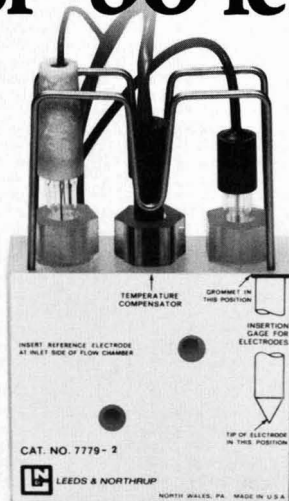# Environmental

Science & Technology

Keeping
a watch on
air pollutants
678

Environmental Improvement Exposition 725

New anti-fouling pH electrodes:

Leeds & Northrup beats the mess for $80 less!

Environmental
Science & Technology

contents

Viewpoint

Feature

Outlook

Departments

Current research

Oxidation of sulfur dioxide in polluted atmospheres—A review **685**

M. Bufalini

Reduced visibility is one noticeable physical effect which is traceable to aerosol particles, and now there is abundant evidence that the photochemical mechanism provides an efficient means for converting gaseous sulfur dioxide to particulate sulfur compounds. Both gas-phase and aerosol-forming reactions are included in this review (through 1970) of 80 references including reactions of sulfur dioxide with other atmospheric pollutants such as CO, NO_x, and hydrocarbons.

Uranium concentrations in surface air at rural and urban localities within New York State **700**

P. McEachern, W. G. Myers, and F. A. White

Uranium is certainly one heavy metal that has been found in the air over the state of New York. Its concentrations (which ranged from 0.10–1.47 ng/m^3 of air) are below present standards and its presence is attributed to naturally occurring sources. The analyses were made by mass spectrometric and fission track analysis, a combination of analytical techniques which may prove useful in the future to monitor nuclear industry activity.

Evaluation of rat eradication programs **704**

J. W. Gentry

A mathematical model has been developed for evaluating the numerous eradication strategies—poisoning, sterilization, and combinations thereof. The model can be used to evaluate the effectiveness of combined poisoning and sterilization treatment. To be successful in eradicating 75% of a rat population by the chemical sterilization procedure alone, for example, the rats must be treated with androgens during each reproductive cycle.

Model ecosystem for the evaluation of pesticide biodegradability and ecological magnification **709**

R. L. Metcalf, G. K. Sangha, and I. P. Kapoor

A model ecosystem is described which will find use in the screening of not only promising new pesticides but also new industrial chemicals for potentially disadvantageous environmental effects. The model has a terrestrial-aquatic interface and a seven-element food chain; the relatively simple method will yield useful information that is needed before the registration of new products.

Communication

Accumulation of DDT by Daphnia magna **714**

D. G. Crosby and R. K. Tucker

Certain links in the food chain are capable of concentrating certain environmental pollutants. For example, Daphnia magna, an important and first animal link in the aquatic food chain, can accumulate the pesticide DDT in 16,000–23,000-fold quantities from dilute DDT water suspensions in 24 hr. Interpretation of the significance of such data must be done with extreme caution.

Correspondence

Sludge dewatering by high-rate freezing at small temperature differences **716**

J. B. Farrell

The problems in developing a practical method are discussed. One of the most serious stumbling blocks is the need for a large freezing surface area per unit of sludge processed.

TECHNICON® AUTOANALYZER® SYSTEMS take the guesswork out of municipal wastewater treatment

Without effective monitoring instruments, wastewater treatment is all guesswork. Technicon AutoAnalyzer systems are capable of monitoring the level of critical chemical pollutants automatically, with almost instantaneous results in direct concentration terms. Run one, two, three or more parameters simultaneously for continuous analysis of major nutrients, including phosphates, or perform individual analyses at up to 80 samples per hour.

In addition, AutoAnalyzer systems from Technicon provide a most logical basis for joint treatment plants to determine surcharges to industry by measuring the level of noxious chemicals accurately before they become part of the treatment process. Further, Technicon instruments can help you meet the monitoring requirements of the federal guidelines for wastewater treatment facilities.

Ease of operation and automatic analysis based on "Standard Methods" make the AutoAnalyzer an ideal system for use in municipal wastewater treatment facilities. When you've reached the design stage, Technicon will work with your consulting engineer by providing technical information and instrument recommendations for specific water analysis requirements.

For more information about Technicon AutoAnalyzer systems, including the AutoAnalyzer II, CSM®6, and Monitor IV, write to Department 141.

Technicon Industrial Systems
A Division of Technicon
Instruments Corporation
Tarrytown, New York 10591
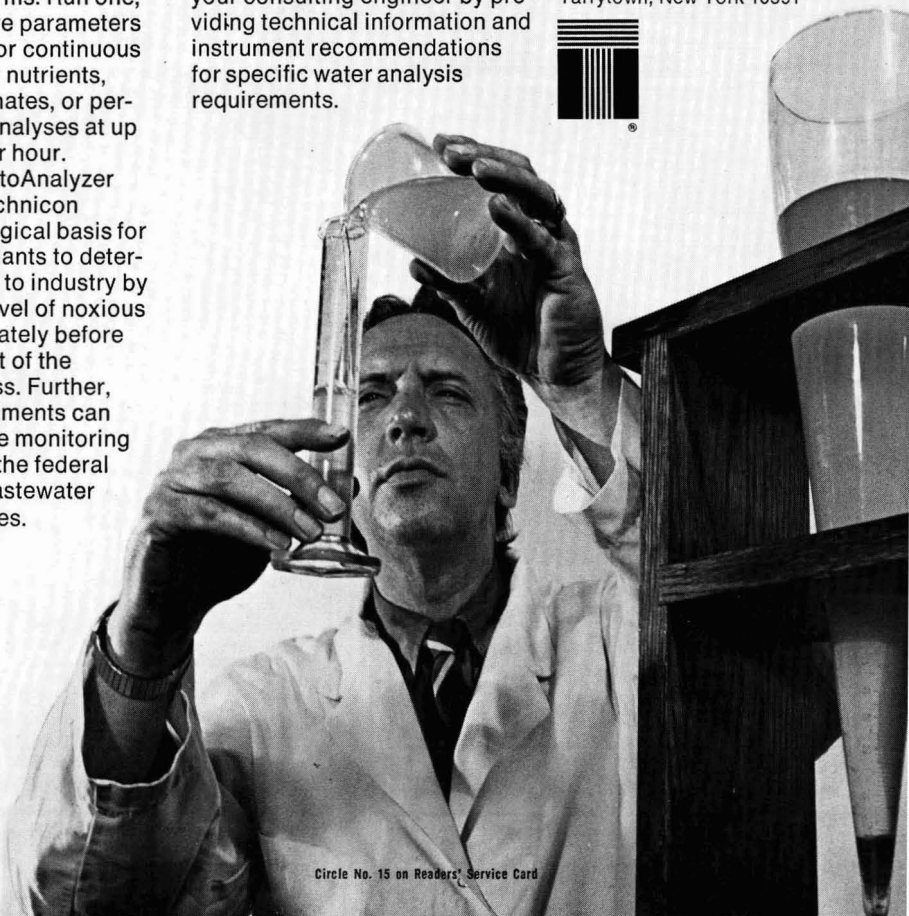
letters

How much protection?

DEAR SIR:

Ernest Tsivoglou in his article, "Nuclear power: the social conflict," ES&T, May 1971, states on page 409 "the AEC and the industry insist that nuclear plants must have the right to release radioactive wastes to the full extent allowed, according to the current radiation protection standard . . . . On the other hand, there is an increasingly strong movement among conservation groups and pollution control agencies to heed the admonitions of the ICRP and FRC." This strong implication that the AEC and the nuclear industry are at variance with the ICRP and FRC has no basis. In fact, Tsivoglou himself states that GE and Westinghouse have announced near zero gaseous emission systems. Here at the National Reactor Testing Station, at the cost of extensive waste processing, liquid effluents are far below guide values, and average personnel exposures are less than 10% of guide values.

Mr. Tsivoglou also states that "there is no conclusive proof that (the) currently applied radiation standard is either adequate or inadequate for long-term protection of the public." Because of the many existing environmental conditions which we know do adversely affect the public, and because of the large variance of response by biological systems to adverse conditions, there can never be conclusive proof that any single agent does not contribute in some small way to adverse biological responses.

G. J. Briscoe
Idaho Nuclear Corp.
Idaho Falls, Idaho 83401

● *Dr. Tsivoglou specifically stated in the May ES&T article: ". . .neither the AEC nor the nuclear industry wishes actually to practice a policy of maximum radiation exposure."—Ed.*

Fossil fuels the felons!

DEAR SIR:

Dr. Tsivoglou's exposition of nuclear power (ES&T, May 1971, page 404) is an eminently sensible discussion of a topic that has been much maltreated in print. He takes the sound engineering approach in urging that radiation hazards be limited by "bottling up" the offgases.

The more one looks at the energy problem, the more apparent it is that fossil fuels represent the villainous characters on the environmental scene. Nuclear energy, subject to proper controls, can greatly ease the impact of energy production on the air–water environment near power sites. However, the nuclear technology involved in power production is so complex that it intimidates the adversary process of a democracy. This means that the engineering community needs to exercise itself to bring into play a system of

checks and balances so that the public health and safety are assured.

Engineers have a special responsibility in this matter, because of the critical importance of core cooling systems designed to act in an emergency. One must never lose sight of the fact that nuclear power plants constitute a hazard unique in the history of engineering.

Ralph E. Lapp
7215 Park Terrace Dr.
Alexandria, Va. 22307

Economic Snow job?

DEAR SIR:

The article, "Pyrolysis of refuse gains ground," that appears on page 310 of your April 1971 issue, in addition to presenting Enviro-Chem's Landgard system for the pyrolysis of municipal refuse, offers some rather philosophical comments attributed to Curtis Snow. Mr. Snow states, "What good does it do to recover goodies from solid waste if you can't find a home for them in the economy?" Experimental work done at West Virginia University shows that the pyrolysis of solid waste materials could result in supplying the equivalent of 10–15% of the daily natural gas requirements for each person in the United States. Conserving our natural gas resources would appear to be an adequate "home" for these "goodies."

Mr. Snow further states, "There are lots of wonderful things you can do with science, but you can't always afford to do them." We are seeing enough results of this attitude of placing economic values above environmental considerations. There are lots of wonderful things you can do with science, and you can't always afford to *ignore* them.

Mr. Snow apparently places little value on the opinions of ecologists, politicians, and the average citizen. According to Mr. Snow, "Recycling and recovery hold a lot of fascination for politicians and the lay mind. There's been a lot of garbage generated about garbage." It is this type of attitude which has placed our ecological system in its present condition, and we certainly do not need another Snow job.

R. C. Bailie
Robert S. Burton III
Dept. of Chemical Engineering
West Virginia University
Morgantown, W. Va. 26506

Red tape—blessing in disguise

EPA and the cause of clean water will eventually emerge
as beneficiaries of the current chaos over permit system

Many of our readers who are in industry will, by the time this issue of ES&T reaches subscribers, have become familiar with the discharge permit system run by the Army Corps of Engineers, about which we first alerted readers in December 1970. In view of the considerable misconceptions, misapprehensions—and in some cases, hostilities—engendered by the federal government's recourse to the provisions of a 70-year-old water pollution statute, it might be as well to ask whether, after all the wrangling is over, the cause of clean water in the U.S. will have been well served. After some inner misgivings, we conclude that, on balance, it will have been.

The biggest single reason for our positive view is that the permit system will enable the government—and possibly the rest of us, if confidentiality of information is dispensed with, as the Environmental Protection Agency (EPA) has strongly hinted it will be—to find out for the first time ever just what is being discharged into the nation's waterways. It is difficult to believe, but nonetheless true, that in an industrially based society like ours, no one person or organization has ever had anything approaching a full idea of what waterborne pollutants are being discharged, in either qualitative or quantitative terms. For years, the Federal Water Pollution Control Administration was urged by some congressmen to find out, by undertaking a full inventory, but bureaucratic delays stymied the attempt. When, in late 1970, the FWQA finally obtained Office of Management and Budget permission to send out a questionnaire form, the supplying of information was left on a voluntary basis (see ES&T, January 1970, page 20). Now that the 1899 Refuse Act has been resurrected, with its mandatory provisions for supply of discharge information, the earlier FWQA inventory project seems to have faded away into obscurity.

Those of us whose job it is to sit on the sidelines and watch industry and government wrangle over the form of the permit system are forced to admit that skeptics who see it quite simply as a case of the blind leading the blind can certainly make a good case. The Corps of Engineers, which is the middle man in this case, has been embarrassed at turn after turn. Not being familiar with the ins and outs of water pollution has put it in the unfamiliar position of being on the defensive. And many industrialists who would normally act like thoroughly assured and confident individuals have been reduced to the role of pathetic whiners and procrastinators. Industrial managers, indeed, have in the main shown an almost pathetic ignorance of what was expected of them, only partly excusable by the fact that just what is expected of them has not really been totally explained.

The beneficiary of the system, and of the arguments it has brought to the fore, is the EPA. The agency, which will (under a formal agreement with the corps) make all the important decisions regarding the issuance or withholding of permits, will be in a much stronger position to curb water pollution. For industries whose polluting activities were previously cloaked in secrecy will now be forced to show their hand. Those of them which have been under scrutiny from EPA in past months as a result of enforcement conferences, for instance, will have to act fast or risk having a permit withheld. And those without a permit may confidently expect visitation from the Justice Department.

It may justly be asked why such a lot of agony, red tape, and ill feelings should be necessary to get a decent water pollution control program going, and it's a fair question. But until we get a new federal water pollution control law that has some real teeth in it—and we may get one this year—the permit system promises results that will in the long run justify the broken bones and hard feelings.

D. H. Michael Bowen

Still growing... with a new name.

VWR Scientific — A VWR UNITED Company

VW&R

Will

Progress Report...We're expanding in the East. Already there are four new facilities in the East bringing the total to over 300,000 square feet. We're modifying, modernizing, improving, enhancing . . . to bring you peak service. Our Eastern sales force has been increased by over 40%. And soon there'll be the unsurpassed computer facilities now serving our Western customers. Video displays that interlink all offices and warehouses—providing instantaneous readouts of inventories and total customer sales histories. And we are installing the latest automated materials-handling systems that reduce costs, expedite deliveries.

East or West, VWR Scientific offers the broadest line of highly-regarded instruments and supplies. The lines we sell come from proven-quality manufacturers and are accepted only if they meet our standards of excellence. In addition, a unique group of top-quality products under our VAN-LAB® label, designed and packaged for user convenience, is available.

We're dedicated to providing you with the finest selection of superior products, optimum service and unexcelled value. That's why we're growing. Look for us . . . if we're not there already . . . we'll be there soon. We're still growing.

Formerly—VW&R/Will Scientific • Albuquerque • Anchorage • Atlanta • Baltimore • Boston • Buffalo • Columbus • Denver • Detroit El Paso • Honolulu • Kansas City • Los Angeles • New York City • Phoenix • Portland • Rochester • Salt Lake City San Diego • San Francisco • Seattle • Tucson • West Sacramento

viewpoint

I. W. Abel

President, United Steelworkers of America

Smoke vs. jobs — end of a myth

We are increasingly being confronted by claims from industry that the demands made on it by citizens and government will not control pollution but rather will bring about complete stoppage of plant operations. This is a throwback to the antiquated escape route of "smoke means jobs"; it is environmental blackmail of the worst sort. The use of this argument—that margins of profit are inadequate to absorb the costs of social responsibility—is nothing new. It is an argument that unions have had to face ever since their inception. And we have countered that stance, despite industry's before-the-fact claims, without bringing about the demise of industrial progress. To the contrary, the wealth and technology of this nation have grown in geometric proportions simultaneously with the recognition of the need for social responsibility within the business world.

