same amount of water to remove the surfactant. The residues were finally extracted with methanol and benzene, and TCDD was determined in the obtained solutions. Untreated contaminated soil samples were used as reference standards. These experiments were set up with the following solvent solutions: 0.05 M sodium dodecyl sulfate (SDS), 0.05 M 1-hexadecylpyridinium chloride, 2% w/v polyoxyethylene sorbitan monooleate (Tween 80), and methanol. Parallel solubilization studies were carried out on pure TCDD: samples of 5 and 12 mL of a benzenic solution of TCDD (8.18 μg/mL) were vacuum evaporated, and the residues were treated, respectively, with 4 mL of the test solvent solution (0.02, 0.05, and 0.08 M SDS; 0.02, 0.05, and 0.08 M CPC; 0.02, 0.05, and 0.08 M hexadecyltrimethylammonium bromide CTAB; 1, 2, and 3% w/v Tween 80) and kept in a dark place at room temperature and checked periodically for UV absorbance until equilibrium was reached (48 h); methanol was used as a reference solvent for these dissolution tests.

Results and Discussion

Results obtained from solubilization experiments on soil and pure TCDD are reported in Table I. In soil experiments, CPC appears to be the best solubilizing aqueous agent among the other surfactant solutions. With pure TCDD only slight differences can be observed; nevertheless, good qualitative agreement can be observed for the two sets of experiments. The more effective solubilization of the pollutant in the cationic detergent (more evident for experiments on soil) can be related to the more compact structure of cationic detergent micelles when compared to the anionic ones (5) and to the nature of TCDD molecules. But the main and more interesting differences among the micellar solutions of the tested surfactants are related to TCDD decomposition; in fact, micellar solutions of TCDD are stable when stored in the dark, whereas solubilized TCDD can be decomposed when exposed to sunlight or to UV irradiation.

Photodecomposition data for different solutions are given in Figure 1 where the percentage of undecomposed TCDD in solution is plotted as a function of time of irradiation. Here the rate of photodecomposition in CPC micellar solution is evident. In our experimental conditions the time required for total TCDD decomposition is only 4 h for CPC solutions, whereas 8 h are required for SDS solutions and about 18 h when the best solvent (MeOH) is used. TCDD photodegradation can be spectrophotometrically observed. The absorption maximum of TCDD rapidly disappears after UV exposure, and at the same time a new maximum at 278 nm can be observed. This is coincident with the absorption of 2-phenoxyphenol, the last step photodegradation product of TCDD (1).

An appreciable turbidity was observed when 98.16-μg samples were used for dissolution tests. This can be related to the properties of surfactants that are both solubilizing and wetting agents. Therefore, substances like TCDD, which are water insoluble, may enhance their solubility when taken up

Table I. Solubilization of TCDD

	Experiments on soil[a]		Experiments on pure TCDD[b]			
Solubilizer	Surfactant concn	Solubilized TCDD (%)	Surfactant concn	Solubilized TCDD (%)	Surfactant concn	Solubilized TCDD (%)
MeOH	. . .	97.5	. . .	100	. . .	100
CPC	0.05 M	75.0	0.02 M	75	0.05 M	78
SDS	0.05 M	60.0	0.02 M	71	0.05 M	75
Tween 80	2% w/v	45.0	1% w/v	72	2% w/v	73

[a] Each 90-g sample contained initially 6.3 μg of TCDD. [b] Initial amount of TCDD: 40.90 μg. CTAB solubilizing capacity is between that of the anionic surfactant and CPC.
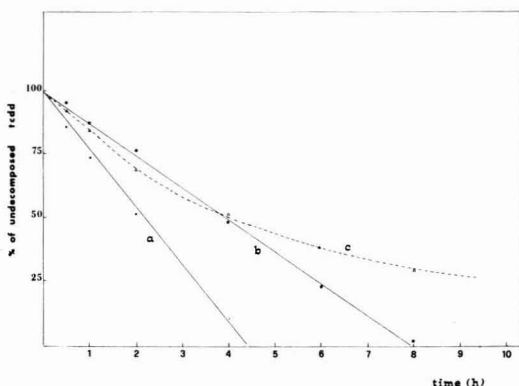
Figure 1. Degradation of TCDD as a function of time in different solvents

Plot a: 0.02 M CPC solution; plot b: 0.02 M SDS solution; plot c: methanol. Initial concentration of TCDD: 8.0 μg/mL

by micelles and can also be more easily dispersed because of the interaction with surfactant monomers. Furthermore, when such turbid micellar solutions of TCDD are exposed to UV irradiation, they clear quite rapidly. Such effects can be related to the observation that only TCDD in solution can be decomposed by light (6); therefore, as dioxin degradation proceeds, more substance is solubilized within surfactant micelles.

The reason for the faster photodecomposition of TCDD in CPC micellar solution is not completely known at the present time; however, we have observed that the molecular structure of CPC decomposes after UV exposure, and a new sharp absorption maximum appears at 374 nm. Also, when TCDD is enclosed in micelles, degradation of CPC is sharply reduced.

This can be interpreted in terms of a stabilizing interaction between the surfactant and TCDD molecules; it appears reasonable to suppose that π-π interactions between the pyridine ring and aromatic TCDD system take place, leading to an energy transfer from one molecule to the other, which enhances the photodecomposition rate of "bound" TCDD. Further investigation on this reaction mechanism is still in progress in our laboratory.

In conclusion, this method seems to be appropriate and effective for the decontamination of buildings, furniture, and personal belongings from TCDD. Its application to soil decontamination should involve the use of the same techniques applied in mineral dressing procedures and, if requested, in repeated "washing" treatments.

A worthwhile feature of this method is the possibility of a rapid photodecomposition of an aqueous detergent solution with the simultaneous degradation of both the solubilizing and the polluting agents.

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Characterization of Contaminant Concentrations in Enclosed Spaces

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■ Generalized equations for contaminant concentration buildup and decay are developed for an enclosed, ventilated space. The generalized equations take local mixing factors and source characteristics into account, and the illustrative cases show that the usual method of estimation can be totally erroneous.

The estimation of transient and equilibrium concentrations of contaminants in enclosed, ventilated spaces is important for both personal comfort and safety of the occupants. Based on the solution of the mass balance equation, if the air in the room under consideration is well mixed, the decrease of pollutant after a single release will be an exponential decay. The nonideality of mixing is usually accounted for by the utilization of a mixing factor, k. The values of k are normally estimated to be from $1/3$ to $1/10$ for small spaces (1–3), and it is possibly lower for very large spaces. The experimental verification of the concept of the mixing factor in the exponential decay has been excellent. The traditional physical meaning attached to the mixing factor is the ratio of the characteristic time for one theoretical air change to the characteristic time for one actual air change as calculated from the experimental results. This concept can lead to theoretical difficulties and indeed to erroneous results if continuous or cyclic sources are present in the room under consideration. Instead of the above-mentioned, a physical description of the mixing factor may be proposed without the alteration of its numerical value. In this paper such a definition will be proposed.

In addition, if the room contains multiple sources that operate periodically, then the usual estimation procedure is to equate the generation rate to a single, continuous source by averaging the emission from all of the sources. In this procedure, two important facets of the exposure to the contaminant are overlooked. The procedure does not indicate what the peak concentrations might be; further, the equilibrium concentration calculated is not representative of the mean concentration as will be shown in this paper.

Theoretical Considerations

Consider a room with volume V, a ventilation air flow rate of Q, and an initial concentration of a contaminant C_{in}. The concentration of the contaminant is described by the mass balance, assuming ideally well-mixed conditions and no reaction:

$$V \frac{dC}{dt} = -CQ \qquad (1)$$

the solution of Equation 1 is:

$$C = C_{in} \exp\left(-\frac{Qt}{V}\right) \qquad (2)$$

The factor in the exponent that describes the theoretical characteristic time for one air change is V/Q, and traditionally the mixing factor, k, is described as:

$$k = \frac{V/Q}{t_{\exp}} \qquad (3)$$

With the use of this factor, Equation 2 becomes:

$$C = C_{in} \exp\left(-\frac{kQt}{V}\right) \qquad (4)$$

Note that Equation 4 will satisfy the mass balance only for $k = 1$ or under ideally mixed conditions. Now, let k be defined as the portion of the ventilation air flow, Q, that is completely mixed with the room air. In other words, we imagine that the k fraction of the air flowing in will be totally replaced by the room air, and the remainder is totally unmixed. Under this condition the mass balance is:

$$V \frac{dC}{dt} = -kQC \qquad (5)$$

and the solution of Equation 5 is identical to Equation 4:

$$C = C_{in} \exp\left(-\frac{kQt}{V}\right) \qquad (6)$$

The numerical value of k given in the definition above is identical to the experimentally determined value, and the final equation satisfies the mass balance for all values of k. Now we can generalize this concept to include any number of sources in the room.

