Environmental
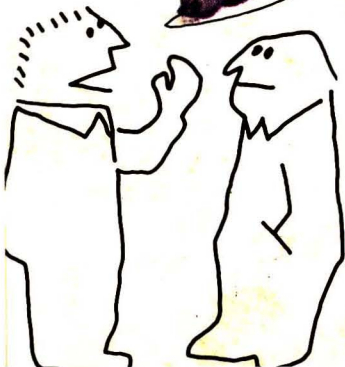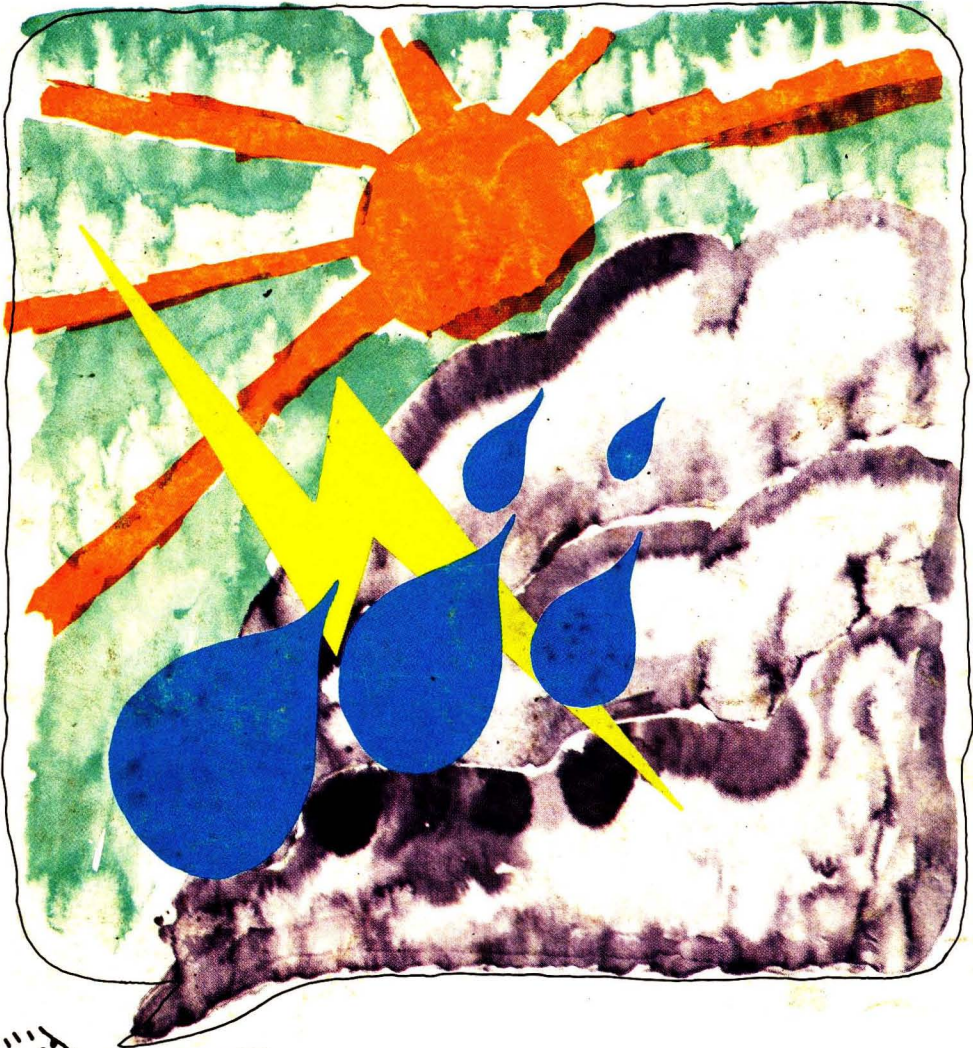## Science & Technology

Watching the weather and atmospheric pollutants 30

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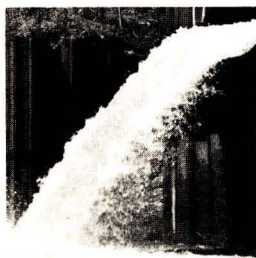
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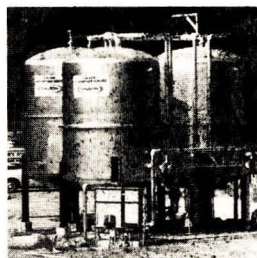
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CONTENTS

CURRENT RESEARCH

Free

LETTERS

Solar energy

Dear Sir: Your November article (*ES&T*, Nov. 1974, p 976) was very interesting but neglected to mention that, as usual with energy sources, in very special cases solar energy can be available at amazingly low cost and in fact at lower cost than atomic energy.

In the St. Clair Solar Energy System a large number of mirrors reflect sunlight on a pile of pebbles, or rather pebbles covered with a lattice brick work, which can be covered by an insulated door when the sun is not shining. When the sun is shining the large numbers of mirrors heat up the surfaces of the lattice brick work and the surface of the pile of pebbles to over 2000°F.

My years of experience with pebble beds in heat exchange have shown me that if you rapidly suck air into the pile of pebbles the heat that hits the surface of the pile of pebbles, can be drawn into the center of the pile of pebbles. Since in special cases the cost of the pebbles is less than 25¢ per ton and you have a heat storage cycle of from 1200°F to over 2000°F the cost of storing the heat of the sun for as much as a year is very low cost. You find the major cost of such a solar heat process in the mirrors. In this way solar heat becomes very dependable and you do not have to put in the large excess of solar heat collectors, as necessary with other processes, in order to get a reasonable amount of solar heat during the winter months when the solar heat collectable is only a fraction of that collectable in the summer.

And besides requiring such a lower area of collectors (mirrors) the solar collectors used are so much cheaper per square foot than the ones described in your article. I have gotten from RANN project workers the cost of mirrors made of metallized plastic film held like drum heads over hoops, and with their rotating mounts cost about $2 a square foot with a good chance of reducing the cost of the mirrors to $1 per square foot. This checks with my own estimates.

John C. St. Clair
London, Ohio 43140

Radioactivity from Pu

Dear Sir: In the Currents section (*ES&T*, July 1974, pp 597–8) the short article, "Ohio's Erie Canal . . ." is written in an extremely inflammatory manner. Certainly plutonium is poisonous but other metals, such as platinum, mercury, etc., are also. Why use the inflammatory adjective "man-made poisonous" when referring to plutonium? Also the sentence, "Plutonium can cause instant death only if inhaled," is certainly inflammatory and probably not true. Plutonium has been inhaled on several occasions (*Health Phys.*, **25** (5), November 1973, p 461) and "instant death" or even delayed death has not resulted. Objectivity is desperately needed by all those reporting on technology today. Certainly an ACS journal should be foremost in objective reporting.

N. Dean Eckhoff
Kansas State University
Manhattan, Kan. 66502

ENVIRO NMENTAL MONIT ORING
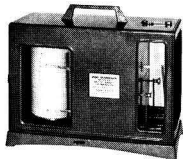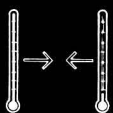
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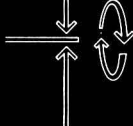
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Even before these problems reached crisis proportions, Chiyoda—Japan's leading engineering firm—was developing technology that will help ensure both environmental integrity and efficient energy production.

For example, to minimize air pollution and alleviate the shortage of low-sulfur fuels, Chiyoda has built about half the fuel oil desulfurizers in Japan. We've developed an indoor fume controller to collect the most harmful fume, consisting of particles of less than 3.0 microns. And we've introduced the Chiyoda THOROUGHBRED series of pollution control systems: new processes for flue gas desulfurization, the simultaneous removal of sulfur dioxide and nitrogen oxides, and waste water treatment.

These days "technology assessment" has become a fashionable expression. In our fields, we've been practicing it for years.

EDITORIAL

Energy and cleanup

This time last year, *ES&T* called for a rally round the cleanup flag. Judging from the response, we are not at all certain that anyone heard the call. Now with mid-term elections over, environmental goals appear to be holding the line against renewed drives for energy conservation. It simply does not appear that energy will break the proverbial environmental camel's back. But that is not to imply that the economics of controls will not destroy the cleanup struggle once and for all.

In any case, this month's feature author, a Federal Energy Administration spokesman, details the impact that pollution control measures—mandated by the Clean Air, Clean Water, and Resource Recovery Acts—have on energy consumption. The impact is small: the sum of all the increased energy requirements amounts to about one year's normal growth in energy use. In other words, the incremental energy required for operating a clean air, water, and solid waste operation, as opposed to a dirty one, is slightly more than 3% overall, according to this FEA spokesman.

In no case does this energy requirement for operating pollution controls approach a double digit number. So, present energy growth rates cannot be attributed solely to operation of cleanup systems.

This spokesman places in perspective the energy implications for operating various environmental cleanup strategies. The energy required to operate such cleanup strategies is summarized, but, unfortunately the installation costs, which everyone keenly watches in these days of double digit inflation, are not considered.

Conserving energy is obviously everyone's responsibility. But finding that energy will not break our camel's back should be somewhat reassuring. Less reassuring, of course, are the installed cost implications. These costs obviously cannot be ignored and await the test of another year of cleanup experiences.

Stanton S. Miller
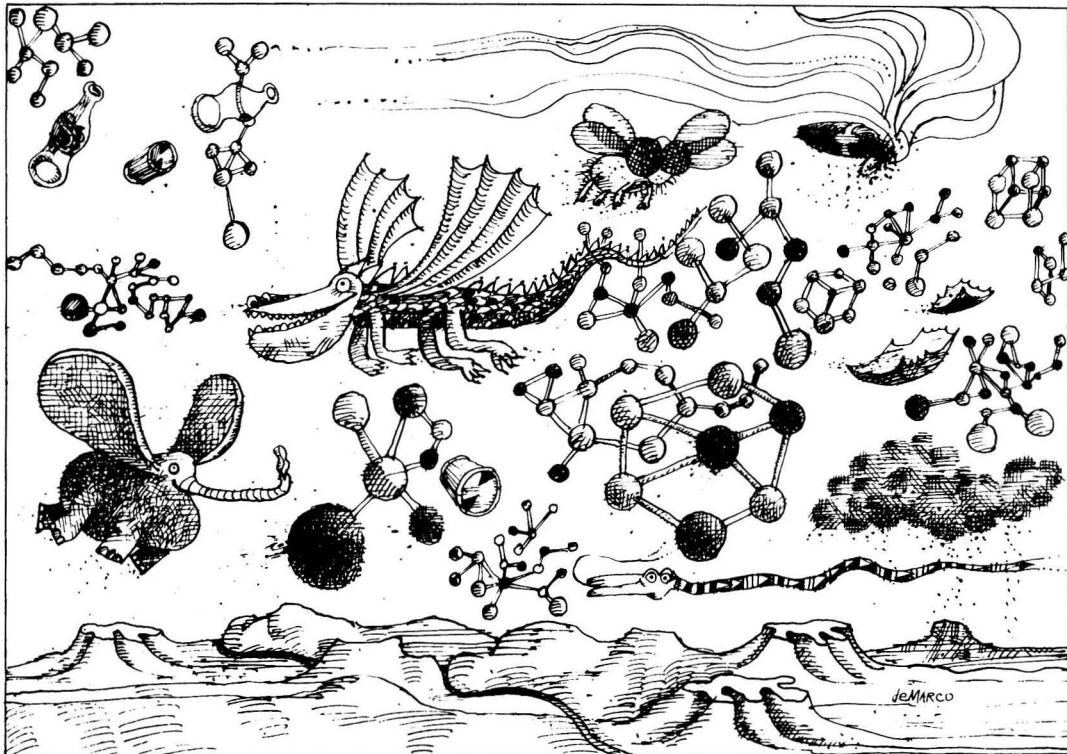
What's in the air for 1975?

There'll be the same cast of characters floating around up there: NO, NO$_2$, O$_3$, SO$_2$, CO, and the rest of the gang. But we can bring a lot of your air quality surveillance problems down to earth, with new developments in analyzers, calibrators and data handling systems.

For instance, the Dual Channel* Chemiluminescent NO$_x$ Analyzer we pioneered last year is now widely accepted, and widely imitated. But this year we've added ISOFLO for improved span stability, plus MOLYCON converters for longer life and improved performance. We've also applied the same technology to a brand new O$_3$ analyzer, Model 8410.

Of course no analyzer is more accurate than its calibration. That's why we've improved our Model 8500 Dynamic Gas Calibrator, already the industry leader with accuracy traceable to NBS. Now it has gas phase titration, an improved zero air source, and new remote control capability. And you can add our new Model 8530 Calibration Controller for automatic station calibration.

In 1975, many people will give up the costly, time-wasting process of manual strip chart interpretation. Because digital data gathering pays its own way with the ML System 9400 Data Logger. The 9400 is designed especially for air quality data gathering needs, with unique monitoring modes and data verification features. We've also added computing capability for calculating EPA averages.

If you have more than six remote monitoring sites in 1975, you deserve, and can economically justify, a System 7000 Computer-Based Network. It automatically oversees system maintenance, calibrates with computer precision, and preedits data for reporting in the EPA SAROADS format. Many System 7000 users are consistently obtaining more than 95% valid data. And they're saving money on data reduction, site operation and equipment maintenance.

No matter what you have in the air for 1975, you'll want to see what's new in air quality instrumentation. So write Monitor Labs, Incorporated, 4202 Sorrento Valley Blvd., San Diego, CA 92121. Tel. (714) 453-6260, TWX 910-337-1278.

*Patent Pending.

ML MONITOR LABS

CURRENTS

INTERNATIONAL

The first meeting at the ministerial level of the OECD's Environment Committee was held in Paris, November 13–14. Discussed were future environmental policies under changing international economic and energy situations. The 19 ministers from member countries of the Organization for Economic Cooperation and Development formulated a 10-year plan to reduce pollution, use natural resources rationally, and improve land use planning.

The National Swedish Board of Occupational Safety and Health has published a new list of maximum allowable concentrations of chemicals in the working environment, effective January 1, 1975. Two types of values are included—maximum allowable concentrations, and threshold limit values. Substances whose values have decreased include acetone, toluene, formaldehyde, chromium salts, cadmium, nickel, benzene, vinyl chloride, and arsenic.

Forty-three Japanese companies agreed to pay 2000 persons the equivalent of $11 million in compensation for deaths or illnesses resulting from industrial pollution. The companies in the heavily industrialized city of Kawasaki will split the cost according to the volume of their discharged pollutants from 1970–1973. For death, the payments will range from $20,000–$40,000; patients suffering from diseases attributable to pollution will receive from $3,300–$8,300.

WASHINGTON

EPA announced a national study of drinking water supplies to determine the amount and potential effects of the organic chemicals present. This follows in the footsteps of the New Orleans study which found that city's water supply to contain minute quantities of 66 organic chemicals, some of which may be hazardous to human health. The nationwide study will monitor untreated and treated water to determine the scope of the problem, the sources of the chemicals and their health effects, and an
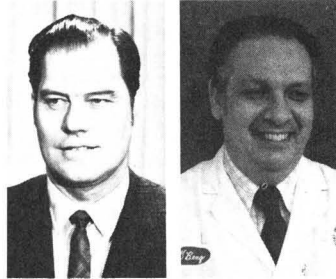
EPA's Robeck & Berg

assessment of corrective measures required, according to EPA's Gordon Robeck. In another study, an outgrowth of the American Public Health Association's conference on viruses in water held last June, Dr. Gerald Berg and others released a list of 10 recommendations on the detection and control of waterborne viruses.

EPA's thermal discharge guidelines have been challenged in court by Con Edison. The utility claims the standards could force the expenditure of $270 million to install cooling towers at four power plants. The towers would cost the utility about $120 million a year to operate, and would represent about 7% of the utility's annual revenue.

A study conducted by NOAA, EPA, and others showed that smog decreases, by as much as 35%, the amount of ultraviolet radiation received by urban and rural populations. The solar radiation measurements were made at six sites in the greater Los Angeles, Calif., area during autumn months; the data were added to those collected previously from two sites in the St. Louis, Mo., region during summer months. The decrease was most severe in urban areas, and was greater for Los Angeles than for St. Louis. This program, part of the photochemical pollution field experiments of the Los Angeles Reactive Pollution Project (LARPP), will result in the development of mathematical models of photochemical smog.

The Dept. of the Interior's Office of Land Use and Water Planning is conducting research to assess federal, state, and local legislation and programs concerned with the designa-

tion, preservation, and management of land resource areas. The study, scheduled for completion June 30, 1975, will result in a guidebook for use by technical and policy development personnel. In a separate tally, the Interstate Commerce Commission revealed that applications are pending for abandonment of more than 6000 miles of railroad rights-of-way in 45 states. When authorized, these could be converted to ribbons of wildlife habitat, recreational trails, or open space relief in heavily developed areas.

The Natural Resources Defense Council (NRDC) has filed a petition with the Consumer Product Safety Commission to ban the use of pressurized products, such as aerosol sprays. These products release fluorocarbon propellants into the atmosphere that destroy the earth's protective ozone layer. The NRDC has estimated that constant use of these sprays will deplete the ozone layer by 16% within 25 yr, and allow more ultraviolet rays to reach the earth's surface. The Council estimates that this will cause 100,000–300,000 additional skin cancer cases per year in the U.S., and from 500,000–1,500,000 additional cases per year worldwide.

STATES

Philadelphia Electric Co. voluntarily agreed to install scrubbers at three of its coal-fired power plants. The scrubbers will cost more than $68 million, take more than three years to install, but will allow the utility to continue to burn low-cost coal and still comply with clean air standards. These scrubbers will create no waste sludge, and the end-product—sulfur or sulfuric acid—will be salable. The savings to its customers would be $35 million a year less than conversion of the system to low-sulfur oil, according to company estimates.

The University of Texas' Center for Energy Studies received two grants from the electrical power industry to study the feasibility of geothermal energy for the state. The source of geothermal energy beneath the Texas coast and extending into the Gulf of Mexico is geopressured

CURRENTS

sands. The interdisciplinary study, headed by Myron Dorfman of the University's Petroleum Engineering Department, will take three years and cost about $3 million. The Gulf geopressured sands may be able to produce 15,000–30,000 MW of electricity over a 50-yr period. A preliminary study was supported by the University and the Atomic Energy Commission.

The Minnesota Pollution Control Agency's (MPCA) Division of Solid Waste will study the state's hazardous wastes. In 1974 the State legislature asked MPCA to adopt standards for the handling and ultimate disposal of the identified wastes. The first phase of the study will be a statewide inventory of the sources of wastes.

Alyeska Pipeline Service Co. has purchased an oil spill recovery vessel with containment equipment. The vessel, to be used in the event of a spill, is stationed at Valdez Port, Alaska, during the construction and op-

Containing spilled oil

eration phases of the Alaskan pipeline. The equipment cost about $100,000, and includes a 24-ft oil spill recovery vessel and a "Vikoma" inflatable floating boom.

The City of Tallahassee (Fla.) has contracted with Research-Cottrell, Inc. to build a mechanical draft cooling tower for its Arvah B. Hopkins Generating Station, a fossil fuel unit. Scheduled for completion in 1977, the six-cell tower is designed for 127,000 gal/min, and will be approximately 382 ft long and 62 ft high. The cooling tower will cost the city approximately $2.4 million. The tower was designed by Research-Cottrell's Hamon Cooling Tower Division to the specifications of U.S. utilities.

New Orleans has begun construction of a resource recovery plant to dispose of its trash and garbage. The facility named Recovery I is scheduled for operation in 1976. It will process 650 tpd of refuse and reclaim ferrous and non-ferrous metals including aluminum, color-sorted glass, and some paper. The residue will be landfilled. Waste Management, Inc. of Oak Brook, Ill., will build and operate the plant, and manage the construction of the sanitary landfill. The National Center for Resource Recovery based in Washington, D.C., will act as technical advisors during construction and operation, and will conduct a test and evaluation program of the system during the first three years of operation. Pennsylvania's Department of Environmental Resources has issued a permit for construction by Palmer Township, Northampton County, of a 160 tpd resource recovery facility. The system is also planned for operation in 1976.

MONITORING

Analysis of water for trace metal pollutants by X-ray fluorescence has been made possible by the U.S. Naval Research Laboratory (NRL), Washington, D.C. A modification of NRL's successful air pollutant measuring device based on the same principle, the present NRL system detects trace quantities of elements whose atomic weight equals or exceeds that of calcium. Contaminants are excited by an X-ray tube; background is minimized with a vacuum sample chamber; and intensity and energy of each contaminant's fluorescence radiation is measured with an energy dispersion, solid-state X-ray detector.

TECHNOLOGY

Decontamination of drinking water for human consumption, with iodine, will be a major topic in a campaign by the American Iodine Institute (AII, Lancaster, Pa.) to educate the public, according to Richard Polley, president of the AII whose consulting scientists point out that iodine does not have certain disadvantages that they say chlorine has. For example, chlorine has been named as a possible cause of cancer, and, in polluted

water, it can form chloroform and carbon tetrachloride, both considered carcinogenic. Moreover, iodine can neutralize certain dangerous forms of bacteria unaffected by chlorine, according to the AII.

Control of hydrogen sulfide (H_2S) in waste treatment systems can be effected by means of "Tysul" WW, a hydrogen peroxide-based chemical produced by Du Pont, Co. It has been known for many years that hydrogen peroxide (H_2O_2) can oxidize sulfides in water. Thus, it was decided to apply this principle to sewage, in which the H_2O_2 could destroy H_2S, thereby neutralizing a source of bad odor and corrosion, and kill sulfate-reducing bacteria that produce H_2S. Tests run at Hershey, Pa., on wastewater from commercial and industrial sources (75% generated by industry) as well as 8000 residents, resulted in very marked odor decreases.

Simulation of ocean conditions will be a function of the Oil and Hazardous Materials Simulated Environmental Test Tank (OHMSETT), a $3 million, one-of-a-kind testing facility the EPA recently dedicated at Leonardo, N.J. OHMSETT is a pool 667 ft long, 65 ft wide, and 10 ft deep, complete with its own wavemaking machinery. Able to produce regular, irregular, and "confused" waves up to 2 ft high to simulate "real life" situations, the "artificial ocean" will test equipment for containing and cleaning up spills of oil and other pollutants.

Meeting strict auto emissions standards of 1977 has been accomplished by General Motors with a Chevrolet Impala V-8 engine converted to stratified charge. While fuel economy was comparable to a catalyst-equipped conventional engine tuned to meet 1977 standards, engine and exhaust design were more complex. Meanwhile, a new engine, based on a combination of atomizers, vaporizers, and centrifugal separators, invented by Edward and Robert LaForce, both of Vermont, might increase nearly pollution-free gasoline efficiency by up to 80%. The LaForce engine will have to undergo stiff EPA tests at Ann Arbor, Mich., however, before a breakthrough can be officially acknowledged.
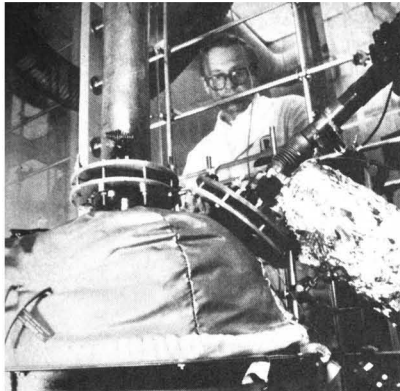
Recycling polyurethane foam

Recycling polyurethane foam, thereby conserving this petrochemically-based polymer, shows promise, because of a technique developed by General Motors Research Laboratories. The process breaks the foam into its original "chemical building blocks," which can be used again. The waste foam, normally sent to sanitary landfills, decomposes very slowly. It can be burned with a heat value similar to that of coal, but a petrochemical resource is then lost. The process recovers the polyol component of the foam by means of steam at 600° F and 1 atmosphere. Diamine is also produced; this leads to isocyanate, also needed in the process, which is explosion- and oxidation-proof because of its configuration.

Do electric fields affect plants, animals, and soils? Westinghouse Electric Corp. will try to answer this question under a 3-yr, $375,000 contract from the Electric Power Research Institute (EPRI), and learn what effects electric fields near and under high-voltage transmission lines may have on plants, animals, and soils.

INDUSTRY

Air Products and Chemicals, Inc. is working on the final design and supply of the world's largest oxygen-activated sludge environmental system (OASES) which will treat 600 mgd for the Detroit Metro Water Department. This system will remove over 90% of Detroit's wastewater pollutants on a continuous basis, and will use about 400 tons/day of 98% oxygen. Start-up is scheduled for 1978. Cost of the Detroit facility is reported to be about $39 million. By the time the Detroit OASES system goes on stream, Air Products will have supplied OASES plants to seven U.S. municipalities to process a total of over 800 mgd (*ES&T,* December 1974, p 1073).

Reynolds Metals Co. dedicated its newest and most modern aluminum recycling plant at Williamsburg, Va. David Reynolds, the company's executive vice president and general manager, reported that when the program is completed, the original 12 recycling centers will be increased to a total of 83, and that over 100 mobile units will be on the road, literally "taking recycling to the people." There will be Reynolds plants in 30 states, and recycling activity in about 45. A full list of recycling centers is available from The Aluminum Association (New York, N.Y.).

Ciba-Geigy Corp. has entered the environmental field by forming EN-CAS Systems (Environmental Concerns And Safety), which is operating in Greensboro, N.C. EN-CAS will help firms in the textile, leather, paper, soap and detergent, dry cleaning, and cosmetics industries "cope with the bewildering complexity of federal, state, and local regulations relating to the environment and to occupational safety and health." George Dominguez is the general manager of the new company.

Southern Co.'s Vogtle

Alvin Vogtle, Jr., president of The Southern Co., said that the issue is "Whether utilities will be permitted to select the most cost-efficient methods for attaining safe levels of air quality while providing their customers with enough electricity at reasonable prices," and "not how well scrubbers can be made to operate." Vogtle also pointed out that "any reasonable environmental regulation should be open to all available options and be consistent with what is needed specifically to achieve and maintain clean air." He said that the EPA approach eliminates all options other than scrubbers, although "tall chimneys and constant monitoring can assure that standards will be maintained."

Georgia-Pacific (G-P) will use 15 million ft^3/yr of by-product hydrogen gas, derived from breaking down salt brine, to replace "scarce" natural gas as boiler fuel, at its chlorine and caustic soda manufacturing facility at Bellingham, Wash. This facility is to be expanded by 36,300 tons/yr of additional capacity, and is aimed at meeting the acute shortage of chemicals for city water purification, municipal sewage treatment, and industrial uses. R. Pamplin, G-P chairman and president, described this project as "unique in the industry."

The National Association of Metal Finishers (NAMF, Upper Montclair, N.J.), together with the U.S. EPA, is running a nationwide survey to determine the kinds of wastes that are destined for land disposal. Such wastes include spent chemicals, sludges, and other process wastes that normally go to lagoons, landfills, or open dumps. The study will cover numbers of plants, waste characterization, treatment and disposal technology, and detailed cost analyses.

"Moving forward with municipal recycling systems as fast as possible," is the way that public policy in America would best be served, according to Peter Stroh, president of The Stroh Brewery Co. (Detroit, Mich.) and chairman of the U.S. Brewers Association. He pointed out, "only $5 billion spent for energy recovery from this country's waste streams will produce 2.5% of the increase in energy available to meet future needs." Stroh alluded to a National Academy of Engineers and National Academy of Sciences study, which estimated that each 1% increase in energy supply would cost $5–6 billion. He characterized energy recovery from waste as "one of the best energy-related investments this country can make."

The B.F. Goodrich Co. (Akron, Ohio) may make capital investments of over $42 million over the next 3–4 years to reduce vinyl chloride (VC) exposure in its plants "to the lowest level attainable with currently feasible technology." The company says that the OSHA standard is unachievable with present technology, unless employees in affected areas use respirators for VC levels up to 25 ppm (optional in 1975; mandatory in 1976).

INTERVIEW

EPRI's Chauncey Starr

Is the Electric Power Research Institute (EPRI) an offshoot of Edison Electric Institute (EEI)? Not directly. It is the follow-on to something called the Electric Research Council (ERC). The Electric Research Council included EEI which is a trade organization for the investor-owned utilities, the American Public Power Association, the National Rural Electric Cooperative Association, the Tennessee Valley Authority (TVA), and several other publicly-owned electric utility generating systems. The ERC coordinated the funds of these organizations in areas of common research interest. When EPRI was formed in 1972 as a non-profit scientific research organization, it took over the activities of the ERC. We moved into our present site at Palo Alto in September 1973, and began to assemble staff.

Since EPRI has assumed the R&D functions of EEI, what are the functions remaining to EEI? EEI is a trade organization. It represents the national business interest of the investor-owned utilities relative to federal regulations, rate structures, tax matters, criteria and regulations of the Environmental Protection Agency (EPA) as they affect power plants, and the activities of the Federal Power Commission as they affect power operation. These administrative and legislative matters are very important to the industry, but they do not involve technical development.

Who are members of EPRI? We now have 88% of all the electrical generating capacity of the country as members. Our Board of Directors consists of fifteen people, two-thirds of whom come from the investor-owned utilities, and one-third from the publicly-owned. This is roughly the ratio of power generation in the U.S. We have nearly 500 members, all voluntary. They include the bulk of the investor-owned utilities in the U.S., the American Public Power Association which includes all municipal and other locally-owned utilities, the NRECA (National Rural Electrical Cooperative Association), the REA's which include the farmer coopera-

tives, and TVA which is a government-owned but independent utility reporting to Congress, and the Department of the Interior which operates Bonneville and several other electrical power generating plants that have emerged from the Department's hydroelectric development program.

What is the organizational structure of the Institute? There are four major divisions that report directly to me: Nuclear Power; Fossil Fuels and Advanced Systems; Transmission and Distribution; and Energy Systems, Environment and Conservation. Each division is further divided into departments. For example, the Fossil Fuel Department studies include all the problems associated with using coal and oil as fuels; the Advanced Systems group studies solar, MHD (magnetohydrodynamics), geothermal, nuclear fusion—the exotic areas which are in the research or early developmental stage.

JOINT PROGRAMS

What is the Institute's working relationship with government agencies? EPRI is funded to handle all problems in the energy areas that are of concern to the electric utilities—from the raw fuels to delivery of electricity to customers. The problems are enormous, and EPRI can only choose areas of high priority. The federal government, because of its larger budget, especially now with the establishment of the Energy Research and Development Administration (ERDA), is in a much better position to assume a big share of the R&D activities. Federal agencies and EPRI have recognized this from the beginning, and have had cooperative program planning on a completely voluntary, professional, open-discussion basis to eliminate duplication of effort. The agencies involved include the Atomic Energy Commission (AEC), the Office of Coal Research (OCR), and Bureau of Mines, the

Chauncey Starr has been president of the Electric Power Research Institute since its formation in January 1973, after resigning as Dean of the School of Engineering and Applied Sciences, UCLA. He tells ES&T's Lois Ember of the Institute's sponsorship of research to develop environmental and economic technology to meet future energy needs. Perennially bow-tied, knowledgeable and glib, Dr. Starr discusses EPRI's joint programs with federal agencies, exotic forms of energy, Project Independence, the tall stack controversy and nuclear safety. As a member of the Manhattan Project and the designer of the only nuclear power reactor to operate in space, he advocates open discussion of nuclear energy as a power source.

National Science Foundation, NASA and, most recently, the EPA.

We have just entered into a Memorandum of Understanding with the AEC that provides a framework for cooperative work over the entire field of electric energy R&D. It establishes a mechanism for joint program planning, for exchange of information, for joint funding and management of selected projects, and for carrying on parallel but complementary projects. That agreement will now apply to relationships with ERDA.

There is a basic difference of objective between the federal government and the electric utility industry which is very important when you look at the joint activities. The federal government has responsibilities for the nation's general welfare and for concerns that are beyond the control of any one industry, such as fuel resources, the availability of energy on a national scale, the way energy systems exchange. These are matters of federal policy because they involve foreign trade, survivability of the nation, and economic growth. The federal government's concentration has been on resource development and technology for new energy resource systems. The utility industry's primary function is the generation and delivery of electricity to consumers; the federal government, except for TVA & Bonneville, has no responsibility for the delivery of electricity to the consumer. So, our interest focuses heavily on the technology of generation, transmission, distribution, and end-use.

Can you cite an example of joint program planning? In the nuclear area, the AEC is primarily concerned with the performance of nuclear fuels in relations to nuclear plant safety. We also have that concern, but since they are funding that part of the work, we are funding the portion of the nuclear fuel performance which has to do with the reliability of the fuel, and the economics of the fuel cycle which determines the cost of power to the consumer. But, as you make the fuel more reliable you inherently decrease the safety issues resulting from fuel failure.

Will agreements be signed with other agencies? Yes, there is an agreement under way with the Department of the Interior, and we are discussing agreements with other federal agencies in the energy sector. With the establishment of ERDA all of these will automatically become part of this Agency. The establishment of ERDA is a great thing for the country because it means that the energy programs will have a broad overview that considers both the consumer's needs and the national welfare.

RESEARCH CONTRACTS

Who is a typical recipient of an EPRI contract, and what is the average length of a contract? The bulk of the smaller contracts are distributed to non-profit research institutions like Battelle, Denver Research Institute, or Stanford Research Institute, and to universities. Increasingly large numbers are going to scientific and engineering departments in universities for applied science areas. When the programs get involved in hardware development, the project is apt to go to a manufacturer skilled in the hardware area, but for whom the risk of development is high. Most programs and the projects that are part of them, run 3–5 years. The contract may be written for the whole project, but the funding is year-to-year, just like federal funding.

EPRI AT A GLANCE
1975 program

Fossil fuels 30%
Transmission and distribution 20%
Nuclear power 25%
Advanced systems 17%
Energy systems environment and conservation 8%

Research programs — millions of dollars

1973: 93
1974: 265
1975*: 350*

* estimated   **Number of projects**
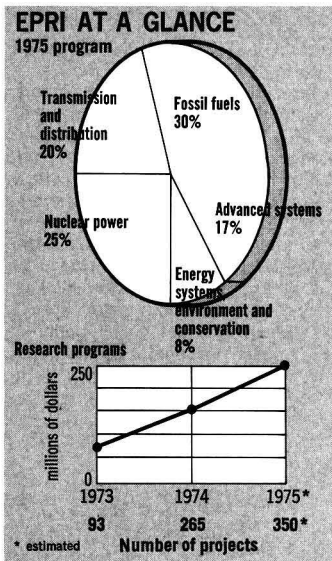
Can you give an example of a program? An example is our program in the field of superconductive rotating machinery. Now, superconductivity is a very interesting, somewhat exotic phenomenon, but its application to rotating machinery may be novel to your readers. Rotating machinery gets bigger as the power station gets bigger, and as the power plants get bigger the ability to expand this machinery becomes limited by the physical strength of the materials. If you build such a machine from a superconductive assembly, you can shrink its size, at least on paper. EPRI has a program at MIT to explore the basic problems of building such machines, and then manufacturers—GE and Westinghouse—work closely with MIT to build prototypes. I don't expect to see a large-scale superconductive rotating machine for at least the next 10 years.

How is the information derived from these contracts disseminated? Through all the traditional channels that any scientific research institute uses. The reports, including progress statements, written for EPRI are immediately disseminated to all member-companies. Copies of these reports are sent to anyone in the energy business who is interested. The scientists performing the experimental work are encouraged during the work, and at the completion of the work to write professional papers, and appear at professional meetings to present status reports.

When you talk about the research programs, are you talking about applications that will come about in the near-term future? Let me give you some arbitrary definitions. Anything that will actually be used by utility systems as part of their regular operation prior to 1990, is considered near-term. What this means is that if it isn't in laboratory pilot operation now, it is not going to be in use by 1990. Now, things that are still in the scientific conceptual stage will be on-line after 1990. Our thinking goes 40–50 yr ahead. Roughly half our money is devoted to near-term projects and the other half to long-term projects.

What are some of the environmental considerations integrated into EPRI projects? First, roughly half of our work is focused on helping the utility industry meet environmental criteria in the delivery of electricity—things like stack gas cleanup, coal gasification, coal liquefaction, reducing nuclear plant effluents. The other half is devoted to developing advanced technologies for reducing the cost of electricity generation. The environmental considerations are the issues of public concern—nuclear safety, land use, aesthetics, environmental impact of chemical pollutants—all these problems are concerns of ecologists, physiologists, and public health officials. We are not assuming that any of today's standards are necessarily those for the next 30 yrs. Thirty years from now there may be more stringent or different environmental criteria, and we want to anticipate these, to develop the technical options to meet them.

RISKS AND INDEPENDENCE

The deadline for achieving national air quality standards is mid-1975. Are the electric utilities going to make this deadline? If you are asking me whether the technology is available for the utilities to do this in any sensible way, I don't see it. What the utilities need to justify installation on

their systems is evidence that the capital investment that they're going to put into the system will result in useful functions, and that the capital investment can be amortized over the life of the power plant. If the life-time of the equipment is 3 or 5 yr, anything less than 10 yr, the cost to the consumer will be enormous, and I don't think any utility management could justify such an investment— except under legal duress.

Now, if you ask me whether the technology is available for a long-term investment, it isn't now. The utilities are in a great dispute with the EPA on this issue and I am sure that it is going to be solved administratively and legally. Whatever happens the con-sumer is going to pay for it.

clear—so that the U.S. doesn't have to rely on imported oil. The U.S. should be pushing conservation mea-sures in parallel with development of alternative energy sources so that ten years from now we won't be de-pendent on Arab oil. The issue here is not just economics; it's an issue of world political pressure.

According to an unpublished Federal Energy Administration report "Nucle-ar energy, while a clean energy source in terms of air quality pre-sents the greatest potential hazard to human health of all fuels." What are your comments? I don't believe it, I would like to see the report. The statement is completely assinine, and I don't know the basis for it. If

What have been the advances in high voltage transmission in the past few years? The biggest advances in high voltage transmission have been the increasing reliability of 350–750 kV power lines, and the interconnec-tion of networks so that system per-formance prevents the failure of one network from shutting-down the whole system. The next biggest area has been the development of high voltage dc. Transmission lines in this country are traditionally ac lines. If you go to direct current and high voltage, the size of the right-of-way decreases, and your losses de-crease; you can carry more power at lower cost.

"Every professional and analytic study that has been made on the hazard to the public from nu-clear power plant effluents . . . has indicated that the risk to the public from nuclear power and all of its possible effluents is much less, by big fac-tors, than the risk of the alternative—fossil fuels."

EPRI's Starr
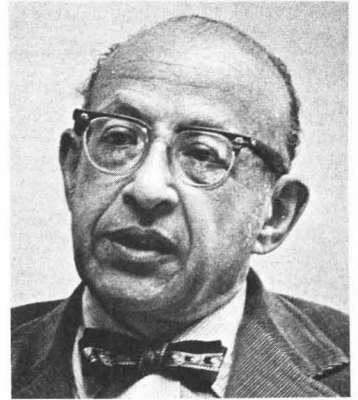
Are **tall stacks, without scrubbers or precipitators, sufficient to eliminate the discharge of harmful pollutants to the environment?** The basic issue of the tall stack is an issue which is technologically and scientifically in dispute. The issue is whether contin-ued fall-out of slightly acidic sulfate compounds, over large reaches of the country, will result in long-term ecological damage. If the alternative to tall stacks is a very high-cost stack gas cleanup system, then you have to decide whether the uncer-tainties of the tall stack dispersal system justify huge capital invest-ments for stack gas cleanup. I don't think the answer to that question has been arrived at yet.

Regarding Project Independence, when will the U.S. become self-suffi-cient in energy? I don't think that there is any possibility within the next decade, even under a crisis situation, of the U.S. being self-sufficient in en-ergy. It might be possible in the next 30 yr to develop enough indigenous energy sources—coal, oil, and nu-

there is such a report I would like to see it and I would like to see who wrote it.

Why do you feel that this statement is incorrect? Every professional and analytic study that has been made on the hazard to the public from nuclear power plant effluents, and the poten-tial hazards from the nuclear fuel cycle systems 30-, 40-, 50-years in the future has indicated that the risk to the public from nuclear power and all of its possible effluents is much less, by big factors, than the risk of the alternative—fossil fuels. The risks have all been analyzed in great detail. The professional studies that have been made by people con-cerned with the biological issues have been very definitive on the fact that while there is much to be done to improve the safety to the public, nuclear power safety as it now stands presents fewer risks to the public than the risks associated with the alternative power sources. There is no risk-free power source available yet for public use.