While we do agree with industrial spokesmen when they say that unreasonable environmental demands would be disastrous for them and for the workers, and while we always have endorsed provisions within federal antipollution legislation which call for standards to be set in accordance with what is technologically and economically feasible, we have found that far too many "unreasonable demand" claims simply are not so. Tragically, however, the worker who is threatened with a job loss, or the community which is faced with the threat of a tax base loss, usually does not have the time, the ability, or the legal authority to sift through the clouded claims to make an objective analysis. In these cases, the burden of proof clearly should be placed on those who are the violators. At present, this placement of the burden does not effectively exist. As we have in the past, the United Steelworkers of America continues to call for the right to subpoena the records of any plant which threatens a shutdown or worker layoff in response to standards' compliance. We also believe that public hearings should be conducted in these instances. Only through these avenues can the public receive the knowledge it needs to prevent environmental blackmail.

We are mindful that many obsolete plants use environmental control as a convenient public relations tool to justify a production decision to terminate operation and rationalize past failures to modernize facilities. The truth must come to light in such situations to prevent false strength being given to other claims of "necessary" industrial pollution.

Armed with the essential information, pragmatic strategies for the control of air emissions and water effluents can be established and implemented within specific time limits. I think we all can agree that it would be foolish to jump immediately to a confrontation crisis point by placing workers in an untenable position by demanding whether they are willing to sacrifice their jobs if all forms of industrial pollution do not stop instantly. Too many environmentalists have not yet gone beyond the stage of fighting for ambient standards. They must now enter the arena of the control strategy and they should not immediately assume that workers' jobs must necessarily be lost. Otherwise, they will provide a fertile field for the environmental blackmailer.

Often we are told that the labor movement should focus its pollution control efforts through collective bargaining. We feel that this is not the proper arena, however, because the technical details and amplitude of controls are far more extensive than the confines of a labor agreement. Moreover, an emission strategy for a region cannot be developed through piecemeal bargaining efforts of individual unions. The emission standards must be established by public authorities through consideration of all industrial sources so that the emission controls might be not only comprehensive and effective but equitable and flexible.

The Steelworkers, both as a union and as individuals, have long been involved with environmental action through educational conferences, participation in public hearings, and legislative support.

The United Steelworkers of America will continue to be an active force for pollution control on all fronts because we never have subscribed, nor will we ever do so, to the theory that social ills are a necessary cost that must accompany technological advancement.
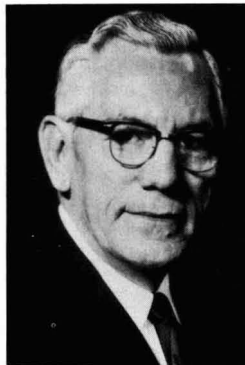
I. W. Abel, president of United Steelworkers of America, is also a member of the President's Task Force on Air Pollution and a director of the National Center for Solid Waste Disposal

Big Problems Come in Small Packages

Like beakers, bottles, capsules, crocks, flasks, jars, trays, tubes and vials. Whatever is required to package an effluent sample, Environment|One's Measurement Services Division (MSD) will use it . . . wherever and whenever it's required.

With analysis capabilities of hundreds of samples simultaneously, MSD offers a total environmental measuring service to industry, government and consulting engineers. This means full-scale characterization studies of WATER SUPPLY, INDUSTRIAL and COMMUNITY WASTEWATER, and ATMOSPHERIC CONSTITUENTS. All backed by the most sophisticated laboratory instrumentation, branch labs in selected metro areas, mobile equipment for field stack sampling and wastewater analysis surveys, specially equipped aircraft for wide area ambient air or plume tracing studies, and a large staff of licensed treatment plant operators, professional engineers, meteorologists, chemists and technicians. Our small packages are available for your big problems 24 hours a day, 7 days a week. Call collect (518/346-6161) or write James L. Setser, Manager, Measurement Services Division.

environment | one
CORPORATION
PROTECTING MAN'S ENVIRONMENT
2773 Balltown Road • Schenectady, New York 12309

environmental currents

Federal government flexes its clean air procurement muscle

By an Executive Order of June 29, President Nixon has instructed each federal agency, which either lets grants, loans, or contracts for the procurement of goods, materials, or services to let them only to companies and the like which are living up to the provisions of last year's clean air amendments (ES&T, February 1970, page 106). Periodically, the EPA administrator will publish lists of those facilities that have been convicted of clean air violation offenses; these companies become ineligible for federal monies until they correct their violations. The order does not apply to contracts, grants, or loans involving the use of facilities located outside the U.S.

1975–76 Clean Car Goals

Emissions	Grams per mile
CO	3.4
Hydrocarbons	0.41
NO$_x$	3.0[a]
	0.4[b]

[a] Beginning 1973 models. [b] Beginning 1976 models.

EPA: Automobile goals for 1975–76 are finalized

The regulations for '75–76 automobiles which have been promulgated by the Environmental Protection Agency certainly meet the 90% reduction requirement that was spelled out in last year's clean air amendments. "The costs resulting from implementation of these requirements will be substantial both to the industry and the consumer," says EPA's William Ruckelshaus. But realizing that in the U.S. automobiles are responsible for more than two thirds of the CO burden, one half of the hydrocarbons burden, and two fifths of the nitrogen oxides burden, the controls are necessary to protect the public health. The new test procedure which went into effect with the '72 test model vehicles consists of both cold and hot start tests; results are weighted 43% on the cold data and 57% on the hot data. In a move to take the lead from California in setting the national pace for automobile pollution controls, the EPA denied a waiver to California for its assembly-line testing of every vehicle manufactured for sale in the state; the testing would have started with 1973 production models.

AID sets up environmental protection watchdog

The State Department's Agency for International Development recently formed a committee on environment and development that will help developing countries to meet their upcoming environmental obligations. Under the direction of James Fowler, the committee will examine carefully the environmental impact aspects of proposed AID projects and consider environmental effects before authorizing loans for dams, bridges, airports, power plants, roads, and the like. AID is also encouraging developing nations to participate in the 1972 U.N. Stockholm conference on the human environment, and points out that education and better understanding are the operational watchwords in dealing with these nations.

NSF project: How to assess the U.S. quality of life?

As part of the National Science Foundation's Project RANN (research applied to national needs), a $3.1 million award has been made to the University of Michigan's Institute for Social Research (ISR) to answer this question. ISR Director Angus Campbell says that special emphasis is to be placed on social indicators which he defines as statements about the social health of all or some parts of the nation. Priority also will be given to so-called social variables, ranging from the quality of products and services to public safety and the environment, which can be improved by change in policies. Hopefully, these indicators will be useful as they are linked to social policy and administration.

ISR's Campbell

STATES   **West Virginia, Virginia toughen stand on coal-area pollution**

The West Virginia Air Pollution Control Commission has ordered the Preston County Coal and Coke Co. to phase out business within two years for failure to meet air pollution regulations. The company looked at pollution control methods for its beehive coke ovens and concluded there were none. The commission has ordered 50% reduction by July 1972 with all operations ceasing by July 1973, but will reconsider should the company solve its pollution problem. The Virginia State Air Pollution Control Board, inspecting the state's coal-producing areas this month is developing rules on pollution from coal refuse areas, coke ovens, and charcoal kilns.

Polluting industries barred from Delaware coast

Gov. Russell Peterson signed landmark legislation in June barring heavy industry from Delaware's coastal areas. The immediate effect of the legislation is to block Shell Oil Co.'s construction of a $100 million refinery near Smyrna. The governor said that heavy industry was incompatible with recreation and would lead to pollution of the popular beaches on Delaware's lower bay and Atlantic Ocean coast. "Jobs (created by new industry) are very important to our people," emphasized Peterson, "but so is the overall quality of our environment."

Gov. Peterson

Western states create geothermal energy council

Last month, a steering committee formed by the Washington Department of Natural Resources met to establish the Western States Geothermal Council. The purpose of this semitechnical organization will be to encourage a broad spectrum of R&D programs in the geothermal energy field. This group thus far includes representatives from the U.S. Department of the Interior, California, Washington, Oregon, New Mexico, and Mexico.

Tennessee to reopen formerly polluted lake

Lake Nickajack, one of Tennessee's most scenic lakes, will open once more to recreation this summer. The Tennessee Valley Authority posted "warning" signs three and one-half years ago because of water pollution from the Chattanooga area at the head of the 46-mile lake. However, Chattanooga's new $8 million secondary sewage treatment plant is scheduled for operation this summer, and water in the lower portion of the lake is expected to be satisfactory for swimming and water skiing when the plant is in full operation.

Chicago ordinance muffles urban noise

A comprehensive antinoise ordinance aimed at muffling urban noise sources became effective last month in Chicago. Based on the A-weighted decibel scale, the ordinance sets specific noise limits on the major sources of urban noise—vehicles, construction equipment, and various powered tools. Noise levels were also established along boundary lines among manufacturing, business, commercial, and residential districts. (For more on noise, see ES&T, September 1970, page 720.)

environmental currents

Membrane halts groundwater contamination by landfill

The Warner Co. (Philadelphia, Pa.) has been awarded a patent for a landfill method which the company says protects groundwater from contamination. Key to the package is a liquid impermeable membrane which covers the landfill sub-base. The membrane is sloped to a sump collection point, and solid waste is deposited in the usual fashion. Water flowing through the refuse in the landfill filters through the pile until it reaches the membrane, drains to a collection point, and is piped away for treatment. Compaction is facilitated, the company says, making it feasible to create mountains of solid waste for ski resorts.

Low emission automobiles are gearing up

The first three contracts to develop low-emission vehicle prototypes under the Federal Clean Car Incentive Program have been announced by the Environmental Protection Agency. Awards were made to Austin Tool Co. (El Monte, Calif.) for development of a small diesel-powered vehicle; the Chemical Construction Co. (New York, N.Y.) for development of a new approach to catalytic mufflers; and Petro-Electric Motors, (New York, N.Y.) for development of a hybrid powered vehicle using a heat engine-electric battery combination. Another hybrid car is being developed by a student–faculty team at the University of New Hampshire (UNH) without EPA support. The UNH car has a combination battery–propane power plant.

Unleaded gas use produces dirtier exhaust

Cars using unleaded gasoline yielded 57% more particulate matter than similar cars burning leaded gasoline, according to Du Pont scientist John M. Pierrard. To simulate road conditions, the test was performed in an idle tunnel on the Pennsylvania Turnpike. Filters were used to collect and compare particulate matter from four-car fleets of 1970–71 automobiles which were driven according to the federal automotive test cycle. Commercially available premium unleaded fuel with high aromatics content and leaded, average aromatic content gasoline were used. Tests also showed a reduction in atmospheric visibility as measured by intensity of white light. Auto exhaust from cars burning unleaded gas decreased light intensity 84% when compared with exhaust from cars using leaded fuel.
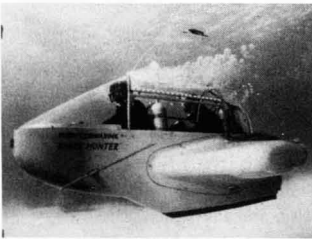
Submarine for pollution monitoring of outfalls

Pollution patrol sub

For the pollution control official who has everything, Perry Oceanographers, Inc. (Riviera Beach, Fla.) is offering the Perry Submarine Shark Hunter—a two-man submarine that has been developed for close-up detection, inspection, and monitoring of pollution sources. The Shark Hunter is a wet submersible sub, one in which the hull is flooded during operations, and looks like a single-wing airplane. Operators in scuba gear can descend to depths of 150 feet to inspect outfalls. The submarine is driven by a 4.5 hp motor and has two forward and two reverse speeds. The battery lasts for 2.5 hr at cruising speed and 1.5 hr at top speed of three knots.

INDUSTRY

Chemical company abandons deep well injection system

Hercules, Inc., will phase out a system of experimental deep well injection sites at its dimethyl terephthalate plant (Wilmington, N.C.). In 1968, Hercules received a five-year permit from the state to dispose of 300,000 gallons of weakly acidic waste per day by deep well injection, but various mechanical problems recently have plagued the installation including a pressure leak. Although the offending wells have been sealed and new units are working fine, Hercules will switch to surface treatment facilities by July 1, 1973, the day after the permit expires. State environmental agencies are taking a harder look at deep well injection, Hercules notes, and the company concludes that surface treatment will be more attractive in the long run.

Metallic can pickup

Steel industry execs plan to recycle all their cans

Seven major steel companies have announced plans for 80 additional can collection stations in 39 cities in 13 states. Eventually, each of the 60 billion bimetallic cans that are made each year could be recycled. Some 168 centers are operating now; more are planned in the future. "Of all the raw materials used to make steel in this country during the past 30 years, between 52 and 57% has been scrap," says George A. Stinson, president of National Steel. The other half-dozen steel companies include Bethlehem, Jones & Laughlin, Kaiser, United States, Wheeling-Pittsburgh, and Youngstown Sheet and Tube Co.

Nonphosphate detergent manufacturers: "A safe product"

Sears, Roebuck and Co. and the maker of its Sears Phosphate-Free Laundry Detergent, DeSoto, Inc., have told the Federal Trade Commission that their nonphosphate detergent is both safe and effective. Responding to charges by spokesmen for phosphate detergents that no safe substitute for phosphates exists, Sears cited evidence from independent testing laboratories which, the company says shows the Sears formulation has cleaning efficiency "comparable to phosphate detergents in either hard or soft water." The Sears detergent contains no sodium metasilicate, a substance used as a builder in several phosphate-free detergents which the FDA says may pose a health hazard. Tests show the Sears formulation is "equally as safe as the major namebrand phosphate detergents now on the market," DeSoto says.
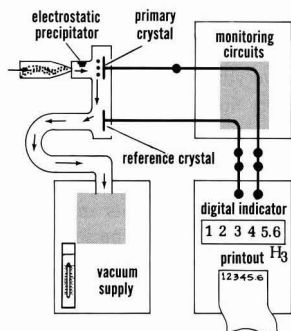
Thermo-Systems develops particulate matter monitor

A unique piezoelectric particle microbalance for monitoring particulates in the atmosphere has been developed by Thermo-Systems, Inc. (St. Paul, Minn.). Called the particle mass monitor, the instrument can effectively replace the filter-weighing procedure commonly used for determining particulate matter (for a discussion of instruments and procedures used in atmospheric monitoring, see page 678 of this issue). The sensor is an oscillating quartz crystal. An electrostatic precipitator deposits particulate matter on the surface of the crystal, and the resonance frequency of the crystal decreases linearly with the mass of particle deposition. Mass is monitored and recorded with a digital counter and printer.

environmental currents

Canadian clean air bill becomes federal law

Concurrent with June's 64th annual meeting of the Air Pollution Control Association in Atlantic City, N.J., the Canadian Air bill became the first major federal law dealing with air pollution. The Canada Water Act (joining federal and provincial powers) was passed in 1970 (see ES&T, July 1970, page 547, "Canada cracks down on pollution"). APCA's new president is W.B. Drowley, director of the air management branch, Ontario Department of Energy and Resources Management.

Economic growth encouraged; emissions must be regulated

West Virginia representatives explained the state's regulation VII, limiting the solid and liquid particulate matter emitted from manufacturing processes, which is the basis for the EPA implementation plan process weight curves. As is, the EPA plan does not allow for increased emissions due to industrial expansion. In the West Virginia statute, any expanded portion of the manufacturing plant may have the same efficiency percentage for emission control as the older portion of the plant, thereby encouraging industrial growth.

Pneumatic pipeline reduces coke oven emissions

Allied Chemical Corp. discussed a new process to eliminate as much as 70% of the total emissions from coke oven operations. Coal—dried and preheated in a continuous fluidized bed—is conveyed to the coke ovens via a pneumatic pipeline system (instead of the conventional larry charging car) using superheated steam. This process not only reduces air pollution emissions, but increases productivity as much as 45%.