In the development of the general equation that describes the concentration of a specific contaminant in a room of volume V and for a ventilation volumetric flow rate of Q, the following assumptions will be made. It will be assumed that there are a number of sources of the contaminant in question, and that each source will have a time dependent generation rate, G_{ij}, for the ith time interval for the jth source. In reality the generation rate for a given source in a given time interval is not constant; however, the function that describes the generation rate is usually not known and is difficult to obtain. Therefore, the generation rate, G_{ij}, will be assumed to be constant over a given interval, i, and for a given source, j. The air supply system that defines the ventilation of the room in question may have a portion of the air supplied from ambient air and a portion recirculated. The recirculated portion may pass through a collector. Therefore, it will be assumed that the ventilation flow rate is composed of a portion that is recirculated, Q_R, and a portion that is supplied from the outdoor air, Q_o. It will be further assumed that a collection device of efficiency E is present in the recirculation loop, a concentration of C_o of the contaminant is present in the makeup air. The room has an initial concentration of C_{in} and a known mixing factor k.

It is possible to develop the controlling equations for a single periodic source in the room and then to generalize it to any number of sources periodic, or otherwise, in the final form. Consider a source with generation rates G_i for time intervals i and let the time interval duration J_i be such that during α_i fraction there is generation and $1 - \alpha_i$ fraction inactivity. The mass balance for the room is:

$$V \frac{dC}{dt} = G(t) - kQ_o C - kQ_R EC + kQ_o C_o \qquad (7)$$

Equation 7 does not include a reactive term, i.e., it is tacitly assumed that the contaminant is conservative. The solution

of Equation 7 for completion of n cycles may be shown to be:

$$C(t) = C_{in} \exp(-\beta_o t) + \frac{Q_o C_o}{Q_o + EQ_R} [1 - \exp(-\beta_o t)]$$
$$+ \sum_{1}^{n} B_i(P_i + R_i) \quad (8)$$

where

$$\beta_i = \frac{k_i(Q_o + \eta Q_R)}{V} \quad (9)$$

$$P_i = 1 - \exp(-\beta_i \alpha_i J_i) \quad (10)$$

$$R_i = \exp\left[-\beta_i \left(t - \sum_{1}^{i-1} J_i\right)\right] [1 - \exp(-\beta_i \alpha_i)] \quad (11)$$

$$B_i = \frac{G_i}{k_i(Q_o + EQ_R)} \quad (12)$$

In Equation 8 the local mixing is adjusted by the definition of a mixing factor k_i for each cycle and a mixing factor for the entire space, k_o, where the source has no contribution. If a number of sources are present in the room then each source, j, will have n_j cycles over the time period, t; hence:

$$C(t) = C_{in} \exp(-\beta_o t) + \frac{Q_o C_o}{Q_o + EQ_R} [1 - \exp(-\beta_o t)]$$
$$+ \sum_{j=1}^{m} \sum_{i=1}^{n_j} B_{ij} R_{ij} + B_{ij} P_{ij} \quad (13)$$

In Equation 13 the double subscripted parameters contain k_{ij}, α_{ij}, G_{ij}, and J_{ij} and the definitions of these parameters are obtained by substituting the double subscripted variables for the single subscripted variables in Equations 9–12. The numerical evaluation of Equation 13 involves the knowledge of the parameters of each individual cycle for each individual source. However, in practice, this is neither tractable nor necessary. What is of importance is an estimate of the average concentration and an estimate of the peak concentration. The average can be obtained for a time $\theta > 0$ by:

$$C_a(\theta) = \frac{1}{\theta} \int_0^\theta c(t) dt = C_{in} \left[\frac{1 - \exp(-\beta_o \theta)}{\beta_o \theta}\right]$$
$$+ \left[1 - \frac{1 - \exp(-\beta_o \theta)}{\beta_o \theta}\right] \frac{C_o Q_o}{Q_o + EQ_R}$$
$$+ \sum_{j=1}^{m} \sum_{i=1}^{n_j} B_{ij} \frac{\alpha_i J_i}{\theta} - \frac{1 - \exp(-\beta_{ij} \alpha_{ij} J_{ij})}{\beta_{ij} \theta}$$
$$+ \frac{[1 - \exp(-\beta_{ij} \alpha_{ij} J_{ij})]}{\beta_{ij} \theta}$$
$$\times \left\{1 - \exp\left[-\beta_{ij}\left(t - \sum_1^{i-1} J_{ij} - \alpha_{ij}\right)\right]\right\} \quad (14)$$

Now Equation 14 may be simplified to a tractable form (albeit approximate) by the assumption that the properties of each cycle may be satisfactorily expressed with an average value for each source. Since

$$n_j J_j = \theta \quad (15)$$

then, it may be shown that for $\theta > J$:

$$C_a(\theta) = C_{in} \left[\frac{1 - \exp(-\beta_o \theta)}{\beta_o \theta}\right] + \frac{Q_o C_o}{k_o(Q_o + EQ_R)}$$
$$\times \left[1 - \frac{1 - \exp(-\beta_o \theta)}{\beta_o \theta}\right] + \sum_{j=1}^{m} B_j \left\{\alpha_j - \right.$$
$$\frac{[1 - \exp(-\beta_j \alpha_j J_j)][\exp[-\beta_j(1 - \alpha_j)J_j]][1 - \exp(-\beta_j \theta)]}{\beta_j \theta [1 - \exp(-\beta_j J_j)]}$$
$$(16)$$

Similarly,

$$C_{\max}(\theta) = \frac{Q_o C_o}{Q_o + EQ_R}$$
$$+ \sum_{j=1}^{m} \beta_j \left[\frac{1 - \exp(-\beta_j \alpha_j J_j)}{1 - \exp(-\beta_j J_j)}\right] [1 - \exp(-\beta_o \theta)] \quad (17)$$

Equations 16 and 17 can be further reduced for conditions when $\beta_j \theta > 200 \alpha_j$ and $\beta_j \theta > 20$. This condition is sufficiently near the equilibrium value where $\beta_j \theta \rightarrow \infty$ so that the deviation from the equilibrium is less than 5%:

$$C_{a(\text{Equil})} = \frac{Q_o C_o}{Q_o + EQ_R} + \sum_{j=1}^{m} B_j \alpha_j \quad (18)$$

and

$$C_{\max(\text{Equil})} = \frac{Q_o C_o}{Q_o + EQ_R} + \sum_{j=1}^{m} B_j \left[\frac{1 - \exp(-\beta_j \alpha_j J_j)}{1 - \exp(-\beta_j J_j)}\right] \quad (19)$$

Discussion of Results

Note that in the expressions developed above, one has a complete generality: $\alpha_j = 0$ implies that there is no emission from the source; $\alpha_j = 1$ implies that the source is continuous. Furthermore, the β values are locally calculated for each source. The local calculation of the parameters for each source is especially important for large rooms. This can be illustrated by a simple, realistic example: a person who does not wish to be exposed to intense tobacco smoke from a smoker can move away from the smoker. This is equivalent to the nonsmoker's choosing a place with a higher k value with respect to the nearest smoker.

The equations developed in this paper can now be compared to the usual expression for the contaminant concentration. In the equation generally used, all of the sources are assigned to one overall generation factor, and the equation does not involve the k factor in any place besides the decay exponent (4):

$$C(t) = C_{in} (-\beta t) + \frac{Q_o C_o t G}{Q_o + ER} [1 - \exp(-\beta t)] \quad (20)$$

This equation implies that the equilibrium concentration at any place in the room will be the same regardless of the mixing factor. This condition is erroneous because if it is true, then the mixing factor must be uniform, i.e., $k = 1$. As a simple illustration, the case of smoker and nonsmoker can be used again. Since both the smoker and nonsmoker are in the same room by Equation 20, both the smoker and the nonsmoker are exposed to the same concentration. This is obviously incorrect; for the smoker, k_i is much lower than for the nonsmoker. Another extreme example can be given by a warm room where cold air intake and exhaust are located very near the floor; the mixing under this circumstance will be very poor, and in fact the equilibrium concentration of a contaminant emitting from a high source will be quite high. According to Equation 20, relocation of the intake and exhaust and utilization of proper diffusers to mix the air will result in the same equilibrium concentration. This again is obviously incorrect. Furthermore, Equation 20 will result in lower values than the equations developed here, hence leading to optimistic estimates that can prove to be hazardous to the health of the occupants.

Nomenclature

$$B = \frac{G}{K(Q_o + EQ_R)}$$

C = contaminant concentration
C_a = average contaminant concentration
C_{in} = initial contaminant concentration

C_o = contaminant concentration in the incoming air
E = efficiency of the collector
G_{ij} = generation rate of jth source at ith interval J_i = duration of ith interval
$P = 1 - \exp(-\beta\alpha J)$
Q = volumetric flow rate
Q_o = volumetric flow rate of makeup air
Q_R = volumetric flow rate of recirculated air
V = room volume
K = mixing factor
M = total number of sources
n_j = total number of cycles for jth source over θ time
t = time

Greek Letters

α = fraction of time for generation

β = decay coefficient
θ = averaging time

Subscripts

i = time interval index
j = source index

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CORRESPONDENCE

SIR: Studies of problems in the area of water quality control, the application of geothermal energy, the desalinization of water, sewage treatment, and bioengineering all must treat aqueous solutions containing ionic species. An enormous need for reliable quantitative data on ionic equilibria has become very apparent in recent years, particularly with the development of large scale models that attempt to simulate complex aqueous ecosystems (1).

The purposes of this letter are to point out that many equilibrium constants involving ions in solution can be extracted from existing tables of evaluated thermochemical data, and to provide three tables of data applicable to studies of the water environment. The tables give thermodynamic equilibrium constants for the association of alkaline earth cations with various ligands and the thermodynamic properties of a number of other species. From the latter the user can construct equilibrium constants pertinent to specific studies. The method used to obtain the equilibrium constants is summarized as an aid to the user.