Can they underground high voltage? High voltage undergrounding is ex-tremely expensive, and it is limited in voltage by the insulation materials. EPRI has a major R&D program studying methods to increase the carrying capacity of underground ca-bles. Incidentally, superconductivity is one of the long-range possibilities in this area, but improvement in insu-lation materials is another.

Will they have to underground for aesthetics? You have to underground in any case when you get in a city, especially like New York. The issue of aesthetics is going to be one of great public discussion, and one which has other than a technological input. The point is that to eliminate overhead transmission lines is going to be extremely costly. The transmis-sion and distribution grid of the coun-try represents a bigger capital invest-ment than the power generation fa-cilities of the country. These are not trivial expenditures, and the public really has to be willing to pay for un-dergrounding.

Recovering chlorine from waste HCl

Hoechst-Uhde Corp. has constructed electrolysis plants which produce 300,000 short tons of chlorine annually; other plants under design will bring the aggregate chlorine output by its direct electrolysis process to 425,000 short tons per year

Essentially all chlorine is presently produced from alkaline chlorides such as common salt by the conventional electrolytic method. In 1970, some 22 million tons of this chemical were produced. At the same time, considerable quantities of aqueous hydrochloric acid or hydrogen chloride gas result each year as by-product materials from chemical manufacturing activities.

These industrial wastes are also being converted to chlorine by an electrolytic process. In this way, a valuable chemical material is recovered from an otherwise discarded industrial waste stream. Existing and proposed regulations prohibit the

Mobay plant manager Elliott
"first U. S. use will be expanded 50% by 1976"

dumping of this hydrochloric acid into waterways, and underground injection of such acid has raised environmental objections.

The most successful designer of hydrochloric acid electrolysis plants was Friedrich Uhde GmbH. The company gained sufficient valuable experience in the two plants it constructed in Germany. Developed through the joint efforts of Farbwerke Hoechst AG and Friedrich Uhde GmbH, the first commercial unit was constructed in 1963. The first electrolysis unit in the U.S. was built in 1971–1972 at the Mobay Chemical Corp. plant at Baytown, Texas. It is the largest one built to date, averaging 180 metric tons per day of chlorine production.

Mobay plant manager Fred B. Elliott explains that hydrochloric acid is not easily disposed of. "The electrolysis process puts the waste by-prod-

uct back into the manufacturing stream," he says. "The unit also avoids the cost of neutralization. Process-wise, we are quite pleased with the unit. Of course, there were some mechanical and construction material problems but these problems have now been overcome. In fact, Mobay is expanding by 50% the electrolytic process unit. Completion date is expected by early 1976."

Sources of industrial HCl

The major portion of gaseous HCl obtained in the chemical industries originates from organic chlorination processes, some 50% of the chlorine used in many chlorination processes. A number of other industrial HCl-producing operations include the chemical manufacturing operations for the production of isocyanates—intermediates in the production of polyurethane polymeric materials—as well as other chemicals of commerce—organic fluorine compounds used as refrigerants and aerosol propellents and silicones.

In its manufacturing operation, Mobay has two or three sources of hydrogen chloride gas, all stemming from isocyanate manufacture. The majority of the Hoechst-Uhde electrolysis units have been installed and are used today with isocyanate manufacturing operations. In the early 1970's Uhde secured contacts for four other plants with a daily aggregate capacity of 520 metric tons.

It is worth noting that three of these plants, including the Mobay

plant, are not combined with an alkaline chloride electrolysis plant, which meant that special care had to be taken to ensure that the isocyante and hydrochloric acid electrolysis plants were tailored to each others needs. Two of these plants were equipped with so-called chlorine recovery facilities, in which the chlorine is almost completely recovered from the bleaching liquor obtained when the plant is started up or shut down and in the hydrogen scrubbing unit (98% yield). In the production of isocyanates, the total amount of chlorine introduced into the reaction in the form of phosgene is recovered as gaseous HCl.

Other disposal techniques

Electrolysis of alkaline chlorides is still the most common method used for the production of chlorine, and as a result considerable quantities of sodium hydroxide have risen also. However, the demand for sodium hydroxide has not risen to the extent of chlorine. Consequently, there is a definite need to produce chlorine without obtaining caustic alkali as co-product. So, recovery of valuable raw materials is a must.

Other processes have alleviated to a certain degree the disposal problem of excess hydrochloric acid. These processes include the oxychlorination in the production of ethylene dichloride as starting material for vinyl chloride; the use of hydrochloric acid in the metallurgical acid for pickling purposes as well as its

Where industrial hydrochloric acid is generated

	Reactions
Production of chlorine bearing solvents	
Production of raw materials for detergents	$RH + Cl_2 \rightarrow RCl + HCl$
Production of chlorination products	
Production of Frigens	$RCl + HF \rightarrow RF + HCl$
Production of silicones	$4RCl + 2Si \rightarrow 2R_2SiCl_2$
	$2R_2SiCl_2 + H_2O \rightarrow \underset{R}{\overset{R}{Si}}..O..\underset{R}{\overset{R}{Si}} + 2HCl$
Production of isocyanates	$COCl_2 + RNH_2 \rightarrow RNCO + 2HCl$
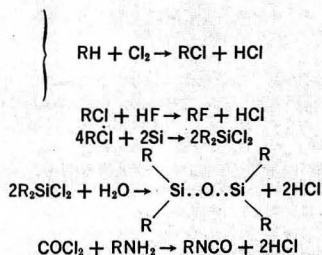
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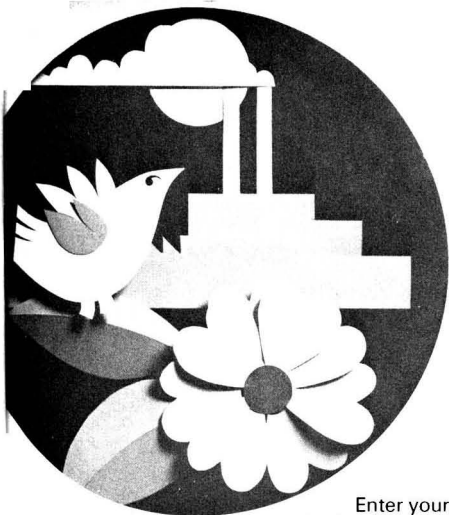
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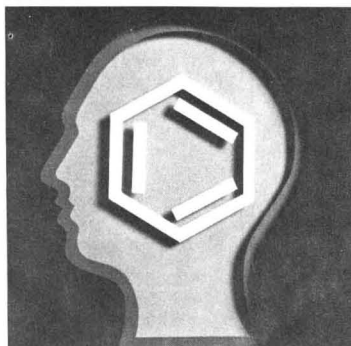
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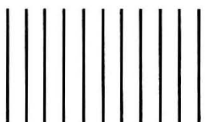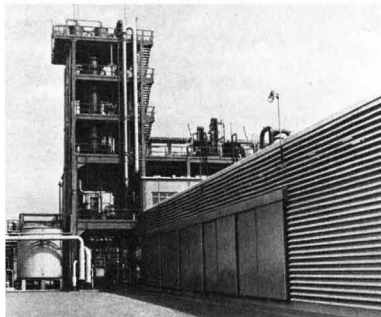
use for phosphate rock digestion. Nevertheless, these processes did not constitute a universal solution to the HCl disposal problem.

At the same time, there are four known processes for the production of chlorine from hydrochloric acid. Three are based on indirect electrolysis via metal salt solutions but only the direct electrolysis has been widely adopted and used on a commercial scale since 1964, despite the fact that the decomposition potential is considerably higher than in the case of the indirect processes.

One reason chemical producers have preferred the direct process is probably because the other processes each consist of two independent stages working at different rates and efficiencies and are more costly and require larger reactions vessels. Another aspect is the fact that the high current densities that are possible in the direct process cannot be achieved in the indirect one.

How it works

In the electrolytic decomposition of aqueous hydrochloric acid, efficiency must be realized at the minimum power requirements for the two reactions—$2 Cl = Cl_2 + 2 e$ at the anode and $2H + 2 e = H_2$ at the cathode. The theoretical minimum electrolysis voltage between the two electrodes is the potential of the chlorine-hydrogen cell of about 1.36 volts. In practice, this voltage will increase in line with the polarization at the two electrodes at the commonly used current densities. To this voltage at the electrodes must be added the voltage drop in the electrolyte that depends on the cell construction and the operating conditions selected. The voltage will further be influenced by factors such as the diaphragm permeability and the specific conductance of the hydrochloric acid.

The cell voltage depends on the hydrochloric acid concentration. It rises sharply for hydrochloric concentrations under 20% because of the decrease in conductivity. Optimum concentration of hydrochloric

acid for best conductivity is between 20-22% at a temperature of 80°C. At concentrations above 22% the conductivity again decreases. Hydrochloric acid at any concentration above 20% can be used in the process. Usually, in consideration of the rising vapor tension of the acid, its concentration is kept below 26%.

Temperature also affects the cell voltage. This effect is very marked at temperatures between 40–50°C, but less noticeable at higher temperatures. Although the voltage can be improved at temperatures higher than 80°C, this value should normally not be exceeded so as not to impair the durability of construction materials used in the cell.

Development progress

In 1938–42, the I.G. Farbenindustrie, as it was then known, began to develop hydrochloric acid electrolysis in its central German works at Bitterfeld and to dispose of excess hydrochloric acid in this manner. The company used the process on a commercial scale at Wolfen from 1942–44 when its operations were interrupted during World War II. In the 1950's Farbwerke Hoechst AG, one of the successor companies formed from I. G. Farbenindustrie, and Friederich GmbH continued to develop the Bitterfeld cell.

The first experimental cell had all the characteristics of today's cells. It was, in fact, the first bipolar cell to be used in the chlorine industry. In the electrolysis, two gases are formed which must not mix, whereas the anolyte and catholyte may be mixed.

Today's Hoechst-Uhde electrolyzers consist of 30–36 single elements

working at current densities from 4–5 kA/m^2. A typical electrolyzer with 30 elements is about 3.5 m long, 2.2 m wide, and requires a floor space of 4 × 4.8 m. The electrolyzers are of simple and rugged construction. The cell itself consists of a frame of phenol formaldehyde or cresol formaldehyde-based plastics, containing ducts for the products and for the feed and effluent hydrochloric acid. Fixed into the frame is the bipolar graphite plate with slots on both sides for the purpose of withdrawing the gaseous products obtained. Normally, the entire unit is of the open-air type.

The gases rise along the vertical electrodes and are distributed at the upper edge of the graphite plate through a system of ducts into the discharge openings. Together with the anolyte, the chlorine is directed toward one end and the hydrogen with the catholyte to the other end. The diaphragm is fixed to the side of the frame. The electrolyzer is closed at each end by a steel plate with rubber-lined inside surface. The end plates and cell frames are held together by eight spring-loaded tie-rods in a manner similar to a pressure filter. Electric power is fed to the graphite plates mounted in the end plates through graphite nipples with stuffing boxes. The electrodes of the Hoechst-Uhde electrolyzer have an effective surface of 2.5 m^2 and can withstand a current load of up to 12,000 amps. The diaphragm consists of a PVC fabric specially developed for this purpose and serves to separate the electrode chambers, and consequently to prevent the two products from mixing. The electrolyzers are supported by steel frames which, in turn, rest on ceramic insulators.

Status of HCl electrolysis units

Client	Location	Capacity T/D Chlorine[a]	Status
Bayer Leverkusen	Germany	89	Built 1962/63
Farbwerke Hoechst	Germany	120	Built 1963/64
Mitsui	Japan	33	Engineering completed; Plant not built
Bayer Dormagen	Germany	89	Built 1968
Bayer Uerdingen	Germany	89	Engineering completed; Construction deferred
Bayer Shell	Belgium	146	Built 1971/72
Mobay Chemical Corp.	USA	180	Built 1971/72
		90	50% expansion planned
Eurane	France	106	Built 1971/72
Asahi Glass	Japan	106	Under construction
Sud Italia Resine S.p.A.	Italy	106	Under construction

[a] Metric tons/day
Source: Hoechst-Udhe Corp.

OUTLOOK

Coal can be a clean fuel

Redevelopment and expansion of U.S. coal resources are economic necessities.

Non-polluting use of coal is a health and social necessity.

NCA's meeting at Louisville was a first big step toward reconciling these necessities

"Thank God for coal," Secretary of the Interior Rogers Morton told a dinner session of the "Coal and the Environment" conference, organized by the National Coal Association (NCA, Washington, D.C.), convened at Louisville, Ky., last October. Secretary Morton foresees that coal will play the key role in the U.S. "energy matrix" over the long haul. He looks to coal as the only near-term hope to reduce the U.S. financial drain of $3 million/hour for the purchase of foreign oil.

Secretary Morton
"Coal will play key role"

Bridging the oil gap with coal, however, poses some hefty environmental challenges—of mine drainage, strip mining, reclamation, refuse handling, and air pollution problems. To start meeting these challenges, the NCA conference, the first of its kind, with about 2000 in attendance, and 112 firms exhibiting, was held.

Among the environmental objections to the use of those types of coal that are presently less expensive and more available in the U.S. is the introduction of large amounts of SO_x and particulates into the air, and the primary and secondary effects of the SO_x and particulates. In order to allay these objections, one has a few options:

- remove the SO_x and particulate sources from the coal before or during combustion
- use tall stacks and intermittent controls, a technique the TVA and other interests advocate, at least as a temporary measure, but which does not have EPA approval
- scrub particulates, SO_x, and perhaps other contaminants from effluent gases after the coal is burned, and before the exhaust goes out of the stack.

Stack cleaning

Perhaps no subject of air pollution control (apc) technology has been the subject of such spirited debate in recent months as has stack scrubbing. One side, which includes the EPA, states flatly that stack scrubbing is a here-and-now technology ready for application (apparently the EPA did not overemphasize cost-effectiveness). The other side states just as flatly that stack scrubbing is beyond the state-of-the-art, and not cost-effective, at least while this technology is under development. The latter view has been graphically presented in frequent advertisements by the American Electric Power System (New York, N.Y.) in many of the nation's leading newspapers.

The M.W. Kellogg Co. is participating tangibly in the great scrubber debate by announcing an exclusive license to offer a "proved" SO_x and particulate removal scrubber developed by Alexander Weir, Jr., of the Southern California Edison Co. (SCE). Operated with a lime slurry, this scrubber has a design capacity of 450,000 scfm, (170 MW equivalent) but has treated up to 544,000 scfm (206 MW equivalent) with no major operating difficulties. The Weir horizontal scrubber operates with an average concentration of 200 ppm of SO_2, but a 30,000 scfm unit has suc-

cessfully handled 400–3000 ppm of SO_2. Removal of 90% or better is achieved at a liquid-to-gas ratio of 20 gal/1000 scf per stage.

Particulate removal has proved efficient, with 0.007 g/scf in exit gas achieved for inlet loadings up to 0.1 g/scf. According to the company, with this achievement in particulate and SO_x treatment, not only federal standards, but the much more stringent standards of Clark County, Nev. (0.15 lbs of SO_2/million Btu), where the units are being tested at SEC's

SCE's Alexander Weir, Jr.
Developed horizontal scrubber

Mohave plant (1580 MW) are constantly being met.

According to M.W. Kellogg Co., the Weir scrubber is small, consumes little power (about 1.5% of power generated), and has an unlimited turndown ratio. It also has an effective demister and wash system that inhibits scale formation. It has required two operators per shift, and has been in virtually continuous operation since January 16, 1974. If the scrubber is still working well by January 16, 1975, as it has so far, it will be deemed to have passed its tests.

Numerous other companies are working in the scrubber field. Catalytic, Inc., for example, scrubs with recyclable ammonia. Dravo Corp.

Weir scrubber horizontal module
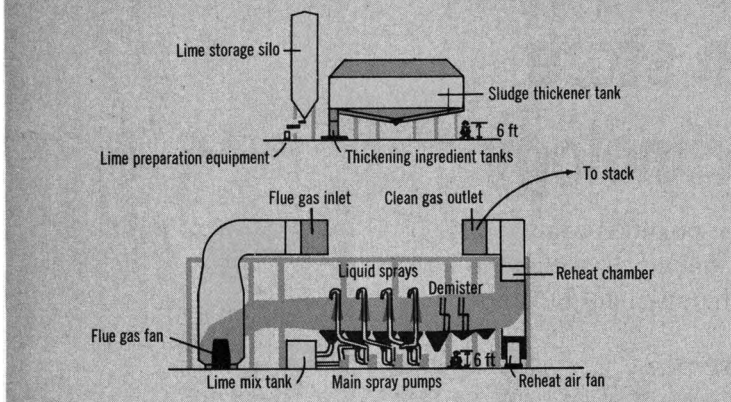
balances lime with magnesium oxide ("Thiosorbic lime") to increase SO_x removal efficiency. Stauffer Chemical Co. captures SO_2 in buffered aqueous sodium phosphate, and reacts the SO_2 with hydrogen sulfide (H_2S) to obtain sulfur. Westvaco uses an activated carbon system.

Coal cleaning

Another approach to apc is to remove pollutants from coal before it is burned. Sometimes called "coal preparation," this approach is considered by A. Deurbrouck and P. Jacobsen of the U.S. Bureau of Mines Pittsburgh (Pa.) Energy Research Center to be a "viable technology."

The main "pollutants" in coal are organic sulfur, pyritic sulfur, ash, and certain trace elements. Probably the least expensive and most highly developed removal method, according to Deurbrouck and Jacobsen, is the physical removal of pyritic sulfur. The methods of removing pyritic sulfur include the wet concentrating table, the Humphreys coal-cleaning spiral, electrokinetics (electrophoresis, deemed uneconomical because of power-input requirements to go even to pilot stage), and froth flotation, the last developed and patented by the Bureau of Mines. Some coal-cleaning equipment innovations include:

- the fine-coal cleaning jig (600 ton/hr capacity), being reintroduced into the U.S. from West Germany and Japan
- the Eis clarifier, a high-capacity sedimentation device built by the Enviro-Clear Co., and presently in use at the Grapevine Oreparation plant of U.S. Steel (Thacker, W. Va.)
- screen-bowl Bird centrifuges, to dewater the froth flotation coal product; a screen-type unit was developed by CMI, Inc.
- water-only cyclones.

Organic sulfur, an integral part of the coal matrix, generally not removable by direct physical separation, comprises 30–70% of the total sulfur of most coals. Usually, with higher total sulfur content of coal, the ratio of organic to pyritic sulfur is lower.

Additional methods of obtaining clean fuel from coal include gasification, liquefaction, and solvent refining (ES&T, June 1974, p 510), among others. For example, substitute natural gas (SNG) made from coal is now being used by housewives in one town in Scotland (ES&T, December 1974, p 1070). Coal liquefaction and solvent refining are being actively pursued on a pilot scale with the COED liquefaction project and others, the 50 ton/day Fort Lewis, Wash., solvent refining plant (which should be in operation this month), and additional efforts being conducted by public and private interests.

Material recovery

In the Weir scrubber system, the addition of magnesium makes it possible to oxidize all of the calcium sulfite in the product stream to calcium sulfate. The resulting slurry contains essentially pure gypsum that settles rapidly and forms a by-product that is over 70% solid. This by-product is drier and more compact, and requires less pond area than do by-products of many other lime or limestone scrubbing systems. This by-product could alternatively be thickened and filtered to produce a high-solids cake suitable for use as dry landfill material, or convertible to a marketable item such as wallboard.

Material recovery is being attempted by other companies and by government agencies, both at the stack and in the coal-cleaning process. For example, the Westvaco activated carbon process returns spent gas to the boiler and yields elemental sulfur as a by-product. Catalytic, Inc. uses an ammonium salt-scrubbing technique with which the "blue plume" normally associated with ammonia scrubbing is eliminated; sulfur is pro-duced; and ammonia is recycled to the system. In some cases, the latter process can be adapted to convert spent "brine" into fertilizer-grade ammonium sulfate; or, in the case of sulfite pulp mills, the spent SO_2 absorbent can be recycled to the digester without additional treatment, other than a filtration step.

Davy Powergas Inc. (Lakeland, Fla.), formerly known as Wellman-Lord Inc., captures SO_2 with sodium sulfite, changing it to sodium bisulfite. The bisulfite is thermally decomposed to regenerate sodium sulfite, and the SO_2 is then further processed. At Northern Indiana Public Service Co. (Gary, Ind.), for example, sulfur will be produced from this SO_2. The basic system is now on stream at six commercial installations in Japan (ES&T, December 1974, p 1070), and at four in the U.S. By 1977, a Wellman-Lord system will treat 1.8 million scf of stack gas for Public Service Co. of New Mexico and Tucson Gas and Electric Co., at a jointly owned coal-fired power plant at Fruitland, N.M.

Interestingly enough, the Wellman-Lord system was originally developed to try to find a cheap, plentiful sulfur source during the sulfur shortage of 1965–1967. Similar material recovery and by-products, derived by different techniques, can be expected from processes that clean coal prior to burning.

Taking technical risks

Every so often, the press carries assertions by various "authorities" that coal, shale oil, solar energy, nuclear breeders, fusion—in short, any energy source except petroleum—will never really be able to meet economic or environment requirements, or some combination of these.

As Secretary Morton reminded his audience, "If we had always viewed our technological prospects so negatively, we would never have seen the development of the Model T or the flight at Kitty Hawk." These developments, as many others, entailed varying degrees of technical risk. Development of alternative, environmentally acceptable energy sources will also entail technical risk, and such risk is inherent in the evolution of improved fuels from coal.

The economic and geopolitical risks involved in heavy dependence on the availability of foreign oil, however, far outweigh the technical risks encountered in diversifying the domestic energy supply base in an environmentally acceptable manner. To accomplish a first major step toward diversification, and once more to refute technological negativism, the material to which the nation will first turn will be coal.   JJ

Changes are in store for pulping technology

Economic considerations and air pollution regulations are causing the pulp and paper industry to weigh the risks and advantages involved in non-sulfur pulping

In recent years, the paper industry, once considered to be a major air and water polluter, has been making significant progress in air and water cleanup and solid waste handling. While much remains to be done, cleanup progress is certain to continue at a very brisk pace. Indeed, this industry is estimated to have made capital investments of about $2 billion in this direction during 1974. Often, it had to resort to untried technology, or develop technology where none had previously existed.

Many pollution problems arise from the use of sulfur systems—kraft, or acid or neutral sulfite. About 85%

TAPPI's vice president Harris Ware

"New methods and improvements needed"

of a total of 48 million tons of wood pulp, expected to be processed in 1974, will have been produced in sulfur systems. Of this total about 34 million tons would be kraft. To approach problems of environment and technological change, does one therefore stay with sulfur systems and fit or retrofit mills with appropriate pollution control (pc) equipment, or does one seek methods of pulping that do not require sulfur?

The Technical Association of the Pulp and Paper Industry (TAPPI, Atlanta, Ga.), together with the American Paper Institute and the U.S. Department of Agriculture's Forest Products Laboratory convened the Non-Sulfur Pulping Symposium at Madison, Wis., last October to address the question of "getting away" from sulfur systems in pulp and paper mills.

Kraft pulping

Nearly a century ago, the kraft process, the one most used for pulping, was conceived. By the 1930's, this process had gained the most acceptance.

However, TAPPI's vice president, Harris Ware, said that the Kraft process may have passed its prime. For example, while the kraft process "is the best we have at the moment," it suffers from high hemi-cellulose losses from yield. Also, liquors and vapors have a high sulfur content, with all that this implies with respect to air and water pollution potential. High bleaching requirements and complexity of processing equipment lend further credibility to Ware's feeling that "the kraft process is old and may be on the threshold of obsolescence in its present form."

In addition, rather sharp modifications must be made to the kraft process if it is to meet today's environmental standards. These modifications could entail huge capital expenditures—more than $11 million for a 1000 ton/day mill, in January 1972 dollars. If, as Ware points out, "the kraft process is obsolete for capital cost reasons," and if "the industry's earning and financial strength cannot justify new kraft capacity to meet increasing pulp demand," capital spending on kraft process pc systems would be equally unjustified. Indeed, Ware said, "The pressure is severe for either a new pulping process or a major modification of the old process."

Non-sulfur approaches

Non-sulfur pulping itself is not new, for it was in use during the late 1850's as the so-called soda process. Nevertheless, until about a decade ago, not much work was done on non-sulfur method updating. Increasingly stringent environmental guidelines and standards, however, have caused research institutes, paper companies, and public agencies to take a long, hard second look at non-sulfur techniques, and try

Air pollution control costs for a typical mill

	Capital investment (thousands of dollars)
Recovery boiler	1200
Evaporation	920
Pulping	780
Auxiliary boiler	720
Recausticizing	580
Washing and screening	205
Bleaching	195

Annual operating costs are estimated at $313,000
Mill produces 1000 tons/day of pulp by kraft process
January 1972 dollars

to modernize them. With non-sulfur pulping methods, "there can be' eliminated most of the pollutive factors that are readily and most easily sensed, such as the volatile and malodorous sulfur compounds from kraft mills," as Matti Saukkonen and Ilpo Palenius of the Finnish Pulp and Paper Research Institute explained to the TAPPI symposium.

What is relatively new in non-sulfur pulping is oxygen pulping—usually with alkalies, such as sodium bicarbonate, carbonate, or hydroxide—and oxygen bleaching. This method shows promise for achieving low odor from mills, as well as low wastewater color through counter-

current disposal of high-color bleaching wastes, according to William Major, technical director of Westvaco's Bleached Board Division (Covington, Va.). The Pulp and Paper School of North Carolina State University and several Canadian concerns have been actively exploring this concept. Westvaco itself has been operating a non-sulfur process since September 1971.

The Hammermill Paper Co. (Erie, Pa.) has also operated a non-sulfur pulp mill since 1971. As of last October, this mill included a 640 ton/day digester, two stages of diffusion washing, brown stock screening, and a bleach plant. Hammermill initially experienced major problems with black liquor evaporation, and with malodorous "kraft-like" emissions that caused citizen complaints.

Process modifications helped to solve Hammermill's black liquor problem with only a small loss in steam economy, but, also with a means of reducing the total alkali used. As for odor control, the symposium learned that the "kraft-like" odors did stem from sulfur. However, the sulfur came from fuel oil, raw lake water, alum treatment of lake water, and impurities in purchased limestone, rather than from the non-sulfur process itself. Changeover to gas about May 1973, and installation, in mid-1974, of a scrubber system that scrubs with residual chlorine in mill effluent, have greatly alleviated the odor problem.

Owens-Illinois Co. (O-I, Big Island, Va., and Tomahawk, Wis.) recently announced a non-sulfur process that the company believes will pulp all species of hardwood currently in use. This process also allows recovery of sodium compounds used, a 10–20% reduction in other chemical use, and production of corrugating mediums of quality at least equal to those made by the neutral sulfite semi-chemical process. Both O-I and Westvaco are licensing non-sulfur processes; the O-I process has been licensed to about 5 paper companies.

A Japanese view

The view that Toyo Paper Company, Ltd. (Tokyo, Japan) presented to the TAPPI symposium was that environmental considerations were the principal stimulus for the search for "new and novel" pulping processes less polluting than those presently in use. Toyo is looking to its HOPES process to provide this new pulping technique, with air pollution control (apc) as the principal objective.

The HOPES process is a two-stage process in which oxygen pulping with sodium carbonate as the alkali is being tried. Preliminary results suggest that pulp similar in quality to kraft pulp is obtainable. According to the firm, all preparation and testing of handsheets produced by the method were performed according to TAPPI standards.

No fast changes

To be sure, sulfur pulping methods, be they kraft or sulfite, will still be in use for a long time to come. The processes involved are largely known and proved. In a number of cases, it may be economically justifiable to install technology that would control emissions of SO_x, hydrogen sulfide, and mercaptans. Indeed, these measures might be taken in instances in which the environmental, economic, and cost-benefit pictures look right to management.

A question that arises is, then, will the environmental, economic, and cost-benefit pictures look right? TAPPI's vice president Ware is not sure that they necessarily will. Not only could capital expenditures be large, but the modifications necessary to achieve environmental acceptability, even for apc alone, could entail the development of what could amount to a new technology. Perhaps the cost-benefit situation would justify the installation of such technology in a new or nearly new mill, but retrofitting an old mill, and

modifying that mill enough so that it can "interface" with new, sophisticated pc equipment may be too heavy a financial burden.

This burden could indeed be heavy. Ware told the symposium that between 1970 and 1973, for example, the paper industry's average after-tax net profit to net sales was 3.78%, and after-tax net profit to net worth was 8.45%. These statistics showed a steady decline from the 1950–1959 period, when these profit figures were 5.32% and 10.78%, respectively. Ware said that these figures are "in fact not good enough to support the capital requirements for the industry." Exacerbating these capital problems, for environmental control or anything else for that matter, are high rates for capital, as well as low availability, though this unhappy picture may change somewhat this year.

Other problems

The use of non-sulfur pulping methods, as well as the major modification of sulfur pulping methods, to curb air pollution, does not directly attack the problem of water pollution or solid waste. Other technology must be installed if water cleanup requirements are to be met by even the newest non-sulfur pulping methods. Moreover, capital problems of retrofitting older mills for water pollution control technology are similar to those encountered where apc technology is required.

Nonetheless, to meet environmental requirements, and to combat the erosion of profits from an aging technology, process modifications, including modernized non-sulfur pulping methods, will appear on the scene increasingly. TAPPI's Ware has the greatest confidence that his association's members could supply the "flash of genius" needed to devise these new methods, improve on old ones, and reduce the new methods and improvements to practice, "thereby accelerating progress." JJ

An integration of water pollution service capabilities under one roof

As a new independent subsidiary of The Dow Chemical Co., Hydroscience Associates, Inc. aims to help its clients tackle these pollution problems "from one end to the other"

"We are moving out of the time when the minimum legal requirements for effluent treatment are all that need be met. We are moving into an era in which we ask ourselves, 'why just treat; why not recover materials?'" This is the assessment of the current water treatment situation by Edwin Barnhart, who is designated to be president of Hydroscience Associates, Inc. (HAI), when it opens its doors at Emerson, N.J., as an independent subsidiary of The Dow Chemical Co., this month.

HAI president Edwin Barnhart
"Why just treat; why not recover?"

HAI will comprise three component divisions. One such division will be Hydroscience, Inc. (HI, Westwood, N.J.), incorporated in New Jersey in 1962 by Wesley Eckenfelder, Donald O'Connor, and Barnhart, and acquired by Dow in October 1972. The second is the former Dow Environmental Control Services, now Environmental Systems, which will move from Dow headquarters, Midland, Mich., to Knoxville, Tenn., during the middle of this year. Finally, there is the Resources Planning Division, which will be located at Emerson, N.J. Future acquisitions may occur.

Mathematical modeling

HI's new president is John Mancini. Its principal efforts are directed toward mathematical modeling of natural water systems and process

design. This year, HI will do about $1.5 million worth of modeling studies. These include determination, for the State of California, of effects that may result from the southward diversion of northern California water; for example, what may happen to algal growth and turbidity in the brackish zone of the San Francisco area. Another model, worked up for the U.S. Army Corps of Engineers, will predict what may happen to the Tidal Basin at Washington, D.C. if more water is impounded or diverted from the upstream Potomac River water for municipal water supply purposes.

HI is also engaged in biological/chemical treatment and process design studies, as well as studies for wastewater treatment (wwt) projects. Business is about 90% industrial and 10% municipal, and includes process design for consultants. Some clients are Du Pont (about $100,000), Shell Chemical Co. (about $120,000), and the American Textile Manufacturers Institute ($50,000). A municipal client is the

City of Roxbury, N.J., for which HI designed and operated a pilot facility so that the city engineer could design a finished plant. HI employs about 100 people at its facilities at Westwood, N.J., Dallas, Tex., and Walnut Creek, Calif.

Recovery

The Environmental Systems Division (ESD) expects to employ 80 people. Its president is Kenneth Honeycutt. One of ESD's principal efforts is directed toward recovery of water, heat, and by-product chemicals for dischargers. For example, ESD is completing a system for a pulp and paper company, which would allow recovery of acetic acid, furfural, and methanol from effluent. HAI's Barnhart estimates that the system would have a 4–5 year payback, and then generate a return.

ESD also works in incineration and disposal of industrial by-products. In this effort, ESD did a $5 million project for 3M, and is completing one for Eastman Kodak.

The HAI organization

The Dow Chemical Co. (Midland, Mich.)
Functional products and systems department
Louis Carmouche, general manager

Hydroscience Associates, Inc. (Emerson, N.J.)
Edwin Barnhart, president

Hydroscience, Inc. (Westwood, N.J.)
John Mancini, president

Resource Planning Division (Emerson, N.J.)
Edwin Barnhart, president
Rita Meyninger, manager

Environmental Systems Division
(to be located at Knoxville, Tenn.)
Kenneth Honeycutt, president

Future acquisition

Future acquisition

Future acquisition

Planning

While Barnhart will be president of the Resources Planning Division (RPD) for the time being, management will be by Rita Meyninger. RPD, which expects to employ 30 people —mostly biologists, geologists, ichyologists, and mathematical modeling experts—will focus on environmental assessments. Such assessments could assist federal regulatory agencies with preparation of environmental impact statements. Other RPD work will involve land use and land disposal techniques.

Among RPD's clients are the U.S. Army Corps of Engineers, cities of northern New Jersey, and the Milliken Chemicals Division of Deering-Milliken Co., a large privately owned textile firm.

Uniqueness

Barnhart told *ES&T* that HAI's uniqueness will be found in the firm's capabilities to look at two important questions:

● Why just treat wastewater; why not recover materials?

● If recovery is not feasible, what is the environmental impact of treated effluent discharge?

HAI would then answer these questions completely "from one end to the other." Barnhart believes that HAI's capabilities will help a discharger to prove that his effluents are environmentally compatible, and are not causing problems, according to a stiffer set of industrial discharge permit regulations Barnhart confidently expects. Another uniqueness of HAI, Barnhart said, is a staff of full-time professionals who have been in the field over the last 15 years.

The "track record" of the HAI components, with many customers among the "Fortune 500," is certainly impressive. HAI's one-year business backlog stands at $6 million, conservatively, and may prove to be as high as $10 million. HI and ESD are profitable now, and RPD is expected to generate profit shortly. Moreover, there is international business in England, Italy, and Switzerland.

Barnhart said that HAI may also be in the enviable position of being able to benefit from the present economic "stagflation." One reason is that with government spending cutbacks, additional planning was mandated, for example, under Section 208 of the Water Quality Act. Another equally compelling reason Barnhart gave is that industrial companies, faced with tighter regulations and higher chemical costs, could turn to HAI for help in devising recovery systems that offer opportunities for payback on investment, and, perhaps, eventual profit.   JJ

Disposing of liquid wastes underground

This half-century practice, used with reluctance, steadily increases as surface waters become overwhelmed by municipal and industrial wastes

Deep wells as a liquid waste management technique are used with great reluctance because of their potential for adverse impact on the environment. Nevertheless, since *ES&T* has been following the developments in this area (*ES&T*, December 1973, p 1106), the permitted number of wells has steadily increased from 30 in 1964 to 333 today. Of this total, 278 are actually drilled, and only 178 are being used. The average increase has been 23 new wells drilled each year with 19 placed in operation, according to the Environmental Protection Agency's (EPA) report "Compilation of Industrial and Municipal Injection Wells in the United States."

Relevant data

The disposal of wastes by injection into deep wells has been practiced for nearly 50 yr. But, only within the past 10 yr, as surface waters became less capable of receiving effluents without violating standards, has this disposal technique become attractive. The variety of wastewaters injected include, in order of volume, chemicals, petrochemicals, pharmaceuticals, hydrocarbon refining by-products, metal manufacturing wastes, and municipal sewage.

Since the effects of subsurface pollution are not fully understood, all relevant data pertaining to this disposal method were collected. Included in EPA's survey were those deep-well injection systems that use saline aquifers—oil field brine injection wells, storage wells, and private domestic sewage wells were excluded. Of the inventoried wells, 90% are

drilled to a depth greater than 1000 ft, 87% inject wastes at a rate less than 400 gal/min, and 78% have a surface pressure head less than 600 psig. For 97% of the wells where sufficient data were available, the minimum distance the wastewaters will have travelled within 10 yr was calculated as less than 3000 ft, and less than 6000 ft after 50 yr.

Twenty-four coterminous states and Hawaii have permitted wells; Texas, understandably, has nearly one-third of these wells. More wells were drilled in 1969 while more operations were terminated in 1972 according to the report. The most rapid growth for operating injection wells occurred between 1964 and 1970.

Aquifer characteristics

Most rock types have, under the proper conditions, sufficient porosity and permeability to accept large quantities of fluids. However, an aquifer used for the injection of liquid wastes should possess:

• a zone with sufficient permeability, porosity, thickness and area to act as a storage reservoir; and

• a zone that is vertically below fresh water circulation and confined by rock stratum impermeable to waste liquids.

Of the three major zones of injection in the U.S., the Tertiary sands of the Gulf Coast possess the required characteristics for injection wells for the states of Texas, Louisiana, and Alabama; the Cambro-Ordovician Arbuckle carbonates of the central plains serve the states of Kansas and Oklahoma; and the Cambrian Mt. Simon sandstones provide the pri-

mary injection zone for wells in Michigan, Ohio, Indiana, and Illinois. Tertiary sands and sandstones are the most commonly used aquifers followed by the carbonates, evaporites, shales, and metamorphics.

For adequate protection of potable water, the aquifer should be so structured that waste liquids are injected to a zone at least 1000 ft (300 m) below the land surface, and one or more strata impermeable to the vertical movement of wastes are present. The wastes should also be separated horizontally from the fresh water. Most permitted injections wells in the U.S. have been drilled to depths between 1001 and 2000 ft, but wells greater than 8000 ft exist.

Difficult decision

In a recent decision, the Atlanta (Ga.) regional office of the EPA ruled that the City of West Palm Beach's water pollution control facility could include injection wells to dispose of sewage-treated effluent. Speaking at the groundbreaking ceremonies, Deputy Regional Administrator John C. White termed the decision "traumatic," although the alternative, rejected by the EPA, was disposal of the effluent through an ocean outfall one mile out to sea.

The Florida project, scheduled for completion in 1976, will hopefully meet existing and 1983 federal treatment requirements, and serve as a proving ground for the method used to treat the effluent and its disposal. The initial 3500-ft deep well is being constructed to be used for test injection purposes, and subsequently as a monitoring well. A potential aspect of the project is that the treated water pumped underground may represent a viable water supply at some future date. LRE

Typical injection well*
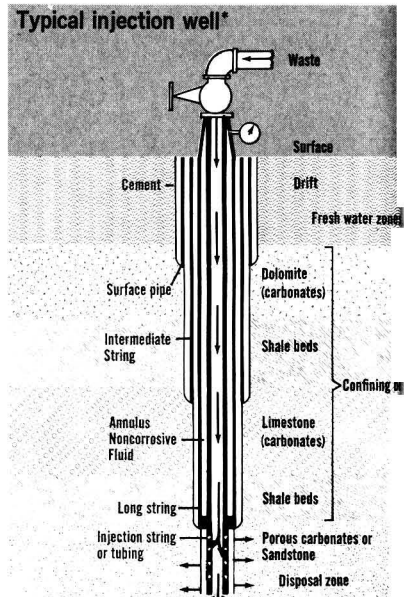
FEATURE

Energy implications of cleanup operations

The environmental thieves of modern society—air, water, thermal and noise pollution, congestion, poor land use, and solid waste management—pilfer our already limited energy supplies

Eric Hirst

Federal Energy Administration, Washington, D.C. 20461

National concern for environmental quality on the one hand, and energy supplies on the other, appear to conflict in two distinct ways. Environmental quality considerations limit fuel supplies to those that can be extracted and burned in environmentally acceptable ways. Some limitations are strip mine regulations, sulfur content limitations for coal, and power plant siting restrictions. The second area of conflict is in the amounts of energy required to operate pollution control systems. By outlining the energy implications of operating various environmental protection systems, the second area of conflict is broadly reviewed. Since technology and the law are changing rapidly, required levels of pollution abatement and optimal strategies for meeting these legal requirements have, in many cases, not yet been determined.

The limited problem areas examined were:

- urban passenger traffic
- wastewater treatment
- solid waste management
- air pollution abatement
- waste heat dissipation.

However, the energy implications of resolving other environmental problems might be significant. For each of the problem areas considered, the energy costs required to *operate* specified systems, but not costs associated with *construction* were considered.

The hypothetical parameters used to evaluate energy implications are based on 1970 data. These energy costs are probably upper limits since the parameters were designed to meet stringent goals. Technological and legal changes could alter these figures.