Small precipitator tackles large cleanup jobs

Recently introduced by American Standard (Hightstown, N.J.), the Mirror Grid precipitator is a unit far smaller than a conventional electrostatic precipitator but which accomplishes comparable results. Mirror Grid can increase the efficiency of existing air pollution control equipment, enabling users to meet or exceed existing air pollution control codes. Initially, American Standard foresees the use of their new precipitator on power plants and cement companies, two industries for which performance standards for new stationary sources were proposed last month.
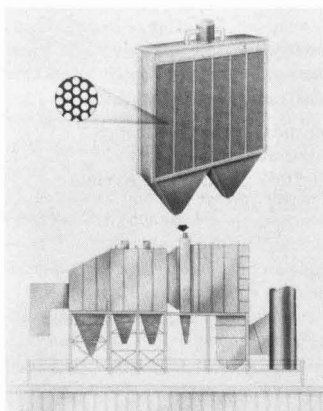
Mirror Grid unit

Municipal incinerator emissions studied at NYU

New York University professors, Arrigo Carotti and Elmer Kaiser, tested gaseous emissions from a typical, modern U.S.-designed incinerator located in the town of Babylon, L.I., N.Y. Results showed that chloride is a major constituent of the flue gases from the municipal refuse incinerator as well as carbon dioxide, carbon monoxide, and water vapor. Organic acid emissions are at levels comparable to those for NO_x and SO_2 which are receiving most of the environmental attention today. Fluoride also occurred in significant concentrations.

Can plastics be incinerated safely?

The United States leads all other countries in the world in many things including per capita production of solid waste handled by municipal authorities. Of this solid waste (more than 190 million tons per capita each year) 1.9% is plastic, a seemingly small percentage. But the amount of plastics is increasing each year, and the present problems associated with their disposal are large. By 1980, plastics are forecast to account for 2.8% of the collectible waste, according to a Manufacturing Chemists Association (MCA) study by DeBell & Richardson, Inc. (Enfield, Conn.).

As more and more areas of the country turn to incineration as a means of waste disposal, certain legitimate questions have been raised about what happens to plastics during and after incineration. Are plastics one of the environmental villains? Do they play a major role? Do plastics break down to emit hazardous air pollutants? Scientists say no, but the public at large does not yet seem convinced.

Packaging materials account for the majority of plastics added to municipal refuse. And this is seemingly where the problem lies and perhaps much of the current plastics dilemma. In today's world of plastics, the types of plastics are just as divergent as their uses (see box). Polyolefins—polypropylene and polyethylene—account for 55% of the total plastics in solid wastes; polystyrene, 20%; polyvinylchloride (PVC), 11%; and all others, the remainder.

At present, four solid waste management practices are available for the disposal of solid wastes containing plastics. Each has its advantages and disadvantages. The practices include:

• Sanitary landfill. Cities are running out of open space for landfills, and in existing landfills, plastics do not rot or degrade, but this can be considered an asset by preventing excessive settling as well as producing no water or air pollutants.

• Reuse. Although this practice is on the upswing, it does not yet enjoy wide acceptance because of economics.

• Biodegradable products. Research is presently underway to develop plastics to degrade from exposure to ultraviolet light from the sun, but such exposure may also adversely affect shelf life of packaged items.

• Incineration. The reduction in volume of solid wastes is nearly zero (up to 95% volume reduction). However, people fear noxious chemicals as products of incineration.

There are several types of incineration—industrial, commercial, and municipal. Industrial incinerators have specialized problems in dealing with large amounts of selected refuse. In a case like this, if incineration is chosen as the disposal method, advanced technology must be applied to both equipment and process. For commercial establishments (restaurants, stores, etc.) plastics used in packaging may also be in large amounts. If municipal disposal facilities are not used, commercial incinerators have to be equipped to handle high concentrations.

Incinerating any refuse (containing plastics) in obsolete, inefficient municipal facilities can create certain problems. Incomplete combustion results in particulate matter emission by most materials and possible clogging of grates by both plastics and other materials. Furthermore, incinerating any organic material (natural or synthetic) releases some gases which can result in corrosion of some metallic components in the incinerator.

In Japan and Sweden, for example, the percentage of plastics in solid waste has already reached the level forecast for the U.S. by 1980. Technical reports state that no new problems occur when refuse containing plastics is incinerated. Furthermore, many European incinerators are actually power plants, utilizing the Btu content of refuse. The newest municipal unit similar to European models in the U.S. is in Chicago (see ES&T, March 1971, page 207, "Plants burn garbage, produce steam").

"We're wasting a great resource by sending it all up in smoke," comments Ralph L. Harding, Jr., executive vice-president, Society of the Plastic Industry, Inc. (SPI). Plastics mixed with ref-

Uses of common plastics

polyethylene
films and sheets for packaging and covers
molded containers, tubing, and piping
electric wire insulation
coatings on metal, paper, and other surfaces
bottles
textiles
bristles
upholstery
window glazing
cordage

polyvinyl chloride
electric wire insulation
garden hose and other tubing
gaskets
shoes
rainwear, aprons, and other garments
curtains, draperies
upholstery, wall coverings
floor tiles, panels
phonograph records
packaging, frames
household appliances
luggage

polystyrene
refrigerators
air conditioners
packaging
wall tiles, cabinets
dishes, tumblers, lids, handles
lamination of fabrics
bonding of adhesives

polyurethane
household appliances
padding for mattresses and upholstery
interlinings for overcoats and sleeping bags
soundproof walls
heat insulation
life preservers
foam rubber applications
cigarette and air filters
packaging

use in low percentages not only burn readily but aid combustion. Although plastics rarely comprise more than 1.9% of collected municipal solid waste, the heat value in Btu's per pound of refuse is raised considerably and improves incineration efficiency of wet garbage. Incomplete combustion is minimal with good incinerator design and reasonable care in operation.

Incineration

Packaging wastes constitute a significant and growing faction of the total solid waste load. Each year 2.55 million tons of plastic is thrown away, according to the National Industrial Pollution Control Council (NIPCC) report, "Plastics in Solid Waste." For too long, solid waste collection and disposal have been classified as low priority.

A variety of waste is emitted by incinerators. These include fly ash, smoke, and gaseous products such as carbon dioxide, water vapor, sulfur oxides, hydrogen chloride, and others. No smoke is emitted if combustion is complete. Scrubbers then can remove gases and trap particulate matter before their discharge to the atmosphere.

Incinerator gases can be cleaned by scrubbers using water as the scrubbing medium. The method is used on municipal incinerators in the U.S. where stringent regulations are in effect. The gaseous products—hydrogen chloride, sulfur dioxide, sulfur trioxide, organic acids, and aldehydes—can almost completely (up to 90%) be absorbed by the scrubber water. Hydrogen chloride and sulfur trioxide are removed with high efficiency through intimate contact with water. When acidity builds up in the runoff water, soda ash may be added to raise the pH. Carbon steels and ordinary stainless steels used in scrubber construction are attacked by hydrogen chloride, sulfuric acid, and nitric acid, but scrubbers with rubber, ceramic, or even PVC linings resist acid attack.

Emissions

Of course, emissions are the major criticism of plastic incineration, especially PVC. Hydrogen chloride, reported to corrode incinerators and pollute the air, results from burning PVC. Polystyrene can cause dense smoke and objectionable odors, and polyolefins may melt and drip through the grates or clog the system if burned at too low a temperature.

The fact that PVC emits hydrogen chloride gas when burned links the gas with possible air pollution and corrosion damage to incinerators. However, the plastic industry argues that properly designed and properly operated incinerators will easily handle PVC in the typical municipal waste load without damaging the incinerator or the environment. "If all plastics were removed from incinerator refuse, the materials remaining would still contain a substantial amount of chlorides and other corrosive and polluting agents. If our incinerators were properly equipped and operated, emissions of all pollutants, including hydrogen chlorides, would be within accepted standards," according to NIPCC.

Most plastics in municipal refuse "don't create severe problems in the incinerator," says a spokesman for the Environmental Protection Agency (EPA). "The specific question with plastics—the major controversy—has to do with halogenated plastics, PVC in particular." From both the industrial and consumer point of view, PVC is a good plastic. It is inexpensive to produce, and has excellent properties—clearness, rigidity, alcohol resistance, and impact resistance.

Due to the controversy over hydrogen chloride corrosion of incinerators burning residue containing PVC, EPA is supporting at least four specialized research projects (Syracuse University, Battelle Memorial Institute, University of Michigan, and the University of Texas at Austin) to investigate plastics and incineration.

"Corrosion is manageable," emphasizes SPI's Harding; "You cannot say that the hydrogen chloride from plastics isn't contributing to corrosion, but it is documented that it is not a major or prohibiting factor." The amount of hydrogen chloride emitted from the stack becomes an academic point when a scrubber is used. There is no air quality standard for HCl from scrubbers yet, but the point is, continues Harding, "the scrubbers that you're going to need anyhow for the other things being incinerated are going to take care of any other air pollution problems," as far as hydrogen chloride is concerned. If plastics were taken out of all inadequate incinerators, they (the incinerators) still would not meet clean air standards.

NYU study

In view of the notorious reputation of plastics' effects on the environment, SPI sponsored a New York University

(NYU) research project designed to pinpoint the effect of burning plastics on incineration systems and the environment in general. In June, Elmer R. Kaiser and Arrigo A. Carotti, from NYU's Department of Chemical Engineering, announced the results of a year's experimentation.

Kaiser and Carotti added individual types of plastics at the rate of 2% and 4% to municipal refuse burned at the Babylon, L.I. incinerator. Four plastics were used in these tests—polyethylene, polystyrene, polyurethane, and PVC—as representative of commonly used plastics. Each test was run with a specific plastic that was mixed with others already in the refuse.

The Babylon plant (with two furnaces feeding one stack) does not meet present New York regulations (fly ash emission requirements)," explains Kaiser. "It was built in 1966 with a water spray system to clean flue gases of fly ash to a certain point." Since there were no scrubbers, Kaiser and Carotti built pilot scrubbers to treat sample airstreams, and ran tests simultaneously, with and without adding plastics to use the same base refuse. Odor was measured, and also, a smoke meter drew hot flue gas through for Ringlemann readings.

Findings

Results of the four plastics tested agreed with predictions. Polyethylene, with its high Btu content, speeded up combustion as expected. On a Ringlemann scale of 1–5, polyethylene emission was less than 1. The flue gases had a slight odor which disappeared after being diluted in the stack. As far as emissions are concerned, the chloride content did not vary much from those furnace gases without the added plastics. There was a small amount of fluo-

rine—from aerosol cans containing Freon gas. As more plastic was burned, the resulting higher temperature caused more NO_x emission, (which is small compared to power plants). The organic acid content is the result of incomplete combustion; therefore, it was higher without the added polyethylene (whose Btu contribution aided combustion).

Polystyrene has the same general story as polyethylene. The burnout was good; smoke rating was zero. (Polystyrene has the reputation of being quite a smoker when burned in the open.) "In the temperature turbulence and high oxygen condition in a municipal incinerator, polystyrene burns beautifully, and by chemical analysis (reflecting its hydrocarbon nature) it should," explained Kaiser.

In this incinerator polyurethane volatized easily, leaving a very fragile shell of carbon that breaks and completely burns. There was slightly more smoke in the incinerator, which was not noticeable in the stack outside. The NO_x content increased due to increased temperature, and the aldehydes were higher than in the other plastics, but still were at a very low level.

For PVC, more detailed tests were run to check its characteristics thoroughly. The question is how much is caught in the scrubber.

"After measuring chloride in base refuse and the total chloride added, we found less chloride coming out through the stack than went in," continues Kaiser. Then, "85–95% chloride is captured by the scrubber. Despite the fact that hydrogen chloride is being produced from burning refuse and plastics, something can be done about it." If a scrubber is added, it will remove hydrogen chloride.

As for the question of hydrogen chloride corrosion of incinerator parts, Kaiser and Carotti removed sections of the grates to examine and test them for corrosion. There was some reaction with the grate, and chlorine was detected in the tests. "There will be some chloride attack, but many other kinds of attacks occur at the same time," explains Kaiser. Incinerators are also damaged mechanically—large pieces of materials hitting the furnace, wear by sand or grit, and heat. "The main chloride attack occurs in the scrubber (if made of nonresistant materials)," summarizes Kaiser.

Kaiser explained that inefficient incinerator operation causes many of the problems. Incineration plants will become more efficient as emission standards are set.

However, Kaiser points out, plastics have not and will not contribute to incineration costs. In fact they add to the Btu value, which has proved to be quite handy during rainy spells. (The incinerator operators at Babylon asked to keep the extra plastics for a rainy day). Furthermore, plastics are not the sole cause of adding scrubbers to incineration equipment.

What other components in municipal rubbish cause real problems in incinerators? Grass presents one of the worst problems, especially during the summer season. It sifts through the grates, mats, does not distribute easily, and emits chlorine and nitrogen. Watermelon rinds and garbage containing much water may be seared on the outside while completely unburned on the inside (creating quite an odor). If more than a few auto tires per ton of rubbish are added, there will be problems with smoke. Aluminum melts and runs down through or piles up on the grates. Magnesium reacts thermally with iron oxide to form globs of steel on the grates. Sodium (from chemistry labs) can cause serious fires. Ammunition is a problem. Aerosol cans will pop and can damage equipment and injure employees. Also fats —a 5-gal can of lard once melted and ran through to the firebox below the grates. The extra high temperatures caused the steel to twist and distort. Plastics, in undistributed loads, can-

not burn properly and may run into the firebox where they will eventually burn out. So where does the real problem lie?

New products

Several new plastics have recently come on the scene that do not give off any harmful emissions when incinerated. Barex 210 resin (Vistron Corp., Cleveland, Ohio) is an ultrahigh barrier packaging plastic and "is safely disposable by incineration without producing noxious or harmful gases or ashes," emphasizes Jim Idol, Vistron's polymers research manager. This plastic is 75% acrylonitrile but still has all the desirable packaging characteristics.

Monsanto's Lopac is a nitrile-based polymer. "The combustion products of municipal wastes containing significant quantities of Lopac containers do not differ significantly from combustion products without Lopac containers," explains M. F. X. Gigliotti, Monsanto's special projects director. (Kaiser and Carotti also studied the incineration of both Barex and Lopac and found no significant differences in municipal incinerator emissions.)

Presently, Coca-Cola is market testing over three million Lopac containers, and Pepsico has been conducting similar tests with Barex 210.

American Cyanamid's XT polymer, an acrylic multipolymer, contains no halogens that would form toxic gases on incineration. XT is presently used to contain peanut butter, olive oil, salad dressings, spices, and other food items. Eastman Kodak, Celanese, and others have cellulosic materials in sheets or films that will combust into harmless products.

Legislation

Many states and local areas are considering legislation to tax, restrict, or ban the use of plastic products. "Many of the bills are obviously aimed only at assuring voters that their representatives are concerned," says SPI's general counsel, Jerome H. Hechman. At present, legislation directed at plastics is pending in at least 13 states. (Roselle Park, N.J., has recommended that pending restrictive plastic legislation not include Lopac or Barex.) In New York City, the city council recently passed a tax of 2¢ per plastic container. (At press time, SPI was planning a lawsuit contesting the constitutionality of such a measure.)   CEK

Direct dumping will probably
not be satisfactory for long; burning
is the most likely solution

Sludge handling: the hardest

Sludge, like gold, is where you find it. And you find it virtually everywhere. It is, according to Robert S. Burd, deputy director of the Water Programs Office's Portland-based Region X, "the most troublesome phase of sewage and industrial waste treatment." All indications are that things will be more "troublesome" in the next few years—hardly good news to municipalities and industries already knee-deep in the slop of civilization—as conventional sludge disposal techniques get disapproving looks from the Environmental Protection Agency.

Operationally defined, sludge is any semiliquid waste with a solids concentration in excess of 2500 parts per million. It may be municipal or industrial in origin. Either type may be further classified as primary sludge—derived from sedimentation with no additional treatment—or secondary sludge, which includes activated sludge, mixed sludges, chemically precipitated sludge, and the like.