Two comprehensive series of thermochemical tables contain the data of interest. These are "Selected Values of Chemical Thermodynamic Properties" (2–7) issued by the U.S. National Bureau of Standards and "Termicheskie Konstanty Veschestv" (8) issued by the Institute of High Temperatures of the Academy of Sciences of the USSR. Both tabulate thermodynamic properties of individual substances from which those for particular processes can be derived. The properties of interest that are tabulated here are the Gibbs (free) energy of formation of a substance from the elements, $\Delta G_f{}^\circ$, the enthalpy of formation, $\Delta H_f{}^\circ$, the absolute entropy, S°, and the heat capacity, C_p, all at 298.15 K. Typical defining reactions for formation processes of a salt and of an ion are, respectively:

$$2\text{Na(c)} + \text{S(c)} + 2\text{O}_2\text{(g)} = \text{Na}_2\text{SO}_4\text{(c)}$$

$$\text{Ca(c)} + 2\text{H}^+\text{(aq)} = \text{Ca}^{2+}\text{(aq)} + \text{H}_2\text{(g)}$$
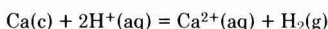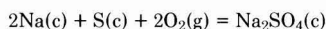
where (c) is condensed phase, (aq) is aqueous, and (g) is gas. The advantage of using either of these tables as a starting point for the construction of equilibrium constants lies in the fact that the data therein are evaluated and self-consistent. In other words, experts have decided which experimental data are likely to be most reliable and have arranged them on a common scale. This relieves the user of the necessity of deciding which of several often discordant results should be used.

Equilibrium constants are determined as follows. The standard Gibbs energy change accompanying a chemical process, ΔG°, is obtained by the relationship:

$$\Delta G^\circ = \sum_i \nu_i (\Delta G_f{}^\circ)_i - \sum_i \nu_i (\Delta G_f{}^\circ)_i \qquad (1)$$
$$\text{products} \qquad \text{reactants}$$

where the superscript ° refers to standard state conditions, the f identifies the formation process, and the ν_i's are the stoichiometric coefficients of the reaction. The standard Gibbs energy change is directly related to the equilibrium constant, K, via

$$\Delta G^\circ = -RT \ln K \qquad (2)$$

where R is the gas constant, T is the absolute temperature in Kelvins, and ln denotes the logarithm to the base e.

As an illustration, the equilibrium constant is calculated for the process forming an ion pair, MgOH^+, in aqueous solution, at 298.15 K:

$$\text{Mg}^{2+} + \text{OH}^- \rightleftharpoons \text{MgOH}^+ \qquad (3)$$

The data needed are listed in Tables I–III and can be obtained from refs. 2–7. Table I presents the data for selected species of alkaline earth salts, and Tables II and III are provided as a ready reference for Gibbs energies of formation for selected cations (Table II) and anions (Table III). Table I lists various common dissolved species, thought to exist in the aqueous environment, the formula weight, the $\sum \nu_i (\Delta G_f)_i$ for the product (ion pair) and the reactants (individual ions), and the ΔG° for the reaction (see Equation 1). All thermodynamic functions are expressed both in kcal·mol^{-1} and in kJ·mol^{-1}. Also listed are the association equilibrium constants and their logarithms to the base 10. Tables II and III simply provide the $\Delta G_f{}^\circ$ of the ions which are used to derive ΔG° for a reaction by means of Equation 1. Tables II and III provide a selection of ions found scattered throughout the Tech. Note 270-series (refs. 2–7) and may be used in conjunction with this 270-series, thus eliminating the need for a comprehensive search for individual, simple ionic species.

For Reaction 3 using Equation 1:

$$\Delta G^\circ = \Delta G_f{}^\circ(\text{MgOH}^+) - [\Delta G_f{}^\circ(\text{Mg}^{2+}) + \Delta G_f{}^\circ(\text{OH}^-)] \qquad (4)$$

Thus,

$$\Delta G^\circ = -149.8 - (-108.7 - 37.594)$$
$$\text{and } \Delta G^\circ = -3.506 \text{ kcal} \cdot \text{mol}^{-1} \qquad (5)$$

Then, from Equations 2 and 3 and the definition of the thermodynamic equilibrium constant, K

Table I. Equilibrium (Association) Constants for Aqueous Species of Alkaline Earth Salts[a]

Ionic species	Formula wt/g·mol⁻¹		kcal·mol⁻¹ $\Delta G_f°$ (Ion pair)	$\Delta G_f°$ (Ions)	$\Delta G°$ (reaction)	kJ·mol⁻¹ $\Delta G_f°$ (Ion pair)	$\Delta G_f°$ (Ions)	$\Delta G°$ (reaction)	$\log_{10} K$	K_A
$Be_3(OH)_3^{3+}$		78.0587	−430.60	−385.03	−45.57	−1801.63	−1610.97	−190.66	33.4037	2.53 E + 33
$MgOH^+$		41.3194	−149.80*	−146.29	−3.51	−626.76	−612.09	−14.67	2.5700	3.72 E + 02
$MgIO_3^+$	Undissoc[b]	199.2146	−140.30	−139.30	−1.00	−587.02	−582.83	−4.18	0.7330	5.41 E + 00
$MgSO_4$	Undissoc	120.3736	−289.74	−286.70	−3.04	−1212.27	−1199.55	−12.72	2.2284	1.69 E + 02
$MgP_2O_7^{2-}$		198.2554	−577.20	−567.40	−9.80	−2415.00	−2374.00	−41.00	7.1836	1.53 E + 07
$Mg(C_2O_4)_2^{2-}$		200.3518	−436.90	−430.90	−6.00	−1827.99	−1802.89	−25.10	4.3981	2.50 E + 04
$MgHCO_3^+$	Undissoc	85.3293	−250.30	−249.00	−1.30	−1047.26	−1041.82	−5.44	0.9529	8.97 E + 00
$Mg(C_2H_3O_2)^+$		83.3570	−198.70	−197.00	−1.70	−831.36	−824.25	−7.11	1.2461	1.76 E + 01
$Mg(NH_2CH_2COO)^+$	Undissoc	98.3717	−188.70	−184.00	−4.70	−789.52	−769.86	−19.66	3.4452	2.79 E + 03
$MgFe(CN)_6^-$	Undissoc	236.2661	−286.80	−283.00	−3.80	−1199.97	−1184.07	−15.90	2.7855	6.10 E + 02
$MgFe(CN)_6^{2-}$	Undissoc	236.2661	−280.00	−274.79	−5.21	−1171.52	−1149.72	−21.80	3.8190	6.59 E + 03
$CaOH^+$		57.0874	−171.70	−169.90	−1.80	−718.39	−710.86	−7.53	1.3194	2.09 E + 01
$Ca(C_2H_3O_2)^+$		99.125	−222.10	−220.60	−1.50	−929.27	−922.99	−6.28	1.0995	1.26 E + 01
$CaFe(CN)_6^-$	Undissoc	252.034	38.10	42.00	−3.90	159.41	175.73	−16.32	2.8588	7.22 E + 02
$CaFe(CN)_6^{2-}$	Undissoc	252.034	28.60	33.79	−5.19	119.66	141.38	−21.71	3.8044	6.37 E + 03
$Ca_2Fe(CN)_6$	Undissoc	292.114	−105.60	−98.51	−7.09	−441.83	−412.17	−29.66	5.1971	1.57 E + 05
$SrOH^+$		104.6274	−172.40	−171.30	−1.10	−721.32	−716.72	−4.60	0.8063	6.40 E + 00
$Sr(C_2H_3O_2)^+$		146.665	−223.50	−222.00	−1.50	−935.12	−928.85	−6.28	1.0995	1.26 E + 01
$SrFe(CN)_6^-$		299.574	36.70	40.59	−3.89	153.55	169.83	−16.28	2.8514	7.10 E + 02
$BaOH^+$		154.3474	−174.60	−171.60	−3.00	−730.53	−717.97	−12.55	2.1991	1.58 E + 02
$BaNO_3^+$		199.345	−159.35	−160.63	1.28	−666.72	−672.08	5.36	−0.9383	1.15 E − 01

[a] All data refer to standard state, $m = 1$ mol·kg⁻¹. 1 Joule = 4.184 calories. [b] Undissoc = not dissociated into ions, i.e., an ion pair. The ion pair is not a precipitate but exists in solution as a separate and distinct species.

$$\ln K = \frac{-\Delta G°}{RT} = \ln \frac{a(MgOH^+)}{a(Mg^{2+})a(OH^-)} \tag{6}$$

where the a's are the thermodynamic activities of the ionic species.