Urban passenger traffic

Transportation causes several major urban environmental problems including air pollution, noise, congestion, inefficient land use, and accidents. Of the many possible solutions to these problems, the energy implications of three: (a) shift from automobiles to mass transit, (b) use of air pollution control devices on automobiles to reduce emissions, and (c) redesign of automobiles to improve fuel economy are discussed. Item (c) is a method of counteracting the energy costs of item (b).

Mass transit is often suggested as an environmentally attractive substitute for automobiles because of its lower air pollution emissions, smaller land requirements, greater safety, and improved fuel economy. The automobile is particularly energy intensive because of its low seating capacity relative to weight; existing mass transit systems are half as energy intensive as autos. The nearly completed BART system in San Francisco, with its advanced lightweight design, is expected to be even less energy intensive than existing electric transit systems. Table 1 compares energy requirements for several urban passenger systems.

Energy requirements per passenger mile are strongly dependent on the load factor (percentage of seats occupied). The higher the load factor, the less energy intensive the system. Thus, a fully loaded bus operating only during rush hours will be much less energy intensive than a bus operating for a full day.

Only a small and declining fraction of urban passenger traffic is carried by mass transit—down from 15% in 1950 to 3% in 1970. Of the 20 billion passenger miles carried by mass transit in 1970, 35% was carried by electric systems and 65% by buses.

It is difficult to predict how many new transit systems will be built in the future, how widely they will be used, and the extent to which existing systems will be revitalized. Assuming a 10% shift from urban auto traffic to mass transit in 1970, at approximately 3500 Btu/passenger mile and 690 billion urban auto passenger miles, use of mass transit would have saved 320 trillion Btu. This savings is almost 6% of the 1970 urban passenger

TABLE 1
Energy use for urban passenger transport in 1970

Vehicle type	Energy per passenger-mile		Load factor, %	Seats per vehicle
	Btu[a]	kWhr[b]		
Electric mass transit (1970 system)	4100	0.353	26	58
BART	2400	0.207	20[c]	72
Motor bus	3700		18	50
Automobile	8100		28	5

[a] Gasoline converted at 136,000 Btu/gal. [b] Power plant heat rate (including transmission and distribution losses) taken as 11,600 Btu/kWhr. [c] Load factor is assumed equal to 1970 load factor for all urban mass transit.

Fuel consumption as a function of vehicle weight for 1971 and 1972 model cars.

Energy intensiveness (Btu/vehicle-mile)

1971 U.S. average (FHWA)

Automobile weight (lb)

TABLE 2
Energy intensiveness for several automobile engines

Engine	Btu Vehicle ton-mile	EI relative to 1973 IC engine[a]
1973 IC	5600	100%
1976 prototype IC	6600	118
1973 Wankel	8200	146
1973 prototype stratified charge	4700	85
1973 diesel	3100	56

[a] EI = energy intensiveness; IC = internal combustion.

traffic energy budget, equivalent to 0.5% of total U.S. energy consumption (67,400 trillion Btu) for 1970.

The federal Clean Air Act of 1970 established air pollution emission standards for automobiles designed to reduce hydrocarbon, carbon monoxide, and nitrogen oxide emissions by about 90%. Meeting these standards will probably worsen fuel economy by 10–30%. According to recent tests conducted by the Environmental Protection Agency (EPA), the fuel penalty caused by emission controls on 1973 model cars is 10%. Use of catalytic converters to meet 1975 standards improved fuel economy considerably.

Applying an average fuel penalty of 20% to 1970 urban auto traffic shows an increase in fuel use of 1100 trillion Btu. This represents a 19% increase in urban passenger traffic energy use, a 1.6% increase in total energy use for that year.

Because of concerns over domestic oil shortages and the need to import large quantities of petroleum, there is considerable interest in improving the energy efficiency of our transportation system. Since the automobile consumes a larger share of the transportation energy budget than all other modes combined, an examination of this mode for potential efficiency improvements is crucial.

The single most important determinant of auto fuel economy is vehicle weight. Fuel economy in the *Consumer Reports* test trip (1971) ranged from 35 mi/gal for the 1600-lb Datsun to 11 mi/gal for the 4600-lb Mercury Marquis. The 1971 average auto fuel economy, as reported by the Federal Highway Administration, was 13.7 mi/gal.

Other methods to reduce fuel use include redesign of auto shapes to reduce aerodynamic drag, use of low-loss tires such as radials, use of cars with lower horsepower-to-weight ratios, redesign of the internal combustion engine, and use of alternative power sources. Table 2 shows fuel economy for a number of engines tested by the EPA. The diesel engine (which met the 1975 standards) and the prototype stratified charge engine (which met the 1976 standards) provided fuel savings of 44% and 15%, respectively, relative to the 1973 internal combustion engine.

Combining all the energy-conserving options could cut auto fuel use by as much as one half, but this is unlikely. More likely, average auto fuel economy would be improved sufficiently to offset the expected fuel penalty caused by emission control. Such an improvement could be achieved by a 25% shift to small cars weighing one half the average, plus a 25% shift to diesel engines.

If no offsetting actions are taken, energy requirements for urban passenger travel could increase because of auto emission standards. Fuel savings owing to increased use of small cars and greater use of more energy-efficient auto engines were assumed to balance the incremental fuel costs for pollution control. Applying these assumptions to the 1970 situation would have yielded a net energy savings of 320 trillion Btu/yr, owing to the assumed 10% shift from autos to mass transit.

Wastewater treatment

Wastewater treatment can take a variety of forms, depending on the use to be made of the treated water (and the strictness of water quality standards). Much wastewater in the U.S. is presently untreated or inadequately treated. One third of the total wastewater effluent comes directly from homes; the remaining comes from commerce and industry, particularly chemical, food, pulp, and paper manufacturers.

Domestic wastes require about 0.17 lb of oxygen per person per day for biological oxidation. The load of a treatment plant is usually expressed in terms of population equivalents (PE), which is the total biochemical oxygen demand (BOD) divided by 0.17 lb.

Figure 2 gives the annual electricity cost per PE as a function of plant size for conventional primary treatment, and for primary/secondary (activated sludge) treatment. Also shown is the kWhr requirement for the 7.5-million-gal/day Lake Tahoe Advanced Waste Treatment (AWT) plant. Major economies of scale exist in the kWhr consumption for operation of treatment plants. Negating the use of large plants are the costs of piping and pumping water from long distances to a central plant.

Electric energy requirements for sewage treatment as a function of plant size.

Annual electricity use (kWhr/PE)

Primary/activated sludge

● AWT

Conventional primary

PE, Population equivalents
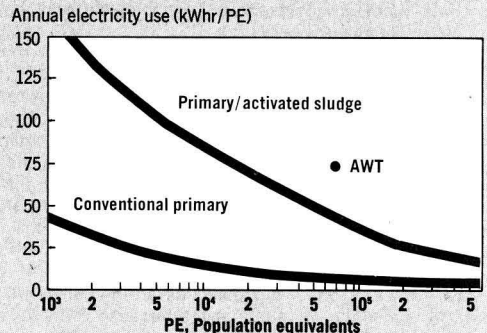
TABLE 3
Energy use for solid waste disposal by landfilling

City	Energy, Btu/ton
Oak Ridge, Tenn.	190,000
Los Angeles, Calif.	300,000
New York, N.Y.[a]	510,000

[a] The estimate for New York includes energy used for street cleaning and is, therefore, too high.

A rather small plant size of 30,000 PE yields an energy consumption of 41 kWhr/PE-yr. The ratio of PE to population in 1970 was 3; thus, electricity use for primary/secondary treatment of *all* wastewater in the U.S. would have been 25 billion kWhr/yr, 1.8% of total 1970 electricity use. This is equivalent to 290 trillion Btu/year, 0.4% of total energy use.

The incremental kWhr cost for tertiary treatment is about equal to that for the primary/secondary system. For the Lake Tahoe AWT plant, primary/secondary/tertiary treatment requires 70 kWhr/PE-yr. In addition, 1.4 million Btu/PE-yr of natural gas is consumed for a total AWT energy cost of 2.2 million Btu/PE-yr.

Solid waste management

Approximately 250 million tons of residential, commercial, and institutional solid waste were produced in the U.S. during 1969. Of this, 25% was uncollected, 68% was disposed of in open dumps and landfills, and 6% was incinerated. Only a very small fraction was recycled.

Energy, primarily petroleum, is required to collect, transport, and landfill solid wastes. Table 3 gives estimates of the energy required for these processes for three very different cities.

A reasonable average value for solid waste collection, transportation, and disposal in landfills is 300,000 Btu/ton. If all solid waste had been properly landfilled in 1970, the total energy cost would have been 75 trillion Btu, 0.1% of total energy use that year.

Incineration of solid waste yields heat at a rate of about 10 million Btu/ton. This heat can be used to generate electricity. For example, the Union Electric Co. in St. Louis burns 300 tons of municipal refuse a day to generate 12.5 MW of electrical power. Similarly, the General Motors Truck & Coach Division recently installed two boilers specifically designed to burn processed plant rubbish. About 55,000 tons of refuse will be burned annually. If 10% of the 1970 solid waste had been incinerated, 25 billion kWhr/yr could have been generated, equivalent to 1.8% of total electricity consumption (0.4% of total primary energy use for that year).

A partial alternative to solid waste disposal is recycling. When materials are recycled, various processes associated with virgin material cycles (e.g., mining, crushing, grinding, milling, separation, transportation to

TABLE 4
Production data and estimated energy use for basic materials

	Total 1970 production,[a] 10⁶ tons	Percent of production from old scrap	Energy coefficients, million Btu/ton	
			Existing methods	100% recycle[a]
Steel	132	26	23	8
Aluminum	4.0	4	218	9
Paper	52.5	18	28	21

[a] Recycle energy coefficients include 2 million Btu/ton for solid waste separation, transportation, and miscellaneous uses.

smelter, oxide reduction) are not needed. On the other hand, waste products must be collected, separated into components, shipped to refiners, remelted, and then (as with virgin materials) shipped to finishing plants for fabrication.

For steel, aluminum, and paper, primary energy consumption for production from recycled scrap is considerably less than energy required to make these materials from raw ores. For example, the energy required to produce raw steel from scrap is about 25% of the energy required to make steel from virgin ores. For aluminum, the figure is less than 5%, and for paper 60–70%. These energy estimates do not include collection, separation, and transportation of solid wastes. Table 4 lists basic production statistics for steel, aluminum, and paper and estimates of the primary energy required to produce each material using existing methods and using 100% recycled scrap.

Approximately 50 kWhr/ton is required to separate solid wastes into useful components. Transportation of recycled materials to processing plants is assumed to require one million Btu/ton, and an additional 50 kWhr/ton is included for miscellaneous purposes.

If one third of the U.S. production of these three materials had been obtained from recycled scrap in 1970, the overall energy savings, considering all steps from mine or solid waste to primary production, would have been about 440 trillion Btu, almost 0.7% of total energy use. The electricity savings would have been 23 billion kWhr, 1.7% of total 1970 use. Although major institutional and economic problems that inhibit greater recycling of energy-intensive materials have been ignored, it can be seen that greater recycling would reduce energy consumption, conserve resources, and help alleviate solid waste problems.

Air pollution abatement

The major sources of air pollution, by weight, in 1970 were: transportation 55%, stationary power sources 17%, industrial processes 14%, solid waste disposal 4%, and miscellaneous 10%. Emissions can be reduced with pollution control equipment which trap emissions before release to the atmosphere, by fuel substitution, or by process changes.

Legislated pollution control devices for automobiles will substantially reduce air pollution levels in both urban and rural areas. Substituting mass transit for autos in urban areas would reduce total energy consumption and, thereby, lower pollution levels further.

Particulate emissions from stationary sources are commonly removed with electrostatic precipitators. The electricity required to operate 95% efficient precipitators at electric power plants is typically less than 0.1% of power plant output. Limestone scrubbing to remove 80% of the sulfur from stack gases would consume 4 to 8% of power plant output. Other sulfur removal processes may require much less electricity—the molten carbonate process is expected to use less than 1% of plant output for 90% efficient sulfur removal. Energy costs for nitrogen removal are not yet known.

The electricity requirement for 90% efficient particulate and 70% efficient sulfur removal at power plants, furnaces, cement plants, incinerators, and fossil fuel cleaning facilities was estimated at 26 billion kWhr/yr for 1970. To account for increasingly strict air quality standards and the fact that several industrial air pollution sources were not considered in the above list, the air pollution control electricity consumption was arbitrarily increased by 50% to 39 billion kWhr/yr.

The primary energy requirement for 90% efficient particulate and 70% efficient sulfur removal at the stationary sources listed above was estimated at 560 trillion Btu for 1970. This includes the electricity noted above plus 260

trillion Btu for heat. Increasing the total Btu requirement by 50% yields a primary energy requirement for air pollution control at stationary sources of 840 trillion Btu for 1970, 1.2% of total 1970 energy use.

Waste heat dissipation

For every kilowatt-hour of electricity generated in the U.S., about 7100 Btu of waste heat are discharged at or near the power plant, a consequence of the 32.5% average thermal efficiency with which electricity is now generated. Much of this heat is discharged to natural water bodies adjacent to power plants that use once-through cooling, with the remainder lost in-plant and up the stack.

In some cases the ecological impact of thermal discharges to natural water bodies may be sufficiently adverse to warrant the use of alternative condenser cooling systems, such as cooling ponds or cooling towers. In 1970, about 20% of the installed steam–electric capacity was cooled with towers and ponds. By 1990, at least 35% of all power capacity is expected to use cooling towers, and an additional 13% is expected to use cooling ponds.

Energy is required for operation of cooling towers to pump cooling water to towers, in towers, and back to condensers. Mechanical draft towers require energy to operate fans that blow air through the towers. Increased turbine back pressure caused by use of closed-cycle towers results in a loss of electricity production.

Use of mechanical draft, wet cooling towers results in a power penalty, relative to once-through cooling, of about 1% for fossil plants and 2% for nuclear plants. For natural draft wet towers, the comparable figures are 2% and 3%. Natural draft towers use more power, in spite of the fact that no fans are required, because of their higher turbine back pressures. Nuclear power plants require additional power because they operate at lower efficiencies and use more cooling water.

For dry cooling towers, the power penalty is higher than for wet towers because of a greater increase in turbine back pressure. The power loss for dry towers is about 6%. Because of their higher capital costs, dry towers are not likely to be extensively used during the next decade or so.

The power penalty for cooling ponds is small relative to once-through cooling.

If 50% of all power plant capacity had been equipped with wet cooling towers in 1970, the electricity consumed would have totaled 14 billion kWhr, 1% of total consumption assuming that the average power penalty is 2%. The primary energy equivalent of this electricity is 160 trillion Btu, 0.2% of total 1970 energy consumption.

Conclusions

The National Petroleum Council (NPC), as part of its work on the *U.S. Energy Outlook*, examined energy requirements for environmental improvement. The NPC total and that given here are in close agreement—roughly 3.5–4.0% of total energy use.

In spite of the assumption and limitations used in developing the present estimates, several interesting and useful conclusions can be drawn. First, the quantities of energy required to achieve various environmental quality goals are relatively small. For example, the 840 trillion Btu estimated for air pollution at stationary sources is only 1.2% of total 1970 energy use. At an annual energy growth rate of 3.5%, this represents four months' energy growth in 1970. The sum of *all* the increased energy costs (Table 5) amounts to about one year's normal growth in energy use. This suggests that present energy growth rates cannot be attributed to operation of environmental protection systems.

Second, energy needs for environmental protection can be more than offset by various conservation measures. Increased recycling, generation of electricity with solid waste, shift from autos to mass transit, redesign of autos to improve fuel economy, and increased building insulation could significantly reduce energy growth. Such energy conservation measures would reduce pollution, conserve scarce energy resources, and generally save money for consumers.

Third, the conclusions in regard to *primary energy* closely correspond to those for *electric energy*. An earlier study by the author found that "the quantities of electricity required to achieve various environmental quality goals are not large" relative to total 1970 electricity use. According to a survey conducted by the Edison Electric Institute, industrial use of electricity in 1971 for pollution control equaled 3% of total electricity use for that year.

Additional reading

J. C. Bravard et al., "Energy Expenditures Associated with the Production and Recycle of Metals," 87 pp, Oak Ridge National Laboratory Report ORNL-NSF-EP-24, November 1972.

E. Hirst, "Energy Implications of Several Environmental Quality Strategies," 31 pp, Oak Ridge National Laboratory Report ORNL-NSF-EP-53, July 1973.

R. L. Michel, "Costs and Manpower for Municipal Wastewater Treatment Plant Operation and Maintenance, 1965–1968," *J. Water Pollut. Contr. Fed.*, **42**, (11), 1883–1910, November 1970.

Office of Air and Water Programs, "A Report on Automotive Fuel Economy," 39 pp, U.S. Environmental Protection Agency. October 1973.

M. Ross et al., "Energy Costs of Limiting the Degradation of the Environment." University of Michigan, prepared for the Energy Policy Project, draft report, June 1973.

TABLE 5
Energy use for hypothetical 1970 environmental quality measures

	Increase, trillion Btu	Savings, trillion Btu	Percent of total energy use[a]
Urban passanger travel			
Mass transit		320	−0.47
Automobile pollution control	1100		+1.63
Redesign of automobiles		1100	−1.63
Secondary level sewage treatment	290		+0.43
Solid waste management			
Landfilling	75		+0.11
Incineration, electricity generation		290	−0.43
Increased recycle		440	−0.65
Air pollution control at stationary sources	840		+1.25
Waste heat dissipation with cooling towers at power plants	160		+0.24
TOTALS	2465		+3.66
		2150	−3.19

[a] Total 1970 energy consumption was 67,400 trillion Btu.
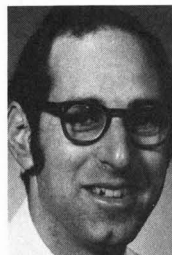
Eric Hirst is director of the Office of Transportation Research, Federal Energy Administration, Washington, D.C. The work described here was done while he was a research engineer in the Environmental Program at the Oak Ridge National Laboratory. Dr. Hirst's work deals with energy-use patterns and methods for improving energy efficiency, particularly for transportation.

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Current, accurate pollution control requirements.
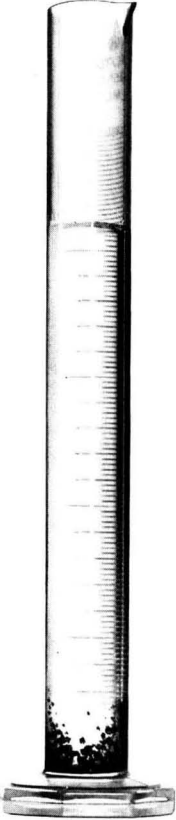
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Global atmospheric monitoring

Meteorology is able to look back on more than one hundred years of international cooperation and progress. The World Meteorological Organization (WMO) and its predecessor, the International Meteorological Organization created in 1873, have been the focal points of these international efforts. They have been remarkably successful in bringing together the national capabilities of member countries for monitoring atmospheric and related geophysical parameters, and in coordinating the exchange of observed data. A continuous technical evolution in methods of communication and observation has permitted a steady development, extension, and improvement of systems for monitoring the physical properties of the atmosphere on a global scale.

With the development of new approaches to forecasting weather, particularly the use of satellites and computers, it became obvious that the then present system (1960) was not sufficient to cover completely the atmosphere horizontally or vertically, and was not capable of data exchange with sufficient speed. It was realized that to make use of modern techniques to extend weather forecasting from 24 hours to several days, it would be necessary to expand the network of observation stations over many land areas in developing parts of the world not yet covered and, even more importantly, over large ocean areas, particularly those in the southern hemisphere. Improved observations from the upper atmosphere were also needed.

This thinking induced the General Assembly of the United Nations in 1960 to adopt unanimously a Resolution that called upon the WMO to develop a plan that would ensure "that these new devices are fully used in man's constant endeavour to improve his basic knowledge of the atmosphere and that this knowledge will be applied in practical and peaceful ways for the benefit of all peoples of the world."

The World Weather Watch

In response to this Resolution, WMO formulated plans for a new world weather system to which the name World Weather Watch (WWW) was given. The World Weather Watch program, which was launched by the World Meteorological Congress in 1963, constitutes the basic part of the WMO monitoring enterprises and involves three elements:

- the Global Observing System (GOS)
- the Global Telecommunication System (GTS)
- the Global Data-Processing System (GDS).

The first system ensures that meteorological observations are made regularly at fixed international times at a network of stations covering, as far as possible, the whole surface of the globe. Some 9,000 stations form the present network of synoptic land stations. In addition to

Maintaining a watch on the weather and other air pollutants is becoming a worldwide concern

Carl C. Wallén

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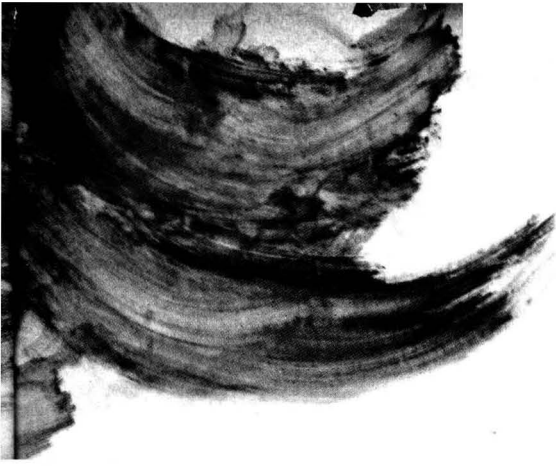
these observations, the GOS provides data from about 6,000 merchant ships at sea, from special ocean weather ships, and from a large number of aircraft. In recent years, an overwhelming amount of worldwide data from meteorological satellites are also being made available to all countries through the WWW.

For monitoring the physical properties of the atmosphere, the GOS provides synoptic (usually 6 hourly) observations of such common meteorological parameters as air pressure, temperature, wind, humidity, clouds and precipitation, as well as many other types of geophysical observations. The GTS provides for these observations to be exchanged within a few hours on regional, hemispheric, and even global scales between various centers. Many of these centers, in view of the vast quantity of data now available, are equipped with modern data-processing equipment, including high-speed electronic computers. The World Centers are located in Melbourne, Moscow, and Washington, D.C., with 21 Regional Centers spread around the continents.

Single-purpose systems

In addition to the multipurpose basic monitoring system, designated by the name WWW, the WMO coordinates a series of specialized single-purpose systems, each specifically tailored to the needs of the user. These systems, of three different types:

- support research activities in atmospheric science
- support studies and application of environmental problems
- support special applications of meteorology.

Monitoring systems in the first category include a limited number of stations for solar radiation, atmospheric ozone, and atmospheric electricity. The solar radiation network consisting of several hundred stations around the world measures incoming and outgoing radiation at the surface of the earth; data from this network are collected under the auspices of WMO, and published annually by the Main Geophysical Observatory in Leningrad.

The network for monitoring ozone in the atmosphere includes, at present, 32 stations. Data are collected under the auspices of WMO and published annually by the Atmospheric Environment Service of Canada. Nineteen stations under joint coordination of the International Union of Geodesy and Geophysics (IUGG) and WMO are making regular measurements of the earth's electrical field and its relation to atmospheric processes.

Monitoring the world's climate is very essential for many application purposes and, in particular, for studies of the human environment. An extensive network of climatological stations in all WMO member-countries provides the basis for such studies and applications. The network, including the special networks established for recording precipitation, consists of more than 100,000 stations that measure elements indicative of the physical properties of the atmosphere. This network is similar to the stations in the WWW system, but they generally report on a monthly basis. Some of the data in the climatological monitoring system are exchanged on WWW facilities.

For application purposes, WMO coordinates and provides guidelines for meteorological observations, and the processing of data from special national networks serving marine activities, air transport, agriculture, and water resource development. In the latter case, WMO is responsible for the coordination and guidance of hydrological observations.

The multipurpose basic WWW system acts in support of all the specialized systems; in any country, all or some of its constituent elements can simultaneously be part of a specialized system. For example, the Global Telecommunication System of WWW is also used for the exchange of data from specialized systems.

Monitoring chemical properties

It is only recently that meteorologists, who for so long have monitored the physical properties of the atmosphere, have begun to follow and study its composition and chemical properties systematically.

In the 1950's a scientific interest in atmospheric chemistry developed in Scandinavia and spread to western Europe and the U.S., stimulated mainly by the famous meteorologist, the late Professor C. G. Rossby, then at the University of Stockholm. Unofficial networks of research stations were established in these countries for observing the chemical content in precipitation. Data from these networks were collected in the Department of Meteorology of the University of Stockholm and published in the geophysical journal *Tellus;* data on the CO_2 content of the atmosphere over Scandinavia derived from aircraft observations were also published. Several important contributions to our knowledge about atmospheric chemistry were derived from these data and published in *Tellus.*

It is interesting to note that until the mid-1960's these research studies in atmospheric chemistry were little stimulated by environmental concerns. WMO's Technical Commission of Aerology in 1957 established a working group on atmospheric chemistry whose main responsibility was to evaluate methods and standardize instrumentation in atmospheric chemistry, with particular reference to the problem of ice and condensation nuclei. At the subsequent session of the Commission in 1961, the working group on atmospheric chemistry was re-established and charged with the collection, sampling, and analysis of atmospheric chemistry data with no reference to the problem of air pollution.

In 1965 the Commission on Aerology recognized for the first time the continuous need for monitoring and research in atmospheric chemistry and, in particular, the problem of air pollution. A new working group was established to study implications of meteorology to both local and background atmospheric pollution. The working group was requested to consider, even at this early date, the possibility of establishing a worldwide network of stations to monitor atmospheric pollution at a background level.

The changes detected in the composition of the atmosphere over the last decade have had, from the point of view of the human environment, the effect of degrading the atmosphere. We are all well aware of the unpleasant health effects and other obvious problems related to highly polluted air in cities and industrialized areas, but few of us realize that some pollutants gradually accumulate in the atmosphere and have environmental consequences not only locally but over large areas, and that ultimately the earth's climate may be affected.

Text labels within the figure:

SYNCHRONOUS METEOROLOGICAL SATELLITE (SMS)

TEMPERATURE HUMIDITY AND RAINFALL

LOCAL, REGIONAL AND NATIONAL CLOUD COVER PICTURES

SEA BUOYS

ALL ENVIRONMENTAL DATA

RIVER AND STREAM GAUGES

COMMAND AND DATA ACQUISITION STATION

MERCHANT VESSELS
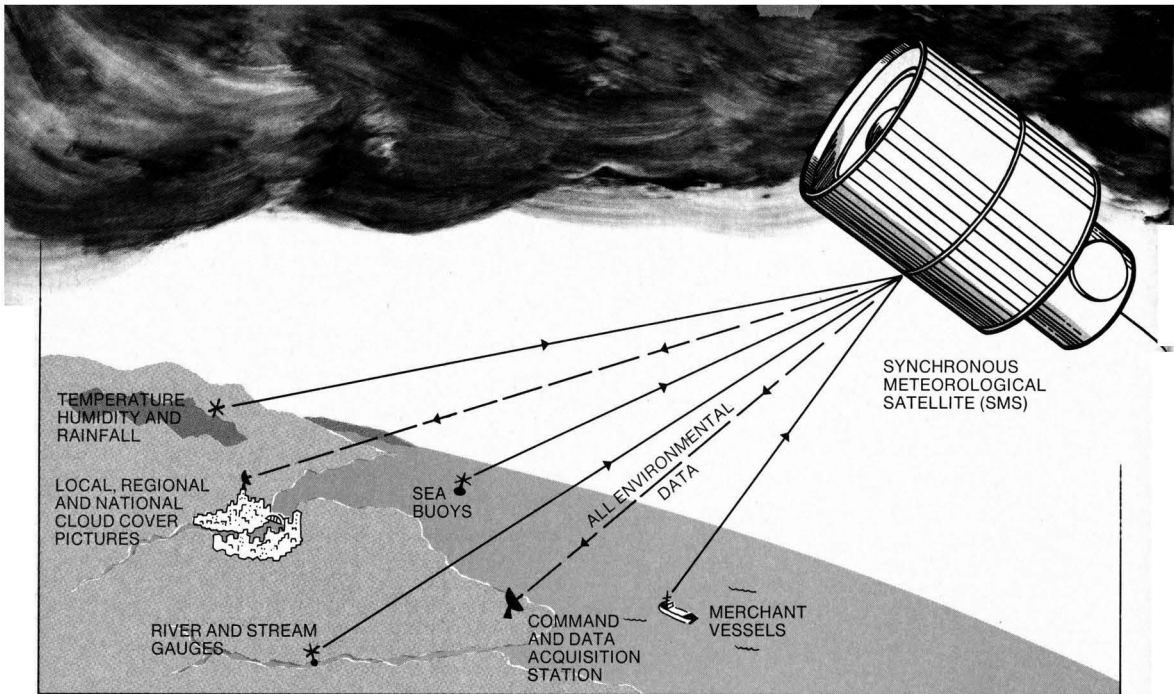
Monitoring background pollution

In view of the possible detrimental consequences of a gradual increase of low concentration pollution, the atmospheric chemistry working group in 1969 proposed the establishment by WMO of a global system for monitoring atmospheric pollution at a background level. In 1970, the Executive Committee of the Organization accepted the proposal to establish a network, and the project became operational following approval by the World Meteorological Congress in 1971.

The observation stations within the global network are located sufficiently remote from industrialized areas so as not to be influenced by short-term fluctuations in pollution from local sources. The network consists of two types of stations with different objectives:

• *regional air pollution stations* intended to reveal long-term changes in atmospheric composition that may be related to changes in regional land-use practices or other activities. Parameters measured at these stations are turbidity and chemical composition of precipitation. Samples are analyzed for SO_4^{--}, Cl^-, NH_4^+, NO_3^-, Ca^{++}, Mg^{++}, Na^+, K^+, heavy metals, alkalinity, conductivity, and pH.

• *baseline air pollution stations* designed to document long-term changes in atmospheric, environmental parameters of particular significance to weather or climate, with a minimum of influence from local or regional factors. Parameters measured at these stations are turbidity, chemical composition of precipitation (as at regional stations), and carbon dioxide in air samples.

As a result of a request to all member-countries to establish at least one regional station per 500,000 m^2 of territory, the network of regional stations has expanded gradually and, at present, around 130 stations in 58 countries are proposed or identified. Around 15 of these need further consideration regarding the suitability of their location. Of the remainder, around 50 are at least partially operating and more stations are gradually coming into operation as means become available. It is hoped that ultimately 150–200 regional stations will become operational around the world.

Continued and increasing interest is being devoted to the baseline stations. So far, 10 members have proposed

locations for 12 stations. About a third of these stations are either partially operating or being tested for operation. The project calls for the ultimate establishment of 10 to 15 baseline stations around the world but, in view of the considerable costs involved, it is anticipated that this goal may not be reached for 5–10 years.

As far as the collection of data is concerned, it was agreed that the two World Centers of the WWW in Washington, D.C., and Moscow would collect all data available. It was further agreed that the U.S. would publish the data annually; special forms have been developed for entering data before their submission to permit publication by computer.

Baseline stations measure the following additional constituents in air samples on an optional basis:

Sulphur dioxide ⎫ or total
Hydrogen sulphide ⎭ sulphur
Oxides of nitrogen (NO and NO_2)
Ammonia
Total ozone
Total precipitable water
Particle composition of dry fall-out
  (Cl^-, SO_4^{--}, NO_3^-, NH_4^+, Ca^{++}, Mg^{++}, Na^+, X^+)
Carbon monoxide

Methane
Nitrous oxide (N_2O)
Ozone at ground level
Condensation nuclei
  (Aitken nuclei)
Particle size distribution
Heavy metals (Pb, Hg, Cd) in air
Total light hydrocarbon compounds
  (excluding methane)

Standardizing methods

The standardization of observations at the stations is obviously an important although difficult problem. In this new field, methods have not yet been tested and agreed upon by specialists. In many cases, the low concentration of pollutants in air or precipitation may even prevent analysis by existing methods. Nevertheless, WMO has made attempts to obtain a consensus regarding the methods to be applied. The WMO panel of experts on meteorological aspects of air pollution has supervised the preparation of manuals on methods of observation and analysis to be used at regional and baseline stations. The

first part dealing with regional stations was issued in 1971, and the second part dealing with more complicated methods to be applied at baseline station is to be published later this year. Fairly final proposals for methods are presented in Part I of the manual but it has been agreed that it is still premature to demand the standardization of techniques to be used at baseline stations. Part II will, therefore, be published in the form of guidelines for methods to be applied at baseline or regional stations; this will permit the early initiation of observations, even in the absence of final recommendations. As accepted new methods become available, the manual will be supplemented with new guidelines.

An important problem now facing the Organization is the extension of the network into areas where governments have not yet volunteered to establish stations. This is particularly the case in developing countries. Realizing the great importance of this monitoring network, the WMO Congress in 1971 decided that the network should become an integral part of the World Weather Watch. In this way, it will be possible to support the establishment of stations in developing countries through the WMO Voluntary Assistance Programme (VAP) and, indeed, a number of developing countries have made requests for support to establish background air pollution stations. The VAP provides for donor countries to voluntarily make available means for helping developing countries to improve their meteorological networks and facilities within the framework of the WWW. With the program's assistance, it is hoped that a number of countries will be able to join the background air pollution monitoring system.

Relationship with UNEP

WMO, through its regular program, will make provision for advice on general standardization of methods, for coordinating the activities relating to the system and for general administration. With the very limited funds available, the Organization will not be able to provide means for advice to developing countries, for support to purchase equipment, and for the erection of stations. There is also need for the training of personnel and the granting of fellowships.

In an attempt to get support for the latter types of activities, WMO has turned to the United Nations Environment Program (UNEP). The UN Conference on the Human Environment held in Stockholm in 1972 requested the WMO to continue its efforts to establish a monitoring system for background air pollution. The Organization then indicated that financial assistance from the Environment Fund for support of the extension of the network in developing countries was needed. UNEP has, in fact, taken a considerable step in support of the program by providing the means for expert advice and equipment to a number of stations in the developing countries during 1974 and 1975.

UNEP's interest in these kinds of activities was further manifested through the Intergovernmental Meeting on Monitoring, which was held in Nairobi on Feb. 11–20, 1974. At this meeting for governmental experts, various aspects of how to organize a global monitoring system for the whole environment were discussed. Objectives and principles of such an overall system were agreed

Present stage of WMO network for monitoring background air pollution

Regional air pollution stations
- ● In operation
- ◐ Planned (located)
- ○ Proposed (non-located)

Baseline air pollution stations
- ■ In operation
- ◧ Planned (located)
- □ Proposed (non-located)
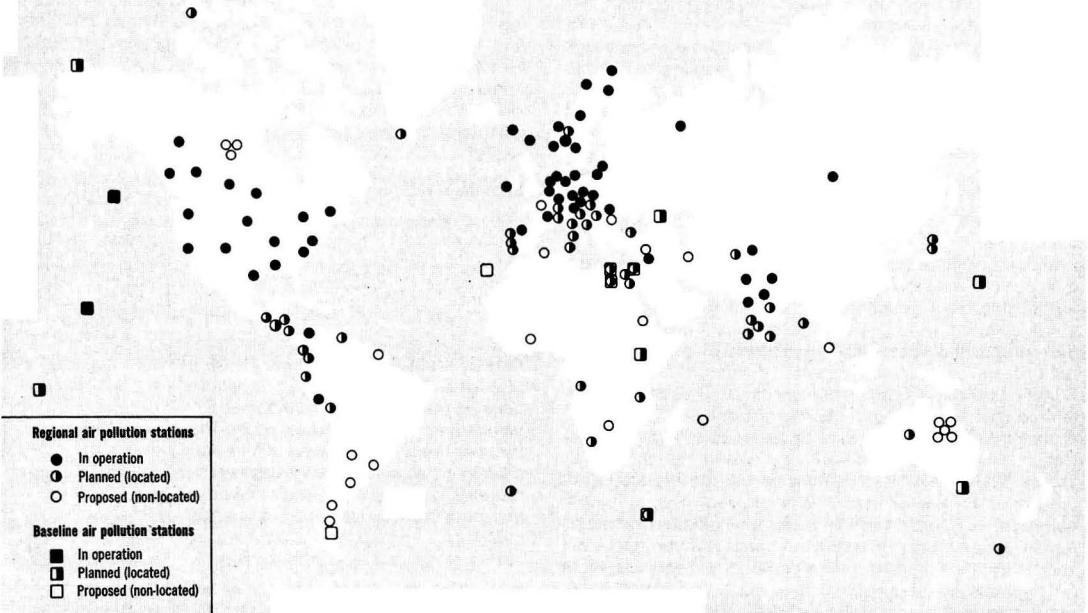
upon. A list of priority pollutants to be monitored in all media of the environment was established, and indications about other environmental factors to be monitored within the Global Environmental Monitoring System (GEMS) were given.

The Governing Council of UNEP has agreed that UNEP should make the necessary administrative arrangements for the preparation and implementation of GEMS, while taking into consideration already existing systems for monitoring the environment. It is to be hoped that UNEP will consider the WMO system for monitoring background pollution as an important system contributing to GEMS, and that WMO will, therefore, obtain further support for its development. The Governing Council has allocated approximately $1 million to support the overall planning and organization of GEMS duing the forthcoming year.

Monitoring high concentration pollution

The concentration of air pollution in cities and in industrialized areas is very much related to such meteorological conditions as wind direction, wind velocity, and the vertical stability of the atmosphere. The study and forecasting of dispersion patterns, and the concentration of air pollution in cities and industrialized areas requires the careful and specialized monitoring of meteorological parameters in addition to the pollutants themselves. WMO has for some time, through the activities of a working group, studied both the dispersion and forecasting problems in connection with air pollution in high concentration. Close cooperation with the World Health Organization (WHO), which is responsible for the monitoring of pollutants in view of their health effects, is continuously going on. A WMO contribution on air pollution meteorology to a manual on air pollution control is to be published shortly by the European office of WHO. A Technical Note on methods in the application of past weather and climate data to the assessment of the climatological poten-

tial for air pollution will be published later this year by WMO.

A recent decision of the Executive Committee of the WMO calls for increased activities in the area of application of meteorology to problems of air pollution in cities and industrialized areas. In particular, meteorology should be applied to monitoring activities and to the development of air pollution control systems.

The WMO coordinates its monitoring activities regarding the atmospheric environment not only with the UNEP and WHO. Close collaboration is maintained with OECD on long-range transport of air pollution and its impact on vegetation, soil, and water; with the Economic Commission for Europe of the UN on economic aspects of air pollution; and with the Council of Europe on the legal aspects.

Additional reading

WMO Operations Manual for Sampling and Analysis Techniques for Chemical Constituents in Air and Precipitation. WMO-No. 299, 1971.

Dispersion and Forecasting of Air Pollution. Technical Note No. 121, 1972.

Carl C. Wallén *is chief of the Division of Special Environmental Applications of the World Meteorological Organization. Dr. Wallén has edited the journals* Tellus *and* Geografiska Annaler, *and was regional editor for the journal* Agricultural Meteorology. *He has published several papers on climatology, glaciology, agricultural meteorology and environmental meteorology.*

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CURRENT RESEARCH

Effects of Ambient Concentrations of Peroxyacetyl Nitrate on Navel Orange Trees

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■ Young navel orange trees and branches of a mature tree were enclosed and exposed for two years at Riverside, Calif., to activated carbon-filtered air, carbon-filtered air plus ambient levels of peroxyacetyl nitrate (PAN), or ambient air. The growth of the young trees was reduced by the addition of synthetic PAN at levels in ambient air. Leaf drop increased. With enclosed branches, significantly less growth occurred with PAN. Trends toward reduced yield of mature fruit were seen. Short-term apparent photosynthesis was not affected by fumigating a young tree with 20–80 ppb of PAN.

Peroxyacyl nitrates, produced in sunlight from unsaturated hydrocarbons and oxides of nitrogen, are highly phytotoxic to some species (1, 2). The effects of peroxyacetyl nitrate (PAN), the most abundant compound of the series, has been studied in some detail. It produces a glazing, silvering, or water-soaked condition on the lower surface of several leafy vegetables (3, 4). Lettuce, chard, and spinach are especially sensitive. These lesions later dry up to give yellow or brown spots which may extend through the leaf. Taylor (2) reported that exposure to 14 parts per billion (ppb) of PAN for 4 hr produced acute injury on petunia and tomato plants.