Although sludges vary widely in solids content, composition, and handling characteristics, sludge handling falls roughly into three categories—conditioning, dewatering, and final disposal. By and large, the technologies available for sludge handling have been around for a long time.

Conditioning of sludge is most often accomplished by chemical means. The theory is that small, dispersed, charged particles can be made to coalesce by adding a chemical which ionizes in water to provide charges of the opposite sign. The chemical conditioner reduces the charge on the suspended particle and thus decreases its tendency to bind water. Settling by gravity or mechanical means is thereby enhanced.

Washing sludges with freshwater—a process known as elutriation—is sometimes done if it is desirable to lower the alkalinity of the liquid portion of the sludge. Elutriation often reduces the amount of conditioner which must be used. The most commonly used chemicals for flocculation are ferric chloride and lime—either separately or together depending on the type of sludge.

Synthetic polymers can also be used to promote flocculation. Such polymers are water-soluble and have end groups which ionize in solution to provide binding sites for charged sludge polymers. Polyelectrolytes can be either anionic or cationic. Sometimes nonionic polymers are used that promote settling by forming bridges between particles in suspension.

Recently, a steam-heating process has been substituted for chemical conditioning with promising results (see "Porteous process unit readied for startup," ES&T, December 1968, page 1068).

Dewatering

After conditioning, sludge is dewatered to the greatest extent practical. A wide variety of methods for sludge dewatering is available, depending on the type and amount of sludge to be treated, availability of land, and plant location. By far the most popular method of mechanical sludge dewatering is vacuum filtration which offers a relatively cheap, rapid means for removing solids from nearly all types of sludge.

A typical vacuum filtration unit consists of a cylindrical drum which revolves through a vat of sludge (see below). A vacuum applied through the drum and filter belt traps particles on the belt as the drum rotates through the vat. The vacuum further drys and dewaters the deposited solids as the drum rotates out of the vat. Just before the solids cake would return to the vat, it is scraped from the belt and collected for final disposal. Various engineering refinements such as filter-medium cleaning systems and conditioning equipment combine with the basic design to produce a cake with a high solids content—a significant advantage where the final disposition of sludge is to be combustion.

Another frequently used mechanical method of dewatering is centrifugation. The design most commonly used today combines a rotating outer

Belt-type vacuum filter

Filter medium belt
Sludge solids
Drum
Discharge roller
Cake deflector
Vacuum
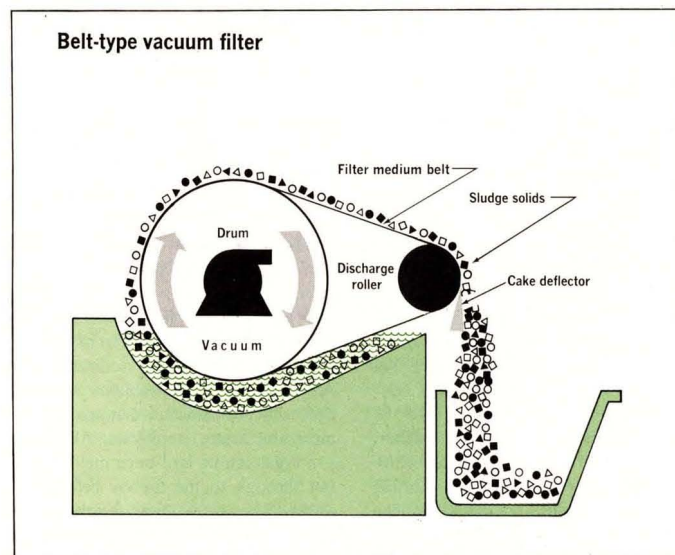
phase of waste treatment

bowl with an inner screw-type conveyor (see diagram below).

Sludge is pumped through the hollow conveyor shaft along the axis of the horizontal rotating bowl. Sludge is flung against the inner wall of the bowl through openings in the shaft and solids are compacted in the bowl by centrifugal force.

Both the screw and the bowl rotate in the same direction, but the conveyor rotates slightly more slowly. Compacted solids are moved by the conveyor to one end of the bowl and discharged while the liquid portion, or "centrate," is discharged over wiers from the opposite end of the bowl. Filter presses which physically squeeze the water from sludges offer an alternative method of sludge dewatering for some applications. They offer the advantage of high solids concentration but since they are, by and large, batch process machines, high labor costs make them impractical for dewatering large volumes. The recent addition of automated cake discharge and better engineering have resulted

in an upsurge in popularity of filter presses—particularly among industrial users. Some municipal treatment facilities in the United Kingdom are using filter presses with encouraging results.

Despite the emphasis on mechanical processing, however, land methods of sludge dewatering continue to be the cheapest and most widely used. Sand beds and lagooning are often the most practical ways to deal with large quantities of sludge. Dewatering on sand beds takes place by drainage and evaporation. Beds may be either open or enclosed and supplied with artificial heat. Although widely used for sewage sludge, sand beds are generally acceptable only for dewatering digested sludge. The availability of land and climatic factors weigh heavily in determining whether or not sand beds can be used.

Lagooning is the most popular method of industrial sludge dewatering and is also widely used to dewater municipal sludge. Drying lagoons are periodically cleaned of settled solids

and can then be reused.

Whatever the method of sludge dewatering, final disposal of the solid residue poses problems. With or without conditioning or dewatering, sludge can be disposed of by landfill, barging or pumping to sea, or by incineration. Where land is available and local codes permit, there is no more economical method than landfill. Direct dumping to land or the sea can cost as little as one sixth the amount which would have to be spent in mechanical dewatering and sludge combustion, according to EPA's Burd. But, in Burd's view, so cheap an option is unlikely to be available for very long. Although EPA has no present legal authority to prevent ocean dumping of sludge, EPA is working to extend its authority to prohibit these practices. Water bills now before Congress contain provisions strengthening the authority of EPA to regulate sludge disposal. In the meantime, the agency is twisting arms by refusing to approve applications for federal funds for municipal treatment plants which do not measure up in their proposed sludge-handling procedures.

Although several processes for disposing of sludge show promise—among them pyrolysis—Burd thinks incineration will prove to be the most valuable. Burd is a "great believer" in incineration and thinks it is easier to clean up emissions from properly designed and operated incinerators than it is to control pollution from dumped sludge. An ideal system for sludge disposal, Burd says, would be a combination of mechanical sludge dewatering, incineration, and sanitary landfill of the ash.

Interestingly enough, Burd remarks, the ever increasing amount of sludge being produced is partly the result of more extensive treatment of waste waters. More sophisticated treatment methods are resulting in sludges that are more difficult to handle. This, he notes, intensifies the need to dispose of sludge by methods other than barging or landfill. HMM

Horizontal sludge centrifuge

Conditioned sludge in

Liquid centrate discharge

Sludge solids discharge
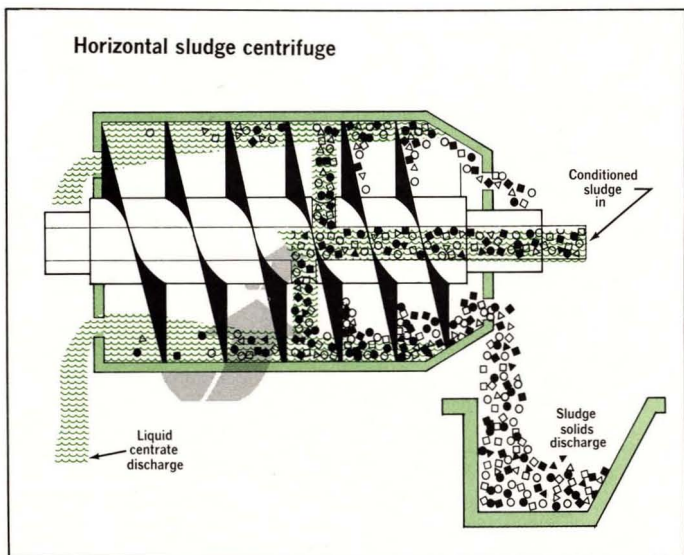
Tax incentives for clean industries

Economic relief for pollution control facilities is possible with existing regulations including grants in aid, property tax exemptions, income tax credits, and accelerated amortization

To the economy-minded industrial executive, the next best thing to not having to make any pollution control expenditures is to be able to write them off quickly on his corporate income tax. Or so a whole host of governmental agencies—from the federal Internal Revenue Service to the treasury divisions of many state governments—seem to believe, judging from the range of tax incentives now becoming available.

The most redundant thing one can say about spending for pollution control is, of course, that it is generally not revenue producing. So when expenditures are made, any money-saving concessions that government can make are useful to those doing the spending. There are several ways that government can help industry with pollution control expenditures:

• Grants-in-aid. These are sometimes available, usually for processes that have not been adequately demonstrated elsewhere in the same industry (see ES&T, June 1971, page 498).

• Exemption from property taxes. This approach is favored in many states, but may be restricted to that portion of the facility which can be demonstrated to be utilized for pollution control; any portions producing a marketable by-product may not be eligible for the exemption.

• Exemption from sales and use taxes. The exemption applies to the cost of the individual pieces of equipment which together make up the abatement facility.

• Income tax credits. In some states, a fixed percentage of the cost of installation (generally 5%) may be directly deducted from taxes due. A federal 7% investment tax credit which was in force for expenditures of any kind, until suspended in 1966, was retained for pollution control spending, until repealed in 1969 (see below and ES&T, February 1970, page 103).

• Accelerated amortization. Whereas pollution control equipment might in practice be expected to be operated for more than 10 years, many states—and the federal government, see below—have initiated rules by which the entire cost of a pollution control facility can be written off over a much shorter period, usually five years. The proportionate cost is deducted from other taxable income in each tax year.

While each state seems to favor rather different incentives from its neighbor (see box), it is true to say that for many firms the greatest interest of business with tax credits and other incentives lies with the federal government, and more specifically with the Internal Revenue Service. The reason for this, of course, is that the federal tax bite can be much larger than that taken by the state in which the facility is located.

Federal incentives

The first indication from Congress that pollution control expenditures would be given more liberal consideration than other types of spending came in 1966. Then, the 7% general investment credit that had been in force since the investment-stimulating days of the Kennedy administration was suspended, but an exception was made for pollution control facilities. Those who made expenditures for facilities that were demonstrably for pollution control could deduct 7% of the cost from federal income taxes.

The 7% investment tax credit was repealed in entirety by the 1969 Tax Reform Act. In its place were instituted provisions for accelerated amortization of pollution control capital expenses. Conditions under which a facility could qualify for the faster write-off were tightly drawn in the act and, in fact, the detailed regulations were not published in complete form until May of this year. The main reason for the delay, which industry has bitterly criticized, was that qualifying facilities must be federally certified (they must, in addition, be certified by the state in which they are located). Since almost the whole of 1970 was taken up with the wheel-spinning that resulted in the creation of the Environmental Protection Agency (EPA) in December, it was not until 1971 that the federal government was in a position to take on the certification job.

The May 26, 1971, *Federal Register* spells out the EPA's certification requirements. Treasury Department regulations governing the accelerated amortization procedure are given in detail in the May 18, 1971, *Federal Register*. Basically, guidelines and regulations specify that, for expenditures to be eligible for accelerated depreciation:

• The plant to which the facility is attached must have been in operation before Jan. 1, 1969. Treatment facilities attached to plants commencing operation after that date are ineligible, no matter when they were installed. Owners of eligible facilities can write off their cost in 60 months provided several other criteria are met:

• Treatment facilities must be installed after Dec. 31, 1968 and before Jan. 1, 1975.

• Building cost will not be included unless the sole purpose of the building is to house a treatment facility.

• A treatment facility used in connection with plants built before 1969 (which are eligible, see above) and with plants built after 1969 (which are not) may nevertheless be eligible for the fast write-off; EPA will determine how much of the facility's cost

is allowable to the earlier, eligible plant.

If only part of the facility is for pollution control, EPA will make a determination of how much of the total cost can be subject to accelerated amortization. If the facility has a useful life of more than 15 years, only that portion of its cost "attributable to" the first 15 years of its life is eligible for accelerated depreciation; the rest of its cost must be amortized over its actual useful life. If it appears to EPA that the costs of a facility will be recovered by profits (for instance, from sale of a by-product), the facility will not qualify.

Forms for the federal certification procedure will be made available in EPA regional offices around the country (see list of offices, ES&T, June 1971, page 498). State certification, which is also required, must be applied for separately. The necessary certification forms, or letters indicating that they have been applied for, must be submitted with the corporate income tax form. There is no separate schedule for pollution control cost write-offs; the taxpayer must add a sheet to the regular depreciation schedule. Details are given in the May 18 Federal Register.

Reaction from taxpayers

Despite this evidence from state and federal governments alike that industry's efforts in the field of pollution control can earn them a tax break, industrialists have not exactly been falling all over each other in profuse thanks to a munificent taxing authority. In fact, they have been quite critical.

The National Association of Manufacturers, in an official position statement, has criticized several features of the federal accelerated amortization program which, it says, have rendered it "ineffective and its benefits illusory." The particular bones of contention are the requirement for dual—federal and state—certification, the tightly drawn eligibility dates for the facility and plant it serves, and the exclusion of profit-making facilities.

NAM plumps instead for an approach in which investment credits and accelerated depreciation would be combined. Such an approach could lead to much greater savings to companies making the pollution control investments. By the same token, of course, it would also lead to much greater revenue losses to the Internal Revenue Service.

It is probably too much to expect the U.S. Treasury Department—or, for that matter, any state treasury division—to be enthusiastic over plans that rob them of revenue, no matter how noble the goals. Former Treasury Secretary David Kennedy has given his opinion that the effectiveness of the accelerated depreciation provision is "doubtful" and that "overwhelming incentive for industrial pollution control will continue to be governmental antipollution enforcement action, or the threat thereof." He is probably correct, but any help with the spending for control will nevertheless not be refused, despite the critical words from industry.   DHMB

State tax incentives for pollution control facilities

State	Property tax exemption	Sales and use tax exemption	Income tax credit	Accelerated amortization
Alabama	■	■		
Arizona				■
Arkansas		■		
California				■
Connecticut	■	■	■	
Florida	■			
Georgia	■	■		
Hawaii	■	■		■
Idaho	■	■		
Illinois	■	■		
Indiana	■	■		
Kentucky	■	■		
Louisiana	■	■		
Maine	■	■		
Maryland		■		
Massachusetts	■	■		■
Michigan	■	■		
Minnesota	■		■	
Missouri	■	■		
Montana	■			
New Hampshire	■			
New Jersey	■	■		
New York	■	■	■	
North Carolina	■	■		■
Ohio	■	■		
Oklahoma		■	■	
Oregon		■	■	
Pennsylvania				
Rhode Island	■	■		■
South Carolina	■	■		
Tennessee	■			
Vermont	■			
Virginia				■
Washington		■		
West Virginia		■		■
Wisconsin	■			■
Wyoming	■			

Note: some of these incentives are also available for expenditures for other purposes
Sources: The Tax Foundation, Inc. and National Association of Manufacturers

Oil spill technology makes strides

Second joint industry-federal government conference
shows progress on all fronts—prevention, containment,
removal, treatment, and cleanup—in the last 18 months

Oil perhaps is the most widespread of any pollutant in the world's waters—the rivers, the estuaries, and the oceans. The present national and international attention to future oil spills is none too early, at least considering the facts that:
• Each day, 15 billion barrels of oil are moved, and by 1980 the number increases to 18 billion barrels.
• Each year, an estimated 2 million tons of oil enter the oceans from tanker cargoes.
• Last year, there were 10,000 spills.

With the longest wetted coastline of any country, the U.S. understandably is not only involved but is setting the example with its oil spill national contingency plan, which now is being emulated by other nations. But other nations are concerned for different reasons. African nations, for example, are concerned because traffic off their coasts is 20 times more than that off the coast of any country. The United Kingdom, to mention another, is concerned because 75% of the known collisions has occurred in the English Channel.