The numerical value of K is obtained by converting $\Delta G°$ to SI units (J·mol⁻¹) and introducing the value of the gas constant, $R = 8.3143$ J·mol⁻¹·K⁻¹, used in the construction of the NBS tables. Therefore,

$$\ln K_A =$$

$$\frac{-(-3.506 \text{ kcal} \cdot \text{mol}^{-1} \times 4.184 \text{ kJ} \cdot \text{kcal}^{-1} \times 1000 \text{ J} \cdot \text{kJ}^{-1})}{(8.3143 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298.15 \text{ K})} \tag{7}$$

$$\ln K_A = +5.9176 \quad \text{and} \quad K_A = +371.5$$

or in terms of dissociation, where

$$K_D = 1/K_A \quad \text{and} \quad K_D = 2.69 \times 10^{-3} \tag{8}$$

Another example is given as an illustration using the reaction:

$$Mg^{2+} + 2C_2O_4^{2-} \rightleftharpoons Mg(C_2O_4)_2^{2-} \tag{9}$$

$$\Delta G° = -436.9 - [-108.7 + 2 \times (-161.1)]$$
$$\Delta G° = -6.000 \text{ kcal} \cdot \text{mol}^{-1}$$
$$\ln K_A = 10.127 \tag{10}$$
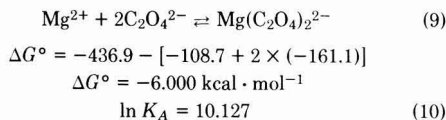
therefore,

$$K_A = 2.501 \times 10^4 \quad \text{or } K_D = 4.00 \times 10^{-5} \tag{11}$$

Several features of this scheme of calculations should be noted. First, the $\Delta G_f°$ values used are those for the substances each in the "hypothetical ideal solution standard state of unit molality". Such data are so labeled in refs. 2–7. Second, the value of R used above differs slightly from the most recently accepted value, 8.31441 J·mol⁻¹ K⁻¹ (9), but is the value used consistently during the construction of the NBS Tech. Note 270 tables over the past decade. The distinction is unlikely to

be important in the calculation of the properties of ions in solution. Third, the derived K, in general, is the thermodynamic equilibrium constant which is expressed on the activity scale, *not in concentrations* (e.g., molarity or molality) of species. In dilute solutions the concentration approaches the activity; therefore, in solutions of less than about 0.05 mol·kg⁻¹, ordinarily concentrations may be used as an estimate if activities are not known.

The equilibrium constants calculated above apply at the reference temperature 298.15 K (25 °C). They may be corrected to another temperature using the following relation

$$\frac{d \ln K}{dT} = \frac{\Delta H°(T)}{RT^2} \tag{12}$$

where, if one can regard $\Delta C_p°$ as a constant (approximately independent of temperature), $\Delta H°$ for the process is:

$$\Delta H°(T) = \Delta H°(298.15) + \Delta C_p°(T - 298.15) \tag{13}$$

and $\Delta H°(298.15)$ and a value of $\Delta C_p°$, can be constructed from refs. 2–7 in a manner analogous to that explained for $\Delta G°$. When the second term on the right-hand side of Equation 13 is small, the approximate formula

$$\ln \left[\frac{K(T_2)}{K(T_1)}\right] = \frac{\Delta H°(T)[T_2 - T_1]}{RT_1T_2} \tag{14}$$

may be used, where T_2 represents the final temperature and T_1, the initial temperature, both in Kelvins. Normally, this will be sufficient for most water environment problems.

The equilibrium constants described above should be exact and sufficient for applications in which activities of dissolved species are important or to be calculated. But when it is desired to calculate the molalities of species, additional steps are necessary. These involve interpretation of activities in terms of activity coefficients, γ, which are functions of molality. The procedure is complicated (although well defined) because only mean ionic activity coefficients for salts are measurable, whereas absolute activity coefficients for individual ions are not.

Table II. Gibbs Energies of Formation for Selected Aqueous Cationic Species [a]

Cation	$\Delta G_f°$ /kcal·mol^{-1}	Cation	$\Delta G_f°$ /kcal·mol^{-1}
Hg^{2+}	39.30	Be^{2+}	-90.75
Hg^{2+}	36.70	Ca^{2+}	-132.30
Cu^{2+}	15.66	Ba^{2+}	-134.02
Ag^+	18.433	Mg^{2+}	-108.7
Ni^{2+}	-10.9	Sr^{2+}	-133.71
Co^{2+}	-13.0		
Fe^{3+}	-1.1	Bi^{3+}	19.8
Fe^{2+}	-18.85	SbO^+	-42.33
Pd^{2+}	42.2	Sn^{2+}(in aq HCl)	-6.5
Pt^{2+}	44.4	Sn^{4+}(in aq HCl)	0.6
Mn^{2+}	-54.5	Pb^{2+}	-5.83
Cr^{2+}	...	Al^{3+}	$-116.$
H^+	0.0	Tl^+	-7.74
		Zn^{2+}	-35.14
		Cd^{2+}	-18.542

[a] All data refer to 298.15 K and a hypothetical standard state of $m = 1$ mol·kg^{-1}. 4.184 Calories = 1 joule.

Table III. Gibbs Energies of Formation for Selected Aqueous Anionic Species [a]

Anion	$\Delta G_f°$/kcal·mol^{-1}	Anion	$\Delta G_f°$/kcal·mol^{-1}
CrO_4^{2-}	-173.96		
$Cr_2O_7^{2-}$	-311.0	N_3^-	$+83.2$
OH^-	-37.594	NO_3^-	-26.61
F^-	-66.64	PO_4^{3-}	-243.7
Cl^-	-31.372	HPO_3^{2-}	...
ClO_2^-	$+4.1$	HPO_4^{2-}	-260.34
ClO_3^-	-0.8	$H_2PO_4^-$	-260.17
Br^-	-24.85	$HP_2O_7^{3-}$	-471.4
BrO_3^-	0.4	$H_2P_2O_7^{2-}$	-480.5
I^-	-12.33	CN^-	$+41.2$
IO_3^-	-30.6	CNS^-	-22.15
S^{2-}	$+20.5$	$C_2O_4^{2-}$	-161.1
SO_3^{2-}	-116.3	CH_3COO^-	-88.29
SO_4^{2-}	-177.97	$NH_2CH_2COO^-$	-75.278
		$HPbO_2^-$	-80.90
$S_2O_3^{2-}$	...	$B_4O_7^{2-}$	-622.6
		$Fe(CN)_6^{3-}$	$+174.3$
AsO_4^{3-}	$-155.$	$Fe(CN)_6^{2-}$	$+166.09$
		HCO_3^-	-140.26
		CO_3^{2-}	-126.17

[a] All data refer to 298.15 K and a hypothetical standard state of $m = 1$ mol·kg^{-1}. 4.184 Calories = 1 joule.

The activity coefficient, γ, of any species is defined by

$$a_i = m_i \gamma_i \qquad (15)$$

where m is the molality of the species (mol·kg^{-1} of solvent).

In a solution of a strong electrolyte where complete dissociation is assumed, the standard state is chosen so that the standard Gibbs energies of the electrolyte are equal to that of the sum of its ions. Then the activity is given by

$$a_{salt} = a_2 = (a_+^{\nu+} a_-^{\nu-}) = a_\pm^\nu \qquad (16)$$

where $\nu = \nu_+ + \nu_-$. For a substance $A_{\nu+} B_{\nu-}$ which forms ν^+ positive ions and ν_- negative ions, the mean ionic activity coefficient $\gamma_\pm$ is defined by

$$\gamma_\pm = (\gamma_+^{\nu+} \gamma_-^{\nu-})^{1/\nu} \qquad (17)$$

and the mean ionic molality is similarly defined

$$m_\pm = (m_+^{\nu+} m_-^{\nu-})^{1/\nu} \qquad (18)$$

or since

$$m_+ = \nu_+ m \text{ and } m_- = \nu_- m; \quad m_\pm = m(\nu^{\nu+} \nu^{\nu-})^{1/\nu} \qquad (19)$$

so that,

$$a_\pm = m_\pm \gamma_\pm \qquad (20)$$

from which the molal concentration of a species may be obtained once the equilibrium quotient is known (Equation 6), and an activity coefficient is available or estimated from the literature.

More details concerning the relationships between concentrations, activities, and equilibria may be found in Chapter 2 of Baes and Mesmer (10); Chapters 19, 20, and 22 of Pitzer and Brewer (11); in Robinson and Stokes (12); or in Harned and Owen (13). These references contain values of mean ionic activity coefficients that may be used in the calculation of molal concentrations from the equilibrium constant equation.

Pitzer and coworkers (14–20) recently published schemes for estimating activity coefficients from theoretical equations, and these relationships may be used to obtain activity coefficients if they are not known.

Critical evaluations of activity coefficients of uni-univalent electrolytes, Hamer and Wu (21); of $CaCl_2$, Staples and Nuttall (22); of H_2SO_4, Staples (23); and of alkaline earth halides, Goldberg and Nuttall (24) have been published more recently. Rard et al. have published reviews of the osmotic coefficients of H_2SO_4 (25), rare earth electrolytes (26, 27), and $CaCl_2$ (28).

It should be apparent that these equilibrium data are for aqueous solutions of one component only and are not intended for equilibria involving multicomponent electrolyte systems found in the real environment. It was not the intention of this letter to delve into the complex relationships of mixed salt solutions. The estimation of properties of mixed electrolyte systems is complex and still somewhat uncertain, although numerous references dealing with this problem are available to the reader.

There are virtually unlimited numbers of examples of the utility of equilibrium constants in practical applications within natural systems. One such example is the involvement of the equilibrium: $Ca^{2+} + OH^- \rightleftarrows CaOH^+$, in the determination of thermodynamic properties of portlandite [$Ca(OH)_2$] for geological implications (29).

A second application utilizes the magnesium and calcium sulfate ion pair equilibria in seawater to determine the percentage of cation that is unassociated in seawater (30).