Elevated levels of PAN have been reported in several areas of the U.S. Taylor (2) measured 58 ppb at Riverside, Calif., in 1967, while Tingey and Hill (5) reported 54 ppb at Salt Lake City, Utah. Mayrsohn and Brooks (6) measured 210 ppb in downtown Los Angeles, which may be an all-time high. Ordin et al. (7, 8) reported that PAN, at high levels, inhibited polysaccharide synthesis in Avena coleoptiles and inhibited the carbohydrate-synthesizing enzyme phosphoglucomutase. Mudd and McManus (9) observed the oxidation of sensitive sulfhydryl groups in enzyme preparations. No evidence of PAN's causing reduced apparent photosynthesis in the absence of visible leaf symptoms has been reported. The entire ambient photochemical oxidant complex has been shown to reduce apparent photosynthesis in isolated lemon branches and in whole trees (10). Also, studies on both lemon and orange trees showed reduced yield and increased leaf drop (11).

The purpose of the present study was to find out if, and if so, how much injury ambient levels of PAN were causing to navel orange trees in the Los Angeles Basin as represented by the Riverside area.

Experimental Methods and Results

Two parallel studies were conducted to test the effects of ambient levels of PAN (occurring in Riverside) on navel orange trees. In one study grafted young orange trees were tested to determine the effects on growth, leaf drop, and other vegetative responses. The second study utilized near equal sized branches from a mature tree. The fruiting branches were enclosed in ventilated, plastic-covered chambers and both leaf drop and fruiting responses were observed. PAN was monitored continuously with an automated PANalyzer (12) at 15-min intervals. Representative weekly values of PAN were obtained by taking the sum of the means of the hourly averages and dividing by 168 hr. Total oxidant levels were measured with a Mast ozone meter and were calculated likewise, but the hourly values were estimated by averaging the continuous strip chart record on an hourly basis (Figure 1).

In the study on young trees, three separate experimental chambers were constructed within an air-conditioned, glass-glazed greenhouse. The air in the greenhouse surrounding the chambers was filtered through activated charcoal to remove ozone, PAN, NO_2, and other readily adsorbed ambient air pollutants. The chambers were wood-framed cubes, $2 \times 2 \times 2$ meters, equipped with ventilating blowers and glazed with polyvinyl fluoride (Dupont Tedlar). Eight cubic meters of air per minute were provided to each chamber.

One experimental chamber was ventilated with the carbon-filtered air (clean) from within the greenhouse; the second, with carbon-filtered air plus levels of synthetic PAN that occurred in outside air (PAN), and a third received outside ambient air that included the photochemical smog complex (e.g., ozone, PAN, NO_2). The amount of PAN dispensed into Chamber 2 was essentially equal to the weekly average shown in Figure 1, but the hourly concentration was adjusted to correspond with the hourly average in ambient air at the same time on the previous
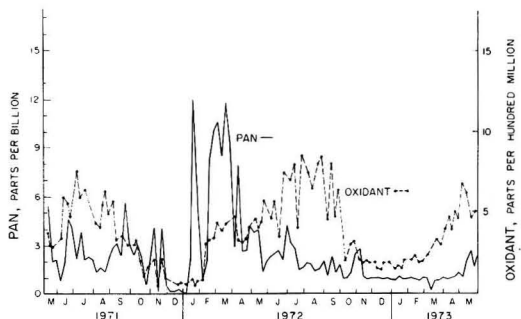

Figure 1. Weekly average PAN and total oxidant levels

Table I. New Leaves and Shoot Growth on 90 Selected Branches Plus Total Growth Measurements and Leaf Retention of Nine Young Orange Trees[a]

		Carbon-filtered air	Carbon-filtered air plus PAN	Ambient air
90 Selected branches	New leaves added	755a	457a	87b
	Shoot growth, cm	1,423c	947c,d	270d
Entire trees	Total no. leaves on trees	11,508e	10,134e	8754f
	% of total leaves dropped	27	25	23
	Av wt of prunings, g/tree	246g	187h	182h
	Av. length cm/tree of prunings	1,387	1,161	1062
	No. leaves on prunings	5,220	4,527	4329
	No. leaves on pruned trees	3,204i	3,033i	2439j

[a] Letters a, b, c, d significance, 99%; e, f, g, h, i, j significance, 95%.

Table II. Average Number of Original Leaves Dropped and New Leaves Set per Tree on Transplanted Orange Trees[a]

	Original leaves, #	Leaves retained, 4/24/72 #	Leaves dropped, #	Leaf drop, %	New leaves, #
Clean	360	169a	191	53.5a	507
PAN	345	100b	245	69.6b	488
Ambient	269	82b	187	68.9b	390

[a] Letters a, b significance, 99%.

day. Concentrations were controlled by a diluting and dispensing system similar to one used previously (*13*).

Soil, one-half meter in depth, was placed underneath the structures and nine young *Frost nucellar* navel orange trees on *Troyer citrange* rootstocks were planted in each. At planting time, the trees were about 1.2 meters in height and had about 200 leaves per tree. An irrigation system plus soil-moisture sensing devices were installed. Cultural practice was such that the young trees grew vigorously. The treatments were begun May 10, 1971, and proceeded with only minor operational difficulties until November 29, 1971.

Ten individual branches were selected on each of the nine trees (90 branches/treatment) and a record of new leaves and increased growth was made. The results, Table I, showed that numerically new leaves and shoot growth on the 10 individual branches were greatest in clean air, less with PAN, and least in ambient. However, variation was large enough that, statistically, in the leaves-added data, the difference of clean vs. PAN was not significant, but clean vs. ambient and PAN vs. ambient were significant at the 99% level of confidence. With growth, clean vs. PAN and ambient vs. PAN were not significant, but clean vs. ambient was significant at the 99% level. Analysis of variance was made by Duncan's multiple range test as modified by Harter (*14*) and Snedecor and Cochran (*15*).

Total leaf drop from the nine trees in each of the three chambers was recorded by raking, drying, counting, and weighing at two week intervals (Table I). The total number of leaves and the percent dropped were greatest in clean air, less in PAN, and least in ambient. The differences in total number of leaves in both clean and PAN were greater than ambient but the percent of total leaves dropped was not statistically significant.

Because the greenhouse which housed this part of the study had to be moved to make room for a new building, the trees were pruned heavily on November 29, 1971, and transplanted to the relocated greenhouse. This is the most dormant season for navel oranges. An attempt was made to remove enough branches to give trees of comparable size and also to remove enough leaves so that the disturbed root system would be able to maintain leaf cell turgor until root function returned to normal. The amount of wood and leaves pruned from the trees and the remaining number of leaves were determined (Table I). The wood and leaves were air dried to constant weight.

Differences in weights of prunings removed from the trees, clean vs. PAN and clean vs. ambient, were significant at the 95% level, but PAN vs. ambient was not significant. Length of prunings showed no significant differences. The total number of leaves remaining on the pruned trees was significantly greater in clean air than ambient at the 95% level, but was not greater than PAN.

The pruned trees when relocated were reduced randomly in number to eight individuals per treatment so that a better fit could be made in the chambers. They grew well as before. Because high levels of PAN and low to moderate levels of oxidant occurred during January to April, 1972 (Figure 1), an evaluation was made on April 24, of the number of original leaves left on the trees that dropped during the period and the number of new leaves which were set. Data in Table II show that leaves retained were greatest numerically in clean air, less with PAN, and least in ambient air. Statistically the clean vs. PAN and clean vs. ambient were significant at the 99% level. PAN vs. ambient values were not statistically different. The differences in percent of original leaves dropped, another expression of the same effect, showed the same levels of significance.

Field Tree Study. For the fruit yield study, nine cubical chambers $0.61 \times 0.61 \times 0.76$ meters, glazed with polyvinyl fluoride plastic and equipped with ventilating blowers were used. These were installed around nine similar sized fruit bearing branches of a mature navel orange tree, and 560 liters of air/min (two times the volume of each chamber) were provided. A PANalyzer and a PAN dispensing system, similar to the one used with the enclosures over the seedlings, were installed.

The same air treatments used with the young trees were carried out. Three chambers received clean air, three PAN, and the three remaining ambient air.

The treatments were begun April 28, 1971, and were continued on an around-the-clock, seven days per week basis. The first evaluation of the performance of the field tree was made January 27, 1972, on 10 marked, newly developed lateral branches. The number of shoots from these branches and the growth were determined. Shoot growth and leaf drop were totaled for the period beginning

Table III. Shoot Growth and Leaf Drop from 10 Marked Lateral Branches on Field Tree, 1971 Season[a]

Total no. of shoots	Shoot length, cm	No. of leaves			
		May 10, 1971	Jan. 27, 1972	# lost	% lost
		Carbon-Filtered Air			
37	328a	270	205	65	21%b
		Carbon-Filtered Air + PAN			
47	347a	306	181	125	37%b
		Ambient Air			
68	446a	472	265	207	43%b

[a] Letters a, b significance, 95%.

Table IV. Shoot Growth and Leaf Drop from 10 Marked Lateral Branches on Field Trees, 1972 Season[a]

	Shoots			No. of Leaves				
Totol #	Orig. length, cm	Growth, cm	Growth, av. % of orig.	Original	Leaves produced	Total	Dropped	Dropped av,%
				Carbon-Filtered Air				
80	349	636	186a	190	359	549	111	20c
				Carbon-Filtered Air + PAN				
48	308	212	70b	208	174	432	221	50c,d
				Ambient Air				
52	310	276	89b	262	268	530	361	71d

[a] Letters a, b significance,95%; c, d significance, 99%.

May 10, 1971, and extending to January 27, 1972. The results (Table III) showed that the differences in growth of shoots between the three treatments were not different statistically. The average percents of leaves on the marked lateral branches that dropped during the period were 21, 37, and 43% for clean, PAN, and ambient, respectively, but these differences were not statistically significant.

A second evaluation of 10 other newly developed lateral branches was made from January 27, 1972, until conclusion of the study on April 25, 1973. The results (Table IV) showed that the growth of shoots was significantly greater at the 95% level in clean air than in the PAN or ambient air treatments. The PAN and ambient treatments were the same statistically. The leaf drop showed a trend with an average of 20% loss in clean air, 50% loss in PAN, and 71% in ambient, but because of individual variation the only difference was between clean and ambient air which was at the 99% level of significance.

The total number of immature fruit dropped, leaf drop, leaf weight and yield of mature fruit were measured in each chamber from May 10, 1971, until January 27, 1972 (1971 season). There was no statistical difference between any of the treatments (Table V, 1971 data). A trend in number of leaves dropped appeared with clean air least, PAN intermediate, and ambient most. Fruit yield showed a trend with clean producing most, PAN intermediate, and ambient least. A second period of measurement of the same parameters was done from March 14, 1972, until April 30, 1973. The results, 1972 season data, showed the same trends as during the previous period, but none of the differences were statistically significant. Statistical analysis of all the basic leaf drop data taken at two week intervals, presented as summaries in Table V, showed that clean vs. PAN was not significantly different, but clean vs. ambient was significant at the 99% level and PAN vs. ambient significant at 95%. The yield of mature fruit for harvest showed the same trends as leaf drop—i.e., clean greatest with PAN intermediate and ambient least, but variability and very small numbers of replicates overshadowed any statistical significance.

An attempt was made to find out what effect short-term fumigations with PAN would have on apparent photosynthesis of navel orange trees. The apparatus for measuring CO_2 exchange by intact leaves, was an adaptation of a system designed by Taylor et al. (16). Hospital grade compressed air enriched with CO_2 to a level of 390 ppm was passed into the plant chamber at the rate of 2 l./min. A Dyna pump was used to circulate air in the chamber and to pass air through a drier and into the sample cell of a nondispersive infrared CO_2 analyzer at the rate of 450 ml/min. The reference cell was filled with dry nitrogen free of carbon dioxide. The excess air in the plant chamber was exhausted through a pressure release valve. The temperature inside the chamber was controlled automatically by circulating cold water through a stainless steel coil. Temperature was controlled at 26–27°C. Light was supplied by two 300-W cool-beam lamps placed over the chamber. A Plexiglas water bath was placed between the lamps and the chamber to absorb heat. The CO_2 enriched compressed air at 390 ppm CO_2 was supplied to the chamber at a flow rate of 2 l./min for approximately 1 hr with lights off before the start of the light period in order to establish an equilibrium with the plant and chamber. After the lights were turned on, reduction of CO_2 could be noticed within 5 min and after 30 min a new equilibrium at a reduced level of 220 ppm CO_2 (44%) was established. After 1 hr, PAN was introduced at 20 ppb. No change in the CO_2 level was observed. Fumigation at this concentration for 1½ hr had no measurable effect on the ability of the plant to fix CO_2. A similar test was carried out on two consecutive days applying PAN concentrations of 40 and 80 ppb. No change in apparent photosynthesis was observed.

Discussion

The replication in this study and size of enclosures for both young trees and branches on the mature trees were

Table V. Field Tree: Immature Fruit Drop, Leaf Drop, Leaf Weight, and Yield[a]

	Fruit drop, #	Leaf drop, #	Total leaf wt, g
	Carbon-Filtered Air		
1971			
Immature fruit	28		
Mature fruit	6	1318	213
Av mature wt, 104 g			
1972			
Immature fruit	88		
Mature fruit	23	2213a,x	410
Av mature wt, 196 g			
	Carbon-Filtered Air + PAN		
1971			
Immature fruit	28		
Mature fruit	2	1955	376
Av mature fruit wt, 99 g			
1972			
Immature fruit	29		
Mature fruit	13	3570a,b,x	570
Av mature wt, 233 g			
	Ambient Air		
1971			
Immature fruit	29		
Mature fruit	0	3638	584
Av mature wt, 0g			
1972			
Immature fruit	98		
Mature fruit	8	6409b,y	798
Av mature wt, 213 g			

[a] Letters a, b significance, 99%; x, y significance, 95%.

limited by the availability of the synthetic PAN required. However, the studies showed that PAN can cause increased leaf drop and reduced vegetative growth in navel oranges. The data in Table I showed that pollutants in ambient air reduced the number of new leaves added and the amount of shoot growth on selected branches of young trees. The effect of the addition of PAN in these data was equivocal. Another expression of the same effect and one that did show statistical significance was the greater weight of prunings in clean air than in either PAN or ambient air (Table I) when the young trees were pruned back for transplanting. This effect occurred during summer and fall of 1971 when PAN was moderately high, but not heavy. The total leaf drop during this period with these young, vigorously growing trees was the same in all treatments indicating that the levels of photochemical oxidant complex that occurred didn't cause additional leaf drop.

In early 1972, after the trees were relocated and high persistant levels of PAN occurred (Figure 1), this pollutant did cause increased, statistically significant leaf drop (Table II), and the remaining pollutants in ambient air failed to show an effect over and above that of PAN probably because ozone, and other principal plant toxicant was relatively low in winter and early spring as indicated in Figure 1. The effect of the total photochemical oxidant complex in causing increased leaf drop was observed previously (11).

The results with mature trees were somewhat similar. A trend toward greater leaf drop was seen with PAN during the first (1971) season when moderately high levels of PAN occurred, Table III. During 1972 and early 1973 when high levels of PAN occurred from January–April, PAN or ambient air caused statistically significant reduction in shoot growth (Table IV), and PAN caused a trend toward increased leaf drop.

The effects of PAN on the drop of immature fruit, total leaf drop, and yield of mature fruit by year (Table V) was inconclusive. The same trends were present with PAN seeming to cause some deleterious effects and the total photochemical complex more injury, but with the limited number of replications no definitive conclusions could be proved.

Fumigating young trees with high levels of PAN for a short time caused no effect on apparent photosynthesis. Why this pollutant has so little effect during the short period requires additional study.

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Identification of Petroleum Products in Natural Water by Gas Chromatography

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■ Gas chromatography on high-efficiency packed columns has been shown to be suitable for the rapid identification of trace quantities of common petroleum products. Concentrations as low as 0.25 $\mu l/l$ of the contaminants may be extracted and identified. Chromatograms of kerosine, diesel fuel, common fuel oils, transmission fluid and lubricating oils are reported. Three examples of use of the method are described.

Gas chromatography with flame ionization detection is ideally suited to the examination of hydrocarbons. It affords a large number of analytical parameters from a low level of material with relatively inexpensive instrumentation. Other techniques such as urea adduction (1) infrared absorbance (2) the determination of n-paraffins in crude oil by differential gas chromatography (3, 4), infrared internal reflection spectrometry (5), and combinations of these (6, 7) have been used; but these methods are time-consuming, resolve compounds only partially, require special instrumentation, and are applicable only with relatively large samples. Mass spectrometry (8) and the recently developed microwave spectroscopy (9) give more information than gas chromatography on high-efficiency columns, but the instrumentation is costly and temperamental.

In a previous paper (10), we described a method for quantitation of gasoline. Here we report its application to the higher-boiling petroleum fractions. This method does not aim to characterize the vast number of components of petroleum products but rather to identify the type of product by a simple gas chromatographic procedure following extraction of the sample by hexane.
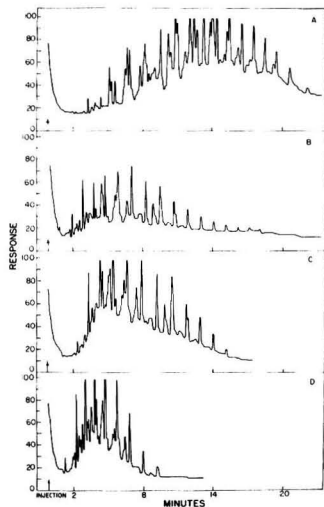
Figure 1. Chromatograms of fuel oils: A, No. 6; B, No. 4; C, No. 2; and D, kerosine

Figure 2. Chromatograms of transmission fluid, A, and diesel oil, B

Crude oil from various geological sources varies widely in composition, and these variations are reflected in the constituents of the various cuts, blends, and refined products arriving on the market. Four main types of hydrocarbon are present in petroleum: *n*-alkanes, naphthenes (cyclic branched alkanes), naphthalenes (bicyclic aromatics), and aromatic compounds. The present note deals with kerosine; diesel oil; fuel oils No. 2, 4, and 6; transmission fluids; and lubricating oils. Their characteristics are described in ASTM Designation, D288-61, and ASTM Designation, D975-68.

Experimental

Reagents. Hexane, nanograde. Anhydrous sodium sulfate, granular, AR grade. Sulfuric acid, AR grade.

Gas Chromatographic Conditions and Equipment. Instrument: Tracor Model MT 220 (Tracor Inc., Austin, Tex. 78121). Column: glass. U-shaped, 2 m × 4 mm i.d., packed with Gas Chrom "Q" 80–100 coated with 4% silicone oil SE-30 or 4% OV-1. Attenuations: input, 10; output, 8. Carrier: Helium (high purity), 40 psi, 110 cc/min. Detector gases: Air (high purity), 40 psi, 285 cc/min. Hydrogen (high purity), 40 psi, 37 cc/min.

The procedure was as previously reported for gasoline analysis (*10*), with the following modifications. Helium (high purity) was used as the carrier gas, at the same pressure and flow rate. The column was programmed at 7.5° C/min to 300° C. The sample was acidified to pH 1–2, and after extraction with hexane (10 ml), the solvent was dried over approximately 1.0 gram of granular anhydrous sodium sulfate. When a grossly contaminated sample yielded a sizable layer of hydrocarbon, it was separated from the water layer, diluted with hexane, and filtered if necessary.

Kerosine can be quantitated by interpolating the height of a chosen *n*-paraffin peak to a standard curve (*10*). When the presence of the lighter fraction, kerosine, had been shown, the extract was concentrated if necessary by passing nitrogen over its surface at room temperature to achieve the degree of sensitivity required to detect the higher fractions that give a lower response in the system. For the resolution of these higher fractions, the oven was
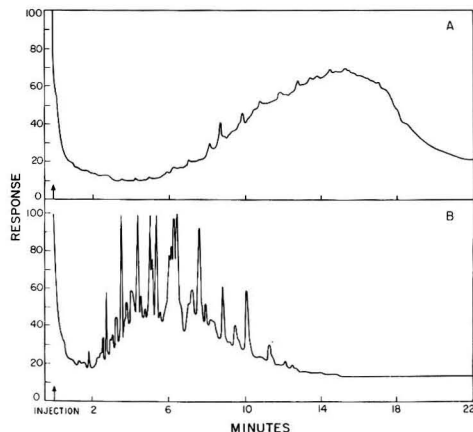
set at 50°C and programmed to rise 7.5°C/min to 300°C and hold. The detector was set at 325°C.

Results and Discussion

Figure 1 gives chromatograms of kerosine and of fuel oils No. 2, 4, and 6. Differentiation of kerosine from the fuel oils and of fuel oil No. 6 from Nos. 4 and 2 is simple. Differentiation of fuel oil No. 2 from No. 4 is more difficult, particularly after the mixture has resided in natural waters. Careful account must be taken of the position of the hump, which represents (to a first approximation) the boiling range profile of the cut, and of the spread of the later peaks. Although No. 2 has as much higher-boiling material, No. 4 contains a small proportion of components with very long retention times.

Diesel oil (Figure 2) can be distinguished from kerosine and from fuel oils No. 2 and 4 because its boiling range spread, represented by the hump, is broader than fuel oil
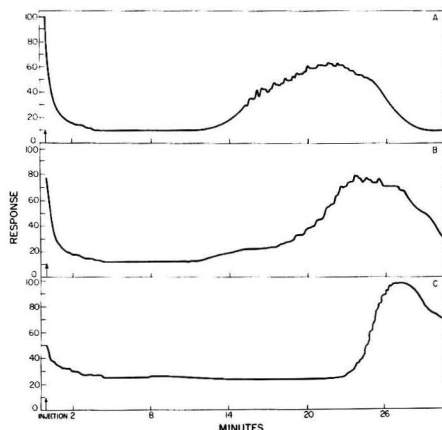
Figure 3. Chromatograms of lubricating oils: A, No. 10; B, No. 20; C, No. 30
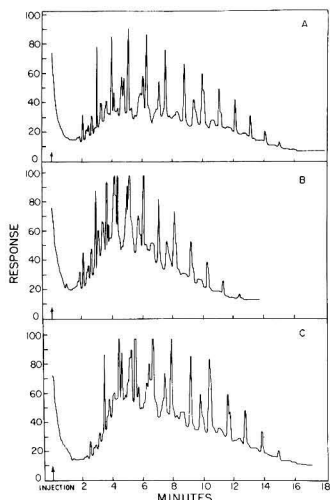
Figure 4. Chromatograms of three samples of fuel oil No. 2 from different manufacturers
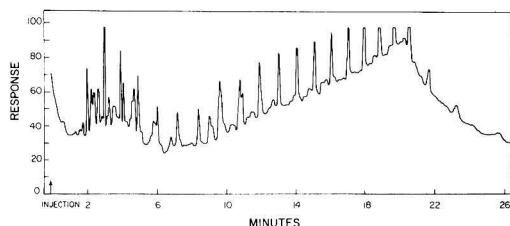
Figure 5. Chromatogram of a water extract from Port of Albany, N.Y., showing pollution characteristics
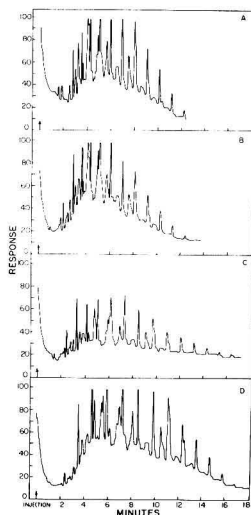
Figure 6. Chromatograms of water extract from the Voorheesville village water supply, A; sample of fuel collected at maintenance site, B; standard fuel oil No. 4, C; and sample of fuel collected at radio station, D

No. 2, though not so broad as in fuel oil No. 4. The later fractions of fuel oil No. 4 are completely absent. Transmission fluid (Figure 2) has a boiling range profile similar to that of fuel oil No. 6 but without the fine structure represented by the major alkanes in the fuel oil mixture.

The lightest lubricating oil shown in Figure 3 can be distinguished from transmission fluid only with difficulty. The more viscous lubricating oils, however, are easily distinguished. Viscous lubricating oils and asphaltic materials take a considerable time to clear from the column. It is very desirable to use the minimum concentration because, even when there has been no apparent recorder response, fresh injections of hexane will wash materials from the column and produce quasichromatograms.

The fine structure of the kerosine, diesel oil, and fuel oil chromatograms allows a high degree of certainty in source identification, if samples can be obtained from the suspected sources. The task of comparing chromatograms of, for example, two fuel oil No. 2 samples is probably best achieved with a computer. However, careful examination of the chromatograms and comparison of the relative peak heights of the most characteristic zones (for example, those with square tops or with points of inflection) make unambiguous identification possible, as the following examples show:

Example 1. Chromatograms of three No. 2 fuel oil samples, collected from three different sources, are given in Figure 4. It is apparent that they are not alike, and unambiguous differentiation would be quite possible, if samples from the suspected sources were available.

Example 2. Figure 5 shows the chromatogram of an extract from a water sample collected in the Port of Albany, N.Y. The water has clearly been contaminated by a spill of a mixture of kerosine and a heavier cut, such as fuel oil No. 6 or a lubricating oil. This indicates that the spill was from the bilges of one suspected ship, rather than from its fuel oil tank or from the fuel oil tank of the other suspect ship, whose bilges were clear.

Example 3. The water supply of the village of Voorheesville in Albany County, N.Y., is a spring located in the face of a limestone escarpment. One weekend in November 1972, the spring started to emanate a strong oily odor. Figure 6 shows a chromatogram from an extract of the water supply, along with those of samples of oil taken from the maintenance area of a nearby park and a radio broadcasting station, where oil deliveries had been made the previous week. It is quite clear that the contamination came from the park maintenance area. Not only is fuel oil No. 2 involved, but the detailed pattern, taking concentration variables into account, shows that the two samples were derived from the same feedstock. The detailed composition of products from one manufacturer varies considerably over time, and it is unlikely that the contamination had occurred from a supply delivered by the same manufacturer earlier. Further inquiry yielded the information that the delivery truck driver had taken shelter from the cold and that the line had slipped from the tank during delivery, contaminating the spring one mile away, the water supply for more than a thousand people.

These examples illustrate that identification is possible in spite of the known changes which occur because of differential evaporation and microbial action. Such changes have been fairly unimportant in our analyses because our samples are relatively uncontaminated with microbial matter, being for the most part drinking water. Also, most are underground water samples or very fresh spills on exposed water, and all samples are transported to the laboratory with the utmost haste. Over 200 samples are being examined annually by the method described.

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Mercury Levels in Lake Powell

Bioamplification of Mercury in Man-Made Desert Reservoir

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■ Flameless atomic absorption analyses of samples from Lake Powell yield mean mercury levels in ppb of 0.01 in water, 30 in bottom sediments, 10 in shoreline substrates, 34 in plant leaves, 145 in plant debris, 28 in algae, 10 in crayfish, and 232 in fish muscle. Trout were unique in having lower concentrations in muscle than in highly vascularized blood tissues. Concentrations increased with increased body weight and higher levels on the food chain. Muscle of some large fish over 2 kg whole body weight exceeded 500 ppb. Bioamplification of mercury up the food chain and association of mercury with organic matter are demonstrated.

The vulnerability of freshwater habitats to mercury contamination was established by Swedish investigations (*1*). Mercury levels exceeding the U.S. Food and Drug Administration "interim guideline" of 500 ppb for flesh have been found in fish from many North American locations. This level is a maximum, allowing an intake of two fish meals per week if the serving averages 150–200 grams. Levels above 500 ppb have been considered evidence for pollution, but these high levels have also been obtained for fish from habitats with no known pollution source (*2–4*). This illustrates the difficulty of determining sources of mercury pollution—a problem that becomes even more complex when we consider inputs from fossil fuel combustion.

Lake Powell, a Colorado River impoundment near Page, Ariz., is a new reservoir remote from major man-caused pollution sources and affords a unique opportunity to establish baseline mercury levels in a reservoir with concentrations resulting principally from the erosion of natural geologic deposits. The extent of bioamplification through the food chain in such a recent, relatively unpolluted lake is of interest.

These baseline levels will be used to evaluate the impacts of rapid recreational development and future operation of large-scale coal-fired power generation facilities near the impoundment.

Lake Powell, a Bureau of Reclamation storage and hydroelectric generation reservoir, was initially impounded in 1963 and reached a 1971 elevation of 1104.3 meters with a volume of 17,860.6 × 10⁶ m³ (14 million acre ft). The lake has a potential storage capacity of 33,304.5 × 10⁶ m³ (27 million acre ft), with a length of 300 km. Annual run-off into the lake is about 14,800 × 10⁶ m³ (12 million acre ft). The deeply dissected sandstones and shales of the canyons of the Colorado River system in southeastern Utah and northern Arizona produce a shoreline characterized by precipitous cliffs, sparse vegetation, and little soil development.

Our purpose is to report baseline mercury levels in water, terrestrial substrates, bottom sediments, and various trophic levels; to provide concentration factors of mercury from one trophic level to the next; and to suggest the need for a clearer understanding of the mercury budget.

Analysis Procedure

Water samples were preserved in glass or polyethylene containers with 3 ml/l. of 50% nitric acid added at the time of collection, and all samples were analyzed in less than two weeks. Samples were not filtered, but were analyzed after concentrating the mercury by the dithizone extraction method. Chau and Saitoh (*5*) reported losses of 35, 82, and 65% after one week if samples were not acidified. Since mercury species may be bound to suspended particulate matter, it is possible that our stated values for mercury are not valid for water alone, but reflect mercury concentration of the unfiltered water with the associated suspended materials. However, concentrations reported by us are low and do not indicate an undue bias.

When sufficient material was available, sample sizes of 1 gram for organic material and 5 grams for mineral material were used, with from two to five replicates. When practical, materials were ground or blended to prepare homogeneous samples. Terrestrial soils and bottom sediment samples were analyzed in the form collected; biological materials, such as floating organic debris, aquatic organisms, and terrestrial plants, were analyzed as recovered from the frozen or air-dried condition. Tissue separation and homogenization were on fish still partially frozen. Portions of sediment and plant samples were weighed and saved for dry weight comparison.

Concentrations of mercury for sediments, soils, and plant materials are expressed on an air–dry weight basis; crayfish and fish data are on a wet weight basis. In each case the material analyzed was in the condition or state in which it would be ingested or passed on through the food chain.

Samples were analyzed using the flameless atomic absorption procedures outlined by Hatch and Ott (*6*) and Uthe et al. (*7*) as modified for use with a Perkin-Elmer

Model 306 atomic absorption spectrophotometer equipped with a Perkin-Elmer mercury analyzer system.

Mean percentage recoveries and mean coefficients of variation (c.v.) for the types of materials analyzed were: water 92.2% (13.0); geological material 96.0% (7.1); plant material 99.8% (14.2); and fish 101.6% (9.81).

Mercury Levels of Water

Mercury levels of unfiltered Lake Powell waters are low. We found mean levels of about 0.01 ppb ($\bar{x}$ = 0.009 ppb, std dev = 0.001). These low levels are expected. Wershaw (8) concludes that mercury levels are 0.1 ppb or less in unpolluted fresh waters and reports USGS results of levels at or below their 0.1 ppb detection limit for 34 of 73 samplings from the Colorado River.

Our levels, averaging 0.01 ppb, are based on 12 water samples from nine widely scattered locations in Lake Powell. Samples were collected from the surface and at 4- or 5-meter depths. Sample variation between locations and depths were expected on the basis of chance alone (0.95 probability level).

Apparently there is little mercury even in the unfiltered water which contains suspended material. It is this water medium through which mercury must pass to become incorporated into mineral and organic matter sediments (9, 10).

Rocks, Soils, and Sediments

Loose rock material collected from the Navajo Sandstone yielded levels less than 30 ppb, dry weight. Analysis of collections from unconsolidated sedimentary rock debris, low in organic material, gave mercury levels less than 30 ppb. Sand was particularly low in mercury content, with 76% of the 17 samples having levels below 5 ppb and only one sample having a level above 10 ppb.

The USGS reports a wide range of mercury levels (<10 to >6,000 ppb) in sedimentary rocks of this region (11). While most strata near the lake gave median levels of 100–260 ppb, the USGS found levels of <10–40 ppb with a mean of 21 ppb at sites near the lake in Navajo Sandstone (12). Our values reflect the lower range of USGS data. However, we did find higher levels where more organic material is associated with the rock debris. These locations include seeps, oak and cottonwood groves, and shallow mudflats. Fifty-three percent of the samples containing appreciable organic matter had levels greater than 10 ppb, with the litter and A-1 horizon from a cottonwood grove yielding 48 ppb, highest of any shoreline substrate analyzed. At Lake Powell, substrates containing appreciable organic matter are probably not abundant enough to be of major importance.

Rock material reworked and deposited at the bottom of the lake contained higher mercury levels. Bottom sediments near the dam had a mean concentration of 49 ppb (95% confidence intervals were 45–53). Since mercury is known to enter bottom sediments close to a point source of pollution we felt that a gradient of mercury concentration might exist in Lake Powell—higher at the headwaters of major tributaries and lower near the dam. This hypothesis was not confirmed by the data, a possible reason being that variable sedimentation occurs in the lake (13). In general, higher mercury levels occurred in midchannel locations where material was finer textured and higher in organic content. With the exception of one collection from the Wahweap Marina, sediments containing more than 20 ppb were either fine-textured or relatively high in organic material. In the tributary Forbidden Canyon, some processed sewage has been released in front of Rainbow Marina (depth about 60 m). The mean level of mercury found in this material was 26 ppb, whereas sediments farther up

the bay, lower in organic material, had a mean mercury level of 14 ppb.

Drake (14) estimates that sedimentation is occurring at the rate of 2.3×10^6 metric tons per month, and that about $\frac{1}{25}$ of the 1971 maximum volume of Lake Powell was filled with sediment during the first eight years of impoundment. As mercury concentrations of sediments are about 3000 times that of the unfiltered surface water, the major portion of the mercury in the lake system can be expected to accumulate in the sediment, from which mercury may be released to the biota and water by both biological and abiotic processes (15).

Plant Materials

Terrestrial vascular plants were within the suggested range of mercury levels for land plants (16). The values were also within the range previously mentioned for rock strata. Leaves gave significantly higher values (15–65 ppb, dry weight) than the stems or roots of the majority of the 19 vascular taxa analyzed. Principal exceptions were the evergreens, Mormon tea (Ephedra), and juniper (Juniperus).

Mercury levels in water-associated plants and nonvascular plants did not differ markedly from those of the typical desert vegetation. However, submerged decomposing snakeweed (Gutierrezia microcephala) from Reflection Canyon had a mean mercury content of 90 ppb compared to 32 ppb for adjacent unflooded snakeweed growing on the same substrate. Mercury levels (43–283 ppb, dry weight) in lake-transported plant debris were significantly higher than those of terrestrial plant materials, further suggesting that mercury is concentrated in some flooded plant material. While biological uptake as previously demonstrated (17, 18) could be occurring in this material, Hannerz (19) and others (9, 20–21) suggest that abiotic sorption is an important uptake mechanism in organic materials.

Even with sparse vegetation, debris impoundment from an extensive drainage and the growth of tamarisk (Tamarix pentandra) and other plants in the drawdown zone provide an additional route for mercury movement into the aquatic system. Through enrichment, plant debris with mercury levels 10^4 times that of the surface water may enter the food chain of the lake. Jernelöv (15) emphasizes the importance of organic matter as an energy source for the biotransformation and biological uptake of mercury. Thus, as a nutrient source, plant material contributes to mercury movement in the lake system.

Invertebrates

Seventeen crayfish collected at the Wahweap Marina had a mean whole body mercury content of 10.0 ppb, wet weight (range 2–23 ppb). On a dry weight basis the mercury content of these crayfish would indicate some accumulation of mercury above the concentrations of the shallow water sediments of Wahweap Bay ($\bar{x}$ = 10.0 ppb). Mercury levels in crayfish are 10^2 times that of the surface waters. Although a low-level source to predatory fish, there was an increase of mercury from 2–23 ppb as whole body weights increased from 1–10 grams. Thus, larger crayfish provide a higher dietary mercury source per unit weight to larger predatory fish than do small crayfish.

Fish

The mercury content of fish tissue ranged from <5 to >700 ppb, wet weight (Table I). As suggested by Johnels et al. (22) patterns of concentration occur between tissues. Axial muscle had the highest mercury content of all tissues analyzed in five of seven taxa. Only in the rainbow and the brown trout (Salmo gairdneri and Salmo trutta)

Table I. Sample Size, Weight, and Mercury Content of Fish (PPB), Wet Weight

	Walleye	Largemouth bass	Trout	Black crappie	Bluegill	Carp	Flannelmouth sucker
No.	8	7	3	7	8	5	3
Mean wt, g	1597	1098	1125	441	193	574	653
Wt range	(300–3350)	(350–2225)	(140–2015)	(300–600)	(151–230)	(513–638)	(650–660)
Muscle	427	314	84.5	204	91.0	252	98.8
	(209–763)	(192–688)	(73–101)	(157–294)	(57–127)	(181–339)	(48–186)
Liver	149	163	186	62.2	86.6	152	36.2
	(42–362)	(53–587)	(27–384)	(38–88)	(62–96)	(55–217)	(9–33)
Heart	135	102	228	22.4	129	66.7	14.6
	(63–320)	(19–421)	(137–404)	(11–37)	(87–158)	(51–84)	(11–25)
Kidney	86.2	144	253	26.9	28.6	180	33.9
	(40–136)	(44–498)	(93–326)	(10–43)	...	(95–251)	(19–56)
Spleen	77.7	168	257	25.6	...	...	29.0
	(28–160)	(26–673)	(192–346)	(9–50)			(28–30)
Stomach	87.3	79.2	89.3	27.2	35.9	32.0	11.6
	(30–158)	(26–280)	(78–107)	(18–47)	(28–47)	(21–43)	(3–25)
Brain	17.2	41.0	98.2	5.5	29.5	86.5	10.9
	(4–31)	(4–74)	(67–152)	(0–10)	(23–36)	(60–120)	(6–14)
Gonads	42.2	34.0	68.7	11.1	23.6	60.4	9.9
	(16–91)	(11–107)	...	(4–16)	...	...	(4–19)
Skin and scales	22.5	17.4	13.1	5.5	40.3	23.7	11.6
	(12–37)	(4–27)	(12–15)	(1–9)	(29–68)	(16–36)	(3–21)
Gills	51.1	42.7	94.4	11.6	15.7	28.1	10.0
	(29–78)	(14–100)	(55–128)	(5–20)	(9–22)	(19–39)	(8–11)
Bone	15.7	18.8	16.4	5.5	10.4	25.2	8.1
	(7–29)	(3–37)	(2–33)	(1–11)	(0–24)	(16–31)	(3–11)

were the highly vascularized blood tissues higher in mercury levels than in muscle (Figure 1). Hasselrot (23) reported similar relative levels for *Salmo* spp., as did Rucker and Amend (24) for tank experiments with rainbow trout. The mercury content of skin and bone was relatively low in all species, as it was for gills for species other than trout. Gonad, brain, and stomach levels were low to intermediate. Higher levels occurred in spleen, kidney, heart, and liver tissue. The ratio of mean mercury content of all nonmuscle tissue to muscle content (Figure 1) seemed characteristic of a species, and suggests that patterns of uptake, accumulation, and elimination differ between species, with that of trout being particularly distinctive.

For those species for which fish of widely differing weights were analyzed, larger fish had higher mercury levels (Figure 2). This relationship is evident for the muscle and liver tissue of walleye (*Stizostedion vitrium*), largemouth bass (*Micropterus salmoides*), and rainbow trout, and for the whole fish analysis of threadfin shad (*Dorosoma petenense*). For the several fish taxa, the mean mercury levels of muscle are positively related to mean body weights. No fish weighing less than 2 kg had mercury levels above the currently accepted guideline of 500 ppb in fish for two meals per week. Of six fish weighing more than 2 kg, four (one largemouth bass and three walleye) had muscle levels exceeding 500 ppb. The mean muscle content of the three large walleye ($\bar{x}$ wt = 2615 grams) was 680 ppb and that of the largest bass (2225 grams) was 688 ppb. A slightly smaller bass (2050 grams) had a muscle content of 394 ppb, while the marked difference of trout was again apparent as a rainbow trout of similar size (2015 grams) had only 101 ppb mercury in axial muscle tissue. A significant finding of this report is that levels exceeding 500 ppb may be common in the larger predatory fish of Lake Powell—a recently impounded reservoir with only very slight and very local pollution.