In the past 18 months, the petroleum industry and the federal government, which shares in the oil spill responsibilities, have made some progress in all areas of the U.S. arsenal—contingency plans, international conventions, removal equipment, treating agents, and the like—since the first oil spill conference in December 1969 (ES&T, February 1970, page 97). At least this was the consensus at the recent second conference, the Joint Conference on Prevention and Control of Oil Spills, which was sponsored by the American Petroleum Institute (API), the Environmental Protection Agency (EPA), and the U.S. Coast Guard (CG).

Operations

The operational rationale on oil spills has not changed in principle in the past 18 months. The various lines of defense remain much the same as they were at the first conference—namely, prevention, first; containment,

second; removal, third; and treatment, fourth.

Prevention

Everyone agrees that prevention of oil release is the route to go, but few agree with the myriad proposals that have come along. To proceed with zero release of oil on the high seas is idealistic, for example, but the real snag with this proposal is that few ports have holding and disposal facilities for receiving such wastes.

Nevertheless, prevention is the marchword of today. Unofficially, the EPA goal is to reduce oil spills 80% by 1975. In addition, the NATO-CCMS (Committee on the Challenges of Modern Society) ministerial conference last December 4 reached agreement on oil spill prevention by 1975 and no release of oil into the high seas by 1980.

The two IMCO conventions—the intervention and liability conventions (ES&T, February 1970, page 99)—which have lain dormant for the last one and a half years are now before the Senate. Ratification by the U.S. would be a first step for dealing with oil spills at the international level. The majority of witnesses who testified at recent Senate subcommittee hearings on the conventions indicated that although these conventions are not perfect, early adoption by the U.S. would set the precedent for other nations to follow. What perhaps is even more encouraging is the fact that the API spokesman Herbert A. Steyn, Jr., indicated that the attitude of European nations was favorable for adoption of the liability convention. Other spokesmen included those from the American Institute of Merchant Ships (AIMS) and the National Audubon Society.

Some senators noted that another IMCO convention has been proposed which is concerned with the formation of a convention fund. The formation of this fund will be the subject for the forthcoming IMCO meeting in December in London. While some senators favor withholding U.S. approval on the two earlier conventions

until the third one has been incorporated, other senators foresee further delay in such a course of action.

Although member governments would not finance the liability insurance under the convention, this would be done by the P&I clubs (the protection and indemnity insurance underwriters for tanker liability), the member governments would, however, certify that the vessel had insurance liability.

IMCO, the Intergovernmental Maritime Consultation Organization—the specialized agency of the United Nations that provides cooperation in all shipping matters—has proved to be the appropriate international forum for oil spill problems since it was formed in 1959. More than likely it will remain the forum for oil despite a number of other forthcoming environmental meetings including the 1972 U.N. meeting on the Human Environment in Stockholm.

Meanwhile, on the home front the Coast Guard last month proposed new regulations for oil spills in the *Federal Register*. After a 60-day period for comment and a public hearing, the regulations will perhaps be finalized by the end of this year. Most likely, the regulations will:
• Prohibit the pumping of bilge and ballast waters into the navigable waters and waters of the contiguous zone.
• Prohibit the carrying of oil in bulkhead sections of tankers.
• Restrict the size of tanks in supertankers. If adopted, new tankers built after Jan. 1, 1972 would have to comply with this requirement.

Containment

With regard to equipment, oil spill personnel realize that today's equipment is more substantial than earlier equipment. The bolstering of equipment comes essentially from recognition of the fact that the equipment must deal with forces of nature; such an appreciation was not evidenced at the first conference.

Even though the nation has **better** booms, a better understanding of re-

moval techniques, and more field data with treating agents than earlier, what need becomes glaringly apparent now is the integration of the various combatants into an optimum system to handle the spill. For example, when to use one technique in preference to another? Under what operating conditions is it better to use one removal system in preference to any other such system or for that matter when to use treating agents in preference to removal?

Removal

Design studies have been completed on a number of removal devices. But additional funds now are needed for prototype development of these devices, followed by later field tests. To be sure, a better understanding of the oil removing capabilities of some promising new pieces of removal equipment was described at the conference. Many of these will be scaled and will undergo field tests in the near future. Such devices, for example, include:

• A floating weir skimmer device—Esso Ltd.,
• Free vortex recovery system—Scientific Associates, Inc.,
• Oleophilic belt scrubber—Shell Pipe Line Corp.,
• Rotating disk oil-removal system—Atlantic Research Systems Div.,
• Rotating disk removal device—Lockheed.

The Lockheed device will be scaled to a device 8 ft in diameter and 10 ft wide. It will have a recovery capacity of 1500 gal of oil per minute, will be installed on a catamaran, and tested in West Coast field trials later this year. With an earlier model of the device, water pickup was less than 1% under quiet sea conditions and approximately 25% under No. 4 sea conditions, according to a spokesman

at the Washington, D.C. conference.

Without question, the largest device at the exhibit was a beach cleaning device of Meloy Labs (Springfield, Va.). Its mobile beach cleaner uses a froth flotation method of separating oil from the sand, a method that was adapted from the minerals-processing industry where the process has been used with great success. Field tests began last October; some 40 have been logged to date. The unit which is capable of cleaning 700 tons of contaminated sand per day, equivalent to 1 mile of beach 32 ft wide and 1 in. deep, will undergo additional tests later this year at the U.S. Navy site at Dam Neck, Va. Earth-moving equipment is used to bring the contaminated sand to the cleaner (see photo).

Nevertheless, it remains to be seen whether the federal government or industry cooperatives will be the purchasers of this $75,000 item. Perhaps, the cleaner will be made available on a lease basis. Surely, the cleaner is a replacement for straw as the No. 1 material for beach cleanup, albeit a frightfully expensive one.

Treatment

The number of chemical combatants remains essentially at 400, the number reported at the earlier conference. When the cleanup operation resorts to treatment techniques four choices are available: sorb it, sink it, burn it, or disperse it. Although sorbents and burning agents seem to hold promise under certain conditions, there seems to be little hope for sinking agents or dispersants.

Fifty sorbent materials have been investigated for their oil-removing capacities by the Naval Ships Research Lab. The materials include synthetic organic foams, which incidentally head the list of sorbents with an oil-

sorbing capacity of 70 grams of oil per gram of material, polyurethane and urea–formaldehyde materials, and hydrocarbon polymers such as polyethylene and polypropylene.

Burning also seems to have a place in the oil spill cleanup action. The method could, for example, be considered for use under high seas conditions. In fact, the Coast Guard reported on open seas burning trials using a few promising burning and wicking agents. But their experiences to date indicate the need for further studies and experiences not only with better ways to apply the agents but a real need for better ignition methods. The use of the Cab-O-Sil agent, for example, required operators to wear protective inhalation equipment, which is awkward at least under sea conditions. Another operational technique in the burning category that remains to be checked involves containment of the slick prior to attempted ignition of the oil.

The problems with sinking agents and dispersing agents are many. Not only must the dispersants be effective but additional constraints have now been placed on such agents. The material must be biodegradable and have a low BOD value. An earlier Battelle literature study showed that all dispersants were toxic at a level of 5 ppm. However, dispersants could be used under one of three extentuating circumstances, one of which cites the protection of endangered species. Dispersants could also be used when recovery was impossible.

Now is the time for further perfection of equipment, field tests, and the gaining of operational know-how with such an arsenal so that if and when an unpredicted dramatic oil spill recurs then the U.S. could stand ready to muster an unprecedented and convincing cleanup action. SSM

Beach cleanup.
Each day the Meloy mobile unit can clean a 1-mile strip of beach, 32 ft wide and 1 in. deep, but it's an expensive substitute for straw
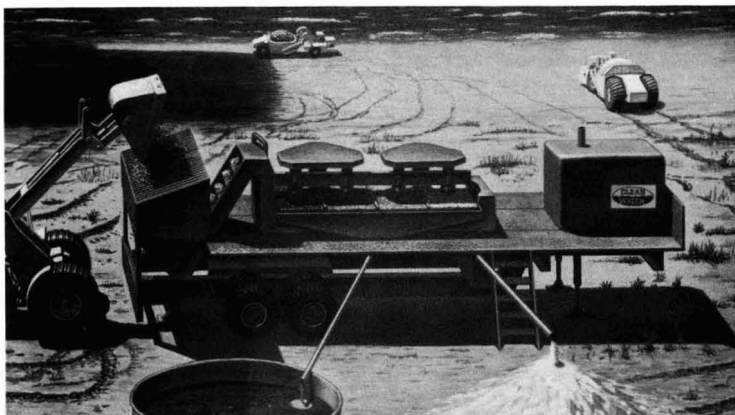
Pollution detection by remote sensing

Environmental surveillance from aircraft or satellites may become global affair to detect changing pollutant concentrations worldwide

The mammoth job of cleaning up the world, most environmental scientists agree, involves more than passing laws or developing specialized technologies. Of critical importance is a global monitoring system—a data-gathering network that will provide a base from which to assess the effects of changing pollutant concentrations, climatological patterns, and demographic shifts on the environment.

To establish such a network with fixed sampling stations would require vast amounts of money, labor, and equipment. The cost of data reduction alone would be prohibitive. With remote sensing techniques—mapping or detection from aircraft and satellites—an integrated instrument package with appropriate data-processing equipment could do the job much easier.
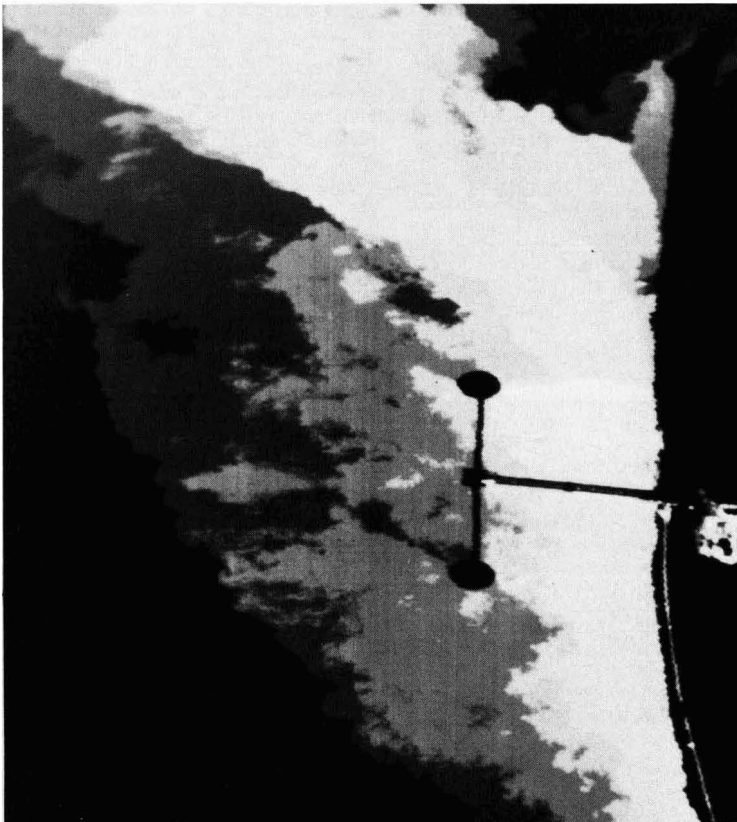
That, at least, is what the National

Aeronautics and Space Administration (NASA) and the U.S. Geological Survey (USGS) think. And to test their ideas, they are collaborating on a limited-scale remote sensing venture called CARETS (Central Atlantic Regional Ecological Test Site). Early next year, NASA plans to launch its Earth Resources Technology Satellite (ERTS) for the collection of remote data on a much larger scale. Then, in 1973, Skylab will provide additional data, perhaps on a global basis. Ultimately, the data will be fed into the Department of Interior's Earth Resources Observation System (EROS) which is administered by USGS; the EROS data center is located at Sioux Falls, S.D.
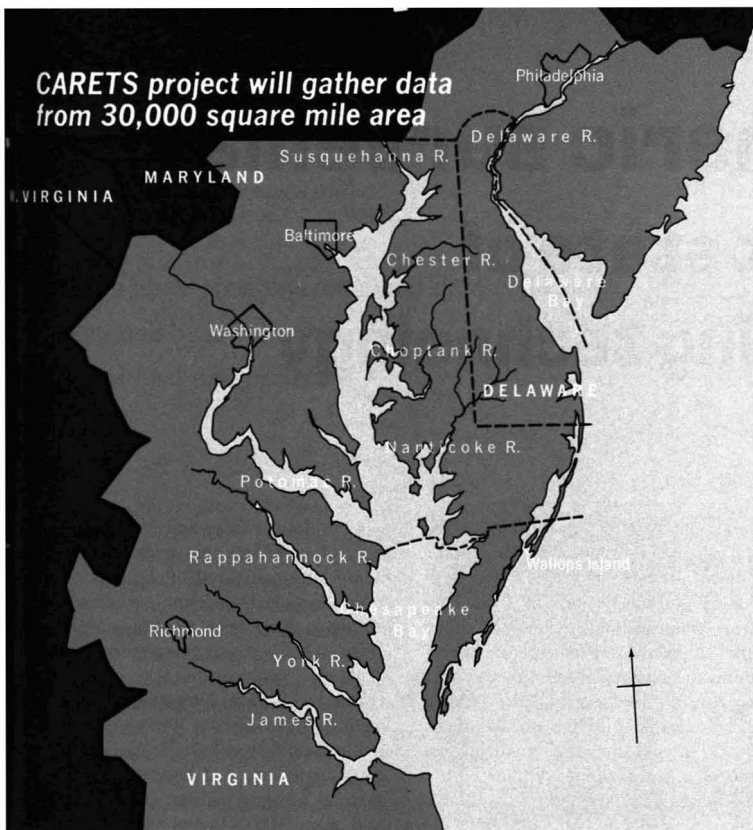
Different techniques

Although remote sensing is a relatively young science, there is a reasonably good assortment of overlapping techniques available for the CARETS program. Broadly defined, remote sensing refers to analytical methods in which there is no physical contact with the sample. It includes radar, sonar, and a host of photographic, spectrophotometric, and geomagnetic processes.

Photography is the oldest remote sensing technique. Both panchromatic black and white and color aerial photography have proved useful in detecting sediment pollution, water current patterns, and air quality in general. Infrared photography is helpful in detecting heat differences in the environment. Both black and white and color infrared photography are capable of differentiating small thermal differences, for example, where heated effluents are discharged into a body of water. Currently available infrared scanners can record heat differences as small as one-tenth of a degree. High-resolution satellite photography has been used to pinpoint plumes and in hydrodynamic mapping. Multispectral photography may be superior to full color in some cases, particularly in delineating pollution outfalls.

Detection. *Helicopter-borne infrared surveillance equipment photographs a power plant's thermal discharge*

CARETS project will gather data from 30,000 square mile area

In addition to the direct-imaging photographic processes, scanning sensors operating in the infrared, ultraviolet, and visible regions of the spectrum can be used as tools to monitor environmental pollutants. Scanning devices with electronically processed signals offer enhanced resolution and make it possible to use computerized storage and retrieval systems. Multispectral scanners which detect several different wavelengths of electromagnetic radiation simultaneously permit computer display of nearly 50 times the amount of information seen by the unaided eye.

One of the newest devices for remote environmental sensing is the correlation spectrometer. Developed by Barringer Research, Ltd. (Toronto), the unit consists of two telescopes (a two-grating spectrometer which disperses incoming light), a photoengraved mask or correlator which serves as a reference spectrum of the pollutant being measured, and appropriate electronics for signal processing. Light matching the mask spectrum is detected by the instrument; the amount of light is a function of pollutant concentration. Barringer has done aerial mapping of sulfur dioxide and nitric oxide burdens over several metropoli-

tan areas and notes that the technique should be applicable to carbon dioxide, carbon monoxide, ozone, ammonia, and methane as well as several other hydrocarbons.