Another example involving the calcium carbonate equilibria in lakes has been cited by Morton and Lee (31). Although the authors did not treat the possibility of ion pair formation, they do conclude that "more accurate ion pair data is needed before the possible role of ion pair formation in dilute lake waters can be determined". The present author feels that the information presented herein will provide a beginning for accurate, consistent equilibrium data.

The Electrolyte Data Center is primarily responsible for maintaining a program to critically evaluate thermodynamic properties of aqueous electrolytes under the direction of the Office of Standard Reference Data. As a result, therefore, a future publication is planned to provide a set of equilibrium constant data for ions in solution, which will be based on data for ionic species tabulated in the National Bureau of Standards Tech. Note 270-series.

Data System was established in 1963 for the purpose of promoting the critical evaluation and dissemination of numerical data of the physical sciences.

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Bert R. Staples

Electrolyte Data Center
Center for Thermodynamics and Molecular Science
National Bureau of Standards
Washington, D.C. 20234

Acurex Corp. (Mountain View, CA) has received a $3.5 million contract from DOE to show that solar energy can supply a large amount of energy for irrigation pumping.

The **Air Correction Division of UOP Inc.** will design, engineer, and build 2 electrostatic precipitators for the Central Iowa Power Cooperative—140 000 acfm at 340 °F—to reduce particulates at 0.02 grains/acf.

The **Chesapeake Research Consortium, Inc.** (Baltimore, MD) has a $53 896 contract from EPA to survey research being done, and data available concerning the Chesapeake Bay.

Logicon, Inc. (Torrance, CA) has an agreement with Intech Laboratories, Inc. for exclusive distribution rights to a line of coaxial communications network components. Wastewater treatment is one application.

Chemico Air Pollution Control (Envirotech) will furnish an SO_2 removal system for the 400-MW Emery Unit No. 2 power Station of Utah Power & Light Co. Startup: June 1980.

Bethlehem Steel now has two 6-story-high water filtration tanks in operation, and related facilities are progressing "on schedule," according to the company. They will clean 10 000 gpm of process water.

Dorr-Oliver Inc.'s desiltors are removing solids from wastewater at a large automotive company foundry at Saginaw, MI.

The **Marschall Division of Miles Laboratories, Inc.** (Elkhart, IN) is providing Trichoderma viride fungus for breakdown of cellulose to glucose. It is usable for cellulosic wastes (*ES&T*, November 1975, p 1011).

AG Brown Boveri & Cie. (Switzerland) has developed water sterilization equipment that uses ultraviolet radiation to destroy almost all microbiological impurities.

SCA Services Inc. (Boston, MA) has rejected an offer on the part of Waste Management Inc., to acquire SCA in a stock transaction valued at $72.3 million.

Nine companies in the solar energy industry will receive 12-mo contracts worth about $4 million, total, to develop low-cost, automated fabrication processes for solar cells. One-third of the firms are small businesses. The aim is mass production.

P. T. Georgia-Pacific Indonesia has a concession from the Indonesian government to reforest harvested timberlands in that country, in Kalimantan (formerly Borneo).

Alten Corp. (Mountain View, CA) will provide a solar hot water system for a new hotel addition in Disneyland. Alten will provide 102 copper/aluminum collector panels, technical supervision, and design assistance.

System Development Corp. (Santa Monica, CA) will do systems integration for a solar heating system for a new library at Saratoga, CA. ERDA and the City of Saratoga are funding the project.

Gilbert/Commonwealth has been awarded a contract to develop a master sewage plan for Lagos, the capital of Nigeria. The plan must include oceanographic studies, and a conceptual design of sewage collection/treatment facilities.

The **Sharples-Stokes Division of Pennwalt Corp.** says that the pollution control market is now the largest segment of its equipment business.

Seaward International, Inc. (Falls Church, VA) has a $197 961 contract from the Coast Guard to study/evaluate the state-of-the-art in oil pollution response technology, and the feasibility of attaining an extreme weather response capability.

Waste Management Inc. has started to perform on the $180 million operational phase of its sanitation contract with the City of Riyadh, Saudi Arabia, part of the most extensive such contract ever made.

Dames & Moore (Los Angeles, CA), and two other firms, will do studies to evaluate potential sites for a possible fossil or nuclear power plant for Delmarva Power & Light Co., in eastern Maryland.

Research-Cottrell (Canada) Ltd. (Toronto) has a $4.5 million order to supply and build four fly-ash precipitators to remove ash (efficiency: 99.5%) from flue gas, for Ontario Hydro.

Englehard Minerals & Chemicals Corp. (Edison, NJ) and Atlantic Richfield Co. have announced a technological improvement that could capture SO_x, from petroleum cracking, on the catalyst, and turn it to sulfur.

Energy Impact Associates, Inc. (Pittsburgh, PA), which works in environmental and energy technologies, and was acquired from Westinghouse by a group of Westinghouse employees, has a backlog of $2.5 million, and $4.5 million projected sales, according to its officials.

Systems Control, Inc. (Palo Alto, CA) will acquire Olson Laboratories, which does automotive emission and fuel consumption testing, from Olson's present principal shareholder, Envirodyne, Inc.

The **Nuclear Energy Liability-Property Insurance Association** has improved its position in the international market by increasing its foreign capacity to $71 million.

Culligan International Co. (Northbrook, IL), prominent in the water treatment field, and Beatrice Foods Co., have agreed "in principle" that Culligan would join Beatrice Foods.

IBM says that computerization will determine whether coal gasification can indeed become a viable alternate energy source, and believes that "mathematical modeling represents what is going to happen."

Air Products and Chemicals, Inc. will supply an "OASES" wastewater treatment system and oxygen generator for a 26 mgd facility for the City of El Paso, TX.

Aluminum Company of America (Pittsburgh,PA) announced that it recycled more than 2 billion aluminum beverage cans during 1977—"about 10 for every American"—and about 34% more than in 1976.

Glazing films
Two types of plastic film are available as the outer and inner glazing materials in liquid or air-type solar flat-plate collectors. The outer glazing material is only 4 mils thick and has a yield strength of 5000 psi. The inner glazing material can withstand stagnation temperatures of up to 400 °F. Chemplast **115**
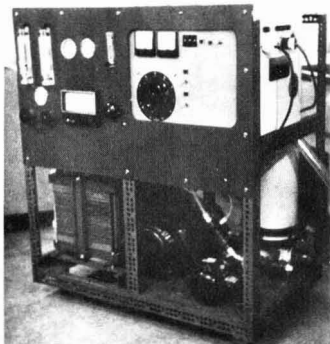
Metal recovery system
The electrodialysis unit returns up to 7 lb/h per unit of nickel metal, reducing nickel loss by 95%. The unit eliminates nickel sludge disposal problems and reduces water consumption. Lea Manufacturing **101**

Cell filter cleaning system
The system permits high air-to-cloth ratio making it possible for the compact cell filter cassettes to do the work of 10 filter bags, and to clean the fumes of an electric arc furnace or oxygen steel-making converter. Maintenance is easy and economical. Bahco Systems **102**

Acoustical foam
This lightweight material is especially designed for low frequency noise problems. The material is produced with an 8-mil insulated membrane that can be impregnated with lead. The material will be produced in $1/8$-in. and 4-in. thickness, with the membrane tailored to achieve sound transmission loss. Accurate Products **103**

Opacity monitor
This optical transmissometer is designed to continuously measure opacity levels in industrial stacks for compliance purposes. Features include unattended operation, automatic correction capabilities for zero and span drift and window soiling and microprocessor-based electronics. Esterline Angus **104**
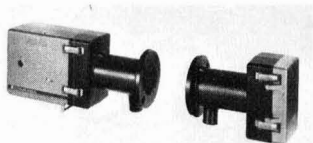
Biological toilet
Because it uses no water, this unit has the capability of saving up to 100 gal of water daily in the average family household. The toilet uses aerobic decomposition that is made more rapid through the use of thermostatically controlled heating coils. An odor-free humus is formed. Biolet **116**

Tapered plug valves
Designed with a minimal number of parts, the valves are available in sizes 0.5–6 in. in stainless steel or ductile iron castings. The tight shutoff valve can regulate flow in refineries and chemical and petrochemical plants. Walworth **117**

Tape recording system
This wideband portable magnetic tape recording system finds application in the field. It offers laboratory grade performance: high-density digital recording at 30 000 bits/in., FM recording bandwidths to 500 kHz and eight standard speeds. EMI Technology **119**
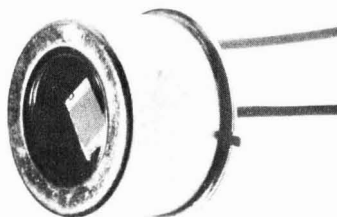
Infrared sensors and arrays
The thermoelectrically cooled lead sulfide and lead selenide detector/cooler modules provide excellent reliability and stability, according to the manufacturer. The units are being used in moisture and exhaust gas analyzers, and industrial process controls. Optoelectronics **105**

Mist eliminators
A solution to the problem of retrofitting existing scrubbers? Yes, according to the manufacturer, this high-efficiency vertical-flow impingent-type separator can be added to existing scrubbers for less than 10¢/cfm of total process flow. The eliminator permits higher than usual velocities without excessive pressure drop. Munters **120**