There was a positive relationship between food habit and mercury levels in stomach and axial muscle (Table I and Figure 3). In Figure 3, representative samples or
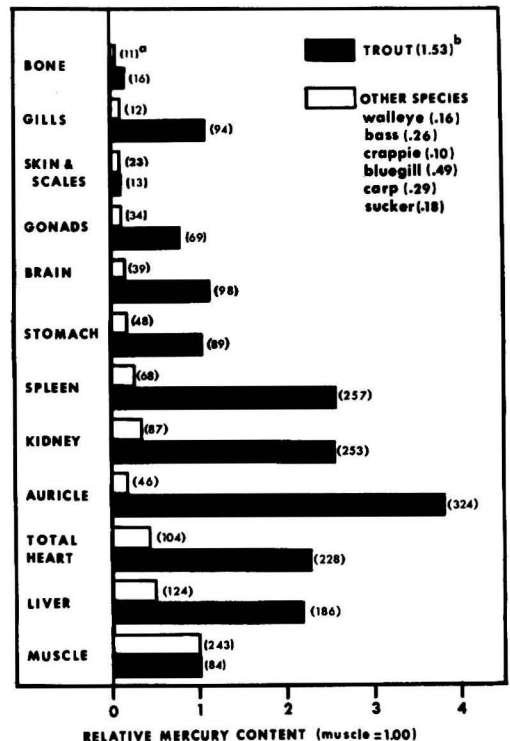

Figure 1. Relative mercury content of fish tissues
[a]Mean ppb values of mercury, wet weight. [b]Mean relative mercury content of taxa nonmuscle tissue compared to muscle as 1.00
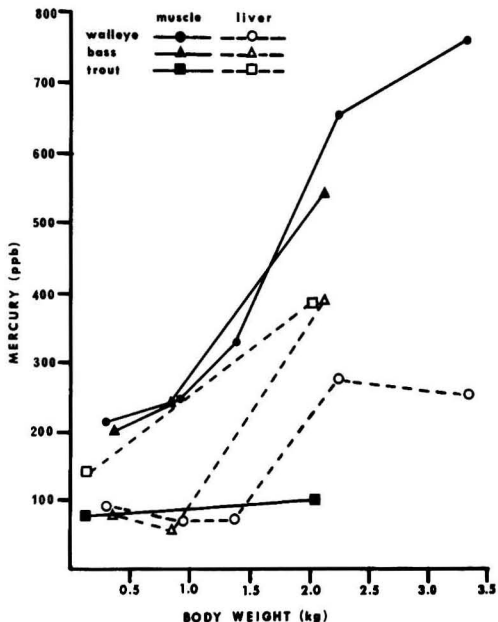
Figure 2. Relationship of the mercury concentration, wet weight, of axial muscle and liver tissue to body weight in walleye ($n = 8$), largemouth bass ($n = 7$) and rainbow trout ($n = 2$)
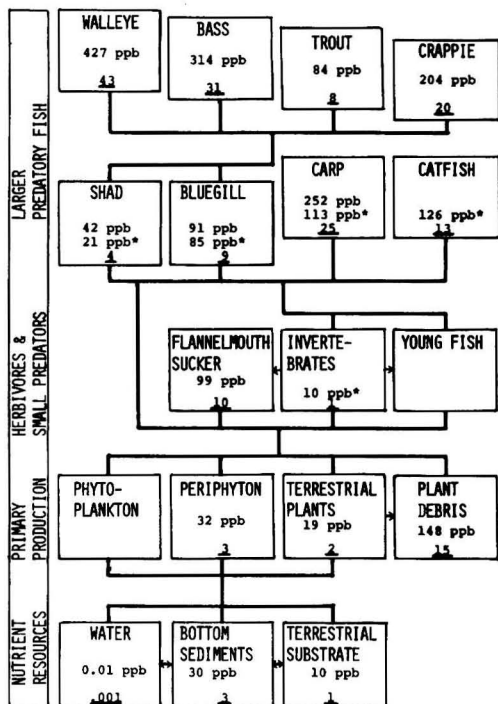

Figure 3. Relationship of Lake Powell trophic levels to mean ppb mercury and magnification factor (underlined) relative to the average concentration of the terrestrial sandstone substrate Magnification factor based on water would be 1000 times greater. Values with an asterisk are whole body analyses; other fish values are of axial muscle

species are arranged in progressive levels: original nutrient sources of water, terrestrial soils, and bottom sediments; primary producers (both terrestrial and aquatic) and decomposing, floating plant debris; herbivores and small predators; and large predators. Principal directions of flow of nutrient and food supply are indicated. Concentrations of mercury in ppb represent means for the samples of that type analyzed. For fish, the concentrations are of muscle tissue unless indicated by an asterisk indicating whole body samples. Data are not available for phytoplankton or young fish. Mercury concentration of unfiltered water averaged 0.01 ppb and that of the terrestrial substrate or soils 10 ppb. The latter was used as the base of one for the bioamplification or magnification factor. To interpret the increase based on water, all underlined magnification factors should be increased by 10^3.

Walleye, bass, and trout (the species with the highest tissue mercury levels) are the highest trophic level fish. Flannelmouth sucker (*Catostomus latipinnus*), a low trophic level fish feeding on plant material and small invertebrates, had the lowest species mercury levels for five of the 11 tissues analyzed. Carp (*Cyprinus carpio*), a low trophic level omnivore, seems to have higher mercury levels than would be expected based on its low position in the food chain. However, plant debris, which we found to have high mercury levels, is a major carp food. Also, its habit of bottom feeding may associate it with a higher mercury environment than that of fish of different foraging habits. The indication of a positive weight–mercury content relationship in threadfin shad, the principal forage fish, and in other fish and crayfish, as well, suggests that fish which take large prey have higher dietary mercury levels—a major reason for the direct relationship of size with mercury levels. However, other factors such as age, surface area, metabolism, habitat, and activity patterns are also important variables affecting the mercury levels in fish of different weight and species (*19*).

A Mercury Budget

Due to bioamplification (Figure 3), mercury concentrations of nonacceptable amounts by FDA standards are being approached in the higher trophic levels. If a mercury content above 500 ppb is confirmed as common to the muscle of large game fish, mercury levels could become a significant factor in the management of the Lake Powell fishery. Imposing consumption limits on large game fish or managing the fishery for a low mercury catch might become advisable, if there is an increase in mercury in the system. As critical levels are being approached, the formulation of a quantitative mercury budget would be desirable in order to evaluate the probability of increased mercury levels due to man's activities in the region.

Using Drake's (*14*) estimate of the natural sediment load of the Colorado River, the net annual degradation of the Upper Colorado Basin is 27.2 million metric tons. Based on U.S. Geological Survey data (*11*), a reasonable estimate of the mercury in the geological material degraded from the Basin would be in the range of 50–200 ppb. If this range were used, the annual weathering of mercury in the Lake Powell drainage would be from 1360–5440 kg of mercury.

If the water of the Colorado River contained from 0.01–0.1 ppb mercury in its 15.3×10^9 m^3 of annual flow (*25*), the unimpounded flow from the upper basin would carry from 153–1530 kg of mercury. At 30 ppb (the mean for our analyses of Lake Powell sediments), the sediment load of the unimpounded river would have carried 816 kg of mercury. Thus, the total estimated annual mercury load for the free-flowing river would be from 969–2346 kg. Any difference between the total mercury transported by the

river and that weathered would represent either net atmospheric transport or accumulation within the system.

In the present impounded system, water flow has been slightly reduced, and the sediment load of the river below the dam has been reduced to <1% of the original load. As weathering and other terrestrial components of the system are basically unchanged, impoundment would logically lead to the accumulation in the lake of most of the original sediment load of the river, suggesting that about 800 kg of mercury may now be accumulating annually. That this accumulation occurs in an aquatic system containing the organisms and energy sources necessary for the uptake and biotransformation of mercury is likely to be the fundamental reason that such impounds may be vulnerable to environmental mercury problems. As well as giving an estimate of the quantities of mercury involved, these computations suggest that a natural equilibrium situation has been converted into a storage system. Both the Lake Powell data and those from other aquatic systems (26) indicate that biological components become the points of maximum concentration of mercury in such storage systems.

If we use data compiled by the U.S. Department of the Interior (27), it should be possible to estimate whether mercury produced by coal-fired power generation facilities will be sufficient to add significantly to the natural mercury budget of the Lake Powell drainage system. In the Upper Colorado Basin (essentially the Lake Powell drainage) three major power plants are contemplated. The Four Corners plant near Shiprock, N.M., approximately 125 miles from Lake Powell and in limited production since 1964, reached a fuel consumption level of 6.5 million metric tons in 1971. The Navajo plant at Page, Ariz., currently being constructed 4 miles south of Lake Powell will consume 5.4 million metric tons annually by 1976. A planned Kaiparowits plant 11 miles north of Lake Powell would burn about 10.8 million metric tons of coal at full capacity. Thus the total annual coal consumption by these major facilities is estimated to be about 23 million metric tons. At this consumption level, an annual mercury output of 23 kg for each ppb mercury in the coal would occur. Based on studies of the Four Corners plant, 96% of the mercury in the coal is released as vapor. As a significant portion of the remaining mercury enters the environment as fly ash or other wastes, essentially all of the mercury in the coal is released into the environment.

Preliminary tests of coal for the Navajo plant indicate coal mercury levels may average 30 ppb. At this level the Navajo plant would produce 162 kg of mercury per year. If we use a current estimate that 40% of this mercury would enter the lake drainage (28), 65 kg of mercury would be added to the system annually, which is 8% of the estimated present annual accumulation of mercury in the lake system and only 1–5% of the estimated natural annual weathering of mercury in the Upper Colorado Basin. Thus, due to the magnitude of the lake system and the movement of natural mercury within it, it is likely that this large power facility can operate adjacent to Lake Powell without significantly affecting lake mercury levels, if mercury levels of coal are in fact near the range that current analyses indicate and assuming a 40% input of mercury into the drainage basin. Later refinements may provide more exacting data.

No data on the mercury content of the coal for the Kaiparowits plant are available. However, if the combined effect of the Navajo and Kaiparowits plants is computed on the basis used for the Navajo plant, enough mercury could enter the system to raise sediment mercury levels by about 24%. While this would represent the addition of only 7 ppb mercury to the sediments, if biological concentration factors remain similar to those found in this study (Figure 3), detectable and environmentally significant elevation of mercury concentrations in the higher trophic levels would occur.

These estimates suggest that both the impoundment of the Colorado River and the projected development of power generation facilities are events of sufficient magnitude to affect the mercury budget of the Upper Colorado River Basin. The definition of the mercury budget of this system, the actual quantities and movement of mercury released by human activity, and the movement of mercury into the biota of the reservoir both currently and as the system ages, should provide the basis for a constructive regional mercury research program. As numerous institutions are already involved in environmental research in the Colorado Basin, a cooperative regional mercury program could appropriately be directed toward the development of a more accurate model of mercury movement that would increase the efficiency of the currently diverse efforts to predict or monitor mercury levels in this major drainage basin.

Summary

Lake Powell is a major storage and hydroelectric reservoir on the Upper Colorado River in northern Arizona and southern Utah. Impoundment began in 1963 with a volume of $17,860.6 \times 10^6$ m^3 (14 million acre ft) being reached in 1971. Samples of organic and inorganic components of the Lake Powell ecosystem were collected during 1971 and 1972 and analyzed for mercury content by flameless atomic absorption.

Surface terrestrial substrates, consisting mostly of sandstones and shales and low-organic unconsolidated materials derived from the sedimentary strata, had a mean mercury content of 10 ppb, dry weight. Where significant quantities of soil organic matter occurred, mercury levels as high as 48 ppb were found.

Leaves of terrestrial plants had a mean mercury content of 34 ppb, air–dry weight, significantly higher than levels in plant stems and roots. Nonvascular plants and water-associated plants had levels in the same range as that of the typical terrestrial vascular plants. Lake transported plant debris had a mean mercury level of 145 ppb, air–dry weight, significantly higher than that of terrestrial plants.

Twelve unfiltered water samples from the upper 5 meters of the lake yielded a mean mercury level of 0.01 ppb, indicating that the lake water with suspended material contains relatively small quantities of mercury.

Mercury in bottom sediments averaged 30 ppb, air–dry weight, with no clear gradient of mercury concentrations relative to distance from the dam. Fine-textured sediments and sediments of relatively high organic content had higher mercury levels than did coarser, low-organic sediments.

Crayfish, the only invertebrate analyzed, had a mean whole body mercury content of 10 ppb, wet weight, and had a positive relationship between mercury content and body weight.

Threadfin shad, the major forage fish of the lake, and three major large predatory fish (walleye, largemouth bass, and rainbow trout) also had a positive mercury content–wet weight relationship. Fish axial muscle levels were generally higher than those of other tissues. Muscle levels on a wet weight basis ranged from 84 ppb in trout to 427 ppb in walleye, with a mean of 232 ppb for all species analyzed. In largemouth bass and walleye, fish heavier than 2 kg had mean muscle levels exceeding 500 ppb ($\bar{x} = 626$ ppb), which is the accepted upper limit safe for human consumption for two meals per week. In rainbow and brown trout, unlike other fish taxa, highly vascu-

larized blood tissues had the highest mercury levels and muscle had relatively low concentrations. In the six other species of fish analyzed, relative mercury levels compared to muscle as 1.00 were: liver 0.51, heart 0.43, kidney 0.36, spleen 0.28, stomach 0.20, brain 0.16, gonads 0.14, skin 0.13, gills 0.12, and bone 0.07.

The results of mercury analyses from water and mineral deposits through the levels of the aquatic food chain provide an excellent example of bioamplification. The terrestrial substrate, mainly sandstone, had mercury concentrations of 10 ppb, diluted to 0.01 ppb in the unfiltered lake water. Increased concentration occurred in the bottom sediments, correlated to fineness of texture and organic matter content, by a factor of three times that of the sandstone and 3000 times that of the water. Bioamplification of mercury, as contrasted to concentration in sandstone as one, increased up the food chain as exemplified by three times in periphyton, nine times in bluegills, and 31 times and 43 times in bass and walleye. Mercury concentrations in some larger predatory fish approached or exceeded the current safe consumption standards.

To evaluate the effects of future human activity on Lake Powell, an estimated mercury budget for the Upper Colorado River Basin is needed. Estimates are that from 1360-5440 kg of mercury may be released by natural weathering in the basin annually, and that impoundment of the river may lead to the accumulation of about 800 kg of mercury in the lake system each year. Currently planned regional coal-fired power generation developments may produce 621 kg of mercury annually, based on conservative analyses of 30 ppb of mercury in the coal, and thus may significantly augment the mercury released by natural weathering in the basin.

Due to the magnitude of the system and the movement of natural mercury within it, the operation of the Navajo power plant currently being constructed adjacent to Lake Powell is not likely to significantly elevate lake mercury levels if the mercury levels of coal are near the current estimate of 30 ppb. However, the combined effects of the two major power plant developments planned near the lake could significantly raise lake sediment levels, and through bioamplification increase mercury levels in large game fish.

The actual impact of power generation facilities will depend upon coal mercury levels and the degree to which mercury output moves into the lake system and through the aquatic food chain. It is concluded that the clearer definition of these major factors of mercury flow can serve as a constructive framework for future regional mercury studies of the Upper Colorado River Basin.

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Methods for Measuring NO$_2$ Photodissociation Rate
Application to Smog Chamber Studies

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The photodissociation of nitrogen dioxide by absorption of solar radiation in 3000-4000 Å region plays a key role in atmospheric chemistry (1, 2), particularly in the formation of photochemical smog (3, 4).

$$NO_2 + h\nu \xrightarrow{k_1} NO + O(^3P) \qquad k_1 = I_0\sigma\phi \quad (1)$$
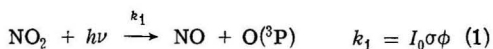
The primary photodissociation rate constant, k_1, serves

as a convenient measure of the intensity of uv radiation in laboratory studies as well as in the atmosphere (5, 6). Several methods have been used previously for the determination of this constant. In this paper these methods will be evaluated on the basis of convenience and feasibility for use in the smog studies.

In principle, k_1 can be determined from the knowledge of the spectral distribution of light intensity, I_0; the quan-

■ Methods for determination of the photodissociation rate of NO_2 have been evaluated critically for application in smog studies. The kinetics and mechanism of NO_2 photolysis at ppm levels in 760 torr N_2 or air were studied in detail using a 45-liter bell jar reactor. Concentration-time profiles of the reactant NO_2 and the products NO and O_3 were monitored continuously by the $NO-O_3$ chemiluminescence method. The decay of NO_2 in N_2 deviated from first-order behavior, this being most noticeable in the early stages of photolysis when the yield of NO is less than a few percent. Thus the commonly used k_d method, based on the assumption of first-order decay, is not applicable. Alternative kinetic expressions have been derived and validated, and values of the relevant rate constant ratios are obtained. In the photolysis of NO_2 in air, the attainment of a photostationary state for NO_2, NO, and O_3 was observed, and the photodissociation rate can be determined from this relationship. Data obtained under various conditions have been analyzed in terms of an 11-step mechanism using numerical integration techniques. A set of rate constants has been derived which can adequately describe the photolysis of NO_2 at ppm level either in N_2 or in the air.

tum yield, ϕ; and the absorption coefficient of NO_2, σ. However, an accurate spectroradiometric measurement of the light intensity is not readily feasible. Therefore, the actinometric determination of k_1 from the photolysis of NO_2 is generally used. Three types of photochemical conditions are often used for this purpose—i.e., A, pure NO_2 at a pressure below a few torr; B, NO_2 at ppm levels in N_2; and C, NO_2 at ppm levels in air. Under these conditions, the primary reaction 1 is followed by numerous secondary reactions (5, 7, 8), as shown in Table I, which should be taken into account in the determination of k_1.

Under condition A, Reaction 3 is the dominant secondary reaction and k_1 can be determined directly from the first-order decay of NO_2 using equation A (9, 10).

$$\frac{d \ln [NO_2]}{dt} = -2k_1 \qquad (A)$$

Unfortunately, this method is often incompatible with existing smog chamber facilities, as it requires an evacuable reactor and low-pressure gas-handling techniques. Namely, the reactor must be free from leaks under vacuum, and the analytical instruments must be able to analyze gases under low pressure. Furthermore, the change in the total pressure of the system during the course of photolysis according to the stoichiometry, $2NO_2 \rightarrow 2NO + O_2$, will add the complication to the calibration procedure for most instruments. Thus, this method is considered less practical and will not be discussed here. The more promising methods, involving conditions B and C, are examined in some detail in the present work.

Under condition B, reactions 3–5 and 8–10 are known to occur, and the determination of k_1 is fairly complex. It has been commonly assumed that the photolytic decay of NO_2 at initial time is a simple exponential process and can be described by Equation B (11):

$$\lim_{t \to 0} \left(\frac{d \ln [NO_2]}{dt} \right) = \frac{-2k_1}{1 + k_4[M]/k_3} = -k_d \qquad (B)$$

The first-order rate constant, k_d, can be thought of as an index of light intensity and has been widely used in smog chamber studies (11–13) despite certain criticisms (6, 14). In the present study, the initial decay of NO_2 deviated from the first-order kinetics given by Equation B. Detailed analysis of this new observation suggests that Equation B is not applicable due to the nonsteady state behavior of the product N_2O_5 in the initial stages, and the results obtained by this method may be subject to some uncertainties. An alternative rate expression for the initial decay of NO_2 and a method for determining k_1 using this system will be discussed.

Under condition C, all 10 secondary reactions, 2 to 11, occur to varying degrees of importance. Due to the regeneration of NO_2 by Reaction 6, its decay is not appreciable; and the concentrations of NO and O_3 remain correspondingly low. Previous work in this laboratory (15) has demonstrated the feasibility of determining k_1 directly from the production rate of NO or O_3 in the early stage of the photolysis—i.e.,

$$\left(\frac{d[NO]}{[NO_2]_0 dt} \right)_{t \to 0} = \left(\frac{d[O_3]}{[NO_2]_0 dt} \right)_{t \to 0} = k_1 \qquad (C)$$

This method has certain advantages over the previous one in that air rather than pure N_2 is used as the diluent gas and k_1 can be derived without the use of other rate constants. This system was examined in the present study, and the "initial rate method" was shown to be too demanding on the response time of the analytical instruments to be of general use. An alternative method to determine k_1 using this system is based on the photostationary state defined by Equation D (3, 4, 15)

$$k_1 = \frac{k_6[NO][O_3]}{[NO_2]} \qquad (D)$$

The validity of this equation is examined in some detail, and a more exact expression is used. Values for k_6 and several rate constant ratios are determined in this study. A set of 11 rate constants is obtained for the photolysis of NO_2 at low concentrations. The computed concentration-time profiles using this set of constants are consistent with all experimental observations both in N_2 and in air.

Experimental

The photolysis of NO_2 was carried out in a 45-liter Pyrex bell jar with initial NO_2 concentration ranging from 1–20 ppm in N_2 and in air. The reactor was mounted on a Teflon-coated stainless steel base with a Viton gasket, and

Table I. Kinetics and Mechanism of Photolysis of NO_2

No.	Reactions	Rate constants	References
1	$NO_2 + h\nu \rightarrow NO + O(^3P)$	5.4×10^{-3} [a]	This work
2	$O + O_2 + Air \rightarrow O_3 + air$	5.6×10^{-34} [b]	(26)
3	$O + NO_2 \rightarrow NO + O_2$	9.5×10^{-12} [a]	This work
4	$O + NO_2 + N_2 \rightarrow NO_3 + N_2$	1.24×10^{-31} [b]	This work
5	$O + NO + N_2 \rightarrow NO_2 + N_2$	1.24×10^{-31} [b]	(26, 27)
6	$O_3 + NO \rightarrow NO_2 + O_2$	1.85×10^{-14} [c]	This work
7	$O_3 + NO_2 \rightarrow NO_3 + O_2$	4.6×10^{-17} [c]	(19)
8	$NO_3 + NO_2 \rightarrow N_2O_5$	3.06×10^{-12} [c]	(32)
9	$N_2O_5 \rightarrow NO_3 + NO_2$	0.23 [a]	(32)
10	$NO_3 + NO \rightarrow 2NO_2$	1.0×10^{-11} [c]	(32)
11	$2NO + O_2 \rightarrow 2NO_2$	2.1×10^{-38} [b, d]	(5, 15)

[a] Sec^{-1}.
[b] Cm^6 molecule^{-2} sec^{-1}.
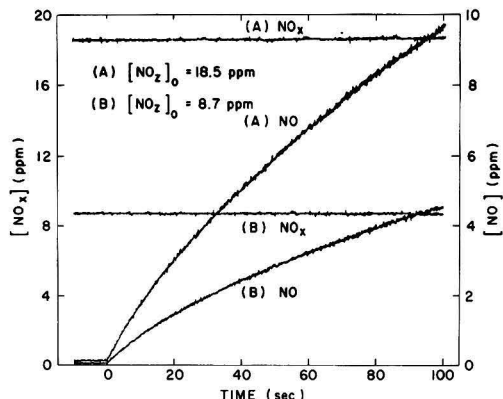[c] Cm^3 molecule^{-1} sec^{-1}.
[d] $k = (1/2)d[NO]/dt[NO]^2[O_2]$.

Figure 1. Some recorder traces of $[NO_x]$ and $[NO]$ in the photolysis of NO_2 in 760 torr N_2

Initial $[NO_2]$ are 18.5 and 8.7 ppm for data sets *A* and *B*, respectively

could be evacuated to below 1 mtorr with a mechanical pump and a liquid N_2 trap. Its leak rate was approximately 1 mtorr min^{-1} upon isolation from the pumping system. The photolytic light source consisted of 24 black light fluorescence lamps (G.E., F40BLB) surrounding the reactor. This arrangement was designed to optimize homogeneity of illumination in the reactor. To ensure a stable light intensity output, the lamps were cooled with forced air and were operated with a voltage-regulated power supply. The light output was monitored by six selenium photocells (International Research, B2M) mounted in circular form at the center of the reactor. A warm-up period of 20–30 min was observed after the lamps were turned on. The stabilized light intensity was reproducible within ±2.5% for a period of over six months. To control the irradiation time accurately, the reactor was equipped with a lighttight cover which could be lifted in about ½ sec.

Nitrogen dioxide (>99% purity) was prepared by adding excess oxygen to prepurified NO, with subsequent O_2 removal via pumping through a liquid N_2 trap. The NO_2 was stored as a white solid at dry ice temperature. Nitrogen (American Cryogenic, ultrahigh purity, stated O_2 purity ≤10 ppm) and air (Air Products & Chemicals, ultrazero grade) were used as received for diluent gases.

The reactant mixtures containing NO_2 at ppm levels were prepared by first filling calibrated volumes with the required pressure and then flushing the contents into the evacuated bell jar with diluent gas until a total pressure reached 760 torr. Reactant pressures up to 5 torr were measured with a pressure transducer (Pace Wiancko, CD25) and total pressures up to 760 torr, by a Wallace & Tiernan gauge. The reactant mixtures of desired concentrations thus prepared could be reproduced within ±2%. The temperature of the gas mixture during the photolysis was determined to be 27 ± 2°C.

Total nitrogen oxides, NO_x, and the products NO and O_3 were monitored continuously with three NO–O_3 chemiluminescence detectors (16, 17) with sample flow rate of 30 cm^3 min^{-1}. The response time of the instruments was less than 1 sec and detectability is 1 ppb. The NO_x detector was equipped with a molybdenum-impregnated carbon convertor (18) to reduce NO_2 to NO quantitatively (greater than 99%), and the sum $[NO_x] = [NO_2] + [NO]$ was measured. There is some evidence that this convertor may be sensitive to other oxides of nitrogen such as N_2O_5 and

NO_3. However, under the present experimental conditions other nitrogen-containing species were less than 1.5% of the NO_x concentration. Thus, the concentration of NO_2 obtained by subtracting the NO value from the NO_x value has very little error. The NO detector was calibrated using a standard mixture of NO in nitrogen. The NO_x and O_3 detectors were calibrated relative to the NO detector using the NO titration method based on Reaction 6. All of these calibrations were cross-checked against the known concentrations prepared in the bell jar by the standard pressure–volume method described above. The results agreed within ±2%. The linearity of the signal vs. concentration was checked from 10^{-3}–10^2 ppm range using the exponential dilution method (17).

Results

Photolysis of NO_2 in N_2. Nitrogen dioxide, with initial concentration ranging from 1–20 ppm, was photolyzed in the presence of 760 torr N_2; and the concentrations of the total oxides of nitrogen, NO_x, and the NO were monitored continuously. Typical recorder traces of such concentration–time profiles obtained for the initial NO_2 concentrations at 18.5 and 8.7 ppm are shown in Figure 1. The rate of NO increase is seen to be very rapid in the early stages of the photolysis and then level off gradually, while $[NO_x]$ remains nearly constant. The noise level is approximately 2% throughout the concentration scale under these experimental conditions. The concentration–time behavior of NO_2 determined by the subtraction method is plotted as circles in Figure 2 for three $[NO_2]_0$ levels. For each initial concentration the photolysis was performed at least three times to check the reproducibility, found to be ±2%. The figure shows only the pair of runs with maximum deviation from each other. The solid curves drawn in this figure and in Figures 3–5 are the computed results to be described later. It is noted that the decay of NO_2 is not a first-order process since the data indicate deviation from the exponential decay with time. This nonlinear behavior is most noticeable in the early stages of photolysis (0–15 sec), where formation of NO is only a few percent. The
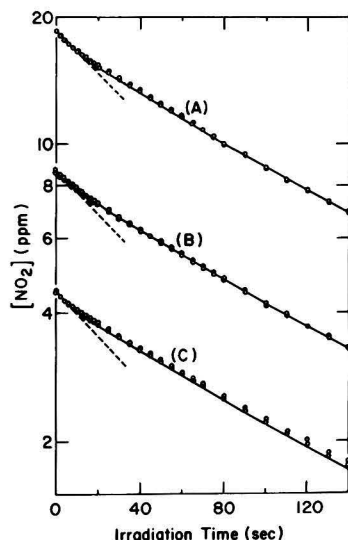

Figure 2. Logarithmic concentration of NO_2 vs. time profiles at three initial NO_2 concentrations, $A = 18.5$, $B = 8.7$, and $C = 4.5$ ppm

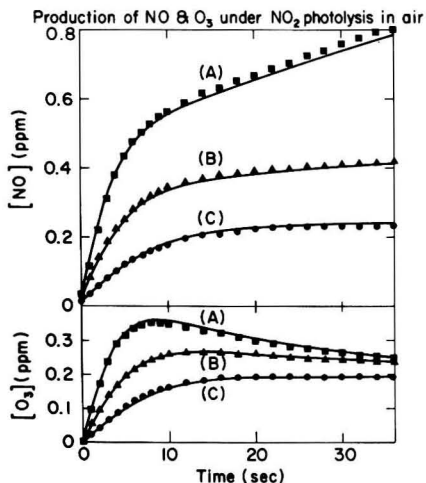Points are experimental data and solid curves, computed results

Figure 3. Concentration–time profile of NO and O_3 in the photolysis of NO_2 in 760 torr air

Initial concentrations of NO_2, A = 19.0, B = 9.2, and C = 4.2 ppm. Points are experimental data, and curves are computed results using rate constants in Table I

Figure 4. Decays of NO and O_3 in dark after the photolysis of NO_2 in air for ~80 sec

Initial concentrations of NO_2, A = 9.2, B = 4.2, and C = 1.95 ppm. The profile of O_3 in set C was shifted up by 0.1 ppm for clarity of presentation. Points are experimental data, and curves are computed results

decay rate is a maximum at zero time and decreases gradually as the photolysis proceeds. This initial rate is estimated to be 0.73 (±20%) min^{-1} as indicated by the dotted lines, and is roughly twice that at later reaction time. The deviation from first-order behavior for the NO_2 decay, particularly in the early stages of the photolysis, was the case for all runs at various initial concentrations of NO_2. These data cannot be described with the simple k_d relationship as defined by Equation B. This observation has not previously been reported.

Photolysis of NO_2 in Air. The major products in the photolysis of NO_2 in 760 torr of air are NO and O_3. These products together with NO_x were monitored continuously. The concentration–time profiles of NO and O_3 are shown as points in Figure 3 for three $[NO_2]_0$ levels. Each data set shown here was taken from the average reading of three runs. The reproducibility of the data was approximately ±3%. In this figure, [NO] increases rapidly initially (0–10 sec) and then continues to increase at a slower rate after the ozone concentration has reached its maximum value. The $[O_3]$ shows a similar fast growth in the early stages but then begins to decay after the maximum. In addition, the profiles of [NO] and $[O_3]$ are nearly parallel from 0–20 sec when $[NO_2]$ is 4.2 ppm or lower; but the deviation of these profiles from each other becomes larger when $[NO_2]_0$ is higher.

When the light is suddenly blocked or turned off during the photolysis, both NO and O_3 are observed to decay until O_3 is completely removed; and [NO] levels off. Figure 4 shows three sets of such "dark" profiles after approximately 80 sec of irradiation. The points are experimental data taken from the average of three runs. The decrements of NO and O_3 are nearly equal under all conditions.

Discussion

Determination of k_1 from the Photodissociation of NO_2 in Air. The initial slope method using Equation C was applied. This equation is valid only when both NO and O_3 are low enough to minimize Reaction 6, and the
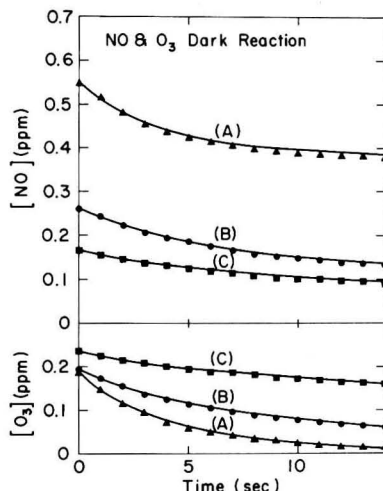
initial slopes have to be measured within a few seconds after the irradiation is begun. During this period, the data are subject to uncertainties associated with instrumental response time, noise in the concentration measurement, and determination of zero irradiation time. Therefore, the values of k_1 determined from this method suffer from a large degree of scatter. They vary between 0.25 and 0.4 min^{-1} with an average value of 0.31 min^{-1}. To improve the precision of the k_1 value using these experimental conditions, an alternative method was sought. When the product, [NO] × $[O_3]$, from the same sets of data in Figure 3 are plotted against time, Figure 5 is obtained. In this figure all [NO] × $[O_3]$ values are seen to reach steady-state conditions after the initial buildup. This indicates that the photostationary state is attained within 10–20 sec of irradiation. The higher the value of $[NO_2]_0$ is, the earlier the system reaches this state. According to
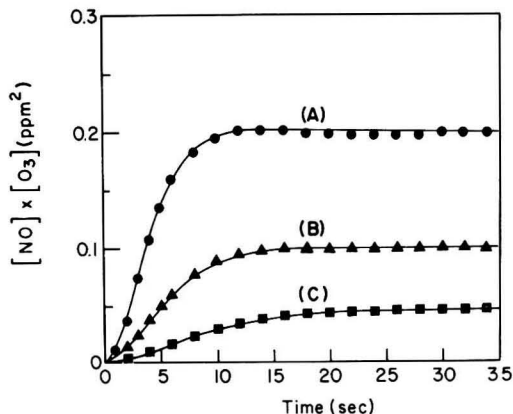

Figure 5. [NO] × $[O_3]$ vs. time profiles during the photolysis of NO_2 in air

Initial concentrations of NO_2, A = 19.0, B = 9.2, and C = 4.2 ppm. Points are experimental data, and curves are computed results

Equation D, the ratio of $[NO][O_3]/[NO_2]$ is equal to k_1/k_6, which should be constant during the photostationary state regardless of the initial NO_2 concentration. However, the values of $[NO][O_3]/[NO_2]$ vary slightly depending on $[NO_2]_0$. Therefore, a more exact photostationary state expression is needed. This can be derived from the kinetic relation of O_3.

Since the O-atom lifetime in air is very short (~ 15 μsec) compared with the experimental time scale, a steady state assumption for this species is valid. The rate equation for ozone formation in the photolysis of NO_2 in air is

$$\frac{d[O_3]}{dt} = k_1[NO_2] - k_6[NO][O_3] - k_7[NO_2][O_3] \quad (E)$$

In the vicinity of the ozone maximum—i.e., $d[O_3]/dt = 0$, Equation E can be simplified:

$$k_1 = k_6 \frac{[NO][O_3]}{[NO_2]} + k_7[O_3] \quad (F)$$

This equation is also a good approximation after the ozone maximum since the rate of ozone decay under the experimental conditions is less than 2% of $k_1[NO_2]$. If both k_6 and k_7 are known, the rate constant k_1 can be determined from the concentrations of NO_2, NO, and O_3 measured during the photostationary state. The rate constant, k_7, has been obtained recently in this laboratory (19), and a value of 7.0×10^{-2} ppm^{-1} min^{-1} (4.6×10^{-17} cm^3 mol^{-1} sec^{-1}) is assigned at $T = 300°K$. The rate constant k_6 can be determined from the data in Figure 4. Because the stoichiometry $\Delta[NO]/\Delta[O_3]$ is observed to be near unity, the major removal process for NO and O_3 under these conditions is Reaction 6. However, for completeness, Reactions 7-10 are also considered. The rate constants k_8, k_9, and k_{10} were taken from the literature values as listed in Table I; but k_6 was treated as a variable. These data, together with initial concentrations of NO_2, NO, and O_3, were used as input to a chemical kinetics computer program (20). The computed concentration-time profiles for NO and O_3 were compared with the observed data. The final value of k_6 was chosen from the best fit to all the data. The value thus derived is 27.5 ppm^{-1} min^{-1} (1.85×10^{-14} cm^3 molecule^{-1} sec^{-1}). The curves in Figure 4 are the computed results using this value. The error range of k_6 was estimated as $\pm 10\%$. Values beyond this error limit give results deviating from the experimental uncertainty. The k_6 value determined here agrees well with the values obtained by the previous investigators (15, 21-23).

The difference between Equation D and Equation F is the $k_7[O_3]$ term, which can be significant, depending on the initial NO_2 concentration. For example, at $[NO_2]_0 = 19$ ppm, it is 7% of the $(k_6\{[NO][O_3]/(NO_2)\})$ term. For better precision, Equation F was used to evaluate k_1. Values of k_1 obtained by this method using the data shown in Figures 3 and 5 are given in Table II.

The average value of k_1 is 0.325 min^{-1} with a standard deviation of 0.005 min^{-1}. The major uncertainty in using this method is the accuracy of k_6 determination and the concentration measurements. When these factors are considered, the probable error in k_1 is estimated to be $\pm 15\%$.

Photolysis of NO_2 in N_2: Determination of Rate Constant Ratios k_4/k_3 and k_5/k_3. The nonfirst-order behavior of NO_2 decay in the photolysis of NO_2 in N_2 (Figure 2) was analyzed using a numerical method. In this case, the reactions to be considered are 1, 3-5, and 8-10. The values of all rate constants are known previously except those of k_3, k_4, and k_5. As we varied these three constants systematically, the concentration-time profiles of the species

Table II. Rate Constant k_1 Determined from Equation F Using Data in Figures 3 and 5

Time, sec	Data set		
	A	B	C
10	$k_1 = 0.315$ min^{-1}		
15	0.323	0.325	
20	0.322	0.331	0.321
25	0.321	0.331	0.327
30	0.321	0.330	0.329
35	0.320	0.330	0.330

in the system were computed and compared with the experimental data. During the process of curve fitting, all computed NO_2 decay curves, however different from the data, showed deviation from the first-order kinetics, with a rapid decay rate in the initial stages similar to that observed experimentally. In addition, the data could be matched well with the computed results using the rate constant ratios $k_4[M]/k_3$ and $k_5[M]/k_3$ both equal to 0.32. The uncertainties of these ratios are estimated to be $\pm 10\%$ and $\pm 25\%$, respectively. The absolute values of these rate constants can be determined from these ratios with a knowledge of any one of three constants. Among them, k_5 has been studied most extensively, and all the literature values are within $\pm 25\%$ (24, 25). If we take the value of k_5 obtained in this laboratory, 6.65×10^{-32} cm^6 molecule^{-2} sec^{-1} for $M = $ He (26) and the relative third body efficiencies for He and N_2—i.e., 0.75 and 1.4 (24, 27), k_5 is calculated to be 1.24×10^{-31} cm^6 molecule^{-2} sec^{-1} for $M = N_2$ at 300°K. On this basis, the values for k_3 and k_4 are determined as 9.5×10^{-12} cm^3 molecule^{-1} sec^{-1} and 1.24×10^{-31} cm^6 molecule^{-2} sec^{-1}, respectively.

The computed results using these rate constants at three $[NO_2]_0$ levels are shown as curves in Figure 2. The initial decay rate of NO_2 was determined from this analysis to be 0.73 min^{-1}, which agrees very well with the experimental observations.

Experimental data of NO_2 photolysis in air were also analyzed numerically using all 11 reactions and the rate constants listed in Table I. The computed profiles of $[NO]$, $[O_3]$, and $[NO] \times [O_3]$ are shown by curves in Figures 3 and 5. The results are in good agreement with the experimental data at various initial concentrations of NO_2.

Kinetic Expressions for NO_2 Decay and Determination of k_1 in Photolysis of NO_2 in N_2. Since a fast decay rate and nonfirst-order behavior of NO_2 are observed both in the experimental data and in the numerical results, the mechanism on which the computational scheme is based appears adequate to explain these observations. Although Equation B was also formulated from the same mechanism, its inapplicability to the system seems to suggest that its derivation should be re-examined. The approximations made in the following derivation are all justified by the detailed analysis of numerical results.