CARETS

"The goal of the CARETS project," says Arch Gerlach, chief cartographer with USGS, "is to provide accurate and timely environmental information to those who make decisions affecting the use of land, water, and air resources." The project is divided into three phases:

• Development of a land use data base and monitoring of its change;

• Assessment, monitoring, and modeling of changes in the total environmental complex;

• Establishment of a regional information service for institutions that will be using remote sensing data.

The CARETS program will apply remote sensing technology to a 30,000 square mile area extending from Norfolk, Va., to Philadelphia, Pa., and from the Potomac and James River basins to the Atlantic seaboard. Several subsites, including the Chesapeake Bay, the lower James, Delaware Bay, the Washington-Baltimore metropolitan complex, and the coastal barrier

islands will be studied in greater detail.

Early last month, high-flying aircraft of the U-2 type began criss-crossing the test area every 18 days. Based at Wallops Island, Va., the planes are equipped with several types of sensors which will collect the information and simulated data that will be generated by satellite later.

CARETS coordinator Robert H. Alexander points out that the project will be organized further into four subprojects. The first—land use data base and change assessment—will permit comparison of environmental and socioeconomic data sets and establish a data base for the entire project. Photomosaics and land use maps on a scale of 1:250,000 will be prepared for the CARETS region, and more detailed maps on a scale of 1:100,000 will be prepared for the Washington-Baltimore urban complex. The maps will be made from RB-57 aircraft photography, ERTS simulation data, actual ERTS sensor data, and later, Skylab photography.

The second subproject will deal with environmental quality and impact assessment. Parameters to be studied include water and air resources assessment, geologic mapping and interpretation, environmental modeling and impact analysis, urban heat island analysis, and assessment of barrier island change.

User services and information systems, another subproject, will establish a data center and explore a standardized graphics format for storage and retrieval of useful information. Limited facilities will be provided in the center for study of indexed imagery, ground truth, statistical data, and reports. Data from the CARETS project will be sold by USGS, but provisions for the loan of limited amounts of imagery and data for special purposes can be negotiated with USGS.

The fourth subproject—systems integration—will result in the preparation of a comprehensive report evaluating the first year of the project. The CARETS project is scheduled to run for an additional two years and draw upon data received from ERTS (1972) and Skylab (1973).   HMM

Atmospheric surveillance
The current state of air monitoring technology

Atmospheric monitoring in the United States today is aimed toward systematically collecting and evaluating aerometric and related data to provide information on pollutant concentrations in ambient air, emissions from polluting sources, and meteorological conditions. Monitoring activities range from operating nationwide and global networks to intensively studying specific problem areas and situations. Whatever the case, monitoring activities produce usable information—collected, structured, and presented for application to problem-solving efforts by the researcher, the pollution control official, the industrialist, and the concerned citizen.

Information derived from monitoring activities is applied in various pollution control activities: assessing pollution effects on man and his environment; studying pollutant interactions and patterns; establishing ambient air quality standards; developing control strategies and regulations; evaluating the effectiveness of these control strategies and regulations when adopted; activating emergency procedures to prevent air pollution episodes or reduce their severity; and guiding efforts to minimize the impact of air pollution by applying mathematical modeling and planning systems.

Knowledge currently available about atmospheric pollutants and their sources is highly variable—ranging from a large body of information about several air pollutants to sparse or nonexistent information about others. For some pollutants, the monitoring techniques are well established and can be considered routine; for others, satisfactory techniques for measurement are still in various development stages.

Consider the large and complex variety of pollutants that must be monitored and measured. Pollutants for which national ambient air quality standards have been promulgated include sulfur dioxide, suspended particulates, photochemical oxidants (ozone), nitrogen dioxide, and nonmethane hydrocarbons. Pollutants currently identified as hazardous are mercury, beryllium, and asbestos. Sulfur dioxide, nitrogen oxides, particulates, acid mist (H_2SO_4), and visible emissions are pollutants currently requiring emission standards of performance at new stationary sources for selected industrial categories. Pollutants presently requiring emission standards for mobile sources are carbon monoxide, hydrocarbons, and nitrogen oxides. Pollutants being studied to determine control needs and optimum control strategies are cadmium, arsenic, nickel,

Seymour Hochheiser,
Franz J. Burmann, and
George B. Morgan

Environmental Protection Agency
Research Triangle Park, N.C. 27711

feature

With more air monitoring and data collection
required by law, instruments are continually being
developed and perfected

polynuclear organics, polychlorinated biphenyls, fluoride, odorous compounds, hydrogen sulfide, fine particulates, vanadium, manganese, chromium, selenium, chlorine, hydrogen chloride, copper, zinc, boron, barium, tin, phosphorus, lithium, aeroallergens, reactive organic compounds, pesticides, and radioactive materials.

In view of this diverse and extensive catalog of contaminants, the technical difficulty of developing instruments and methods with which to monitor them becomes apparent. The criteria for selecting monitoring instruments and methods will be discussed in this article, and the current state of monitoring technology will be described.

Measurement

Methods and instruments for measuring air pollutants must be carefully selected, evaluated, and standardized. Factors that must be considered include:

• Specificity—does the method respond only to the pollutant of interest in the presence of those other substances likely to be encountered in samples obtained from ambient air or pollution sources?

• Sensitivity and range—is the method sensitive enough over the pollutant concentration range of interest?

• Stability—is the sample stable? Will it remain unaltered during the sampling interval and the interval between sampling and analysis?

• Precision and accuracy—are results reproducible? Do they represent true pollutant concentration in the atmosphere or source effluent from which the sample was obtained?

• Sample averaging time—does the method meet the above-stated requirements for sample-averaging time of interest?

National air quality standards reference methods

Pollutant	Averaging time	Reference method	Principle of detection
SO$_2$	3 hr, 24 hr, annual	Pararosaniline	Colorimetric
Particulate matter	24 hr, annual	Hi-vol sampler	Gravimetric
CO	1 hr, 8 hr	Nondispersive infrared spectrometry	Infrared
Photochemical oxidants (ozone)	1 hr	Gas phase O$_3$–ethylene reaction (calibrated against neutral buffered KI method)	Chemiluminescence
Hydrocarbons (nonmethane)	3 hr	Gas chromatographic	Flame ionization
NO$_2$	Annual	24-Hr integrated samples collected in alkaline solution	Colorimetric

• Reliability and feasibility—are instrument maintenance costs, analytical time, and manpower requirements consistent with needs and resources?

For continuous automatic monitoring instruments, further requirements must be considered:

• Zero drift and calibration—is instrument drift over an unattended operation period of at least three days slight enough to ensure reliability of data? Are calibrating and other corrections automatic?

• Response, lag, rise and fall time—can the instrument function rapidly enough to record accurately changes in pollutant concentration that occur over a short time in the sample stream being monitored?

• Ambient temperature and humidity—does the instrumental method meet all of these requirements over temperature and humidity ranges normally encountered?

• Maintenance requirements—can the instrument operate continuously over long periods with minimum down time, maintenance time, and maintenance cost? Is service for the instrument available in the area of use?

• Data output—does the instrument produce data in a machine-readable format?

Reference methods

In standards for ambient air quality or for source emissions of pollutants, the method of measurement must be specified. The method specified in the standard is then known as the reference method. Reference methods and sample-averaging times specified for national air quality standards are indicated above.

In addition to the specified reference methods, other, equivalent methods may be used for atmospheric surveillance to determine compliance with national air quality standards. An equivalent method is defined as one that yields results consistent with those of the reference method. To deter-

mine equivalency, standard tests must be developed and applied to characterize instrument performance. Furthermore, standard methods must be developed for calibrating instruments and for determining the comparability of diverse methods when applied onstream in the field. The Environmental Protection Agency is working to meet these objectives. At present, however, determinating equivalency of diverse monitoring methods must be based on the best judgment of those with extensive knowledge and experience.

Method availability

Mechanized samplers (below) gen-

erally collect integrated samples in the field. The most widely used of these devices is the high-volume (Hi-vol) sampler, which collects particulate pollutants on glass-fiber filters. Analysis of these samples provides information on concentrations of total suspended particulate matter, trace metals, and other organic and inorganic pollutants. In addition to the glass-fiber filters, membrane filters are used to collect pollutants such as zinc, asbestos, boron, and silicates. Impactors of different designs are used to measure suspended particulate matter fractions to determine particle-size distribution in the respirable range.

Mechanized bubbler devices are used to collect sulfur dioxide, nitrogen dioxide, mercury, and other gases and vapors. These samplers, although typically designed for collecting 24-hr integrated samples, can be modified to collect 1- or 2-hr samples in sequence, and thus allow definition of diurnal variations.

In automatic sampler-analyzers, collection and analysis are combined in a single device. These automatic instruments produce continuous analysis, with the output in a machine-readable format or in a form suitable for telemetry to a central data-acquisition facility. Continuous analyzers are now

Common ambient air pollution sampling techniques

Type	Use	Specificity	Common averaging time	Relative cost	Required training of personnel	Remarks
Static						
Settleable particulates (dustfall)	Mapping and definition of special problem areas	Total settled particulates and general classes of pollutants	1 month	Collection, low; analysis, high	Collection, low; analysis, moderate	Well-equipped laboratory required for analysis only for definition of problem areas where a chemical analysis will pinpoint a particular source. Sensitive to temperature, wind, and humidity
Sulfation devices	Mapping and general survey for sulfur dioxide	Responds to oxides of sulfur, hydrogen sulfide, and sulfuric acid	1 month	Collection, low; analysis, high	Collection, low; analysis, moderate to high	
Mechanized						
Hi-vol	Integrated quantification of suspended particulate	Total suspended particulate and multiple specific pollutants	24 hr	Moderate	Moderate	Detailed chemical analysis of Hi-vol and gas samples requires sophisticated laboratory, trained chemists; cost is high
Gas sampler	Integrated quantification of gases	Sulfur dioxide, nitrogen dioxide, mercury, and other gases and vapors	24 hr	Moderate	High	
Spot tape sampler	Relative soiling index		2 hr	Low	Low	Provides only a rough, relative index of particulate soiling
Automatic						
Gas	Continuous analysis of gaseous pollutants	Single gas or group of related gases	Continuous; sample integration usually 1–15 min	Moderate to high	Moderate to high	Continuous measurements allow use of any desired averaging time by computation. Accuracy is generally much better than other methods. Calibration is simplified. Data are available instantaneously
Particulate: soiling (automatic tape)	Continuous analysis of soiling rate	Unknown	Continuous; sample integration usually 1–15 min	Moderate	Moderate	

Cost basis: low, 0 to $500; moderate, $500 to $2000; high, above $2000.
Personnel training: low, maintenance level; moderate, technician; high, experienced technician or professional support staff.

Commercial continuous monitoring methods for common air pollutants [a]
(Not an exhaustive list; without recorder)

SO₂ instruments—cost range, $2000–5000

Manufacturer	Colorimetric	Coulometric	Flame photometric	Electrochemical	Conductimetric
Atlas Electric Devices Co.	■	■			
Barton Instr. Corp.		■			
Beckman Instr. Co.		■			■
Bendix Environmental Sci. Div.				■	
Calibrated Instr. Inc.					■
Combustion Equipment Associates					■
Davis Instrument Co.					■
Devco Engineering					■
Dynasciences				■	
Environmetrics Inc.				■	
Erickson Instruments				■	
Instrument Devel. Co.				■	■
Intertech Corp.				■	■
Kimoto					■
Leeds & Northrup					■
Meloy Labs			■		
Monitor Labs Inc.	■				■
Phillips Electronic Co.		■			
Pollution Monitors Inc.	■				
Precision Scientific	■				
Process Analyzers Inc.		■			
Scientific Industries					■
Technicon Corp.	■				
Tracor Inc.				■	
Wilkens-Anderson Corp.	■				

CO instruments—cost range, $2500–5000

Manufacturer	NDIR	Uv (mercury replacement)
Bacharach Instrument Co.		■
Beckman Instrument Co.	■	
Bendix Environmental Sci. Div.	■	
Calibrated Instrument Co.	■	
Intertech Corp.	■	
Morgan Co.	■	
Mine Safety Appliance Co.	■	

Total hydrocarbons—cost range, $2000–5000

Manufacturer	
Beckman Instrument Co.	
Bendix Environmental Science Div.	
Davis Instrument Co.	(all based on flame
Delphi Industries	ionization detection)
Mine Safety Appliance Co.	
Power Design Inc.	

Methane–CO–total hydrocarbon instruments —cost, approximately $10,000 with recorder

Manufacturer	
Beckman Instrument Co.	
Mine Safety Appliance Co.	(all based on gas chromato-
Tracor Inc.	graphic separation and flame ionization detection)
Union Carbide Corp.	

NO₂–NOₓ instruments—cost range, $2000–5000

Manufacturer	Colorimetric	Coulometric	Electrochemical
Atlas Electric Devices Co.	■		
Beckman Instrument Co.	■	■	
Dynasciences			■
Environmetrics Inc.			■
Mast Development Inc.		■	
Monitor Labs Inc.	■		
Intertech Corp.			■
Pollution Monitors Inc.	■		
Precision Scientific	■		
Raditron Inc.	■		
Scientific Industries	■		
Technicon Corp.	■		
Wilkens-Anderson Corp.	■		

Oxidant instruments—cost range, $1000–7000

Manufacturer	Colorimetric	Coulometric	Chemiluminescence	Uv absorption
Atlas Electric Devices Co.		■		
Beckman Instrument Co.	■	■		
Bendix Environmental Science Div.			■	
Dasibi Corp.				■
Mast Development Co.		■		
McMillian Electronics			■	
Monitor Labs Inc.	■			
Ozone Research		■		
Raditron Inc.	■			
REM Inc.			■	
Spectrometrics of Florida Inc.				■
Technicon Corp.	■			
Triangle Instrument Co.			■	

[a] Mention of companies or products does not constitute endorsement by the Environmental Protection Agency.

available for carbon monoxide, carbon dioxide, nitric oxide, nitrogen dioxide, sulfur dioxide, total hydrocarbons, methane, oxidants, ozone, and hydrogen sulfide. Although a large variety of automatic analyzers is now available commercially, only a few have been properly field-tested to determine their limitations, reliability, and durability, and to provide information about possible interferences.

Solid-state sensors having sensitivity, specificity, and reliability are urgently needed; such sensors would overcome many of the current problems with wet-chemical methods. Furthermore, new techniques will be needed as air pollution control efforts are expanded to encompass less abundant and newly recognized air pollutants.

Commonly used continuous automatic instrumental methods to monitor those pollutants for which national ambient air quality standards have been established are indicated on page 681. Over 70 instrument for measuring air pollutants are currently advertised in the technical literature, and for some of these, several models are available. None of these instruments, however, has yet been collaboratively

tested to evaluate its equivalency to a reference method. The Environmental Protection Agency and the Intersociety Committee, which includes representatives of eight major professional societies in the United States, are working together on plans to conduct these collaborative tests.

Previously, only the colorimetric and the conductometric methods were available for measuring sulfur dioxide. The pararosaniline colorimetric method has been improved and is now the reference method. The method does have the drawback that the liquid reagent in which the sulfur dioxide is collected lacks stability. The conductometric method lacks specificity and may or may not yield results consistent with the reference method in most urban areas. Many compounds might interfere in the method. Recently, certain instruments incorporating flame photometric and coulometric detection principles have been field-tested; these limited tests indicate that the instruments may be acceptable for measuring ambient sulfur dioxide. The most recent procedure introduced for measuring sulfur dioxide is an electrochemical method; this method, however, has not been tested

under field working conditions.

The reference method designated in the national air quality standard for photochemical oxidants (ozone) is the chemiluminescent method, selected because of its specificity for ozone. Past methods for measuring oxidants were based on colorimetric and coulometric principles. Both of these suffered from lack of specificity and stability. An ultraviolet analyzer, recently field-tested on a limited basis, also appears to be specific for ozone.

The most commonly used method for measuring carbon monoxide is based on nondispersive infrared analysis. This technique, employing stable electronics and a mechanism for removing moisture, is the reference method. A recently developed gas chromatographic procedure is both specific and sensitive as well as useful for measuring methane and hydrocarbons.