Air washers/fume scrubbers
These are constructed of polyvinyl chloride (PVC), polypropylene or fiber-glass-reinforced plastic to prevent corrosion and thereby hold down maintenance costs. An access/inspection door permits access to internal components for cleaning or adjustment without shutting the unit down. Air Plastics **121**
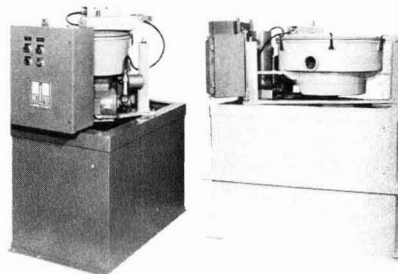
Sludge dewatering system
Especially designed for domestic sewage and industrial sludges, the units have solid bowl and vertical centrifuge design that exerts up to 500 gravities to accomplish separation. Solids concentration typically achieved is 15–20%. Met-Pro **106**

Desktop computer
The system contains a powerful central processor and a large built-in mass storage system. Also featured: a 12-in. CRT display; BASIC interpretive language; applications software; and an optional graphics package. Hewlett-Packard **122**

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Anti-dust helmet
This personal engineering control features powered filtration as an integral part of a hard hat. The hard hat also contains a face shield. Thus the helmet combines respiratory, head, eye and face protection. Racal Airstream **123**

Video imaging system
This master-scanning system can operate independently or interface with most minicomputers. The complete system features a dedicated minicomputer and a bi-polar microprocessor operating in tandem to provide a high-resolution display. Lexidata **124**
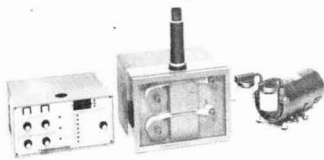
Aerosol monitor
The device uses beta-ray absorption methods to measure aerosol concentrations in ambient air. The instrument can be used to locate sources, and trace movements of respirable particles in "clean" air environments. Particles less than and greater than 3.5 μ can be measured in very short sampling intervals. Meteorology Research **107**

Personal pump
This air sampling device measures 4 × 7 × 10 cm and weighs 255 g. It can be used for filter sampling or bag filling. The pump, equipped with two ports, accommodates sample bags or other collectors at the positive (pressure) port and filters or tubes at the negative (vacuum) port. Calibrated Instruments **125**

Fluorescence detector
This continuously variable wavelength detector is designed for use in high-performance liquid chromatography. Its special feature is a patented 2π steradian interception cuvette. By using a 5 μL cuvette, total emission is intercepted by using an inverted Cassegrain design. Schoeffel Instrument **126**

Flocculating agent
The agent is designed for treating metal finishing effluents, especially where low-flow (under 25 gpm) conditions exist. The flocculant is contained within a fabric sock that is suspended in the wastewater stream. Aqualogic **112**

Gas flow monitors
The instruments, which incorporate solid-state circuitry, can be combined with data acquisition systems for continuous surveying of analog or digital measurements. Five different models are available with alarms and digital display of volume or flow rate, and recorders. Singer/American Meter Div. **108**

Data acquisition system
This self-contained, modular system includes a bus-oriented microcomputer. Features include cassette tape drive, and 16 channel expandable to 256 channel. Rockwell International/Atomics International Div. **109**

Dissolved oxygen analyzer
This portable system measures trace levels of dissolved oxygen as low as 0–20 ppb in boiler feedwater systems. Rexnord Instrument Products **110**

Liquid level sensor
This ultrasonic sensor is designed to detect liquid levels at temperatures up to 450 °F (232 °C). The sensor is unaffected by thermal shocks and temperature cycling; vibration; pressure and reflected light. The sensor can activate alarms, pumps or solenoid valves. Repeatability is within 0.02 of an inch. Envirotech **113**

Benzene detector tube
The tube is designed to be used with the company's toxic vapor detector kit. The direct-reading tube gives accurate readings on benzene threshold level values as low as 0.5 ppm in ambient air, according to the manufacturer. Matheson **114**
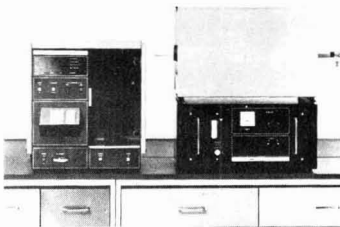
Sulfur analyzer
The unit is completely automated with digital readout. Precision is ±2% and accuracy is ±3%; reproducibility is good. The analyzer can measure sulfur in coal, coke and other fossil fuels with results reported in percentage or ppm. Fisher Scientific **111**

Scrubbers
These counterflow and crossflow fume scrubbers are able to remove gaseous fume contaminants, mists, dust and dirt from the air stream. Output efficiencies range from 85–100%. Scrubber sizes range from 500–100 000 cfm or more. Air Plastics **118**

Stack gas sampler
Measures temperature and velocity and samples condensible gases for analysis; it can also trap and classify particulate matter. The sampler contains a vacuum pump, timer, gas meter, impinger train, digital temperature readout, manometer and controls. AC Incorporated **127**

Portable bag sampler
Reliable operation is assured at temperatures of −10 °C and +50 °C. The number of air samples delivered to the storage bags is as much as 1800/h. This sequential bag sampling system can be programmed to collect 8 to 24 hourly air samples over 24 h or 96 h. Environmental Measurements **133**

Flow meter
This ultrasonic unit with no moving parts and solid-state electronics can reliably monitor the flow of industrial wastewater with an 0.5% accuracy under temperature conditions up to 500 °F. Du Pont **128**

Airsonde
This is a disposable, balloon-borne atmospheric sounding system that can take soundings from the surface to 50 000 ft (15 km). The solid-state sensor package uses 9-v transistor batteries, and descends without a parachute. The unit will find application in air pollution studies. Ambient Analysis **129**

Sample sequencer
This automatic, analyzer-controlled device is an accessory to the company's TOC, TOD and TC analyzers. The automatic sample injection is controlled by the analyzer and eliminates manual injections. Ionics **130**

ES&T
LITERATURE

Pesticide analysis, Brochure, "Baker Resi-Analyzed Solvents", lists solvents effectively used for pesticide analysis. J.T. Baker Chemical Co. **151**

Heavy metal removal. Brochure describes company's patented electrochemical removal system for chromates and other heavy metal contam-inants. Cooling towers, and other applications. Andco Environmental Processes, Inc. **152**

Sewer evaluation. Consulting engineer tells how sewer maintenance contractor's expertise was used for sewer system evaluation survey, and employed videotaped inspection. Value of engi-neer's advice was greatly enhanced. Ace Pipe Cleaning, Inc. **153**

Organics removal. Brochure describes new ULTROX ultraviolet-ozone process for destruction of toxic and re-fractory organic compounds, bacteria, and viruses in water. Treats 1000–10 million gpd. Westgate Research Corp. **154**

Air filtering. Bulletin describes equipment that removes contaminants from compressed air, including some particles as small as 0.01 μ. Odors are controlled. Pure Aire, Inc. **155**

Line strainers. Bulletin 735 describes a complete new line of "Sani-Filtration" strainers for liquid filtration. Specifications, mesh sizes, and material availability are included. Newark Wire Cloth Co. **156**

Limestone analysis. Report, "Analysis of Limestones and Dolomites by Energy-Dispersive X-Ray Fluorescence", provides discussions of accurate, quantitative analysis of these materials so important to air pollution control. EG&G ORTEC **157**

Liquid treatment. Bulletin MW generally describes ultrafiltration, deion-ization, reverse osmosis, carbon/resin adsorption, and other water cleanup systems. Illinois Water Treatment Co. **158**

Solids-handling pumps. Bulletin 7190 describes solids-handling pumps for many municipal and industrial wastewater applications, including storm water, process wastes, and other requirements. Deming Division, Crane Co. **159**

Benzene analysis. Application note AN 228-3 discusses benzene analysis in keeping with OSHA's proposed standards to protect workers. Full technical data are provided. Hewlett-Packard **160**

Airtight/watertight doors. Brochure D-77 illustrates and specifies air-tight/watertight doors for pollution control, clean room, nuclear plant, and other applications. Presray **169**

Ozone meter. Bulletin 8772000 announces availability of the Model 2000 portable ozone meter. Rugged, measures 0.1–1.0 ppm, lightweight. Columbia Scientific Industries **173**

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Carcinogens. Carcinogens—"Working with Carcinogens", DHEW (NIOSH) Publication No. 77-206, tells how to prevent employee exposure to such substances; contains information specifically for the *employee*. NIOSH, Robert A. Taft Laboratories, 4676 Columbia Parkway, Cincinnati, OH 45226 (write direct).

Water savings. Report LBL No. 6817 explains how Californians can save 40% of their water by means of standard measures. Lawrence Berkeley Laboratory, 1 Cyclotron Road, Berkeley, CA 94720 (write direct).

Fossil fuels. "Advanced Fossil Fuels and the Environment". EPA-600/9-77-013. National Technical Information Service, Springfield, VA 22161 (write direct).

Asbestos pipe. "A/C Pipe and Health" addresses the asbestos in drinking water controversy. A/C Pipe Producers Association, Suite 1308, 1600 Wilson Blvd., Arlington, VA 22209 (write direct).

Gas desulfurization. "Electric Utilities' Use of Flue Gas Desulfurization (FGD) in the United States". Federal Energy Regulatory Commission, 825 North Capitol St., N.E., Washington, DC 20426 (write direct).