When we combine the rate equations of NO_2, O, NO_3, and N_2O_5 from the mechanism, Equation G is obtained:

$$\frac{d[NO_2]}{dt} + \frac{3d[N_2O_5]}{dt} + \frac{d[O]}{dt} + \frac{2d[NO_3]}{dt} = -2k_3[O][NO_2] \quad (G)$$

The last two terms on the left side of the equation—i.e., $d[O]/dt$ and $2d[NO_3]/dt$, can be neglected, because they are three to four orders of magnitude smaller than the first two terms. Also, as the lifetime of O atoms in this

system is less than 1 msec, a steady state approximation can be used:

$$[O]_{ss} = \frac{k_1[NO_2]}{k_3[NO_2] + k_4[NO_2][M] + k_5[NO][M]} \quad (H)$$

Substituting Equation H into Equation G, one obtains

$$\frac{d[NO_2]}{dt} + \frac{3d[N_2O_5]}{dt} = $$
$$\frac{-2k_1k_3[NO_2]}{k_3 + k_4[M] + k_5[M][NO]/[NO_2]} \quad (I)$$

In the conventional derivation of k_a, the $3d[N_2O_5]/dt$ term was neglected on the assumption that $[N_2O_5]$ is in a steady state; Equation I would then become Equation B by neglecting [NO] in the initial stage. In fact, this steady state assumption of N_2O is not valid at the initial time. The kinetic expression for $[N_2O_5]$ can be derived similarly from the overall mechanism by neglecting $d[NO_3]/dt$ term and expressed as Equation J.

$$\frac{d[N_2O_5]}{dt} = \frac{k_1[NO_2]}{1 + \frac{k_3}{k_4[M]} + \frac{k_5[NO]}{k_4[NO_2]}} - k_{10}[NO_3][NO] \quad (J)$$

In this equation, $[N_2O_5]$ is governed by two major terms, both being strongly dependent on the concentration of NO. At the initial time, where [NO] is low, Equation J becomes

$$\frac{d[N_2O_5]}{dt} = \frac{k_1[NO_2]}{1 + \frac{k_3}{k_4[M]}} \quad (K)$$

and N_2O_5 is generated at its highest rate. This rate can be as much as 15% of $d[NO_2]/dt$ term and should not be neglected. Multiplying this rate expression by 3 and substituting this into Equation I, one obtains the rate expression for NO_2 decay at zero time

$$\lim_{t \to 0} \frac{d \ln [NO_2]}{dt} = -k_1\left(2 + \frac{1}{1 + \frac{k_3}{k_4[M]}}\right) \quad (L)$$

A value of 0.74 min^{-1} was obtained for the initial NO_2 decay rate from this equation using the values of k_1 and $k_3/k_4[M]$ determined above. This agrees quite well with the rate of 0.73 min^{-1} determined both by experimental observations and numerical results and is much greater than 0.51 min^{-1}, which would be obtained from Equation B. Therefore, it becomes clear that an assumption of an $[N_2O_5]$ steady state does not hold during the initial stages of photolysis, and that this nonsteady state behavior of $[N_2O_5]$ is responsible for the faster NO_2 decay early in the reaction.

As the reaction proceeds, the NO concentration increases and the rate of N_2O_5 formation slows down as predicted from Equation J. The concentration of N_2O_5 reaches a maximum (in about 10–20 sec) and then decays gradually. Under these conditions, the steady state approximation of N_2O_5 holds rigorously and Equation I can be written as

$$\frac{d \ln [NO_2]}{dt} = \frac{-2k_1}{1 + k_4[M]/k_3 + k_5[M][NO]/k_3[NO_2]} \quad (M)$$

This equation shows that the NO_2 decay is not a simple

first-order process, and the logarithmic decay rate will decrease with time due to the increase in [NO]/[NO$_2$] term. To validate this equation quantitatively, the decay rate of NO_2 was calculated from Equation M for [NO]/[NO$_2$] = 0.8. A value of 0.415 min^{-1} was obtained, which agrees well with the experimental values of 0.41 ± 0.01, 0.405 ± 0.01, and 0.405 ± 0.01 (Figure 2). Such agreement was found when the [NO]/[NO$_2$] ratio is equal to or greater than 0.5.

Equation M can be integrated to give

$$k_1 = \frac{1}{2(t_2 - t_1)} \left\{\left(1 + \frac{k_4[M]}{k_3} - \frac{k_5[M]}{k_3}\right) \times \ln \frac{[NO_2]_1}{[NO_2]_2} + \frac{k_5[M]}{k_3}\left(\frac{1}{[NO_2]_2} - \frac{1}{[NO_2]_1}\right)[NO_x]_0\right\} \quad (N)$$

where $[NO_2]_1$ and $[NO_2]_2$ are concentrations of NO_2 at times t_1 and t_2, and $[NO_x]_0 = [NO_2] + [NO]$. This equation allows the determination of k_1 by measurements of $[NO_2]$ at any two reaction times during photolysis, provided $[NO]/[NO_2] \geq 0.5$. Again, the applicability of this equation was checked by substituting the data at $t_1 = 40$ and $t_2 = 100$ sec and the rate constant ratios into Equation N. The values of k_1 thus obtained are 0.32 ± 0.015, 0.32 ± 0.015, and 0.31 ± 0.015 min^{-1} for data sets A, B, and C in Figure 2, respectively.

Conclusion

This work shows that for NO_2 photolysis in N_2 the decay of NO_2 does not follow a simple first-order process, particularly in the early stages of reaction when the NO formation is only a few percent. Equation B is inadequate to describe the system due to the nonsteady state behavior of N_2O_5. Derivation of the rate constant ratio, k_4/k_3, from Equation B can lead, therefore, to an erroneous result. For example, a 10% overestimation in k_d can lead to more than a 30% lower value in the ratio of k_4/k_3. Because the variation in NO_2 decay rate in this initial period (0–20 sec) is large (~30%), the derived values of k_4/k_3 can vary by more than a factor of two. This may partly explain the large discrepancy among the reported values for this ratio (6, 7, 9, 10, 28). If the rate constant ratios k_4/k_3 and k_5/k_3 are to be determined using this system, the curve-fitting method by numerical integration used here seems to be more appropriate, since it takes into account all the data over the entire reaction time, rather than the decay slope of NO_2 at the beginning of the photolysis. The absolute values for k_3 and k_4 determined here agree well with the recent direct measurement of $k_3 = 9.1 \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1} (29, 30) and reasonably well with the critical evaluation of $k_4 = 1.0 \times 10^{-31}$ cm^6 molecule^{-2} sec^{-1} (31).

Although the initial decay rate for NO_2 in photolysis of NO_2–N_2 system and the initial formation rates for NO and O_3 in NO_2–air system can be expressed by Equation L and Equation C, the determination of k_1 from the initial slope is not readily feasible. It requires very fast instrumental response time and more exact control of the starting time of irradiation. Since these requirements are too stringent for existing smog chamber facilities, the method does not seem to be of general use.

The two k_1 determination methods both in air and in N_2 demonstrated in the present study do not suffer from such experimental difficulty. Once the photostationary state is attained, Equation F holds for the entire course of the photolysis. Therefore, the measurement of NO_2, NO, and O_3 concentrations can be made essentially at any time during this period. The application of Equation N needs only the relative values of $[NO_x]_0$, $[NO_2]_1$, and

$[NO_2]_2$. The last two values can be measured at any two reaction times of convenience. This method is similar to that proposed by Holmes et al.(6), except that the present initial $[NO_2]_1$ measurement should be made at a slightly later time, after $[N_2O_5]$ reaches a steady state. However, if there is sufficient NO present in the reactant mixture initially, $[NO_2]_1$ can be determined at $t = 0$; and only one measurement of NO_2 concentration—i.e., $[NO_2]_2$, is needed after the photolysis.

A set of 11 rate constants, of which seven are taken from the literature and four were derived from this study, is listed in Table I. When these rate constants were used in the mechanism (1–11), the concentration–time profiles of all species in the system were computed by a numerical integration scheme. The computed results are in good agreement with all observed data (Figures 2–5). Thus, the kinetics and mechanism derived here adequately describe the photolysis of NO_2 at ppm level either in N_2 or in air.

Acknowledgment

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Removal of Pesticides by Reverse Osmosis

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Pesticides have been widely used to increase not only the production of food and fiber but also the freedom from epidemic diseases and obnoxious plant and animal life. In 1971, a total of 1.34 billion pounds of pesticides were manufactured (1) in the United States. The estimated annual growth rate of poundage manufactured now approaches 16% (2). It is obvious that the use of pesticides has become indispensable to many in the struggle to improve man's life.

Nevertheless, the side effects resulting from the use of pesticides, on the other hand, have become increasingly severe (3). Pesticide residues have been reported to impart an unpleasant odor and taste to water (4). Pesticide residues not only kill noxious pests and weeds but also kill various microorganisms, fish, birds, and wildlife. Moreover, because of their resistance to decomposition, the pesticide residues have appeared in man's immediate food supply through natural food chains. Since 1945, pesticide

■ Two types of reverse osmosis membranes—i.e., cellulose acetate (CA) and cross-linked polyethylenimine, designated as NS-100 by OSW, were evaluated for their removal of a wide variety of pesticides, including chlorinated hydrocarbons, organophosphorus, and miscellaneous pesticides. With each membrane the rejection of pesticides was better than 99%. A considerable amount of pesticide was adsorbed onto the membrane materials. The extent of adsorption is governed by the van der Waals–London forces and hydrophobic bonding between pesticide molecules and the polymeric membrane materials. Membrane rejection of the pesticides is in turn governed by the polarity of the solute molecules in aqueous solution, which is in accord with the theory advanced by Sourirajan.

residues have been reported in milk, tissues of fish and wildlife, and all types of waters, such as municipal, drinking, irrigational, and recreational waters. The amount of residues in the wastewater of pesticide manufacturers is stunning. In spite of extensive treatment of pesticide wastewater generated by pesticide manufacturers, a recent investigation (1) showed that a large amount of pesticide ranging from a few pounds per day to over 1000 lb per day was found in their effluents. All of these facts clearly show the need for an in-depth study of the removal of pesticide residues from water.

Numerous studies have been conducted on processes for removal of all types of pesticides from aqueous solution (2). Several treatment processes, such as activated sludge treatment, chemical oxidation, coagulation and filtration, adsorption (activated carbon, ion exchange, saturated clay systems, hydrous aluminum silicate), liquid–liquid extraction, and photochemical degradation, have been developed as a result of these studies. Hindin and his coworkers (5) have studied the removal of a few chlorinated pesticides, including DDT, TDE, BHC, and lindane, by reverse osmosis using cellulose acetate (CA) membrane. The initial results of their findings have shown that reverse osmosis seems to be a promising treatment process for removing pesticides from water.

Reverse osmosis has become a versatile separation/purification process since the discovery of the asymmetric cellulose acetate membrane in late 1950's (6). This process physically separates contaminants from the water by circulating the solution at high pressure over the surface of a semipermeable membrane. The performance of the membrane process is determined by two parameters—i.e. the degree of contaminant removal, and the flux of purified water permeating through the membrane. These parameters, however, were highly dependent upon the physical and chemical properties of the contaminants as well as the membrane materials (7).

In their recent study, Chian and Fang (7) reported that a number of noncellulosic base membranes, such as aromatic polyamide and cross-linked polyethylenimine (NS-100) membranes, exhibited far better properties of removal of organic compounds and resistance to pH than conventional CA membrane. Because of this advancement in membrane technology, reverse osmosis has been gradually finding application in the treatment of a variety of domestic, industrial, and hospital wastewaters. This work gives an in-depth study of pesticide removal with reverse osmosis, a study needed for fully assessing the potential of this process.

Experimental Procedures

Thirteen major pesticides and two metabolites of pesticides were selected for this study. The selections of pesticides were based upon their chemical compositions, applications, and occurrences in water. The trade and chemical names, molecular weights, classifications, solubilities, toxicities as well as annual productions of pesticides are summarized in Table I. Samples of pesticides were provided by the Pesticides and Toxic Substances Effects Laboratory of the Environmental Protection Agency, North Carolina. The metabolite samples were provided by Illinois State Natural History Survey. All pesticides studied here were of analytical grade.

Nanograde solvents, such as acetone, hexane, ether, ethanol, dichloromethane, and benzene, were used for dissolution and extraction of pesticides in this study. Demineralized water was used to prepare the aqueous solution of pesticides.

Conventional CA membrane and a newly developed cross-linked polyethylenimine membrane were employed in this work. The CA membrane, designated as KP-98, was a product of Eastman Kodak Co. (Kingsport, Tenn.). It possesses an asymmetric structure composed of a dense active layer of approximately 2000 Å supported by a porous layer about 0.25–0.5 mm in thickness. It is the dense active layer which dominates the permeate flux and the solute separation.

The cross-linked polyethylenimine membrane, designated as NS-100 by the Office of Saline Water (OSW), was provided by North Star Research and Development Institute (Minneapolis, Minn.). This membrane has a dominant active layer of polyethylenimine cross-linked with m-tolylene 2,4-diisocyanate and is coated on a porous polysulfone support. Figure 1 depicts the possible chemical structure of the active layer of this membrane. Previous study (7) has shown that the NS-100 membrane is the most promising membrane ever developed with respect to pH stability, permeate flux, and the removal of solutes, especially small polar organic compounds.

While testing an aqueous solution containing 5000 ppm of sodium chloride at room temperature and under a pressure of 40.8 atmospheres (600 psig), a flux of 32 ml/cm²/day (8 gal/ft²/day, gfd) with 96.5% rejection of sodium
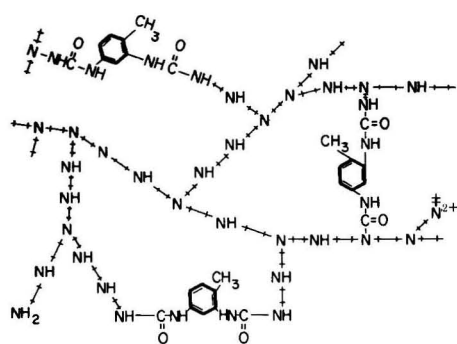
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Figure 1. Idealized structure of cross-linked polyethylenimine and tolylene-2,4-diisocyanate

chloride was obtained with the CA membrane. Under the same testing conditions, the NS-100 membrane yielded a flux of 49 ml/cm²/day (12 gfd) and a rejection of 99.5% of sodium chloride.

The pesticides investigated in this study can be divided into three groups: (1) chlorinated hydrocarbons, including aldrin, lindane, dieldrin, heptachlor, heptachlor epoxide, DDT, and DDE; (2) organophosphorus, including diazinon, parathion, methylparathion and malathion; and (3) miscellaneous pesticides, including randox, trifluralin, atrazine, and captan. Because of their low solubility in water, each group of the pesticides was first dissolved in acetone as stock solutions. Three different aqueous solutions, each containing a specific group of the pesticides, were prepared by dissolving in water a given amount of the acetone stock solution of pesticide mixtures. The final concentrations were adjusted to a level within the solubility limits for each of the pesticides in the groups given above.

The removal of each of the above pesticide solutions with CA and NS-100 membranes was tested using a stainless steel static test cell. Figure 2 depicts the static test cell manufactured by Abcor, Inc. (Cambridge, Mass.). Each of these tests was conducted at room temperature and at a pressure of 40.8 atm (600 psig). The latter was controlled by the pressure regulator on the nitrogen tank. The membrane, with its active surface facing the solution, was supported on a sintered stainless steel plate. During the run, the pesticide solution was agitated by a magnetic stirring bar suspended close to the surface of the membrane. Such circulation is necessary to minimize the effect of concentration polarization on the membrane surface which, in turn, governs the performance of the membrane process. Due to the limitation of the test cell employed in this study, only a narrow range of agitation rate is allowed to be varied. This makes it difficult to evaluate the adequacy of agitation in avoiding concentration polarization. However, the normal agitation rate was maintained throughout the experiment so that results can be related meaningfully to the characteristics of the membranes tested under the identical conditions with 5000 ppm of aqueous solution of sodium chloride.

A fresh membrane was used for each test. The test cell was filled with 150 ml of pesticide solution. After nitrogen pressure and stirring speed were adjusted, the permeate was collected from the low-pressure side of the cell. At the amount when 40% of the original solution was collected, the pressure of the cell was reduced to atmospheric. Both the retentate and the permeate were weighed. The test cell was then filled with 50 ml of extracting solvent. A 50/50 by volume of acetone and water was used for extracting the NS-100 membrane while ethanol was used for extracting the CA membrane. The extraction process was carried out under a pressure of 13.6 atm. The pesticides extracted from the membrane were collected in the permeate. Between experiments the test cell was cleaned and rinsed thoroughly with acetone and demineralized water.

Analysis

Pesticides in feed, retentate, permeate, and the membrane extract were quantitatively and qualitatively analyzed by a Tracor Gas Chromatography Model 550 (Tracor Lane, Austin, Tex.). For all the pesticides studied here, a N_i^{63} high-temperature electron capture detector (ECD) using nitrogen as carrier gas was used. Two 4-mm i.d. Pyrex glass columns were used for the analysis. A 183-cm (6-ft) column packed with 100–120 mesh Supelcoport (Bellefonte, Pa.) containing 1% OV-17 and 3% QF-1 was employed for nonpolar pesticides such as chlorinated hy-
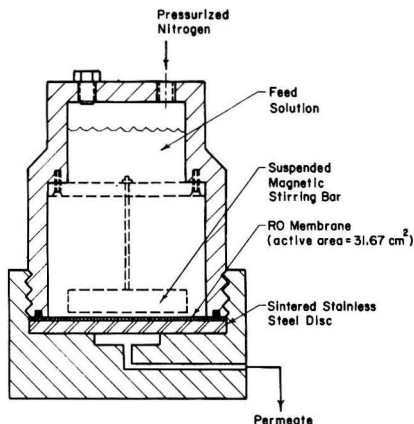

Figure 2. Static test cell for reverse osmosis membrane (Abcor, Inc.)

drocarbons. For organophosphorus and other pesticides, a 61-cm (2-ft) column packed with 100–120 mesh Supelcoport containing 2% OV-17 and 4% QF-1 was used.

Chlorinated hydrocarbons in each sample were extracted with a mixture of ether and hexane in a proportion of 1 to 9. Other pesticides were extracted with dichloromethane. After two consecutive extractions for each sample, the extracted solution was transferred to a 250-ml Erlenmeyer flask equipped with a Snyder condenser; 25 ml of benzene was added to the extracted solution. The mixture was evaporated on a steam bath until 5 ml of benzene solution remained. The content of the flask was then transferred and made up to a 10-, 100-ml, or other volumes to a concentration suitable for injection into the gc column for analysis of pesticides.

Results and Discussion

The average permeate fluxes were 32 and 49 ml/cm²/day (8 and 12 gfd) for CA and NS-100 membranes, respectively. Because of the low concentration of the pesticides (ranged from 0.28 ppm of DDT to 10.53 ppm of trifluralin in the original feed solution), the flux of permeated water was independent of the pesticides tested and remained constant throughout the run. In actual cases, membrane fluxes will depend more upon the concentration of the total dissolved solids (TDS) rather than the concentration pesticides in the water.

The efficiency of the membranes for removing certain pesticides was determined as follows:

$$R = \left[1 - \frac{C_p V_p}{C_f V_f} \right] \times 100\% \qquad (1)$$

where R represents the percentage of pesticide being removed; C and V represent the concentration of pesticide and volume of aqueous solution, respectively; subscripts p and f represent permeate and feed solution, respectively. Tables II, III, and IV show the percentage removal of each group of pesticides with both CA and NS-100 membranes as determined by Equation 1. Percentages of pesticide removal were calculated when 40% of the volume of the original feed solution was removed in the form of permeate.

From a simple material balance made among pesticides present in the original feed, the membrane retentate and permeate as shown in Tables II, III, and IV, it was determined that an appreciable amount of pesticides was lost after the tests. The possibility of decomposition and hy-

drolysis of pesticides that might occur within a period of a few days between sample collection and analysis was not eliminated but seems unlikely in view of the relatively short time involved. This is especially true with the more persistent chlorinated pesticides. The only other possibility which might account for the loss of pesticides would be adsorption of pesticides onto either the wall of the stainless steel (Type 316) test cell or the polymeric membrane

materials. While results of analysis of the acetone rinse from the compartment of the test cell wetted by the feed solution showed trace to nondetectable amounts of pesticides, an appreciable amount of pesticides was, however, detected in the membrane extract.

Quantitative recovery of pesticides was not attained from membrane extracts owing either to lack of adequate solvent for extraction (i.e., solvent having a favorable dis-

Table I. Classification and Properties of Pesticides Tested

Trade name	Chemical name	Mol wt	Chemical classification	Type	Solubility (2,'23), ppm	Oral toxicity (2, 24), LD$_{50}$, mg/kg	Estimated annual sales in 1971 (1), million lb
Diazinon	O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl)-phosphorothioate	304	Organophosphorus	Insecticide	40	76–108	10
Malathion	O,O-dimethyl phosphorodithioate of diethyl mercaptosuccinate	330	Organophosphorus	Insecticide	145	2,800	35
Parathion	O,O-diethyl O-p-nitrophenyl phosphorothioate	291	Organophosphorus	Insecticide	20–25	6–15	15
Methylparathion	O,O-dimethyl O-p-nitrophenyl phosphorothioate	263	Organophosphorus	Insecticide	50	9.4	45
Aldrin	1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo-exo-5,8-dimethanonaphthalene	365	Halogeneous cyclodiene	Insecticide	0.20	55	10
Dieldrin	1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene	381	Halogeneous cyclodiene	Insecticide	0.25	60	<1
Heptachlor	1,4,5,6,7,8,8a-Heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	373	Halogeneous cyclodiene	Insecticide	0.056	130–135	6
Heptachlor epoxide	1,4,5,6,7,8,8a-Heptachloro-3a,2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindene	389	Halogeneous cyclodiene	Metabolite of heptachor	...	...	...
Lindane	1,2,3,4,5,6-Hexachlorocyclohexane	291	Halogeneous aliphatics	Insecticide	7.3–10	90	<1
DDE	1,1-Dichloro-2,2-bis(p-chlorophenyl)ethylene	318	Halogeneous aromatics	Metabolite of DDT	...	...	...
DDT	1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane	354.5	Halogeneous aromatics	Insecticide	0.0012–1	113	45
Trifluralin	α,α,α-Trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine	335.3	Salt of quaternary ammonium bases	Herbicide	24	>10,000	25
Randox	Diallylchloroacetamide	174	Derivative of aliphatic carboxylic acids	Herbicide	19,000	700	10
Atrazine	2-Chloro-4-ethylamino-6-isopropyl amino-s-triazine	216	s-Triazines	Herbicide	70	1,750–3,080	90
Captan	N-trichloromethyl thiotetrahydrophthalimide	301	Mercaptanes	Fungicide	Insoluble	9,000	18

Table II. Removal of Chlorinated Pesticides by Reverse Osmosis

	Membrane	Amount of pesticides (μg) in solutions				% removal	% adsorption calcd[b]
		Original feed	Retentate	Permeate	Adsorbed calcd[a]		
Aldrin	NS-100	142.3	6.9	N.D.[c]	135.4	100	95.15
	CA		29.1	N.D.	113.2	100	79.55
Lindane	NS-100	506.4	440.2	5.3	60.9	98.95	12.03
	CA		157.5	2.5	346.4	99.51	68.40
Heptachlor	NS-100	145.1	5.4	N.D.	139.7	100	96.28
	CA		28.1	N.D.	117.0	100	80.63
Heptachlor epoxide	NS-100	306.9	25.6	0.5	280.8	99.84	91.50
	CA		71.5	0.7	234.7	99.77	76.47
DDE	NS-100	69.0	4.2	N.D.	64.9	100	94.06
	CA		13.6	N.D.	55.4	100	80.29
DDT	NS-100	42.0	2.4	N.D.	39.6	100	94.29
	CA		N.D.	N.D.	42.0	100	100
Dieldrin	NS-100	321.3	14.9	N.D.	306.4	100	95.36
	CA		75.7	0.4	245.2	99.88	76.31

[a] Adsorbed calcd = pesticides present in the original feed less that determined in the retentate and permeate. [b] (Pesticides adsorbed calcd)/(pesticides in original feed) × 100%. [c] N.D. = nondetectable.

Table III. Removal of Organophosphorous Pesticides by Reverse Osmosis

Pesticide	Membrane	Amount of pesticides (μg) in solutions				% removal	% adsorption calcd[a]
		Original feed	Retentate	Permeate	Adsorbed calcd		
Diazinon	NS-100	473.7	273.5	56.6	143.6	98.05	30.31
	CA		334.7	8.3	130.7	98.25	27.59
Methylpara-thion	NS-100	913.1	542.1	4.0	370.6	99.56	40.59
	CA		496.9	4.1	412.1	99.55	45.13
Malathion	NS-100	1057.8	647.0	3.7	407.1	99.65	38.49
	CA		739.9	8.9	309.1	99.16	29.22
Parathion	NS-100	747.3	363.2	1.3	382.8	99.83	51.22
	CA		412.5	0.9	333.9	99.88	44.68

[a] (Pesticides adsorbed calcd)/(pesticides in original feed) × 100%.

Table IV. Removal of Miscellaneous Pesticides by Reverse Osmosis

Pesticide	Membrane	Amount of pesticides (μg) in solutions				% removal	% adsorption calcd[a]
		Original feed	Retentate	Permeate	Adsorbed calcd		
Randox	NS-100	326.8	286.0	4.7	36.1	98.56	11.05
	CA		253.7	91.4	18.3	72.03	5.60
Trifluralin	NS-100	1578.9	530.0	0.1	1048.8	99.99	66.43
	CA		560.1	4.1	1014.7	99.74	64.27
Atrazine	NS-100	1101.7	956.5	24.0	121.2	97.82	11.00
	CA		851.4	176.0	74.3	84.02	6.74
Captan	NS-100	688.9	437.0	N.D.[b]	252.4	100	36.64
	CA		314.7	8.4	440.1	97.78	63.88

[a] (Pesticides adsorbed calcd)/(pesticides in original feed) × 100%. [b] N.D. = nondetectable.

tribution coefficient for extraction) or not enough time to reach equilibrium. Partial recovery of pesticides from the adsorbates, such as soils and clays, is frequently reported (8). However, in some cases, recovery was larger than 100% apparently due to experimental error. In spite of this inability to determine quantitatively the amount of pesticides adsorbed by the membrane material, detection of pesticides in appreciable amounts from the membrane extract strongly supports the notion that the loss of pesticides is mainly due to adsorption onto the membrane material.

Attempt was made to calculate the percentage of pesticides adsorbed by the membrane materials in order to give an insight into the basic mechanism involved in the adsorption and rejection of pesticides by the membranes. It was believed that understanding of these mechanisms would provide a basis for predicting the performance of these membranes tested toward the removal of pesticides other than those tested. In addition, knowledge of the relationship between the chemical nature of the membrane and the individual pesticide will lead to establishing useful criteria for the choice of membrane best suited for the removal of pesticides by reverse osmosis.

Tables II, III, and IV show the percentage of each group of pesticides adsorbed by both CA and NS-100 membranes. The percentage of pesticide adsorbed was calculated based upon a material balance:

$$A = \left[1 - \frac{C_p V_p + C_r V_r}{C_f V_f} \right] \times 100\% \qquad (2)$$

where A represents the percentage of pesticide being adsorbed; C and V represent, respectively, the concentration of pesticides and the volume of the aqueous solution; and subscripts r, p, and f represent the retentate, permeate and feed, respectively.

It is seen from these tables that, with the exception of lindane, the percentage adsorption is the highest for the chlorinated hydrocarbons (Table II). This is followed by trifluralin and captan in the miscellaneous group (Table III), and all of the organophosphorus pesticides tested (Table IV). The poorest adsorption is observed with ran-

dox and atrazine as shown in Table III. The adsorption data reported here are not indicative of the equilibrium data as would normally be required for establishing the empirical Freundlich isotherms. The average contact time of the pesticide solutions with NS-100 was only 40 min and with CA 55 min. In view of this relatively short equilibrium time involved, the adsorption process was by no means in true equilibrium. However, the relative degree of adsorption of various pesticides by the membranes does give an indication of the relative magnitudes of the distribution adsorption coefficient of pesticides between the two phases of membrane materials tested and the aqueous solution. The distribution coefficient is defined by the expression of $(x/m)/C_{eq}$ obtained from the Freundlich isotherms in which x/m represents the weight of material being adsorbed per unit weight of adsorbent and C_{eq} represents the equilibrium concentration of adsorbate in the solution.

The distribution adsorption coefficient is naturally related to the intermolecular interactions of the adsorbate between the solid phase of adsorbent and the liquid phase of aqueous solution. In view of this, the chemical nature of pesticides and membrane materials should be discussed to further explain the degree of adsorption of pesticides by membranes. On the basis of the preferential sorption-capillary flow mechanism (6), solute separation in reverse osmosis is thought to depend upon the chemical nature of solute and membrane. To obtain optimal performance of the membrane, proper balance between the hydrophobic and hydrophilic groups on the backbone of the membrane polymeric structure is essential. For example, the hydrophobic acetyl groups on the cellulose molecular are necessary for reverse osmosis separation of salts. On the other hand, however, the hydrophilic hydroxyl groups are needed for greater passage of solvent water. The widely used cellulose membrane, such as the one employed in this study, contains 2.5 acetyl groups on the average out of the maximum of 3.0 per repeating β-glucoside unit of the polymer. The polar hydroxyl group is responsible for the poor rejection of the highly polar organic compounds (7). Figure 1 shows that the ethylene backbone and the cross-

linked benzene groups are the nonpolar regions, and the urea peptide bond and amines are the polar region of the NS-100 membrane. Chian and Fang (7) have concluded that the NS-100 is more apolar than the CA membrane due to its better rejection of the highly polar organic solutes than the CA membrane.

By the same token, pesticide molecules also comprise polar and nonpolar regions. With the exception of the highly substituted lindane, most of the chlorinated pesticides have nonpolar regions of significant size in proportion to polar regions. They are likely to adsorb onto the hydrophobic region of membrane materials (e.g., acetyl, ethylene, and benzene groups) by means of the van der Waals–London forces. The interaction between the hydrocarbon (nonpolar) regions of pesticides and membranes is amplified further by the tendency of water to form a partial cage of icelike hydrogen-bonded clusters of water molecules around nonpolar regions of both adsorbate and adsorbent (9). This type of interaction derived from the structure changes of water molecules around nonpolar molecules is called hydrophobic bonding, and the interaction force involved is related to entropy generation. In other words, hydrocarbon groups tend to associate with one another and with hydrophobic surfaces in order not to cause additional structuring in the water which involves a decrease in the entropy of the total system, and is thermodynamically rather unfavorable (10, 11).

Table II also shows that the NS-100 membrane has a higher percentage adsorption of the nonpolar chlorinated pesticides than the CA membrane. This indicates that the former membrane is somewhat more nonpolar as compared with CA. It agrees with the conclusion drawn by Chian and Fang (7) that better separation of the polar organic compounds with the NS-100 membrane is attributable to the apolarity of the membrane material relative to CA. Therefore, poor adsorption of lindane, along with somewhat poor separation of this highly chlorinated hydrocarbon with these membranes, suggests that the lindane molecule is relatively polar as compared with the rest of the chloropesticides tested. This is indeed the case. The lindane molecule has a polar region of larger size than the hydrocarbon nonpolar region as shown in Table I. By the same token, poor adsorption of atrazine and randox, along with poor separation of these pesticides by membranes as shown in Table IV, also suggests the polar nature of these pesticides. Hydrogen bonding has actually been indicated for adsorption of s-triazine herbicides to clay surfaces from the study of infrared spectra of adsorbed material (12). The electron-rich π-cloud donor of s-triazine and alkenes and the lone-pair electron donor of secondary amines (Table I) are responsible for the polar nature of atrazine and randox which, in turn, leads to formation of hydrogen bonding.

All of the organophosphorus pesticides tested (Table III), along with trifluralin and captan (Table IV), show intermediate adsorption of pesticides as compared with the nonpolar chloropesticides and the relative polar atrazine, randox, and lindane. The percentage adsorption of organophosphorous pesticides averaged about 40%. This corresponded to the amount of permeate removed from the test cell—i.e., 40% of the feed removed. Therefore, adsorption of organophosphorus appears to result from the direct flow of solution through the microporous structure of the membrane material rather than from adsorption onto the skin layer of the membranes. Strong adsorption of chloropesticides onto the skin layer of the membranes is evidenced by the greater percentage of adsorption—e.g., 75–100%, relative to the amount of solution passing through the membranes (i.e., 40%).

As postulated by Matsuura and Sourirajan (13), one of the most important of the physicochemical criteria governing reverse osmosis separation of organic solute in aqueous solution is the "Polar Effect" of the solute molecule. A measure of the hydrogen bonding ability and the dissociation constants gives relevant expression of polarity of the organic solutes. In general, poor removal of solutes by the CA membrane corresponded to solutes having greater tendency to form hydrogen bonding. Results of this study on solute separation by membranes agree well with the separation mechanism proposed by Matsuura and Sourirajan (13)—i.e., poor removal of pesticides was observed with the relatively polar ones (e.g., atrazine, randox and lindane), which are also adsorbed poorly by the membranes tested. Within this group of somewhat more polar pesticides, the differences in rejection by membranes may be attributable to the size of the molecules which, in turn, governs the rate of diffusion of solutes across the membranes. This explains high rejection of lindane over atrazine and randox (Tables I, II, and IV).

From these findings is provided a general criterion in selecting membrane material for efficient separation of pesticides—i.e., the more apolarity the membrane material is, the better the pesticide removal will be, mainly through the mechanism of adsorption according to this study. Therefore, the relatively nonpolar aromatic polyamide (e.g., Du Pont's B-9 permeator, Wilmington, Del.) and furfural alcohol (NS-200, North Star R&D Inst.) membranes should all be comparable in performance, as compared with the NS-100, according to results of their removal of the model compounds reported by Chian and Fang (7). This, however, would be at the expense of decreasing water flux, an important engineering parameter of the reverse osmosis process, according to Sourirajan's model of preferential sorption of water. Remedies for overcoming the low water flux due to the use of more nonpolar membrane material would be either to employ a reverse osmosis module configuration that would provide a large specific surface area to compensate for the low flux (such as the use of hollow-fiber module) or to control the thickness of the effective skin layer to enhance water flux according to Darcy's law (such as the use of ultrathin membranes).

The effects of pressure, temperature, and concentration of solutes on the performance of the reverse osmosis process have been discussed in great detail by numerous authors (6, 14–17) and will not be the subject of this study. However, attempts have been made to discuss effects of the above operating variables on membrane performance toward aqueous solutions of pesticides.

Pressure Effect

In general, solute separation has usually been observed to increase with feed pressure to either an asymptotic maximum (18) or to approach 100% rejection, as in the case of cellulose acetate (15), although observation of an inverse relationship between separation and pressure with porous glass membranes (14) and polyvinyl alcohol films (17) is not unknown.

The membranes employed in the present study have been tested regarding solute separation vs. applied pressure with a 0.5% sodium chloride aqueous solution. Increase in solute separation with pressure was more pronounced with the partial salt rejection membrane, such as CA. With the high salt rejection membrane, such as NS-100 having a rejection of 99.5% sodium chloride, the effect of pressure on solute separation becomes negligible, probably due to approaching the asymptotic maximum of 100% rejection. In view of the excellent removal of the chloropesticides, organophosphorous pesticides, and trifluralin and captan with both CA and NS-100 membranes,

increase in pressure within a practical range would have little or no effect on improving removal of these pesticides. However, it is anticipated that rejection of the more polar atrazine and randox would increase somewhat with increasing pressure. This will be especially true with the CA membrane due to poorer rejection toward these pesticides. Removal of 72 and 84% of randox and atrazine, respectively, was obtained with the CA membrane, as compared with 98.6 and 97.8% removal of these pesticides with NS-100 membrane.

Temperature Effect

Increase in temperature within an allowable range for the reverse osmosis process normally would result in flux increases in direct proportion to the decrease in solution viscosity according to Darcey's Law for viscous flow in pores. Again, with membranes having poor rejection of solutes, the increase in permeate flux with increasing temperature tends to improve membrane rejection of solutes. Solute transport through the membrane will increase with temperature to a lesser extent when compared to increase in permeate flow. On this basis, rejection of the more polar pesticides, such as atrazine and randox, will increase with temperature, especially with the CA membrane due to its poorer rejection of these pesticides. However, no apparent increase in rejection of the nonpolar and lesser polar pesticides, such as chlorinated hydrocarbons and organophosphorus, would be expected because of their efficient removal of these pesticides in the first place—e.g., an average of better than 99.5% removal. With the strongly adsorbed pesticides, such as most of the chlorinated hydrocarbons, some increase in rejection may be anticipated since the hydrophobic interactions partially responsible for the adsorption of nonpolar pesticides become stronger with increasing temperature (10).

Concentration Effect

Higher feed concentrations generally result in lower flux, since the solvent flow follows the relationship:

$$J_1 = K_1(\Delta P - \Delta \pi) \qquad (3)$$

where J_1 is the flux of solvent; ΔP is the applied driving force; K_1 is the membrane permeability; and $\Delta \pi$ is the osmotic pressure of solutions across the membrane. Since the solubility of pesticides is so low and the molecular weight is so high, the effect of increase in concentration of pesticides on solvent flux is almost negligible because of extremely small changes of osmotic pressure, $\Delta \pi$, involved. However, high feed concentration results in higher flux for solute transport across the membrane due to increased concentration driving force for solute diffusion as given by the following equation

$$J_2 = \frac{K_2}{D_2 M \delta} \Delta C \qquad (4)$$

where J_2 is the diffusional flux of solute across the membrane; K_2 is the distribution coefficient of solutes between the membrane and the solution; $D_2 M$ is the diffusivity of solute in membrane; δ is the thickness of the active skin layer; and ΔC is the concentration driving force.

Therefore, high solute flux, associated with the increase in pesticide concentration, would result in poorer rejection.

Effect of Organic Matter Present in Water

In natural water, persistent pesticides, such as chlorinated hydrocarbons, are normally complexed with humic and fulvic acids (19, 20). These humic substances are ef-

fectively rejected with reverse osmosis membrane mainly because of their high molecular weight (21) on the order of a few thousands to tens of thousands. The removal of pesticides from natural water is thus expected to be even higher than those data shown in Tables II, III, and IV. This is especially important with the poorly rejected polar pesticides, such as atrazine and randox, which tend to form hydrogen bonding and complex with the humic substances.

In view of the strong sorptive characteristics of the membrane materials with most of the pesticides tested, one would expect a leakage of pesticides when the adsorption capacity of membranes is exhausted. The fact that no experimental results show actual exhaustion of the adsorption capacity of membranes is, however, a matter of real concern when long-term tests are conducted. Tardiff and Deinzer (22) have employed reverse osmosis to concentrate river water for organic analysis. With the evidence found in this study regarding strong sorptive characteristics of the persistent chloropesticides onto reverse osmosis membrane materials, effort should be directed toward development of procedures for extracting either pesticides or other trace organics that might adsorb onto the membranes without deleterious effects on membrane.

Conclusions

Excellent performance of CA and NS-100 membranes in removing a wide variety of pesticides, including chlorinated hydrocarbons, organophosphorus, and miscellaneous pesticides, was observed. A considerable amount of pesticides, however, adsorbed onto the membrane materials. The extent of adsorption was shown to be governed by the van der Waals–London forces and hydrophobic bonding between pesticide molecules and the polymeric membrane materials.

Several conclusions can be drawn concerning mechanisms of pesticide removal by the reverse osmosis membranes. Whereas better than 99.5% removal of the nonpolar pesticides, such as chlorinated hydrocarbons and organophosphorus, was observed with both membranes tested, the removal of the more polar pesticides, such as randox and atrazine, was, however, less satisfactory. This is especially true with the more polar CA membrane. The mechanism of pesticide removal from aqueous solution can be explained partially by the polar effect of the solute and partially by the extent of adsorption of the pesticide onto the membrane materials. The former mechanism of pesticide rejection is in accord with the theory advanced by Sourirajan.

The effect of pressure, temperature, concentration of solutes and organic matter commonly found in water—e.g., humic substances—on the performance of the reverse osmosis process has been discussed. It is concluded that the above operating variables has little or no effect on membrane performance with pesticides that are rejected efficiently by the membrane. However, with the membrane rejecting pesticides partially, higher pressure, temperature, and organic content are expected to improve the performance of the membrane on pesticides removal, whereas higher concentrations of pesticides in the feed is expected to have adverse effects.

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Evidence of Atmospheric Transport of Ozone into Urban Areas

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■ In late spring and continuing throughout the summer, concentrations of ozone in excess of 0.08 ppm are commonly found in rural areas of New York State. Widely separated rural sites measure similar ozone concentrations with very slight diurnal fluctuations. During episodes of high rural ozone concentrations, urban areas also experience high ozone peak concentrations, typically in the early afternoon. A transport and mixing hypothesis is made which interprets these urban ozone peak concentrations as primarily the result of the high background level of ozone and not local photochemical generation.

Recently several investigators have measured high concentrations of ozone in rural areas, often in excess of the national ambient air quality standard (0.08 ppm ozone, hourly average not to be exceeded more than once a year). Johnston et al. (*1*) monitored ozone and several other pollutants in rural Garrett County, Maryland, from August 29 to September 25, 1972. The ozone concentration of Garrett County exceeded the air quality standard 11.26% of the time, the average for the period being 0.057 ppm. A previous study by Richter (*2*) found similar high ozone concentrations in the rural Mount Storm area of West Virginia.