Total hydrocarbons have traditionally been measured with a flame ionization detector. Because this method could not distinguish between methane and nonmethane hydrocarbons, the data were limited in use. The recently developed gas chromatographic technique can simultaneously measure
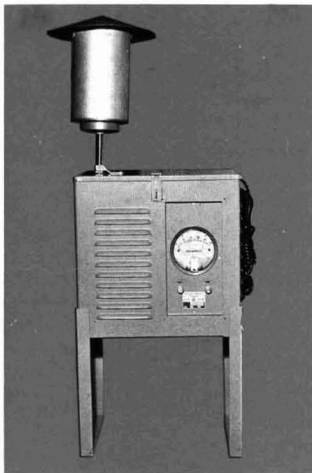
Ambient air pollution samplers are available in various shapes and sizes
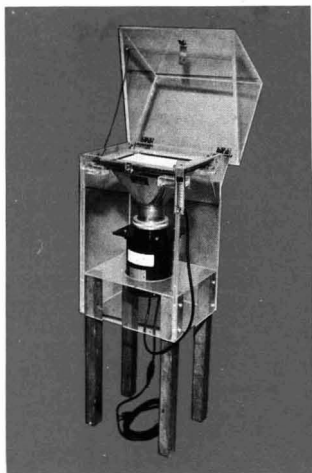
Hi-vol. Mechanized unit uses glass-fiber filters for sampling

24-hr sampler. Instrument can be modified to collect for 1- or 2-hr

Membrane filter. Zinc, asbestos, boron, and silicates are sampled

Other pollutant sampling and analytical methods

Pollutant	Sampling method	Analytical method	Major improvement needed
Hg	Gas bubbler, Hg amalgamation	Flameless atomic absorption, uv absorption	Yes
Be	Hi-vol	Emission spectroscopy, atomic absorption	No
Asbestos	Membrane filter sampler	Electron microscopy	Yes
Pb	Hi-vol	Emission spectroscopy	No
Cd	Hi-vol	Atomic absorption, emission spectroscopy	No
As	Hi-vol	Colorimetric, neutron activation	No
Ni	Hi-vol	Atomic absorption, emission spectroscopy	No
Polynuclear organics	Hi-vol	Chromatography and fluorescence analysis	No
Polychlorinated biphenyl	Not developed	Not developed	Yes
F	Coated–open tubular column	Specific ion electrode	Yes
Odor	Human odor panel	Olfaction	No
H₂S	Continuous automatic analyzer and mechanized tape sampler	Flame photometric, coulometric, colorimetric	Yes
Fine particulates	Impactor	Gravimetric	Yes
V	Hi-vol	Emission spectroscopy	No
Mn	Hi-vol	Emission spectroscopy	No
Cr	Hi-vol	Emission spectroscopy	No
Se	Not developed	Not developed	Yes
Cl₂	Not developed	Not developed	Yes
HCl	Not developed	Not developed	Yes
Cu	Hi-vol	Emission spectroscopy, atomic absorption	No
Zn	Membrane filter sampler	Emission spectroscopy, atomic absorption	No
B	Not developed	Not developed	Yes
Ba	Membrane filter sampler	Emission spectroscopy	Yes
Sn	Hi-vol	Emission spectroscopy	No
P	Not developed	Not developed	Yes
L	Not developed	Not developed	Yes
Aeroallergens	Not developed	Not developed	Yes
Reactive organics	Not developed	Chromatography	Yes
Pesticides	Not developed	Chromatography	Yes
Radioactive materials	Hi-vol	Gross beta and gamma scanning	Yes

methane, total hydrocarbons, and carbon monoxide. This instrument separates carbon monoxide and methane by chromatographic techniques and measures hydrocarbons by a flame ionization detector.

The methods most commonly used for measuring nitrogen oxides are based on the diazotization and coupling technique. The reference method for nitrogen dioxide is the Jacobs-Hochheiser method, in which the pollutant is collected in an alkaline solution and analyzed in the laboratory. Procedures based on coulometry are available but have not been collaboratively field-tested.

Calibration techniques

Continuous automated measurements yield accurate data only if the measuring instruments have been calibrated with a known quantity of gaseous pollutant while the complete system is operational in the field. All other so-called calibration checks performed by the operator or recommended by the manufacturer are nothing more than operational checks. These operational checks are sometimes classified as static calibrations, usually performed with a material having the same effect on the sensor as the material of interest. Only the sensor is being calibrated, however, and not the sample-collecting portion of the instrument.

To calibrate any instrument, the operator must use a method that delivers a known pollutant quantity to the system. The instrument must be calibrated in the monitoring mode and must sample the calibrating gas at identical settings and flow rates at which the instrument will operate in the field. Since air flow rates and sometimes reagent flow rates are involved, this type of calibration is commonly referred to as dynamic calibration.

A fundamental difference between calibration checks and calibration must be emphasized. A calibration check is introducing a known amount of pollutant to verify at one level that the initial calibration is still valid. This operational check, obtaining a span point, should be performed daily on most instruments. True calibration entails measuring and adjusting all instrument parameters or subsystems that have a direct bearing on measurement. Typical parameters, determined and adjusted if necessary in full calibration, are rate of flows, base line, lag and response time, and system response to input of known standard pollutant concentrations over the entire operating range.

Usually, the most difficult part of calibration is generating calibration gases in specified concentrations. For total hydrocarbons and carbon monoxide monitors, acceptable standard gases with certified analysis are obtainable from commercial sources. For sulfur dioxide and nitrogen dioxide monitors, gravimetrically calibrated permeation tubes can be utilized. A permeation tube consists basically of a sealed FEP (fluorinated ethylene

propylene) tube containing the liquefied gas kept at a constant temperature. The sulfur dioxide permeation tube is gaining rapid acceptance, since it can be purchased from the National Bureau of Standards as a primary standard. Preparation, calibration, and use of these tubes are described in the literature.

Applying nitrogen dioxide permeation tubes to dynamic calibration still poses problems, but work currently in progress at the National Bureau of Standards promises to produce a permeation tube system suitable for routine field application.

For calibrating oxidant and ozone analyzers, an ozone source is used. A recently developed ozone source consists of a low-pressure mercury lamp mounted in a quartz tube enclosed in an adjustable metal sleeve. The irradiation and ozone-generation level are controlled by adjusting the open area of the lamp with the sleeve. By carefully controlling the flow of ozone-free air through the quartz tube, the operator generates standards containing constant, known concentrations of ozone. The ozone levels generated are determined by the neutral buffered potassium iodide method.

Sampling and analytical methods for monitoring potentially hazardous or detrimental pollutants are indicated on page 683. Most of these methods require highly trained personnel, and the analysis cost is high. Few of the methods have been standardized. For several pollutants there are no existing methods of demonstrated applicability to monitor ambient air; therefore, both analytical methods and air monitoring instruments must be developed. For others, the available methods must be improved for adaptability to routine atmospheric surveillance.

Future needs

No effective air pollution control program can operate without air quality monitoring. Man must continually strive to develop and improve monitoring methods to meet the challenges of newly recognized pollutants and to monitor more efficiently those already recognized. Research and development of low-cost, reliable instruments is needed for continuous pollutant monitoring in the atmosphere and at emission sources. Methods used to test compliance with standards must be collaboratively tested and standardized so that both the methods and

their results are recognized as valid. Yet today, among all the methods used in measuring air pollutants, only the high-volume method for particulates and the pararosaniline method for sulfur dioxide have been collaboratively tested. Means for determining equivalency of a method to the reference method must be developed. Standard procedures for testing and reporting instrument performance characteristics are needed. And primary and secondary standards for calibrating methods and instruments and an automatic dynamic calibration system are also necessary.

Preliminary research and development on designing air quality monitoring networks has been performed. This work must be intensified and tailored for application at various levels —by state, regional, and local control agencies.

In this presentation the monitoring methods in current use have been described, and promising developments for future application have been indicated. Also, some specific technical problems have been outlined, although, certainly, other problems will arise.

Fortunately, ability to solve these problems is increasing rapidly. In the past two years alone, contributions to monitoring technology have been greater than those developed over the previous 10 years. The pace of technological improvement should continue to accelerate as the nation's technical talents are brought to bear on the task of meeting new air quality standards.

Additional Reading

Environmental Protection Agency, "National Ambient Air Quality Standards," Fed. Regist., April 30, 1971.
Environmental Protection Agency, "The Clean Air Act," December 1970.
Hodgeson, J. A., Stevens, R. K., Martin, B.E., "A Stable Ozone Source Applicable as a Secondary Standard for Calibration of Atmopsheric Monitors." Analysis Instrumentation Symposium, Instrument Society of America, April 1971.
Morgan, G. B., Ozolins, G., Tabor, E. C., "Air Pollution Surveillance Systems," Science, 289–296 (Oct. 16 1970).
Scaringelli, F. P., O'Keeffe, A. E., Rosenberg, E., Bell, J. P., "Preparation of Known Concentrations of Gases and Vapors with Permeation Devices Calibrated Gravimetrically," Anal. Chem. 871–876 (July 1970).
Stevens, R. K., O'Keeffe, A. E., "Air Pollution Monitoring," ibid., 143A–148A (February 1970).

Address inquiries to Mr. Hochheiser.
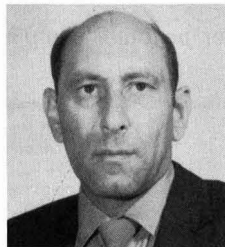
Seymour Hochheiser received his B.S. in chemistry from CUNY. He is presently chief, Air Surveillance Branch, Division of Atmospheric Surveillance, Bureau of Air Pollution Sciences, EPA. Mr. Hochheiser's major areas of activity have been technical assistance, abatement investigations, methods development, evaluation and standardization, and atmospheric surveillance.

Franz J. Burmann, currently chief, Field Studies Section, Air Surveillance Branch, EPA, studied at the University of Frankfort as well as the University of Cincinnati. He holds an M.S. in chemistry from the University of Cincinnati. Since he joined the EPA in 1967, Mr. Burmann's primary area of concern has been instrumentation for continuous ambient air monitoring.

George B. Morgan is director, Division of Atmospheric Surveillance, Bureau of Air Pollution Sciences, EPA. Mr. Morgan received his B.S. in chemistry (University of Georgia) and M.S. in bioanalytical chemistry (University of Florida). His duties include maintaining a national program for surveillance of ambient air quality, emission, and related data.

Oxidation of Sulfur Dioxide in Polluted Atmospheres—A Review

Marijon Bufalini

Division of Chemistry and Physics, Environmental Protection Agency, Air Pollution Control Office,
Research Triangle Park, N.C. 27709

■ A review of the oxidation reactions of sulfur dioxide in polluted atmospheres is presented. The literature is covered through 1970. Emphasis is on the photochemical reactions of sulfur dioxide in the wavelength range of 3000 to 4000 Å alone and in mixtures with nitrogen oxides and (or) hydrocarbons or carbon monoxide. Reactions of sulfur dioxide in the presence of foreign particles and reactions with metal salt solutions are also included. Gas-phase reactions, heterogeneous reactions, formation and chemical identity of aerosols, effect of water vapor, effect of nucleating particles on photochemical aerosol formation, and effect of sulfur dioxide on nitrogen oxides–hydrocarbon reaction parameters are discussed.

O ne noticeable physical effect of air pollution is reduced visibility. Visibility in the atmosphere is reduced by the scatter and absorption of radiation by aerosol particles. The quantitative contribution made by the oxides of sulfur to the total scattering of light in various atmospheres has not been resolved, but sulfuric acid mist and other sulfate particulate matter are recognized as important sources of scattering. Sulfate particulates arise from complex oxidation processes that occur when common atmospheric pollutants interact. The major sulfur pollutant, sulfur dioxide, is produced mainly from combustion processes and is oxidized in the atmosphere either photochemically or catalytically.

Two reviews of the photochemical aspects of air pollution have been published by Altshuller and Bufalini (1965, 1971).

These reviews emphasize the gas-phase photooxidation reactions of hydrocarbon nitrogen oxides systems and only briefly discuss aerosol formation from the irradiation of sulfur dioxide and its mixtures with hydrocarbons and nitrogen oxides. Urone and Schroeder (1969) surveyed the photochemical reactions of SO_2. The material presented here constitutes a review of the chemical aspects of photochemical and catalytic oxidation of sulfur dioxide and its mixtures with hydrocarbons and nitrogen oxides as related to air pollution. The emphasis is on photochemical reactions of sulfur dioxide, both gas-phase reactions and aerosol-forming reactions. Since there is some interest in the reactions of sulfur dioxide in aqueous metal salt solutions due to the relationship of such to fogs, these reactions are briefly discussed.

For a broader review of air pollution problems, the treatise of Leighton (1961) and the three-volume work edited by Stern (1968) may be consulted.

Photochemical Reactions of SO_2

The photodissociation of SO_2 into SO and O atoms requires 135 kcal/mol and is therefore not possible energetically for wavelengths of absorbed light greater than 2180 Å. Since only solar radiation of wavelengths greater than 2900 Å reaches the lower atmosphere, the photochemistry of SO_2 within the 3000 to 4000 Å range can only involve molecular reactions of the electronically excited states of SO_2.

In the 3000 to 4000 Å region, the absorption spectrum of SO_2 shows two bands. The first band is the transition to the first excited state. It originates at 3880 Å, with a maximum around 3840 Å, and is a weak absorption. The second band is the transition to the second excited state. It originates at 3376 Å, with a maximum around 2940 Å, and is a strong absorption. The radiative lifetimes suggest that the first

Table I. Primary Reactions of Sulfur Dioxide[a]

Reaction no.	Reaction[b]	Rate constant[c]
1	$SO_2 + h\nu \rightarrow {}^1SO_2$	$\Phi I_{absorbed}$
2	${}^1SO_2 + SO_2 \rightarrow (2SO_2)$	$2.0 \pm 0.1 \times 10^{10}$ l. mol^{-1} sec^{-1}
3	${}^1SO_2 + SO_2 \rightarrow {}^3SO_2 + SO_2$	$0.18 \pm 0.08 \times 10^{10}$ l. mol^{-1} sec^{-1}
4	${}^1SO_2 \rightarrow SO_2 + h\nu_f$	$5.1 \pm 4.0 \times 10^3$ sec^{-1}
5	${}^1SO_2 \rightarrow SO_2$	$1.7 \pm 0.4 \times 10^4$ sec^{-1}
6	${}^1SO_2 \rightarrow {}^3SO_2$	$1.5 \pm 0.8 \times 10^3$ sec^{-1}
7	${}^3SO_2 \rightarrow SO_2 + h\nu_p$	$0.10 \pm 0.06 \times 10^2$ sec^{-1}
8	${}^3SO_2 \rightarrow SO_2$	$1.3 \pm 0.2 \times 10^2$ sec^{-1}
9	${}^3SO_2 + SO_2 \rightarrow (2SO_2)$	$2.5 \pm 0.5 \times 10^7$ l. $mole^{-1}$ sec^{-1}

[a] Rao et al. (1969a).
[b] Parentheses were used in Reactions 2 and 9 to designate that either chemical change or relaxation to ground-state molecules was occurring.
[c] The rate constant for Reaction 9 was calculated by Rao et al. (1969a) from the data of Strickler and Howell (1968).

excited state is a triplet state ($^3SO_2$) and the second excited state is a singlet state ($^1SO_2$). The precise roles of the excited singlet and triplet states in the photochemistry of SO_2 are unclear. Recent findings by Okuda et al. (1969) indicate that the $^3SO_2$ molecule is the major reactive species within the 3200–2400 Å band. The primary processes in the photochemistry of SO_2 were described by Rao et al. (1969a). The primary reactions and the corresponding rate constants are shown in Table I.