Water reuse. Municipal Wastewater Reuse News. AWWA Research Foundation, 6666 West Quincy Avenue, Denver, CO 80235 (write direct).

Car emissions. "Automotive Emission Regulations and their Impact on Refinery Operations", CONCAWE Report 10/77. Also, "Techniques for the Analysis of Particulate Matter in the Atmosphere", CONCAWE Report 12/77. Stichting CONCAWE, Van Hogenhoucklaan 60, The Hague 2018, The Netherlands (write direct).

Centralized computing/control. Book describes TDC 2000 complete process control system (*ES&T*, December 1977, p 1152). Edwin C. Watson, Honeywell, 1100 Virginia Drive, Fort Washington, PA 19034 (write direct).

Commitment. "Environmental Commitment through 1976" explains costs, efforts, and energy demand for chemical industry to meet environmental standards. Manufacturing Chemists Association, 1825 Connecticut Ave., N.W., Washington, DC 20009 (write direct).

ES&T BOOKS

Methods of Air Sampling and Analysis. Second Edition. 1000 pages. American Public Health Association, 1015 18th St., N.W., Washington, DC 20036. 1977. $45 (add 50¢ for postage/handling), hard cover.

This is a very comprehensive book which tells "how to do it" for many different types of pollutants one may find in the air. It describes techniques and precautions, state-of-the-art, and gives detailed methodology for chemical and biological sampling/analysis of air in the workplace, as well as elsewhere. Some 130 accurate, reproducible sampling/analysis methods are offered.

Fate of Pollutants in the Air and Water Environments. I. H. Suffet, Ed. xx + 484 pages, Part 1; xx + 442 pages, Part 2. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1977. $24, Part 1; $23.95, Part 2, both hard cover.

Part 1 goes into the mechanism of interaction between environments and mathematical modeling, and the physical fate of pollutants. Part 2 takes a close look at the chemical and biological fate of pollutants in the environment. Both parts contain papers on these subjects, given by noted experts in their fields.

Enviroamental Remote Sensing. Vol. II. Eric C. Barrett, Leonard F. Curtis, Eds. vi + 314 pages. Crane, Russak & Co., Inc., 347 Madison Ave., New York, NY 10017. 1977. $32.50, hard cover.

This volume discusses policymaking aspects of remote sensing on the national and international levels, as well as legal implications. It also covers making the best use of data from existing systems, as well as establishment/testing of remote-sensing systems. Oceanographic, air/space, and ground-based remote sensing are discussed.

Handbook of Solid Waste Management. David Gordon Wilson, Ed. x + 752 pages. Van Nostrand Reinhold, 450 West 33rd St., New York, NY 10001. 1977. $39.50, hard cover.

What are properties of solid waste? How is it handled, processed, and disposed of? This book gives a comprehensive answer to these and other questions; looks at health/injury hazards; composting, uses in agriculture and forestry, and many other aspects. Waste generation rates are discussed, as are resource recovery and quality specification for recycled materials.

Environmental Effects of Complex River Development. Gilbert F. White. xi + 172 pages. Westview Press, 1898 Flatiron Court, Boulder, CO 80301. 1977. $14, hard cover.

Development of river basins presents many interesting, complicated, and varied problems. Here is a discussion of these problems and possible approaches toward solutions, as presented by U.S., African, Canadian, and Soviet experts. They discuss climate, water supply, and many other related topics.

Metal Toxicity in Mammals. Vol. 1. T. D. Luckey, B. Venugopal. x + 238 pages. Plenum Publishing Corp., 227 West 17th St., New York, NY 10011. 1977. $21.50, hard cover.

This book provides an understanding of the chemical toxicity of metals, metalloids, and their inorganic compounds. It discusses these substances with respect to mammalian nutrition, physiology, and toxicology, as well as detoxification. Safety standards are proposed, and carcinogenicity and teratogenicity are examined.

Solar Heating and Cooling: Recent Advances. J. K. Paul. x + 484 pages. Noyes Data Corp., Mill Rd., at Grand Ave., Park Ridge, NJ 07656. 1977. $48, hard cover.

Flat-plate collectors—focusing collectors—hot water—cooling—heating—the latest advances and patents are provided in this book. Coatings and storage systems are also covered, as are theoretical aspects and practical applications.

Regionalization of Water Management. Daniel A. Okun. xiii + 377 pages. Applied Science Publishers Ltd., Ripple Rd., Barking, Essex, England. 1977. $36, hard cover.

This book looks at water management in England and Wales, and discusses the promise that the regionalization of water management, as mandated by the British Water Act of 1973, holds.

Air Pollution and Human Health. Lester B. Lave, Eugene P. Seskin. 388 pages. The Johns Hopkins University Press, Baltimore, MD 21218. 1977. $22.95, cloth.

Litter may be an affront, but it is not normally a severe threat to human health. Air pollution, by contrast, can be a most serious threat. This volume traces relationships between air pollution in certain metropolitan areas, and death rates, and justifies its conclusions through careful statistical analysis. It also tells how controls on air pollution sources can help to reduce death rates.

Toxic and Hazardous Industrial Chemicals Safety Manual. 580 pages. Lab Safety Supply Co., P.O. Box 1363, Janesville, WI 53545. 1977. $75, hard cover.

This book covers over 700 chemicals' toxicity and hazard data. It discusses acute/chronic symptoms of exposure, cancer potential, fires, explosions, OSHA and EPA regulations, and many other related topics. It also provides handling and disposal procedures, and practical safety considerations.

The Removal of Sulfur Dioxide from Copper Reverberatory Furnace Gas with the Ammonia Double-Alkali Process. 138 pages. Smelter Control Research Association, Inc., Sixth Floor, 666 Fifth Ave., New York, NY 10019. 1977. $15.

This report describes an SO_2 removal system which, unlike other double-alkali systems, uses limestone for regeneration of the spent scrubbing liquor. It gives a full description of the process by which plugging/scaling are minimal. SO_2 removal was comparable to that of conventional ammonia scrubbing systems.

Introduction to Appropriate Technology. R. J. Congdon, Ed. 224 pages. Rodale Press, Organic Park, Emmaus, PA 18049. 1977. $6.95.

Appropriate technology involves small-scale, people-oriented technology, cottage industries, nonpolluting transportation, and the like. This book explains how both developed and developing countries can introduce such technologies to all sectors of society. Among its topics are "pedal power", water technologies, intermediate chemical technology, energy in rural

areas, and much other practical information.

The Economics of Cadmium. Third Edition. 236 pages. Roskill Information Services, Ltd., 14 Great College St., London SW1P 3RZ, England. 1977. $225.

The Cadmium Conference held in San Francisco, CA, last February (*ES&T,* April 1977, p 336) showed a deep interest in the metal. Now comes a work that discusses many facets of the cadmium scene—economic, environmental, production, end-uses, production, and prices. The demand/supply and other patterns in the U.S., Japan, and other countries are presented.

Energy for Development: Third World Energy Options. Denis Hayes. 43 pages. Worldwatch Institute, 1776 Massachusetts Ave., N.W., Washington, DC 20036. 1977. $2, paper.

It could be that the Third World may get the "jump" on the U.S. and Europe in making a transition to solar (and other renewable) sources of power. Third World countries are well-endowed with sun, green plants, and wind and water power. Some countries have indeed made vigorous efforts in this direction (*ES&T,* September 1977, p 848). Here is a detailed explanation about how all that may be—and, in fact, is—coming about.

Lead in the Environment. National Science Foundation. 272 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402. 1977. $4.

Here is a report concerned with the occurrence, transport, distribution, and possible environmental effects of lead. It is a product of the Research Applied to National Needs program.

Introduction to Appropriate Technology: Toward a Simpler Lifestyle. R. J. Congdon, Ed. xviii + 204 pages. Rodale Press Inc., Organic Park, Emmaus, PA 18049. 1977. $6.95, paper.

Choices of water technologies; ways of obtaining useful substances from nature; renewable energy supplies. These are all useful in developed, as well as developing nations, and are described as "people-oriented." These techniques have been listed and discussed in this book by experts who have worked with the Intermediate Technology Development Group ·in London, and are experienced in developing countries.

Water and Waste-Water Technology: SI Version. Mark J. Hammer. viii + 504 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1977. $15.50, hard cover.

This is a text in the field of municipal water supply and wastewater disposal. Emphasis is on art and practice, and chemistry, biology, hydrology, and hydraulics are among the many basic subjects covered. Advanced treatment, water reuse, and land disposal techniques are also discussed at length.

Coal Desulfurization: Chemical and Physical Methods. Thomas D. Wheelock, Ed. xi + 332 pages. American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. 1977. $25, hard cover.

It is imperative that coal use not breach environmental pollution control standards. One way to assure this is to remove sulfur from coal before using it. This volume discusses, in depth, the latest sulfur removal techniques, and is based on the symposium of the Division of Fuel Chemistry at the 173rd Meeting of the ACS at New Orleans, LA, last March.

ERT Workshop on the 1977 Clean Air Act Amendments. J. E. Mahoney et al. 10 parts + viii pages and appendix. ERT, 696 Virginia Road, Concord, MA 01742. 1977, updated 1978. $70, loose-leaf binder.