During a 1973 investigation, we, too, found high spring and summer levels of ozone (in excess of 0.08 ppm) at a remote rural site operated by the Atmospheric Science Research Center of the State University of New York at Albany (SUNY) in the Adirondack Mountains of New York. Additionally, in this same period, we noted the high ozone concentrations being recorded in the urban areas of New York. As for the rural site, these episodes of ozone concentrations in excess of 0.08 ppm generally first occurred in late spring and continued sporadically throughout the summer. Characteristically, the urban ozone con-

centration peaked in the midafternoon period. Such ozone peaks have generally been interpreted as the result of a local photochemical situation which could be alleviated by a local emission abatement program. The purpose of this paper, however, is to present an alternative mechanism to the local photochemical process as the cause of most urban ozone in the New York State area, a mechanism which could produce high urban ozone levels in excess of the federal standard regardless of local antipollution efforts.

Discussion

In an earlier paper (*3*) we described high ozone concentrations from two rural ozone monitoring sites 160 miles apart (Mt. Utsayantha, elevation 1060 meters, and Whiteface Mountain, elevation 1636 meters) and several urban sites. Figure 1 locates these stations, plus the cities of
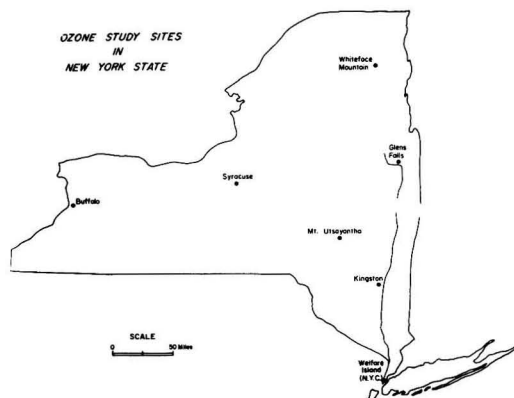
Figure 1. Locations of various sites in New York State
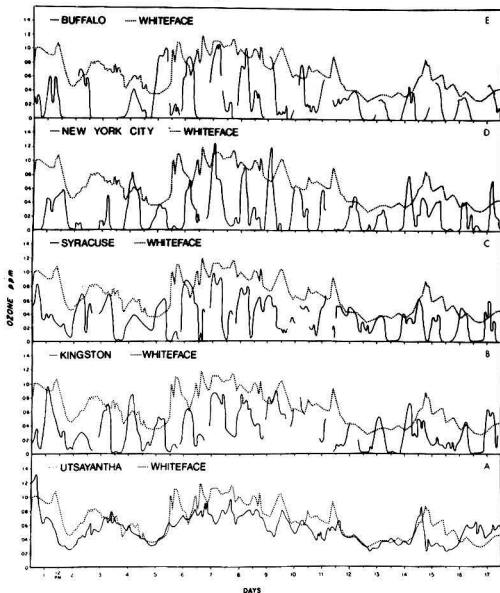
Figure 2. Figure 2A compares the ozone concentration at the two rural sites for the first 17 days of August 1973. Figures 2B–E compare the ozone concentrations at Whiteface with that for the cities of Kingston, Syracuse, New York City, and Buffalo

New York, Syracuse, Buffalo, Kingston, and Glens Falls in New York State. As seen in Figure 2A, the continuously recorded ozone concentrations observed at the rural sites for the first 17 days of August 1973 (the only period when both rural sites were in operation) were quite similar and often exceeded 0.08 ppm of ozone. Chemiluminescent devices were used at all sites. Analysis of the data reveals a very small diurnal fluctuation in ozone concentration peaking shortly after midnight with the maximum average hourly concentration being only 0.01 ppm higher than the minimum average hourly concentration. For this period Ripperton and Worth (4) have also reported high rural ozone concentrations at sites in the Appalachian Mountains. Figures 2B–E illustrate the daily urban maximum ozone concentrations in Kingston, Syracuse, New York, and Buffalo and show a rather strong correlation with the synchronous ozone concentrations recorded at the rural sites as represented by Whiteface.

This correlation, plus some additional data we have acquired, suggests that for those cities studied, local urban photochemical generation of ozone is not the dominant mechanism for ozone production; that, in fact, the high urban ozone concentrations are principally the result of transport and mixing of ozone rich air into the city from the surrounding air mass.

Analysis

Consider the air mass above an urban area and how its characteristics change through the course of a day. This air mass might be expected to exhibit various degrees of turbulence dependent on existing conditions.

That part of the air mass from the ground up, in which relatively vigorous vertical mixing occurs, is characterized by its mixing depth. The maximum mixing depth is usually determined where the dry adiabat drawn through the maximum temperature for the day intersects the sounding

on an adiabatic diagram. In the upstate New York region characterized by Albany, the summer mixing heights average 474 meters in the morning and 1896 meters in the afternoon (EPA Publication No. AP101).

In addition to the mixing process, wind speed increases with height. Momentum is transferred downward toward the surface by eddies of air. The coefficient of eddy viscosity varies with the lapse rate (5). During the day, as the surface temperature increases, the lapse rate and coefficient of eddy viscosity increases so that the high momentum aloft is transported downward by the eddies. The wind at the ground tends to reach its maximum value in the afternoon when the lapse rates are usually the greatest. At night the lapse rate becomes stable, the coefficient of eddy viscosity decreases and there is little exchange of momentum. Thus, surface winds die down.

Therefore, in general, the greatest horizontal movement into and vertical mixing of the air above an urban area will occur in the afternoon when the surface temperature reaches its maximum.

It is well established because of the presence of nitric oxide that urban areas, especially after sunset, are strong sinks for ozone (6). The nighttime destruction coupled with a supposed daytime photochemical generation of ozone yields the classical urban diurnal ozone concentration curve.

On the other hand, if the ozone being measured in urban areas has as its primary source the bulk air mass over the State of New York, the urban ozone will generally reach its peak concentration when the surface winds and temperature reach their maximum, because at this time the urban air mass is undergoing its most rapid interchange with the air above and outside of the city. Of itself, this interpretation is not conclusive since the time of the surface wind and surface temperature maxima is usually in the midafternoon period, a time which coincides with the expected time of the maximum photochemical ozone concentration. However, rural ozone concentrations have similar values across wide areas of the state, and the peak urban concentrations show a correlation to the rural concentrations being measured at the same time, a fact difficult to explain solely through photochemical generation. A transfer and mixing mechanism would suitably explain these correlations.

Results

During the period of this study, the afternoon mixing depth was generally close to 2000 meters. The highest
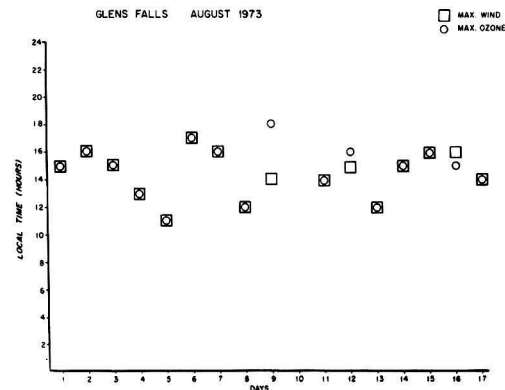
Figure 3. Local time of occurrence for Glens Falls of the daily hourly average wind and ozone maxima for the first 17 days of August 1973
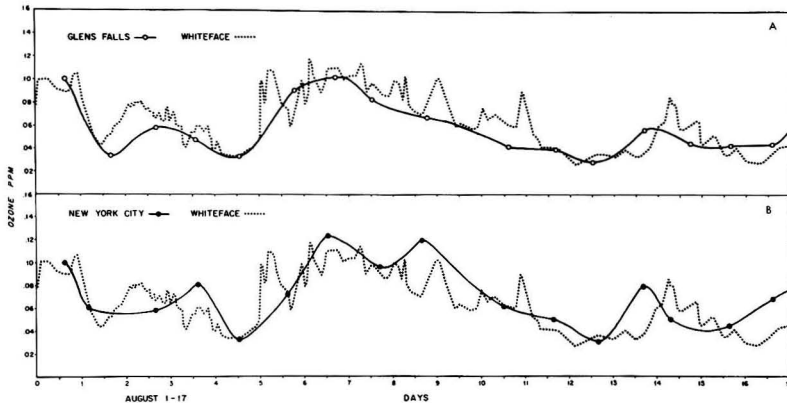
Figure 4. Close correlations between the Whiteface ozone concentrations for the first 17 days of August 1973 and the smooth curve drawn between the Glens Falls and the New York City daily ozone maximums

ozone concentrations were recorded when the winds were light and from the southwest. Cold fronts moved across the area on the 2nd and 12th of August with accompanying wind shifts to the northwest and decreasing ozone concentrations.

To investigate the transport and mixing hypothesis, ozone and wind data were obtained from a monitoring site in downtown Glens Falls, N.Y. This city is in the Hudson Valley, approximately 80 miles south of Whiteface Mountain and has an elevation of 110 meters above sea level. Figure 3 shows the time of occurrence of the daily wind and ozone maxima for the period. A linear regression analysis of these times of occurrences yielded a correlation coefficient of 0.87. Unfortunately, temperature data were not available from this site. Assuming, as we stated earlier, that these ozone maxima would most closely correspond to the rural ozone levels, a smooth curve for the sake of representation was drawn connecting these daily maximum readings. This curve was then compared directly to the continuous Whiteface ozone data covering the same time period. Figure 4A shows the rather close correlation between both curves. Not only are the concentration trends similar, but the actual concentration values are almost identical for the two sites.

Figure 5 indicates the correlation between wind temper-

ature and ozone maximum at Kingston, N.Y., for the period. The correlation coefficients were 0.83 for wind and temperature, 0.81 for wind and ozone, and 0.87 for ozone and temperature. Similar data were taken from a monitoring site on Welfare Island in New York City. Figure 6 shows the time of occurrence of the daily wind, temperature, and ozone maxima for the period. The correlation coefficients calculated from the hourly maximum averages were 0.79 for wind and temperature maxima, 0.76 for ozone and temperature maxima, and 0.59 for ozone and wind maxima.

Connecting the daily maximum hourly ozone values for Welfare Island by a smooth curve yields a curve which exhibits a remarkable similarity to the continuous Whiteface ozone data covering the same time period as seen in Figure 4B. It should be noted that Welfare Island is 250 miles from Whiteface Mountain.

When a weather front passes through an area, the maximum advection of air might be expected to occur with the passage of such a front. As an example of nighttime advection due to a weak front, consider the sharp ozone maximum (0.84 ppm) recorded in Syracuse, N.Y., at 4 a.m. on August 1, 1973. At this same hour the maximum daily wind was also recorded (3.6 meters/sec). As seen in Figure 2A, the rural ozone concentration was close to 0.10

Figure 5. Local time of occurrence for Kingston of the daily hourly average wind, ozone, and temperature maxima for the first 17 days of August 1973
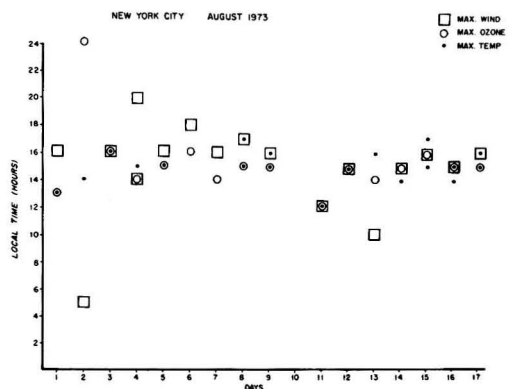
Figure 6. Local time of occurrence for Welfare Island in New York City of the daily hourly average wind, ozone, and temperature maxima for the first 17 days of August 1973

ppm at Whiteface Mountain and 0.12 ppm at Mt. Utsay-antha and falling. This same effect is also seen in New York City on the morning of the 2nd of August. The highest average hourly ozone concentration was recorded at 1 a.m. on August 2, 1973 (0.056 ppm). The wind maximum was recorded at 4 a.m. on August 2nd at 6.7 meters/sec as opposed to 4 meters/sec at 1 a.m. However, as seen from the Whiteface data, the background level was falling rapidly after the frontal passage.

Summary

In general, it is safe to say that a correlation between data from several sites does not necessarily imply a common source. For example, if uv radiation is causing generation of photochemical ozone in one area, the same conditions may exist elsewhere; hence, the trends at the several sites would be similar, but not indicative of a transport phenomena. However, since our rural data at elevated sites have only a slight diurnal fluctuation (and opposite to the urban diurnal fluctuation), it appears that no significant ozone production is occurring at these sites. Furthermore, the actual synchronous ozone concentrations at widely separated sites are almost identical, especially for the Glens Falls maxima and Whiteface continuous data. Therefore, we believe the correlations do imply a common ozone source. We do not intend to suggest that local photochemical production of ozone does not contribute to the total urban ozone burden. The data from New York City show some exceptionally high afternoon ozone concentrations which might be the result of significant contributions from both background ozone and locally produced ozone. How-ever, what the data do indicate is that ozone concentrations in excess of the 0.08 ppm federal maximum hourly standard do exist in rural areas and can be transported into urban areas through advection and vertical mixing.

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Glc Analysis of 2,4-D Concentrations in Air Samples from Central Saskatchewan in 1972

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■ Levels of 2,4-D [(2,4-dichlorophenoxy)acetic acid] in the atmosphere of central Saskatchewan were estimated as butyl and octyl esters using a two-column gas liquid chromatography technique, and then further characterized by chemical derivatization. Glc mass spectrometry confirmed the presence of 2,4-D. Mean total daily levels of 2,4-D (as *n*-butyl ester) found for Saskatoon for 33 days were 600 ng/m^3 of air, and for Naicam for 47 days, 142 ng/m^3 of air. Very little 2,4-D was detected at Rosetown.

Recent work (1) suggests that vapor and droplet drift of the butyl esters of 2,4-D may be as high as 30% after boom spraying in the field. The presence of 2,4-D in the atmosphere has been detected using bioassay techniques (2–5). However, few of these methods are quantitative and are subject to interference by many compounds. For these reasons, it is necessary to measure herbicide levels in the atmosphere directly by physical means. Very little work (6) has been published on the estimation of 2,4-D levels in the atmosphere during the spraying season using direct means. Saskatchewan provides a unique opportunity for the quantitation of 2,4-D derivatives in this way since large quantities (up to 2000 tons) of this herbicide are sprayed in spring and early summer.

Experimental

Air Sampling Procedures. Commercial activated silica gel (60/70 mesh) was treated by Soxhlet extraction for two days using boiling methanol. The gel was then dried in an oven at 200°C for two days. Five grams of the gel was then packed into polyethylene air samplers similar to samplers described previously (1) and shielded from moisture. Sampling stations were established in Saskatoon and at weather stations on farms in the Rosetown and Naicam districts (Figure 1). The samplers were placed on the vertical inlet of a vacuum line, 7 ft above ground level. The samplers were encased in a cage of mesh and the air flow was maintained at 10 l./min. The samplers were changed daily, wrapped to exclude moisture, and stored in a refrigerator until analysis. Weather information was recorded daily, but comprehensive data were available only for Saskatoon.

Analytical Procedures. The silica gel was removed, mixed well, and divided into two equal portions. All solvents used in the following procedures were doubly distilled reagent grade chemicals. All glassware was prewashed in chromic acid, distilled water, and acetone in that order.

Analysis for Butyl and Octyl Esters. One half of the sample was placed on fluted Whatman filter paper (No.
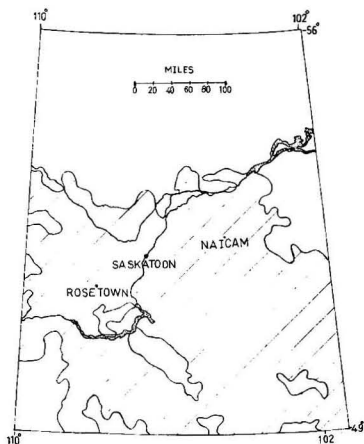
Figure 1. Location of atmospheric monitoring stations in relation to cropland (shaded areas) in Saskatchewan

40) contained in a Pyrex filter funnel. Methanol (20 ml) was then poured through the gel which was then allowed to drain dry. The efficiency of desorption was (66 ± 8)% for the gel loading range of 20–80 ng of radioactive ^{14}C-labeled n-butyl ester vaporized by heat, then desorbed. The efficiency increased to (75 ± 3)% when the loading range was 1–100 μg.

The methanol was then concentrated to about 5 ml, a saturated brine solution (10 ml) was added, and the solution was shaken with hexane (10 ml). The hexane extract was concentrated prior to electron capture gas liquid chromatographic (glc) analysis. The efficiency of this one-step extraction process was (50 ± 5)% in the concentration range 20–80 ng of radioactive ^{14}C-labeled n-butyl ester in the original methanolic solution, and (97 ± 2)% in the concentration range 1–100 μg, using glc–electron capture for quantitation.

The samples were analyzed using two glc columns. The first, Column A, was a 5% ethyl acetate extract of Dow Corning high-vacuum grease impregnated on 80–100 mesh Chromosorb W(AW-DMCS) contained in a 6-ft, $^3/_{16}$-in. i.d. Pyrex U-tube column. The effluent from Column A was monitored by a ^{63}Ni detector, with 19:1 argon-methane as carrier at a flow rate of (40 ± 2) ml/min. The temperatures of the column, injector, and detector were 192, 232, and 222°C, respectively. The detector was operated at a pulse interval of 15; maximum sensitivity, about 20 pg.

Column B was 2% SE-30 impregnated 50–100 mesh Chromosorb W (AW-DMCS), contained in a 6-ft, $^1/_8$-i.d. diameter Pyrex spiral column. The detector used with Column B was tritium foil. The carrier gas was nitrogen at a flow rate of 20 ml/min. The temperatures of the column, injector, and detector were 192, 232, and 222°C, respectively. The maximum sensitivity was about 40 pg.

Pure iso- and n-butyl, and iso-octyl and n-octyl esters were used as external standards. Coinjection also was used to confirm retention times. Peak areas were evaluated using a planimeter. The error in the measurement of peak areas was about 7%.

Analysis for Total 2,4-D by Conversion to n-Butyl Ester. The unextracted half of the silica gel sample was placed on a Buchner filter and washed with boiling methanol (7 × 15 ml) under suction. The solution was concentrated to about 1 ml on a rotary evaporator. The efficiency of desorption was (96 ± 1.2)%, by using radioactive ^{14}C-labeled n-butyl ester vaporized by heat, and then desorbed from the gel in the loading range of 20–80 ng of ester.

Sodium hydroxide solution (10 ml, 2M) was added to the residue, and the mixture was refluxed for 15 min. The basic solution was extracted once with benzene (10 ml) to remove any nonacidic or nonphenolic matter. It was then acidified with concentrated hydrochloric acid (pH2, Universal Indicator Paper), and extracted with benzene (3 × 10 ml) to extract all free 2,4-D.

The combined extracts were concentrated to about 1 ml on a rotary evaporator. The residue was butylated by refluxing with BF$_3$/n-butanol solution (2 ml of 36% BF$_3$ in n-butanol, plus 10–12 ml of n-butanol) for 15 min.

After the solution was refluxed, water (10 ml) and benzene (10 ml) were added, and the resulting layers separated. The aqueous layer was extracted with benzene (3 × 10 ml). The combined organic extract was concentrated to a volume of 1–2 ml. The efficiency of the entire hydrolysis, extraction, and butylation procedure was (91 ± 1.2)% as indicated by use of radioactive n-butyl ester, and by glc techniques (20 replicates) in the range of 20 ng to 100 μg of starting ester.

One microliter of concentrate was injected into Column C (Pyrex U-tube, 6 ft long and $^3/_{16}$ in. i.d., packed with 10% SE-30 impregnated on Chromosorb W (AW-DMCS). The temperatures of the column, injector, and detector were 190, 222, and 232°C, respectively. The flow rate of 19:1 argon-methane carrier gas was (45 ± 5) ml per min. The ^{63}Ni electron capture detector was operated at a pulse interval of 15. The maximum sensitivity was about 0.1 pg.

The retention times were compared with those shown by external standards of n-butyl ester, and by coinjection. The esters were also quantified by the external standard method, and, taking into account the known initial volume of concentrate, the total ester thus was calculated for each sample. The error in the ester levels was calculated to be about 8–12%. The presence of the ester was further confirmed by mass spectroscopy. Some samples had to be amalgamated and concentrated.

Control blanks were also run. Laboratory air containing no 2,4-D was sucked through silica gel samplers for a day. The silica gel from each sampler was halved and treated by the two analytical procedures given above. A negligible background was observed at the retention time of the butyl- and octyl-ester peaks.

Each glc attenuation setting used was individually calibrated for both analytical procedures.

Results and Discussion

Criteria for Presence of Esters. In the analysis of butyl and octyl esters using the two-column technique, the following two criteria had to be met before the presence of 2,4-D esters was deemed likely.

The retention time of the suspected peak had to be within ±0.25 min of the retention time of the standards run under the same conditions. This range was chosen on the basis of the possible 5–10% error in flow rate of carrier gas through the column and on the temperature stability of the column oven.

Both glc columns had to show a peak, fulfilling the first condition.

A third condition should be that the concentrations estimated on both columns be approximately the same. Perusal of Tables I–III and Figures 2–4 show that the levels obtained on Column A are generally lower than those on Column B from the same samples. These levels have been corrected for efficiency of desorption (75%) and extraction (97%). The question of which column will give the most realistic levels must be considered. The retention time for the isobutyl ester on Column A was approximately 5.2 min, whereas the retention time on Column B was 1.5

Table I. Ester Levels[a] for Saskatoon
In ng per m³ per day

Date	Column A	Column B	Column C (butylation)	Date	Column A	Column B	Column C (butylation)
May 27				June 21			391 ± 53
28				22	N[b]	147	300 ± 33
29			2,850 ± 290	23			377 ± 89
30				24			199 ± 21
31				25			196 ± 20
June 1	20	43	488 ± 46	26			260 ± 30
	63[c]	52[c]		27			193 ± 20
2			1,730 ± 150	28			438 ± 44
3	N[b]	42	1,650 ± 175	29			—
4	105	31	21,400 ± 3,500	30			—
5	40	311	31,800 ± 9,500	July 1			—
6			455,000 ± 42,000	2			—
7			208,000 ± 24,000	3			—
8			355,000 ± 39,300	4			—
9	322	105	32,900 ± 3,600	5	53	84	—
10			2,900 ± 425	6			—
11			2,890 ± 321	7			—
12			1,560 ± 170	8			—
13	97	168	1,120 ± 265	9			—
14	56	217	764 ± 197	10			—
15	38	242	332 ± 66	11			—
16	38	223	347 ± 69	12			—
17	N[b]	147	202 ± 21	13	N[b]	24	—
18			363 ± 21	14			—
19			208 ± 13	15			—
20			—				

[a] i-Butyl ester levels unless specified otherwise. [b] N = negligibly small amount. [c] Iso-octyl ester levels.

Table II. Ester[a] Levels for Rosetown
In ng per m³ per day

Date	Column A	Column B	Column C (butylation)
May 27	N[b]	40	
28			80 ± 7
30	44	53	
	15[c]	39[c]	
31	43	22	
June 7	36[d]	63[d]	
21	65	42	
22	110	136	
July 1	56[d]	51[d]	
10	100	331	

[a] i-Butyl ester levels unless specified otherwise. [b] N = negligibly small amount. [c] i-Octyl ester levels. [d] n-Octyl ester levels.

min. Since many peaks are observed on each chromatogram and more are observed on Column A than on Column B, there is a greater possibility that overlapping peaks may increase the peak size of an apparent isobutyl ester peak on Column B. In spite of these limitations, approximately half of the ester levels obtained on the two columns agreed very well.

As is well known, glc retention times do not positively identify specific compounds. Even a multicolumn approach does not conclusively *prove* the identity of a suspected compound, although the probabilities for correct identification are greatly increased. Thus, spectroscopic techniques or chemical derivitization have to be used to confirm the presence of suspected compounds. Use of the former is limited because of sensitivity problems, and this was borne out in the present study by the fact that no

Table III. Ester Levels[a] for Naicam
In ng per m³ per day

Date	Column A	Column B	Column C (butylation)	Date	Column A	Column B	Column C (butylation)
May 29	19	28	—	June 21	22	121	103 ± 13
30	18	21	99 ± 10	22	18	90	83 ± 10
31	15	44	—	23	18	90	117 ± 9
June 1			235 ± 26	24			454 ± 45
2	25	29	688 ± 70	25	25	153	128 ± 25
3	58	57	197 ± 20	26	22	90	284 ± 30
4			209 ± 18	27	21	197	340 ± 30
5			—	28			212 ± 25
6			—	29	26	133	291 ± 25
7			201 ± 15	30			129 ± 10
8			—	July 1			280 ± 25
9			207 ± 22	2	42	386	232 ± 20
10			126 ± 15	3			232 ± 22
11			81 ± 7	4	39	369	108 ± 9
12			—	5	35	487	—
13			124 ± 10	6			—
14			100 ± 12	7	45	294	—
15			126 ± 14	8	26	240	—
16			124 ± 13	9	75	78	—
17	45	170	134 ± 15	10	47	238	163 ± 15
18			116 ± 10	11	37	60	378 ± 40
19			164 ± 18	12	50	36	105 ± 12
20	17	N[b]	89 ± 9	13	39	96	83 ± 9

[a] i-Butyl ester levels. [b] N = negligibly small amount.

samples in the analysis for the individual esters were concentrated enough to give mass spectral confirmation. However, chemical derivitization via the butylation procedure reported here not only is a cleanup step limiting the final analysis to esters of acids and to individual phenols, but it also retains the advantages of the specificity and sensitivity of the electron capture (EC) detector. Thus, any 2,4-D compound will be converted to free acid, and detected as the *n*-butyl ester.

It follows that samples suspected of containing butyl or octyl esters should also produce positive results by the butylation technique. A negative result for the butylation procedure was taken to mean no confirmation of 2,4-D, even if the two-column technique produced positive results. When the butylation method indicated the presence of 2,4-D but the two-column technique did not, spectroscopic confirmation was again attempted. Only three samples, Saskatoon June 6–8 were confirmed by mass spectroscopy, the 70-eV mass spectra being superimposable on *n*-butyl ester standard. In addition, at 7 eV, only the two peaks associated with two chlorine atoms at m/e 276 and 278 were observed, implying the butyl ester only was present. The butylation results could have been further confirmed by a further transesterification step, but this was impossible for 1972. This procedure should be adopted in any future monitoring program.

Samples containing 2,4-D as indicated by both techniques were amalgamated (except for Saskatoon June 6–8 in the butylation technique) and confirmed quantitatively by glc mass spectroscopy. High eV mass spectra were obtained but not low eV spectra, so that the "purity" of each glc peak could not be ascertained.

General Analysis of Results. Tables I–III and Figures 2 to 4 show that the total 2,4-D levels are generally higher than those of the individual esters. Other esters, free acid, or amine salt forms of 2,4-D may also be present. These would not be quantitated by the two-column technique.

The levels quoted here may be only a fraction of the total amount of 2,4-D originally volatilized into the air, or in aerosol form, as some 2,4-D may be degraded by sunlight, air, heat, or water and because only a small portion of the atmosphere was sampled. It is imperative to try to obtain a mass balance relating all 2,4-D sprayed to the residual 2,4-D left in the environment, and including all products which had 2,4-D as their precursor. Work is still in progress to detect any possible degradation products of 2,4-D in the atmosphere.

Of the 480 samples analyzed, 45 showed the likely presence of butyl or octyl esters, and 28 of these (63%) were confirmed by the butylation technique. This shows that confirmation of glc multicolumn results is definitely necessary.

2,4-D was detected in 65 samples by the butylation procedure. Of these, 28 (43%) contained butyl or octyl ester. Thus, a substantial portion of individual 2,4-D compounds is unaccounted for by the two-column glc technique.

It must be emphasized that the levels quoted in this paper are only those collected at the air flow rate of 10 l./ min through the sampler, and that both vapor and aerosol forms of 2,4-D will be sampled. Thus, extrapolation to total levels in the atmosphere was not attempted as it cannot be assumed that the collected sample was representative of the whole atmosphere. The concentration profile of the herbicide with respect to height has to be known.

However, it is instructive to calculate the total amount of 2,4-D as the *n*-butyl ester in the vapor phase which could be collected by our sampling system at the flow rate quoted above.

The saturated vapor pressure of the *n*-butyl ester of
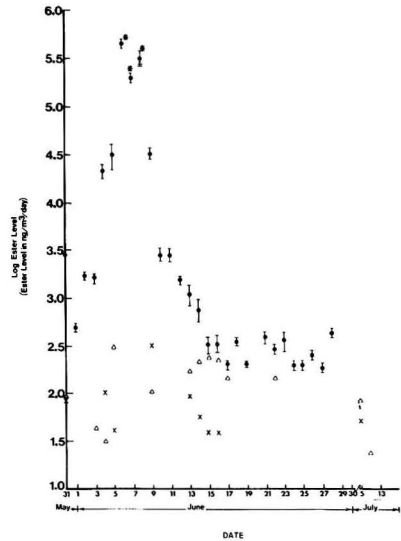
Figure 2. 2,4-D levels at Saskatoon (*confirmed by mass spectroscopy)

✕ Column A   △ Column B   ● Column C
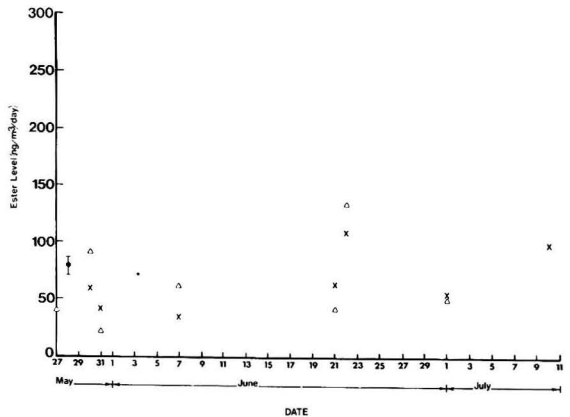
Figure 3. 2,4-D levels at Rosetown

✕ Column A   △ Column B   ● Column C
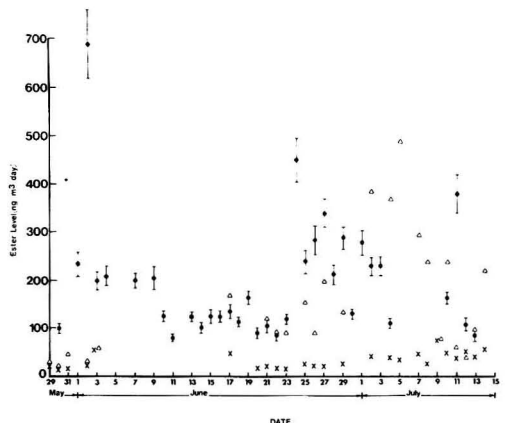
Figure 4. 2,4-D levels at Naicam

✕ Column A   △ Column B   ● Column C

2,4-D at 27°C is about 4×10^{-3} mm Hg (7). If the Ideal Gas Law holds,

$$pV = \frac{mRT}{M} \qquad (1)$$

where

p = the saturated vapor pressure in atmospheres
V = the volume in liters
m = the mass of gas in grams
M = the molecular weight in grams
R = the gas constant in liters atmos^{-1} mol^{-1}
T = the absolute temperature

then

$$\frac{m}{V} = \rho_v = \text{vapor density} \qquad (2)$$

$$= \frac{pM}{RT}$$

$$= \frac{4 \times 10^{-3}}{760} \cdot \frac{277}{0.082 \times 300}$$

$$= 5.93 \times 10^{-5} \text{ g/l.}$$

that is, one liter of air saturated with n-butyl ester contains 5.93×10^{-5} grams.

As the air flow through the sampler is 10 l./min, 5.93×10^{-4} grams are collected every minute.

As there are $(60 \times 24) = 1440$ min in a day, then in one day it is possible that a maximum mass of 853 mg can be accumulated from the vapor component. It would be highly unlikely that the wind would remain saturated all day unless extensive areas were sprayed. However, if more than this amount is collected assuming collector flow rates and temperatures are fairly constant, then aerosol collection must also be important.

Let us consider the results at each station.

Saskatoon. Of the 13 samples containing butyl or octyl esters (Table I, Figure 2), 11 were confirmed by butylation (about 90%). In addition, when these 13 samples were concentrated, glc mass spectroscopy confirmed the presence of the butyl esters. However, the octyl esters could not be confirmed because of inadequate sensitivity.

Of the 29 samples containing 2,4-D as found by butylation, 40% contained butyl or octyl esters.

The most interesting features of the Saskatoon results are the huge levels (a mean of 175 μg per m^3 per day) of total 2,4-D as the n-butyl ester found between June 3 to June 10, and the low levels of butyl and octyl esters in the same time period. The maximum levels occurred on June 6 to June 8, for which no butyl esters were detected. The observed levels of about 3 mg/day are well below the theoretical maximum as calculated above at 27°C for n-butyl ester in the vapor phase. Shorter chain esters than butyl

could easily account for the high values, as these have higher vapor pressures. Further possible explanations could involve localized spraying, or domestic spraying in urban gardens and streets. Apart from this period of time, levels observed for the butyl or octyl esters correlated fairly well with those confirmed by butylation. The mean daily total 2,4-D level to June 28, in terms of butyl ester, except from June 4 to June 9, inclusive, was about 600 ng/m^3. Little octyl or butyl ester was used in the period July 18 to July 28.

Rosetown. Of the eight samples containing octyl or butyl esters (Table II, Figure 3), none were confirmed by the butylation procedure. This illustrates again that very little credence can be given to data "confirmed" on the basis of glc retention times alone for one or two glc columns. Only one sample (about 80 ng per m^3 per day) yielded 2,4-D on butylation (May 28). This sample did not contain butyl or octyl esters.

Naicam. Of the 24 samples containing butyl or octyl esters (Table III, Figure 4), 17 (70%) were confirmed by butylation. Generally, the butyl and octyl ester levels were slightly lower than those found by butylation. The 24 samples on concentration and subsequent glc mass spectroscopy showed the presence of butyl esters.

Of the 35 samples containing 2,4-D as found by butylation, only 50% contained butyl or octyl esters. An interesting feature is that from June 7 to 16, no octyl or butyl esters were detected. The mean daily total 2,4-D level during the period of analysis up to July 14 was about 142 ng/m^3. This level is substantially lower than that found at the Saskatoon station, and together with the low levels at Rosetown, implies that spraying in urban areas sometimes causes more pollution than spraying in rural areas.

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Comparison of Instrumental Methods to Measure Nitrogen Dioxide

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■ A comparison study was performed between the newly developed chemiluminescent $NO-NO_2$ monitor and existing automated NO_2 monitors based on coulometry and colorimetry and the 24-hr manual reference method for the measurement of NO_2. Correlations were obtained among the various techniques by sampling ambient air in a nonurban atmosphere. In addition, a detailed study of maintenance requirements, calibration stability, and typical response patterns of the instrumental methods was obtained. The chemiluminescent monitors successfully measured ambient concentrations of NO_2 under conditions of this study. The coulometric monitor gave lower mean values and the Federal Reference method gave higher mean values than the other measurement methods at this nonurban site. Performance tests show that the chemiluminescent monitors have a faster response time than the coulometric or colorimetric methods and that each method has the sensitivity to measure NO_2 concentrations of 0.01 ppm. Analysis of the calibration data for each instrumental method showed little variation.

Over the past several years a number of new automatic instruments have been developed which are capable of measuring ambient concentrations of nitrogen dioxide (NO_2) and nitric oxide (NO). The most notable is the chemiluminescent monitor for the measurement of NO. When coupled with a NO_2 converter, the same instrument can be used to measure $NO_2 + NO_x$. Fontijn et al. (*1*) described the detector based on the chemiluminescent reaction of NO with ozone (O_3) at pressures of 1–3 torr. Martin et al. (*2*) described the application of the same reaction at or near atmospheric pressure. Sigsby (*3*) first described the use of NO_2 converters for application with the chemiluminescent monitor. Since then, considerable effort has taken place within the Environmental Protection Agency on development and application of NO_2 converters. A number of successful designs have been developed. Most converters use either low-temperature (225°C) surface reactions to convert the NO_2 to NO or high-temperature (600°C) thermal decomposition of NO_2 to NO. Using the procedures described above, a number of instrument manufacturers have constructed prototype and commercial chemiluminescent monitors for the analysis of NO, NO_2, and NO_x.

Existing methods for the measurement of nitrogen dioxide include automated wet chemical analyzers based on coulometry, colorimetry, and the 24-hr manual method, which is the current reference method specified for determining compliance with National Primary and Secondary Ambient Air Quality Standards for NO_2 (*4*). A need exists for the comparison of the newly developed chemiluminescent monitors and associated converter techniques with other available continuous monitors, and with the published manual reference method cited above. This paper describes a three-month study in which chemiluminescent monitors were compared with the colorimetric and coulometric monitors and with the 24-hr manual method. Correlations have been obtained among various techniques on ambient air data from the Research Triangle Park area of North Carolina. In addition, a detailed study of maintenance requirements, calibration stability, and typical response patterns of the instrumental methods was made.

Experimental

The site of the study was the National Environmental Research Center in the Research Triangle Park, N.C. The area is nonurban in nature and typical ambient NO_2 concentrations are near 37 $\mu g/m^3$ (0.02 ppm). The monitors and associated hardware were placed in a laboratory. All instruments and the manual sampler obtained their samples from the same manifold. Sample air was drawn through the laboratory manifold from the roof by a blower at a rate of 20 l./min.

The Beckman 910 was selected as a representative model of a coulometric analyzer and the Technicon IVA was selected as an example of a colorimetric monitor. Two chemiluminescent monitors were used in the study. The Thermo Electron 12A Monitor which operates at a pressure of 3 torr, and the Bendix Monitor 8101B which operates at a pressure of 300 torr. A modification was made on the Thermo Electron so an external converter of our own design could be utilized. This converter reduces NO_2 to NO. A manual 24-hr bubbler box sampler (*5*) was run in conjunction with the continuous monitors.

Two dynamic calibration systems were used for the instrumental methods. The first system used a permeation tube housed in a constant temperature bath to generate known concentrations of NO_2. The tube was weighed on a weekly basis during the study to determine if the weight loss was constant. The second system used in the study was a gas phase titration system as described by Rehme et al. (*6*). Excess concentrations of NO were mixed with known concentrations of ozone from a calibrated ozone generator to produce corresponding known concentrations of NO_2. Calibrations performed by both systems on the chemiluminescent monitors showed an agreement within 5%. Two independent NO_2 generation systems were used because of possible interference of excess NO in the gas phase system with the Beckman and the Technicon monitor.

Continuous sampling was begun after the initial calibration of the instruments. Data was taken from each instrument at 5-min intervals by a data acquisition system. Strip chart recorders were also used to provide a permanent trace of instrument output. The instruments were checked dynamically by a span and zero input every week, and a complete calibration curve of 4 points plus a zero point was determined every two weeks.

Results and Discussion

Response Characteristics. Response characteristics were determined for each instrument prior to the sam-

Table I

Analyzer	Lower dtectable limit, ppm	Range, ppm	Lag time, min	Rise time, t_{95}, min
Bendix 8101-B (NO_2, NO_x)	0.010	0–0.50	0.30	0.80
Thermo electron 12A (NO, NO_2, NO_x)	0.005	0–0.25	0.25	0.50
Beckman 910 (NO_2)	0.010	0–0.50	3.0	15
Technicon IV-A (NO_2)	0.010	0–0.25	4.5	8.2

Table II. Regression Analysis of Calibration Data

Instrument	Equation, $y = mx + b$	Confidence interval of mean
Bendix	$y = 184 (X) + 0.204$	±10.1
Technicon	$y = 387.9 (x) + 0.41$	±4.3
Thermo Electron	$y = 377.5 (X) - 0.40$	±7.4
Beckman	$y = 204.3 (x) + 0.137$	±5.2

pling phase of the study. Lower detectable limit, range, lag time, and rise time are given in Table I. The lower detectable limit for three of the monitors was 19 $\mu g/m^3$ (0.01 ppm) NO_2. The Thermo Electron was slightly more sensitive than the other monitors with a detectable sensitivity of 9 $\mu g/m^3$ (0.005 ppm) of NO_2. Chemiluminescent monitors such as the Thermo Electron operating at 1–3 torr pressure have more sensitivity than conventional monitors or other chemiluminescent monitors that operate at higher pressures.

Two of the monitors were operated on a full-scale range of 0–0.50 ppm full scale and two of the monitors were operated on a full-scale range of 0–0.25 ppm full scale. Other ranges are available on each instrument and the range selected reflected the most effective operating range for the study.

Response time (lag time plus rise time) for the two chemiluminescent monitors was much less than for the coulometric or the colorimetric monitors. Total response time for the chemiluminescent monitors was less than one minute. The Beckman coulometric monitor had the longest response time with a rise time of 15 min and a lag time of 3 min. The Technicon IVA colorimetric monitor had a total response time of 12 min.

Calibration Stability. The calibration data for each instrument were fit by least squares to the line,

$$y = mx + b$$
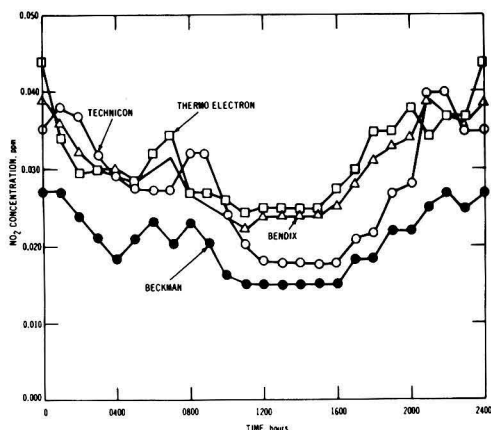
Figure 1. Average hourly concentrations, NO_2, April 25 to May 25, 1972
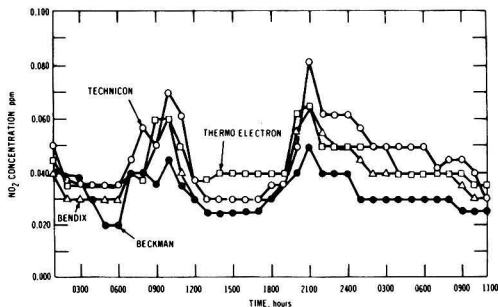
Figure 2. Typical response data for NO_2 monitors, April 25 and 26, 1972

where y is the instrument response in % of chart, m is the slope, x is the gas concentration in ppm, and b is the y-intercept. Table II summarizes the calibration data obtained for each instrument for weekly calibrations over the 3-month period. The y-intercept for each instrument is within 1% of full scale of the origin. The 95% (2σ) confidence interval on the mean is shown for each instrument. The Technicon showed less deviation from the least square line than the other instruments. From the values shown in the table, the variation in the calibration of all instruments is small.

Comparison of Measurements. From the data gathered during the study, a diurnal plot was constructed and correlation coefficients and mean values were obtained. Correlation coefficients and absolute mean ratios were also determined between the instruments and the reference method. Data for each instrument between April 25 and May 25, 1972, was averaged on an hourly basis. Figure 1 contains the hourly averages plotted to show the diurnal variations for the entire sampling period. The response of the two chemiluminescent monitors was similar during peak NO_2 periods which occurred twice a day and at hours when the NO_2 concentration was less than 0.025 ppm. The response of the Technicon IVA followed the two chemiluminescent monitors during peak NO_2 periods but fell to lower values during minimum concentrations. The Beckman coulometric monitor gave consistently lower values during the entire sampling period.

Figure 2 shows a typical daily response pattern (time vs. concentration) of the instruments and gives corresponding peak concentrations of NO_2. Peak concentrations of NO_2 in this nonurban area can be related to traffic patterns occurring in the morning and late afternoon.

Table III gives the correlation coefficients determined for each pair of instruments. The number of pairs represents the number of available simultaneous hourly aver-

Table III. Comparison of Methods

Analyzer	Correlation Coeff	Mean value, ppm	Pairs of numbers
Thermo Electron vs. Technicon	0.72	0.035 0.032	576
Thermo Electron vs. Bendix	0.75	0.035 0.033	1009
Thermo Electron vs. Beckman	0.71	0.035 0.028	456
Bendix vs. Beckman	0.62	0.028 0.025	408
Bendix vs. Technicon	0.80	0.030 0.028	756
Technicon vs. Beckman	0.79	0.028 0.021	696

Table IV. Comparison of Methods

Analyzer	Correlation coeff	Mean value, ppm	Pairs of numbers
Thermo Electron vs. Federal Reference Method	0.72	0.036	14
		0.044	
Bendix vs. Federal Reference Method	0.76	0.030	14
		0.047	
Beckman vs. Federal Reference Method	0.54	0.026	12
		0.040	
Technicon vs. Federal Reference Method	0.40	0.028	12
		0.040	
Federal Reference Method vs. Federal Reference Method	0.86	0.044	18
		0.042	

Table V. Instrument Failures and Maintenance Requirements

Instrument	Instrument failures for 3-month period		Maintenance required, hr/week for 3-month period	% of time in operational mode, 3-month period
	Electronic	Mechanical		
Beckman	2	3	0.5	94
Bendix	1	1	0.5	94
Technicon	2	2	1.5	93
Thermo Electron	0	2	0.5	96

ages from which the coefficients were determined. The absolute values given were determined only over these hours. The correlation coefficients for each pair of instruments ranged from 0.62–0.80. The correlation values were lower than expected among the four monitors. The low correlations obtained among the analyzers may be related to the low ambient NO_2 concentrations which would have increased errors in readability and measurability of some of the analyzers. In terms of mean values, the four monitors agreed closely. The two chemiluminescent monitors agreed within 4% for a thousand pairs of numbers. The Beckman NO_2 monitor gave lower absolute values than the other monitors. Stevens et al. (7) observed the same trend from a field evaluation study in St. Louis.

The comparison of data obtained from the continuous monitors and the reference method is shown in Table IV. The correlation coefficients varied considerably. The correlation with the reference method is higher with the two chemiluminescent monitors than with the Technicon and the Beckman monitors. The absolute values for the manual method were consistently higher than those obtained with continuous monitors. Recent investigations of the manual method have determined that the collection efficiency of the method varies with the NO_2 concentration (8). The values used in this study were calculated using the standard collection efficiency of 35%. At the low concentrations encountered during this study, the true collection efficiency is higher than 35%. If correction is made reflecting the latest research (8), the absolute numbers for the manual method are more closely in line with the instrument values. Variability of the manual method can also be seen in the correlation of only 0.86 from sample to sample within the same bubbler box. This study was performed under carefully controlled conditions and the results cannot necessarily be taken as representative of all sampling done with these analyzers.

Instrument Failures and Maintenance Requirements. During the sampling period, a log was kept of instrument

failures, maintenance requirements, and downtime. Table V shows the data obtained on the above parameters for each instrument. That instrument failures were at a minimum for all instruments may be due to the daily attention given to each instrument by the operator. The two chemiluminescent monitors had the least number of failures. The Beckman instrument encountered the greatest number of problems. The majority of these were related to the water addition part of the system. Failures were easier to correct with the Beckman whereas problems encountered with the other monitors required service personnel. All of the monitors sampled greater than 90% of the time during the three-month period. This did not take into account calibration time. If calibration time were considered, then the longer responding instruments such as the Beckman and the Technicon would show less operating time in relationship to the quick responding chemiluminescent instruments.

Conclusions

From the observations, evaluations, and comparisons made during the study, the following conclusions can be drawn:

The chemiluminescent NO monitor, with appropriate converter, can be used to measure ambient concentrations of NO_2 on a continuous basis under the conditions of this comparison.

In terms of response time and required maintenance, the chemiluminescent monitors have advantages.

The Beckman coulometric monitor while "tracking" with the other monitors gives lower mean values at all concentrations.

The Federal reference method gives higher mean values than the continuous monitors at the generally low concentrations observed at this nonurban site.

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Sulfur Dioxide Pressure Leaching

New Pollution-Free Method to Process Copper Ore

R. A. Meyers,* J. W. Hamersma, and M. L. Kraft

TRW Systems Group, Redondo Beach, Calif. 90278

■ Copper smelters in the United States emit 3.0×10^6 tons of sulfur dioxide into the atmosphere yearly, causing a major air pollution problem in some western states. The current industrial technology which gives rise to sulfur oxide air pollution involves pyrometallurgical treatment of copper sulfide ores. We have discovered a pressure-hydrometallurgical reaction which utilizes sulfur dioxide and hydrochloric acid to recover copper from copper ore while converting both the sulfur dioxide and the ore's sulfide content to elemental sulfur. This embryonic discovery could provide a basis, after full engineering testing and development, for pollution-free refining of copper.

Copper smelters in the United States presently emit more than 75% of the total sulfur oxides generated by the nonferrous smelting industry. An average capacity copper smelter discharges sulfur dioxide into the atmosphere at higher rates than some of the largest United States power plants.

United States copper sulfide ores consist mainly of chalcopyrite ($CuFeS_2$) with smaller amounts of chalcocite (Cu_2S), bornite (Cu_5FeS_4), and lesser copper minerals. Pyrite (FeS_2) is frequently found in the ore matrix. These ores are currently processed by pyrometallurgical techniques involving air oxidation.

Approximately one half of the U.S. smelters roast the ores prior to reverberatory furnace smelting, resulting in sulfur dioxide emissions. After the metal-bearing charge is placed in the reverberatory furnace, it is melted to form copper matte and slug. The matte is then transferred to the converters where air is blown through the matte to eliminate the remaining sulfur as sulfur dioxide, while silica flux is added to remove the iron as a silicate slag.

Because of the multiplicity of flue gas exit locations and the variable sulur dioxide content of the emission streams, stack gas cleaning technology has met with only moderate success. In addition, many of the stack gas cleaning processes which have been tested for the control of sulfur oxides from copper smelters produce one or more products such as sulfuric acid, ammonium sulfate, or calcium sulfate which would be sources of secondary pollution if produced in the large amounts required for industry-wide pollution control.

Consequently, a good deal of activity has been centered on the development of nonpolluting hydrometallurgical techniques which could be substituted for the older pyrometallurgical technology as new copper production capacity comes on stream. We believe that a hydrometallurgical process which could rapidly dissolve the ore copper content while converting the sulfide content directly to elemental sulfur would be most desirable, as elemental sulfur storage would create no secondary pollution problem. The key step in the development of this type of hydrometallurgical process is in finding an oxidizing medium which will rapidly dissolve the ore but will not oxidize sulfur to sulfate.

A number of oxidizing agents have been evaluated for hydrometallurgical processing of copper sulfide ores. These include sulfuric acid, oxygen with ferric chloride, and ferric sulfate (1). Processes based on these agents have been under investigation for more than 40 years. Of these, only the ferric salt leaching systems produce elemental sulfur as nearly the only sulfur product. Although processes based on ferric salt leaching were first described in the 1930s (2), none have as yet reached commercial production. A drawback of this latter system lies in the electrowinning of the copper metal from ferric salt solutions, wherein the ferric ion impedes the plating step.

An unconventional approach for the pressure hydrometallurgical refining of copper ore is presented below. The process is based on a novel reaction, reported for the first time herein, in which solutions of hydrochloric acid and sulfur dioxide convert copper sulfide ores to elemental sulfur and soluble copper and iron chlorides as shown in Equation 1:

$$4CuFeS_2 + 3SO_2 + 12HCl =$$
$$4CuCl + 4FeCl_2 + 11S + 6H_2O \quad (1)$$
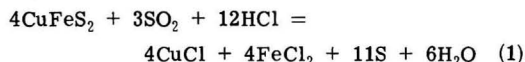
This reaction mode has advantages over other leaching methods as both copper and iron ions are produced in the reduced form, thus less reductant is required for, and ferric ion is not present to interfere with, subsequent copper metal production. In addition, sulfur dioxide removed by flue gas scrubbing from the exit gases of existing pyrometallurgical smelters can be reduced to elemental sulfur by this reaction, thus providing the dual benefit of reducing sulfur dioxide to a storable form while producing copper.

A sample of flotation concentrate from a large open pit mine in the state of Arizona was selected for demonstration of the concept. This concentrate is nearly pure chalcopyrite. The results (Table I) show that 99–100% of the copper and 96–97% of the iron content of the concentrate is dissolved by action of aqueous sulfur dioxide and hydrochloric acid in a maximum residence time of 30 min at 180°C and 180 psig. Initial studies at lower temperatures

Table I. Extraction of Metal Sulfides[a]

Metal sulfide	Residence time, min	Metal extracted,[b] % by wt Copper	Iron
Chalcopyrite ($CuFeS_2$)[c] concentrate	30	99.7 ± 0.05	96.6 ± 0.1
Chalcopyrite ($CuFeS_2$)[c] concentrate	60	98.8 ± 0.05	97.3 ± 0.1
Chalcopyrite ($CuFeS_2$)[c] concentrate	120	99.8 ± 0.05	96.8 ± 0.1
Iron pyrite (FeS_2)[d]	60	...	16.3 ± 0.1

[a] Extraction conditions: 9.77 mM metal sulfide (based on copper for chalcopyrite, on iron for pyrite) extracted with 225 ml of water, $0.86M$ in sulfur dioxide and $3.6M$ in hydrochloric acid at 180°C and 180 psig, in a Fischer and Porter glass pressure reaction vessel with Teflon-coated magnetic stirring bar system.
[b] Percent metal extracted = (1.000 − metal extracted from residue with nitric acid)/(total metal in starting concentration) × 100. Metals determined by atomic absorption spectrophotometry.
[c] Greenlee County, Arizona: molar ratio $Cu_{1.00}Fe_{0.96}S_{1.90}$; 85.2% −200 mesh. X-ray powder fraction pattern shows greater than 95% of the metal content in the form of chalcopyrite with a small amount of pyrite.
[d] E. H. Sargent Co., 95% −200 mesh.
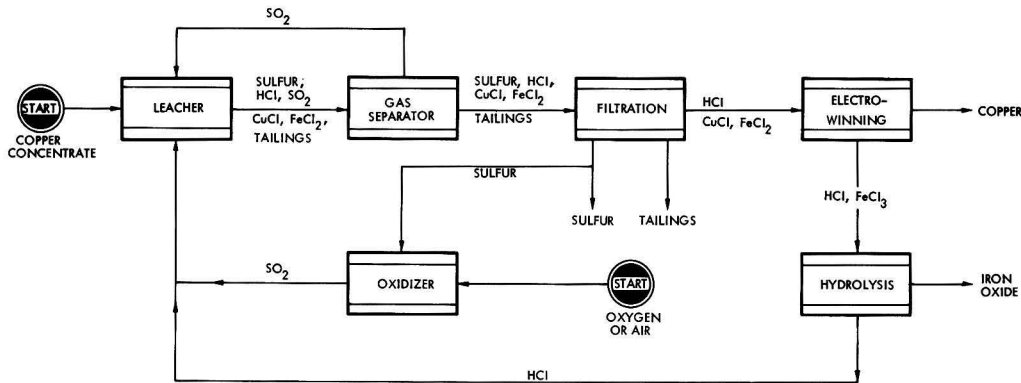
Figure 1. Process flow diagram
(i) Copper concentrate is leached with an aqueous solution of hydrochloric acid and sulfur dioxide; (ii) unreacted sulfur dioxide is vented from the slurry mixture and recycled; (iii) elemental sulfur and copper ore tailings are filtered from the slurry mixture; (iv) makeup sulfur dioxide is obtained by oxidization of a part of the product sulfur; (v) elemental copper product and ferric chloride are obtained by electrolysis of an acid solution of cuprous and ferrous chloride; and (vi) hydrochloric acid is regenerated by hydrolysis of ferric chloride giving iron oxide as a product

showed very little reaction below 150°C (100 psig). It is apparent that the iron content of the concentrate dissolves at a slower rate than the copper content. This is probably due to the small iron pyrite component of the concentrate which reacts more slowly under these conditions, as shown in Table I.

Elemental sulfur and ferrous and cuprous ions were isolated from each experimental extraction in an amount, which corresponds within a relative 5%, to that predicted from the reaction shown in Equation 1. Excess sulfur over stoichiometric (Equation 1) was found for the 2-hr extraction while no excess was noted for the shorter duration runs. Catalyzed disproportionation of sulfur dioxide to sulfur and sulfur trioxide ($3SO_2 = S + 2SO_3$) is possibly responsible for the excess sulfur. Reaction blanks were run under the same conditions as shown in Table I (180°C, 180 psig), where the copper ore was omitted but trace amounts of cuprous ion were added, and in which sulfur was produced in amounts corresponding to the small ex-

cesses noted for the 2-hr extraction. Copper (>99% purity) was plated directly from the above solutions by reduction of the cuprous ion content, after flashing off residual sulfur dioxide.

We believe that a pollution-free process could be developed utilizing the discovery presented herein (in combination with suitable state-of-the-art sulfur dioxide and hydrochloric acid regeneration steps) which could extract copper from copper ore with production of elemental sulfur as the sole sulfur-containing product.

A block process flow diagram of one preliminary process design utilizing the technical approach described above, is shown in Figure 1.

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INDUSTRY TRENDS

Zimpro Inc. has acquired Adrian Manufacturing and Research Div. of Adrian Construction Corp., in order to enter the incinerator business, and made a marketing agreement with D. R. Sperry and Co. to market filter presses for dewatering municipal sludge.

Roy F. Weston, Inc. has established a branch office at Silver Spring, Md., to provide environmental consulting services throughout Maryland. Robert P. Relyea will manage the branch office.

VTN Corp., Irvine, Calif., will complete an environmental impact report relative to NRG NuFuel Co.'s landfill gas processing system on the Palos Verdes Peninsula, Calif. This will be southern California's first landfill gas processing plant.

The Electric Power Research Institute (EPRI), Palo Alto, Calif., awarded a $455,000, two-year contract to Power Technologies, Inc., Schenectady, N.Y., to extend a research program on the design of very compact overhead transmission lines.

ECOKEL, Santa Rosa, Calif., a joint venture of Ecodyne and The M.W. Kellogg Co., received a contract, worth about $20 million, including options, to design, supply, and build two natural draft cooling towers for Commonwealth Edison Co.

Gray Pollution Control Systems, Inc., Englewood Cliffs, N.J., has signed a $3,646,000 contract with New York City's Environmental Protection Administration to rehabilitate and modernize the city's Southwest Brooklyn incinerator.

Robintech, Inc., Fort Worth, Tex., made a joint venture with Nicaraguan investors in Tubos de Centroamerica, S.A., Nicaragua. The Nicaraguan firm will produce PVC pipe and fittings for electrical conduits and pressure and irrigation pipes.

Tracor, Inc., has received a $3.9 million contract from the U.S. Naval Sea Systems Command to continue its current program of assisting the Navy in procurement of sonar systems for missile-carrying submarines.

Combustion Engineering, Inc. will defer major expansion of its Chattanooga, Tenn., nuclear manufacturing facility because of deferred delivery dates requested by a number of utilities. A moderate expansion is still in the works, however.

Continental Oil Co. (Conoco, Stamford, Conn.) received the Department of Commerce's "savEnergy" award from Commerce Secretary Frederick Dent.

Hoyt Manufacturing Corp. (Westport, Mass.) supplied Western Electric Corp. (Weco) with a trichloroethylene solvent recovery system that helped Weco win the environmental improvement award from the Associated Industries of Massachusetts.

Hesston Corp. (Hesston, Kan.) sold a custom-made "Incinerotor" rotary incinerator to the U.S. Department of Agriculture for the department's screw worm eradication project at Mission, Tex. Cost was $119,471.

Emission Abatement, Inc. (Houston, Tex.) has announced that six new vapor recovery processes the firm developed are now available for licensing in the U.S. and abroad.

The American Petroleum Institute (API, Washington, D.C.) voted to allocate $2.31 million toward API's 1975 research program for improvement and protection of the environment.

Benham-Blair & Affiliates, Inc. (Oklahoma City, Okla.), a large design and engineering firm, has acquired the firm of Wildman & Morris (San Francisco, Calif.). Wildman & Morris designed the $1-million control house "nerve center" for the Standard Oil (California) $200 million low-sulfur fuel oil refinery.

Chemfix, Inc. (Pittsburgh, Pa.) has licensed Browning-Ferris Industries (BFI) to employ the Chemfix liquid waste disposal process under special circumstances at BFI sites.

The Orville Simpson Co. (Cincinnati, Ohio), which manufactures screening machines and liquids/solids separators, has changed its corporate name to ROTEX, Inc.

Georgia-Pacific (Portland, Ore.), defendant in a mercury pollution case involving Bellingham Bay, Wash., since 1970, has recently had this case against the company dismissed. The case was never brought to trial.

Ingersoll-Rand's IMPCO Division (Nashua, N.H.) is licensed to use the Scott Paper Company's data and experience concerning bleaching of wood pulp and other cellulosic material with ozone, alkali, and chlorine dioxide, for lowest effluent potential.

NEW PRODUCTS
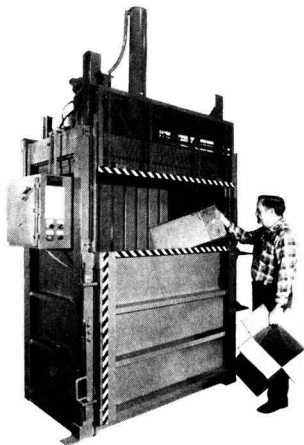
Vertical baler
The unit is designed to handle cartons, boxboard, chipboard, waste paper, and waxed or coated material. The baler compresses reusable waste in bales measuring 60 in. × 48 in. × 32 in. and weighing 600–900 lb. The unit is complete as delivered, requires no special foundation and only a few electrical connections to start-up operation. Enviro Wasteaway, Inc.   **101**

Dewatering centrifuge
Low-speed waste sludge dewatering centrifuge requires less connected horsepower and operating power, and is quieter to operate. The company claims lower speed reduces maintenance and electrical hardware costs. The concurrent flow design results in turbulence-free operation, and improved solids settling and cake compaction. Performance is said to equal high-speed machines. Bird Machine Company, Inc.   **102**
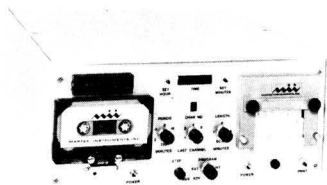
Data printer
Model is designed to record up to 15 analog environmental parameters, and the time of day on digital magnetic tape and a digital printer. Inputs can be scanned continuously or at pre-programmed intermittant rates. In addition, the time of day, channel I.D. number and the measured parameter are individually indicated on LED digital displays. Martex Instruments Inc.   **103**

Ion meter
Concentrations of 16 different ions including arsenic, cyanide, chromium, and others may be determined by using the specific ion electrodes. Portability results from the solid-state circuitry, while high accuracy results from four scale selections. Fields of application include industrial waste control, biological studies, soil analyses, and metal smelting. Devon Products, Inc.   **104**
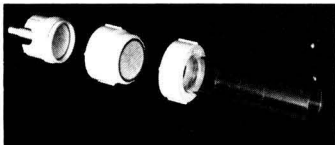
Asbestos detector
The unit, a multiple 47-mm diameter membrane holder, is designed for serial filtration of liquids or gases; it is particularly useful for detecting asbestos aerosols in ambient air. The holder is made of polycarbonate plastic, and is virtually unbreakable, chemically inert in most fluids, and can be repeatedly autoclaved. Nuclepore Corp.   **105**

Delumper
The pipeline delumper, included in any waste pipeline system, permits the economic incineration of commercial or human solid wastes at uniform, controlled rates. The strainless steel delumper operates vertically or horizontally, requires no open pit in sewage work, and is sanitary. It will pulverize large blocks of wood, polyethylene sheeting, stringy materials, and hard-caked slurries carried in water, air acids, and chlorinated hydrocarbons. Franklin Miller, Inc.   **106**

Fecal test
The set consists of sterilized EC medium and fermentation vial assemblies, an incubator, and instructions

for fecal coliform determinations. It can be used to test stream pollution, sewage treatment systems, and water quality checks. This test differentiates between coliforms of fecal origin and those from other environmental sources. Hach Chemical Co.   **107**

Data converter
Device converts analog voltages to a format accepted by teletypes, calculators, printers or computers. Outputs are serial ASCII or parallel BCD. The unit can be inserted between existing communications components. The standard model is equipped with a $3\frac{1}{2}$-digit LED display; its self-contained power supply permits stand-alone usability. Elographics Inc.   **109**
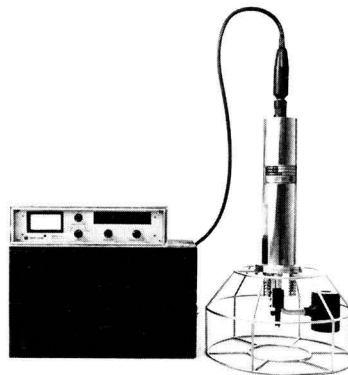
Water monitoring probe
Probe is an oceanographic instrument which senses and transmits conductivity, salinity, temperature, depth, dissolved oxygen, pH, turbidity, and redox. The probe will operate in depths of 0–1000 meters, and may be configured to sense any or all of the above ocean parameters. InterOcean Systems, Inc.   **111**

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Today for tomorrow.

1. AIR POLLUTION: PHYSICAL AND CHEMICAL FUNDAMENTALS

John H. Seinfeld, California Institute of Technology. 1975, 400 pages, $22.50.

The need for a quantitative approach to the basic science and engineering underlying the air pollution problem has been fulfilled in this timely text. The most comprehensive single book available on the subject, it provides an in-depth treatment of air pollution chemistry, atmospheric transport processes, combustion sources and control methods.

2. HYDROLOGY FOR ENGINEERS, Second Edition

Ray K. Linsley, Stanford University, Max A. Kohler and Joseph L. H. Paulhus, formerly with the U. S. National Weather Service. *McGraw-Hill Series in Water Resources and Environmental Engineering.* 1975, 416 pages (tent.), $18.50 (tent.).

Updated throughout, here is the only general hydrology book available to present a detailed description of computer-based hydrologic tools as well as classical techniques. Assuming a limited background in hydrologic science, it offers basic concepts in the techniques of hydrologic analysis relevant to the design, planning and operation of engineering works for the management and control of water resources.

3. INTRODUCTION TO OCEAN ENGINEERING

Edited by Hilbert Schenck, Jr., University of Rhode Island. 1975, 512 pages (tent.), $18.50 (tent.).

Consisting of eleven chapters written by nine experts in their fields, this is the first basic text ever written in ocean engineering. It provides integration of oceanographic theory, especially in the chapters on waves, soil mechanics, underwater acoustics and water quality.

4. SYSTEMS ANALYSIS AND WATER QUALITY MANAGEMENT

Robert V. Thomann, Manhattan College. 1972, 286 pages, $18.50.

Using both mathematical models of environmental responses and management and control schemes, the text 1) provides a series o analytical tools for describing and forecasting the effects of the surrounding environment on the water quality of a stream or estuary; 2) presents information on water quality criteria and wastewater inputs, and 3) establishes a point of departure for evaluating the worth of water quality improvement projects and discusses the benefits of applying cost/benefit analysis to engineering.

5. SOURCE TESTING FOR AIR POLLUTION CONTROL

Hal B. H. Cooper, Jr., University of Texas at Austin, and August T. Rossano, Jr., University of Washington. 1971, 278 pages, $14.50.

A discussion of principles and methods used for testing of gaseous and particulate materials being emitted from industrial, combustion and other sources is presented in this informative text. Organized to give the reader a logical presentation of the steps taken in source testing, the book includes an extensive examination of the equipment, methodology, sampling, and analytical techniques in use for gaseous and particulate particles.

6. AIR POLLUTION CONTROL: GUIDEBOOK FOR MANAGEMENT

August T. Rossano, Jr., University of Washington, and Hal B. H. Cooper, Jr., University of Texas at Austin. 1969, 214 pages, $19.50.

The book provides a comprehensive and balanced treatment of the complex technical and administrative nature of air pollution problems. All major elements of the field are included to provide both a text and background reference of the subject in one volume.

7. ENVIRONMENTAL PROTECTION

Emil T. Chanlett, University of North Carolina at Chapel Hill. *McGraw-Hill Series in Water Resources and Environmental Engineering.* 1973, 560 pages, $17.50. Solutions Manual. A rationale for the management and protection of our land, air, water and energy resources, this book examines the consequences of mismanagement at three levels: 1) effects on health, 2) effects on comfort, convenience, efficiency and esthetics and 3) effects on the balance of ecosystems and of renewable resources.

8. ENVIRONMENTAL SYSTEMS ENGINEERING

Linvil G. Rich, Clemson University. *McGraw-Hill Series in Water Resources and Environmental Engineering.* 1973, 405 pages, $17.50. Instructor's Manual.

Covering a broad spectrum of environmental topics, this quantitative introduction uses a systems approach in the analysis of environmental phenomena and in the selection and design of engineering facilities used for controlling the environment.

9. AIR POLLUTION

H. C. Perkins, University of Arizona. 1974, 407 pages, $15.50. Solutions Manual.

This engineering-oriented treatment of air pollution is sufficiently detailed to enable chemical, mechanical and sanitary engineering students to solve a variety of problems. A discussion of global effects of air pollution is included along with numerous applications-type problems.

NEW LITERATURE

Cooling towers. Bulletin S220/1-0 presents design, construction, and engineering data on the new "Ejector II" cooling tower. No electric motors, fans, shafts, bearings, or similar parts. Baltimore Aircoil Co. **161**

Energy-saving lighting. Case history booklet describes energy-saving lighting. Wattage reduction and improved seeing conditions are described. Title is, "Better Lighting with Fewer Watts." Johns-Manville **162**

Conductivity instruments. Summary catalog lists conductivity instruments and accessories for water system, reverse osmosis, environmental protection, and other analysis applications. Myron L Co. **163**

Water management. Capabilities brochure describes the company's water management and pollution control programs in industrial, commercial, and institutional water facilities. Vulcan Laboratories, Inc. **164**

Pesticide surfactant. Technical data describe SURFYNOL TG-E, an acetylenic liquid nonionic surfactant for use with agricultural pesticides. Toxicity data, water solubility, and physical properties are covered. Air Products and Chemicals Inc. **165**

Crusher. Catalog sheet describes model T150 "Tubar Can & Glass Crusher" that reduces container waste volume 80% for more economical refuse handling. Specifications are included. Uhrden, Inc. **166**

Flaring. New 20-page booklet, "Flare Tips," describes aspects of flaring. It explains steam, gas, air, and water-assist flares, pilots, igniters, seals, and controls. National Airoil Burner Co., Inc. **177**

Chemical feed systems. Bulletin FDP-1050 details line of "dia PUMP" systems. Uses are in chemical treatment of water. ET-P and ET-S Tank Systems are also described. Neptune Chemical Pump Co. **178**

Flow measurements. Form FR 8-74 is a practical guide to fluorometry for flow and time-of-travel measurement for streams, weirs, flumes, sewers, and other channels. Turner Designs **179**

Canning system. Bulletin describes new approach for the cleanup of fruit and vegetable canning effluent, using the company's centrifugal wastewater concentrator and centrifugal thickener. SWECO, Inc. **180**

Optical filters. Catalog describes Grubb Parsons (England) line of optical filters (0.4–1000 μ), beam splitters, laser components, and related items. Ask for Catalog C-14. Baird-Atomic **181**

Paint spray problems. Bulletin 68 tackles problems of sludge accumulations on paint spray booth walls, exhaust fans and ductwork, and waste treatment systems. The bulletin also describes an organic chemical additive that solves the problems. Nalco Chemical Co. **182**

Solid waste management. Publication 674FE describes system than can recover glass, aluminum, and ferrous metals from refuse. The system also can give about 6.7 million Btu/ton of refuse. Garrett Research and Development Co., Inc. **183**

Solvent recovery. Brochure 1259 features systems than can capture and return 85–95% of solvents usually lost through evaporation, thus removing hazardous air pollutants. Hoyt Manufacturing Co. **184**

Centrifuges. Bulletin 1230A covers centrifuges which can treat many sludges without addition of polyelectrolytes. System uses an exclusive design, and is self-cleaning and anti-plugging. Sharples-Stokes Division, Pennwalt Corp. **185**

Hopper feeders. Bulletin 3006 describes tube hopper feeders, packaged pneumatic conveying systems for efficient transfer and rapid discharge of nonfree flowing material. Vac-U-Max **186**

Chemicals. Company's 1975 catalog lists more than 10,000 different chemicals for the laboratory, pilot plant, or factory. Laboratory equipment is included. Gallard-Schlesinger Chemical Manufacturing Corp. **187**

Measuring electrodes. Catalog gives complete line of chemical measuring electrodes, 100 different types, made by Radiometer A/S of Denmark. Full range of applications. The London Co. **188**

Clarifiers. Standard and custom-engineered traveling bridge clarifiers are features in the company's new clarifier brochure. New features eliminate unnecessary downtime. Aqua-Aerobic Systems **189**

Energy publication list. Bulletin 122 fully lists significant publications on energy produced from wood, coal, gas, oil, water, wind, steam, sun,

geothermal heat, hydrogen and helium, and thermonuclear and laser fusion. High Energy Technology Corp. **190**

Reverse osmosis. Bulletin FS-1, entitled "Reverse Osmosis and Ultrafiltration—An Emerging Technology for Liquid Separations," gives an in-depth description of this field. Universal Oil Products Co. **191**

Oil and solids removal. Corrugated Plate Separator Engineering Guide describes means of removing oils and solids from wastewater and process fluids. Heil Process Equipment Co. **192**

Cryogenic grinding. Brochure describing "Cryo-Grind" systems, for liquid nitrogen embrittling and grinding of thermoplastic, elastic, heat sensitive, and scrap materials, is available. Technical services are also described. Air Products and Chemicals, Inc. **193**

Marine pollutant study. Environmental data to assess potential effects of man-generated substances on the marine environment is available from Environmental Science Information Center, Marine and Earth Sciences Library (Fisheries Branch), 3300 Whitehaven St., N.W., Washington, D.C. 20235. (Write direct.)

Waste heat utilization. Bulletin 334 makes recommendations for future work in this area, and lists present uses of waste heat. David C. Flaherty, Ed., College of Engineering, Technical Extension Service, Washington State University, Pullman, Wash. 99163. (Write direct.)

Re-refined oil use. Publication, "Lubricating Oil Never Wears Out; It Just Gets Dirty!" focuses on ways that re-refined oil can contribute to solving the energy crisis. Association of Petroleum Re-Refiners, 1730 Pennsylvania Ave., N.W., Washington, D.C. 20006. (Write direct.)

Air pollution research. Article sets forth a list of work done in air pollution research, funded by state grants. Air Resources Board, 1709 11th St., Sacramento, Calif. 95814. (Write direct.)

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BOOKS

Proceedings, International Conference on Land for Waste Management. 450 pages. Executive Secretary, International Conference on Land for Waste Management, c/o National Research Council of Canada, Ottawa, Canada K1A OR6. 1974. $15, hard cover.

Book covers six themes. These include climate, vegetation, and soils in waste disposal; soil properties and processes; hydrogeology and geomorphology; nature of waste in relation to land disposal; socioeconomic, health, and legal aspects; and present and future designs for disposal. Special problems in the North are discussed.

Automotive Scrap Recycling. James W. Sawyer, Jr. 157 pages. The Johns Hopkins University Press, Baltimore, Md. 21218. 1974. $7.50, hard cover.

The author presents an in-depth analysis of the processes employed by the part of the scrap industry that uses obsolete automobiles as raw materials. He concludes that steel scrap derived from "obsolete" steel represents a very small portion of raw material input to the ferrous materials industry—about 3–4%. Formal mathematical models shed new light on elasticity of this ferrous scrap supply.

Water Pollution. Stanton S. Miller, Ed. ix + 317 pages. American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. 1974. $7.50, paper; $12, hard cover.

Contains articles from Volumes 4–7, *Environmental Science & Technology*, 4–7, published as Outlook or Feature items, between 1970 and 1973. The book covers many aspects of government, business, industry, technology, monitoring, and specific pollutants; and also presents overviews and issues in the field of water pollution. Contributed and staff-written articles are included.

Environmental Law for Non-Lawyers. J. Gordon Arbuckle, Stanley Schroeder, and Thomas Sullivan. xi + 296 pages. Government Institutes, 4733 Bethesda Ave., Bethesda, Md. 20014. 1974. $29.50, paper.

Readers of this book will avoid one of the prime causes of environmental problems—ignorance of environmental laws. They will gain an understanding of environmental law fundamentals, the National Environmental Policy Act, and legal aspects of air, water, solid waste, and noise pollu-

tion control. Land use is also covered. Language is such that the non-lawyer can readily understand the material.

Proceedings of the 1974 National Conference on Control of Hazardous Material Spills. 388 pages. American Institute of Chemical Engineers, 345 E. 47th St., New York, N.Y. 10017. 1974. $25.

This book presents the papers given at the conference. It covers legal and legislative implications, contingency and response, prevention, social and economic impacts, cleanup, removal, containment, surveillance and detection, safe disposal practice, and many other very timely topics. Environmental damage is thoroughly assessed.

United Nations Environment Program. Directory of National and International Pollution Monitoring Programs. 3 Volumes. xv + 1179 pages, with additional pages for forms and index. Smithsonian Institution Center for Short-Lived Phenomena, 60 Garden Court, Cambridge, Mass. 02138. 1974. Three-volume set, $30, paper.

The set of books covers national monitoring programs, listed on an alphabetical basis, from Argentina to Zaire. It stems from a survey undertaken by the Smithsonian Institution to provide the United Nations Environment Program with information to plan the first phase of the Global Environmental Monitoring System (GEMS).

The Chemistry of PCB's. Otto Hutzinger, S. Safe, and V. Zitko. 269 pages. CRC Press, 18901 Cranwood Parkway, Cleveland, Ohio 44128. 1974. $35, hard cover.

The book's main aim is to present a comprehensive summary of what is known about the chemistry of polychlorinated biphenyls and chlorophenyls. It fulfills this aim. Workers involved in research and analysis are provided with an up-to-date survey of PCB chemistry. The book includes nomenclature, composition of technical mixtures, synthesis of individual chlorobiphenyls, chemical reactions, photochemical and metabolic alterations, and spectroscopic properties.

Air Pollution, Part B: Prevention and Control. Joe Ledbetter. xiii + 286 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, N.Y. 10016. 1974. $11.75, paper.

This timely volume is the sequel to Part A which covered analysis. It deals with the abatement of air pollu-

tion, and is directed to senior undergraduate and graduate students in enginering who have no prior instruction in the area of air pollution. For civil engineers, this book is of particular benefit as a reference. Included are topics such as management of air pollution, tall stacks, process change, specific pollutant or pollution source abatement, and related subjects.

Waterfowl and Wetlands: Toward Bioeconomic Analysis. Judd Hammack and Gardner Brown, Jr. 95 pages. The Johns Hopkins University Press, Baltimore, Md. 21218. 1974. $7.00, hard cover.

Migratory waterfowl and their value to mankind, and value as an outdoor recreational resource, are discussed. Hunter demand, biometric relationships, and rough cost-benefit analyses on existing prairie wetlands, are presented. There are also recommendations for future study of this significant wildlife resource.

Handbook of Common Methods in Limnology. Owen Lind. vii + 154 pages. The C. V. Mosby Co., 3301 Washington Blvd., St. Louis, Mo. 63103. 1974. $5.95, paper.

A very practical, concise "how-to-do-it" manual for workers carrying out field assignments in limnology. Physical and chemical limnology, as well as methods of collecting and studying plankton and benthos, are covered, with easy-to-understand instructions. A comprehensive unit conversion table is included.

Water and Landscape. R. Burton Litton, Jr., et al. xviii + 314 pages. Water Information Center, 44 Sintsink Dr. East, Port Washington, N.Y. 11050. 1974. $11.50, paper.

Presents the first concrete set of principles by which environmental enhancement by water can be evaluated, protected, and developed. This is done with a visual classification system for freshwater streams and bodies, creation of criteria for aesthetic quality of landscape, and suggestions as to how design and development of man-made additions to the water scene may be judged for aesthetic merit.

Air Pollution Abatement and Regional Economic Development. William Miernyk and John Sears. xvi + 194 pages. D. C. Heath and Co., 125 Spring St., Lexington, Mass. 02173. 1974. $13.50, hard cover.

Presents not only an economic study, but an amalgam of economic and engineering analysis. Focus is on regional economic development, not on environmental management exclusively. There are detailed estimates of new and replacement investments required to meet standards established by the Clean Air Act of 1970.

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Designed for engineers and others responsible for evaluating particulate collection devices. *Write:* Registrar's Office, Air Pollution Training Institute, Research Triangle Park, N.C. 27709

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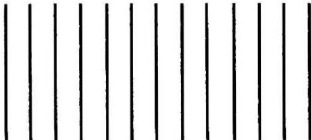
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