The Clean Air Act Amendments of 1977 (CAAA, 1977) are quite complex, but complex or not, there must be compliance, or penalties will be mandatory. What are one's duties, responsibilities, and rights under CAAA, 1977? This workshop book offers a comprehensive, yet uncomplicated discussion, and goes over permits, new source, modeling, enforcement, and all other aspects of the new law. The appendix contains a copy of the Act.

Viruses and Trace Contaminants in Water and Wastewater. Jack A. Borchardt et al. xiv + 249 pages. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, MI 48106. 1977. $29.50, hard cover.

There are many such contaminants in water and wastewater, and also certain theories and practices for setting regulatory standards concerning those impurities. Both wastewater and drinking water are covered in this book, vis-a-vis these contaminants and standards. It grew out of a conference on the subject, held in January 1977 at the University of Michigan.

ES&T MEETINGS

March 22–23 Washington, D.C.
6th Annual APCA Government Affairs Seminar. Air Pollution Control Association
Theme is "The New Clean Air Act: Its Impact on Energy and Growth." *Write:* Public Relations Dept., APCA, P.O. Box 2861, Pittsburgh, Pa. 15230

March 28–31 Philadelphia, Pa.
2nd Annual Workshop on Industrial Toxicology. Thomas Jefferson University
Write: Dean R. C. Baldridge, College of Graduate Studies, Thomas Jefferson University, Philadephia, Pa. 19107

March 29–31 Denver, Colo.
Ninth National Symposium on Food Processing Wastes. U.S. EPA
Write: Kenneth A. Dostal, EPA, Food and Wood Products Branch, 200 S.W. 35th St., Corvallis, Ore. 97330

March 29–31 Las Vegas, Nev.
3rd Annual International Technology Conference on Slurry Transportation. Slurry Transportation Association
Write: Slurry Transportation Association, 490 L'Enfant Plaza East, S.W., Suite 3210, Washington, D.C. 20024

April 3–5 Champaign, Ill.
20th Annual Public Water Supply Engineer's Conference. American Water Works Association, University of Illinois and Illinois Environmental Protection Agency
Write: Dr. T. E. Larson, Illinois State Water Survey, Box 232, Urbana, Ill.

April 3–7 Reno, Nev.
Environmental Impact of Mines and Quarries. Mackay School of Mines
Write: Jan Dunbar, program coordinator, Conferences & Institutes/EPCE, University of Nevada-Reno, Reno, Nev. 89557

April 4 King of Prussia, Pa.
8th Annual Industrial Air Pollution Contamination Control Seminar. American Institute of Plant Engineers
Write: William L. Smedley, American Institute of Plant Engineers, Box 8045, Route 8, Browns Mills, N.J. 08015

April 9–12 Palm Springs, Calif.
Second International Alternate Energy Conference & Exhibit. Solar Energy Development Institute and the University of California–Riverside
Write: International Alternate Energy Conference/Exhibit, University of California Extension, Riverside, Calif. 92521

April 10–11 Denver, Colo.
The New Mine Safety and Health Act: What it Means to You. The Energy Bureau
Write: Robert W. Nash, executive director, The Energy Bureau Inc., 101 Park Ave., New York, N.Y. 10017

April 10–13 Gaithersburg, Md.
Trace Organic Analysis: A New Frontier in Analytical Chemistry. National Bureau of Standards (NBS)
Environmental topics are included. *Write:* Dr. Harry S. Hertz, Chemistry Building, Room A105, NBS, Washington, D.C. 20234

April 10–14 Pensacola Beach, Fla.
Microbial Degradation of Pollutants in Marine Environments: Consensus as to Methodology, Interpretation and Future Research. Environmental Protection Agency and Georgia State University
Write: Microbial Degradation Workshop, U.S. Environmental Protection Agency; Gulf Breeze Environmental Research Laboratory, Gulf Breeze, Fla. 32561

April 10–14 New Orleans, La.
1978 American Occupational Health Conference. American Occupational Medical Association
Write: Howard N. Schulz, conference manager, American Occupational Health Conference, 150 N. Wacker Dr., Chicago, Ill. 60606

April 10–14 Miami Beach, Fla.
1978 National Conference and Exhibition on Control of Hazardous Material Spills. EPA, U.S. Coast Guard and Hazardous Material Control Research Institute
Write: Bobbie Zucker, conference coordinator, Information Transfer Inc., 1160 Rockville Pike, Suite 202, Rockville, Md. 20852

April 11–13 St. Louis, Mo.
Sixth Annual Industrial Pollution Conference. Water and Wastewater Equipment Manufacturers
Write: Frederick Harroun, WWEMA, 7900 Westpark Dr., Suite 304, McLean, Va. 22101

April 12–14 Washington, D.C.
1978 TAPPI Environmental Conference. Technical Association of the Pulp and Paper Industry
Write: W. H. Gross, environmental division administrator, c/o TAPPI, One Dunwoody Park, Atlanta, Ga. 30341

April 17–20 Houston, Tex.
Third Annual Conference on Treatment and Disposal of Industrial Wastewaters and Residues. Hazardous Materials Control Research Institute, University of Houston, American Institute of Chemical Engineers and Information Transfer Inc.
Write: Industrial Wastewater and Residue Conference, Information Transfer Inc., Suite 202, 1160 Rockville Pike, Rockville, Md. 20852

Courses

March 20–22 Washington, D.C.
Fluidized-Bed Combustion. The George Washington University
Fee: $385. *Write:* Martha Augustin, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

March 20–23 Louisville, Ky
Control of Particulate Emissions. U.S. EPA
Fee: $88. *Write:* Registrar, Air Pollution Training Institute, MD-20, Environmental Research Center, Research Triangle Park, N.C. 27711

March 23–24 Atlanta, Ga.
Particle Sizing Seminar. ANDERSEN 2000 Inc.
Fee: $250. *Write:* Neal Hill, ANDERSEN 2000 Inc., P.O. Box 20769, Atlanta, Ga. 30320

March 27–31 Davis, Calif.
Water Surface Profile Computation Using Computer Program HEC-2 (Surface Water Hydrology). University of California at Davis
Fee: $350. *Write:* Charles Lacy, University Extension, University of California, Davis, Calif. 95616

March 28–31 Philadelphia, Pa.
Second Annual Workshop on Industrial Toxicology. Thomas Jefferson University.
Enrollment limited to 50 applicants. Fee: $375. *Write:* Dean R. C. Baldridge, College of Graduate Studies, Thomas Jefferson University, Philadelphia, Pa. 19107

April 3–5 Washington, D.C.
Energy Conservation in the Textile Industry. George Washington University
Fee: $385. *Write:* Martha Augustin, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

April 3–5 Nashville, Tenn.
Development of Design Criteria for Wastewater Treatment Processes: Biological Waste Treatment. Vanderbilt University
Fee: $250. *Write:* Prof. W. W. Eckenfelder, Jr., Vanderbilt University, Box 6222, Sta. B, Nashville, Tenn. 37235

April 3–7 Miami Beach, Fla.
Land Application of Liquid Wastes and Sludges. Leon W. Weinberger & Associates Ltd.

Workshop is limited to 50 registrants. Fee: $450. *Write:* Leon W. Weinberger & Associates, 1160 Rockville Pike, Rockville, Md. 20852

April 3–7 Cincinnati, Ohio
Industrial Hygiene Sampling: Sampling Strategies. NIOSH and CES

Fee: $350. *Write:* CES, P.O. Box 75120, Cincinnati, Ohio 45275

April 6–7 Nashville, Tenn.
Development of Design Criteria for Wastewater Treatment Processes: Physical/Chemical Treatment. Vanderbilt University

Fee: $175. *Write:* Prof. W. W. Eckenfelder, Jr., Vanderbilt University. Box 6222, Sta. B., Nashville, Tenn. 37235

April 11–14 Cincinnati, Ohio
Air Pollution Control Technology, Course No. 431. U.S. EPA

Fee: $88. *Write:* Registrar, Air Pollution Training Institute, MD-20, Environmental Research Center, Research Triangle Park, N.C. 27711

Call for Papers

April 3 deadline
Environmental Aspects of Non-Conventional Energy Resources. Environmental Sciences Division, the Technical Group for Alternative Energy Technologies and Systems, and the Colorado Section of the American Nuclear Society

Conference will be held on September 26–29, 1978, at Denver, Colo. *Write:* Thomas H. Row, technical program chairman, Energy Division, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tenn. 37830

April 15 deadline
5th Annual UMR-DNR Conference and Exposition on Energy. University of Missouri–Rolla and the Missouri Department of Natural Resources

Conference will be held on October 10–12, 1978, at Rolla, Missouri. *Write:* Dr. J. Derald Morgan, conference director, Emerson Electric Professor of Electrical Engineering, Electrical Engineering Dept., University of Missouri–Rolla, Mo. 65401

April 15 deadline
Commercialization of Solar & Conservation Technologies Symposium-Workshop. University of Miami School of Continuing Studies

Symposium will be held December 11–13, 1978, at Miami Beach, Fla. *Write:* Dr. T. Nejat Veziroglu, director, Clean Energy Research Institute, University of Miami, P.O. Box 248294, Coral Gables, Fla. 33124

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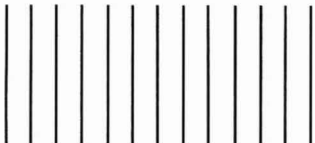
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