The only observed products from the photolysis of SO_2 alone at 3130 Å were SO_3 and S. Hall (1953) reported that the rate of production of SO_3 was proportional to the SO_2 pressure and the quantum yield for the disappearances of SO_2 was about 10^{-2} molecule per quantum absorbed. He postulated that the reaction products arose from the reactions

$$SO_2^* + SO_2 \rightarrow SO + SO_3 \tag{10}$$

and

$$SO \rightarrow SO_3 + S \tag{11}$$
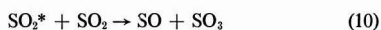
by various steps. The asterisk represents an excited SO_2 molecule.

The unspecified product, 2 SO_2, in Reactions 2 and 9 of Table I has been discussed by Okuda et al. (1969). This product can be ground-state SO_2, SO_3, and SO, and (or) possibly some other chemical products that do not regenerate any excited state of SO_2. The photochemical formation of SO_3 from SO_2 is suggested by experimental evidence, but there is no requirement that SO_3 is indeed the oxidation product. There has been no direct spectroscopic evidence for SO_3 formation in this system. Okuda et al. (1969) state that, conceivably, the primary product may be a metastable dimer of SO_2 (O$_2$S—O—S—O) or even the reactive textroxide of sulfur (SO_4). However, their results at present favor the following more detailed description of Reaction 9:

$$^3SO_2 + SO_2 \rightarrow SO_3 + SO(^3\Sigma^-) \tag{12}$$

Photochemical Reactions of SO_2–O_2 System

Studies of the fluorescence and phosphorescence of SO_2 suggest that the reactivities of the triplet and singlet states of SO_2 are quite different. This was confirmed by the work of Rao et al. (1969b) on quenching reactions of the two states with oxygen. Based on reaction steps 1 through 9 plus the following steps:

$$^1SO_2 + O_2 \rightarrow (SO_2\text{-}O_2) \tag{13}$$

$$^1SO_2 + O_2 \rightarrow {}^3SO_2 + O_2 \,(^3\Sigma, {}^1\Delta, {}^1\Sigma) \tag{14}$$

$$^3SO_2 + O_2 \rightarrow (SO_2\text{-}O_2) \tag{15}$$
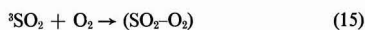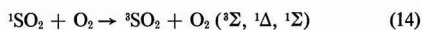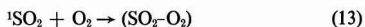
they deduced that $k_2 + k_3 = 1.5 \pm 0.7 \times 10^{10}$ liter mol^{-1} sec^{-1}, $k_{13} + k_{14} = 0.47 \pm 0.22 \times 10^{10}$ liter mol^{-1} sec^{-1}, $k_9 = 1.4 \pm 1.4 \pm 0.7 \times 10^7$, and $k_{15} = 1.1 \pm 0.6 \times 10^7$ liter mol^{-1} sec^{-1}. The values for $k_2 + k_3$ and k_9 agree within experimental error with their previous work. The formation of O_2 in the $^1\Delta$ or $^1\Sigma$ state in Reaction 14 is energetically possible only if the $^1SO_2$ is in a vibrationally nonequilibrated excited singlet state. The rate constant for the quenching of $^1SO_2$ with O_2 is near the collision number, whereas the quenching rate for $^3SO_2$ is much lower. In fact, it is the lowest reported value for a triplet molecule quenching reaction by oxygen. It is suggested that the slowness of energy transfer to oxygen from $^3SO_2$ forming $^1\Delta$ or $^1\Sigma$ states of oxygen is related to the relative unimportance of charge-transfer states in the O_2-$^3SO_2$ collision complex.

An early study of the photochemistry of SO_2–O_2 mixtures was reported by Blacet and Hall (Gerhard and Johnstone, 1955). They obtained a quantum yield of 10^{-3} for the decomposition of SO_2 at 3130 Å. Blacet (1952) reported that when the O_2 concentration is high in comparison to SO_2, ozone and SO_3 appear to be the only products. The secondary reaction steps in the photooxidation of SO_2 were described as

$$SO_2^* + O_2 \rightarrow SO_4 \tag{16}$$

$$SO_4 + O_2 \rightarrow SO_3 + O_3 \tag{17}$$
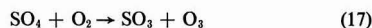
and in the presence of water

$$H_2O + SO_3 \rightarrow H_2SO_4 \tag{18}$$
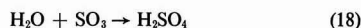
The quantum yield for sulfate production was 10^{-2} to 10^{-3} molecule per quantum absorbed. Blacet (Renzetti and Doyle, 1960) later supplemented the above mechanism by adding the reaction

$$SO_4 + SO_2 \rightarrow 2\, SO_3 \tag{19}$$

Blacet's publications, however, do not present the data for these studies and since there is no proof that ozone is indeed formed, this mechanism can only be viewed as speculative.

Gerhard and Johnstone (1955) studied the photooxidation (3650–2950 Å) of SO_2 at concentrations of 5 to 30 ppm and 32 to 91% relative humidity (RH) under static conditions. The rate of decomposition of SO_2 was determined by measuring the formation of H_2SO_4. The rate of H_2SO_4 formation was found to be first order with respect to SO_2 and was 0.68%/hr. It is difficult to convert this rate into an exact quantum yield, since the authors' only statement concerning intensity of the ultraviolet source is that "the intensity of the ultraviolet in the region from 2950 to 3200 Å in the sunlamp chamber was approximately three times as great as the noon sunlight on a clear day and approximately five times as great as in their natural sunlight reaction chamber." This does not necessarily mean the reaction with their lamp is three times faster than the photooxidation rate in natural sunlight. Their irradiations in natural sunlight indicated the rate of formation of H_2SO_4 to be approximately 0.1%/hr. Hall's (1953) studies under natural sunlight between 10 a.m. and 3 p.m., with 56 to 230 mm SO_2 mixed with 50 to 200 mm O_2 indicated that the rate of formation of SO_3 was first order with respect to SO_2, was independent of the concentration of oxygen, and was about 0.05%/hr.

Renzetti and Doyle (1960), while studying the photochemical formation of aerosol in sulfur dioxide–hydrocarbon systems, did some irradiations in which only SO_2 in air (0.2 to 0.6 ppm) and water vapor were present. They obtained a quantum yield for the disappearance of SO_2 of about 0.3 molecule per quantum absorbed. However, when the concentration of SO_2 was increased to 12.7 mm and the O_2 concentration was 10.6 mm and no water vapor was present, the quantum yield for the disappearance of SO_2 decreased to 0.036 molecule per quantum absorbed. Their data do not indicate whether this decrease was due to the lack of H_2O or to the higher concentrations of SO_2 and O_2. From their light-scattering data, they calculated that the complete conversion of 0.05 ppm SO_2 to aerosol of 50% RH will result in a mass loading of about 460 $\mu g/m^3$ of a 43% solution of H_2SO_4. A mass loading of this magnitude will significantly reduce visibility.

Renzetti and Doyle (1960) suggested that the absorption of a photon by SO_2 promotes it to a highly excited vibrational state of the second electronic level ($^1SO_2''$) which then decays

by various processes to the vibrational ground state of SO_2. Their suggestion was based on Walsh's (1953) molecular orbital calculations which indicated that the first excited electronic state ($^3SO_2$) of SO_2 is a "bent" state, having a different O—S—O bond angle than the ground electronic state. They considered this bent state ($^3SO_2$) to be a biradical having an unpaired electron in a sulfur sp^3 orbital, and thus Reaction 16 would be facilitated. The conclusion was made that the best state is sufficiently stable with regard to collisional deactivation. The recent findings of Rao et al. (1969b) have shown that $^3SO_2$ is the major chemically active species in SO_2 photochemistry both within the first allowed absorption bond (2400–3200 Å) and the "forbidden" bond (3390–4000 Å).

Leighton (1961) suggested that the SO_4 molecule formed would have a peroxy structure, and if SO_2* is a triplet the SO_4 molecule might also be a biradical:

$$\begin{array}{c} O \\ \diagdown \\ \cdot S{-}O{-}O \cdot \\ \diagup \\ O \end{array}$$
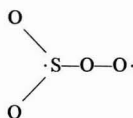
More recently, Urone et al. (1968) irradiated SO_2 (12 and 19 ppm) tagged with $S^{35}O_2$ in air (50% RH). Their system was designed to account for the total amount of SO_2 initially present. The rate of disappearance of SO_2 was approximately 0.6%/hr. It is unfortunate that they choose to express this rate as 0.1%/hr of noonday sunlight rather than the more meaningful quantum yield since they had measured the intensity of their lamps. They could account for 99.5 to 98% of the sulfur.

Sethi et al. (1969) determined quantitatively the quantum yields for the disappearance of SO_2 (Φ_{SO_2}) using a photometric method to monitor SO_2 concentration. The dependence of Φ_{SO_2} on the initial SO_2 (20–100 torr) and initial oxygen (50–390 torr) pressures was studied at room temperature. Over an eight-hr photolysis with an intense ultraviolet light source (10^{18} quanta sec^{-1}), conversions of about 10% were observed. Φ_{SO_2} at 3130 Å was 1.7×10^{-2} molecule per quantum absorbed and over the integrated wavelength range 2800 to 4200 Å, it was 2×10^{-3} molecule per quantum absorbed. In both cases, Φ_{SO_2} was essentially independent of the initial oxygen and sulfur dioxide concentrations. Also, addition of inert gases, such as N_2 and CO_2, had no observed effect on Φ_{SO_2}.

In contrast with these findings are results obtained by Billings et al. (1968) for the photooxidation of 3130 Å of SO_2 in oxygen at concentrations from 60 to 100% SO_2. For pure SO_2, the quantum yield for SO_3 formation was 0.05 molecule per quantum absorbed. As O_2 was added to the system, the quantum yield increased to a value of 0.22 molecule per quantum absorbed for a 60/40 SO_2–O_2 mixture. They explain their results with a mechanism involving formation of an oxygen atom from the reaction of excited SO_2 with O_2.

$$SO_2 + h\nu \rightarrow SO_2^* \qquad (20)$$

$$SO_2^* + SO_2 \rightarrow 2\,SO_2 \qquad (21)$$

$$SO_2^* + SO_2 \rightarrow SO_3 + SO \qquad (22)$$

$$SO_2^* + O_2 \rightarrow SO_3 + O \qquad (23)$$

$$SO_2 + O \rightarrow SO_3 \qquad (24)$$

$$O + O_2 \rightarrow O_3 \qquad (25)$$

$$SO + O_2 \rightarrow SO_3 \qquad (26)$$

$$SO + wall \rightarrow SO\ lost \qquad (27)$$
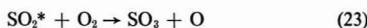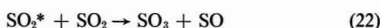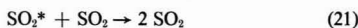
According to this mechanism, SO_3 formation occurs only by Reaction 22 in pure SO_2, and the low quantum yield is due to the effectiveness of ground-state SO_2 deactivating excited SO_2.

Reactions 22–24 and possibly 26 account for the initial increase in quantum yield as oxygen is added. As the oxygen is further increased, the predominant steps become Reaction 23 followed by 24. At lower SO_2 concentrations Φ_{SO_2} would be expected to decrease as a consequence of the competition for oxygen atoms caused by ozone. Although not included, the deactivation of excited SO_2 by O_2 would also be important.

Another point not discussed by the authors is the formation of O_3 in Reaction 25. Although the rate constant for the oxygen atom–O_2 reaction is an order of magnitude less than that for the oxygen atom–SO_2 reaction, the rate of formation of O_3 in Reaction 25 will be 10^4 to 10^5 times greater than the rate of formation of SO_3 in Reaction 24. Thus, if it is assumed that at atmospheric concentration levels Reactions 24 and 27 are unimportant and if k_{22} and $k_{23} = 10^7$ or 10^{10} liter mol^{-1} sec^{-1}, depending on whether SO_2 is in the singlet or triplet excited state (Rao et al., 1969a,b), and (O_2) = 10^5 to 10^6 (SO_2) then the steady-state kinetic expression predicts that the rate of O_3 formation would be approximately the same as the rate of SO_3 formation. Unfortunately, no effort was made to substantiate this mechanism by a check for ozone.

Since SO_3 is a known product of the photooxidation of SO_2 in the 3000 to 4000 Å range, consideration must be given to the photochemistry of this product. Little work has been done on the photochemistry of SO_3, but some earlier work (Fajans and Goodeve, 1936) shows that absorption does occur in the ultraviolet region with weak diffuse bands superimposed on a continuum extending to about 3100 Å. From energy considerations, the following photodecompositions:

$$SO_3 + h\nu \rightarrow SO_2 + O\ (^3P) \qquad (28)$$

$$SO_3 + h\nu \rightarrow SO + O_2\ (^3\Sigma) \qquad (29)$$
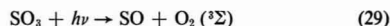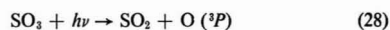
may occur at 3440 Å and 3000 Å, respectively.

In the presence of O_2, Reaction 28 would cause a competition between O_2 and SO_2 for the oxygen atom, with subsequent formation of ozone and SO_3. It would be expected that formation of ozone would predominate because of the high concentration of O_2. A decrease in Φ_{SO_3} would occur to the degree that the photodecomposition of SO_3 occurs.

The SO formed in Reaction 29 would probably react with O_2 to form SO_3, and no net effect on Φ_{SO_2} would likely occur. If both photodecomposition processes were occurring, the net effect would be dependent on the value of the primary quantum yield for the two processes.

In summary, the reason for such a large discrepancy in the reported quantum yields for the disappearance of SO_2 is not readily apparent. The reported values vary from 10^{-3} to 10^{-1} molecule per quantum absorbed. The mechanism is highly speculative. There is no direct evidence for formation of an SO_4 intermediate nor for formation of ozone.

Photochemical Reactions of SO_2–NO_x System

Gerhard and Johnstone (1955) carried out a series of experiments in which 1 to 2 ppm of NO_2 was added to 10 to 20 ppm SO_2 and irradiated with light in the range of 2950 to 3650 Å. No measurable effect on the rate of H_2SO_4 production was observed, and no dark reaction between SO_2 and NO_2 occurred.

In contrast to that work, Renzetti and Doyle's (1960) experiments indicated that the addition of 1 ppm NO_2 to 0.14 ppm SO_2 enhanced the photooxidation of SO_2 (as measured by a light-scattering photometer), whereas the addition of 1 ppm NO to 0.5 ppm SO_2 at a relative humidity of 50% hindered the formation of aerosol. They account for the enhancement of the rate by NO_2 with the reaction

$$SO_2 + O + M \rightarrow SO_3 + M \qquad (30)$$
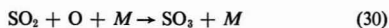
and suggest that the reaction

$$SO_4 + NO \rightarrow SO_3 + NO_2 \qquad (31)$$

can account for the suppressing effect of NO. As Altshuller and Bulfalini (1965) have pointed out, this explanation for the decrease due to NO is not appealing because the end product of the reaction is still SO_3. If, however, more SO_3 is formed by Reaction 19 than by 17, then the net result of Reaction 31 would be a decrease in SO_3. With excess O_2, though, it is unlikely that Reaction 19 will predominate. Altshuller and Bufalini (1965) suggest that the removal of SO_3, or the deactivation of excited SO_2 with NO is a more plausible explanation.

Adding to the confusion are the results reported by Ripperton et al. (1962), who irradiated mixtures of SO_2 (1 ppm) and NO_2 (1 ppm) at a relative humidity of 44%. These experiments showed little SO_2 destruction in comparison with an SO_2 consumption rate of 30% in four hr when SO_2 was irradiated in the absence of NO_2. Their results indicate that NO_2 interferes with SO_2 destruction, at least when the ratio of the two gases is 1/1. They interpret the slower rate of SO_2 disappearance in the NO_2–SO_2 system as an indication that SO_2 is not being rapidly oxidized by atomic oxygen produced from the photolysis of NO_2.

Thus, addition of NO_x to low concentrations of SO_2 seems to produce varying results. To discuss the reactions that occur when mixtures of SO_2 and NO_x are photolyzed in the presence of O_2, the primary reactions of NO and NO_2 when exposed to 3000 to 4000 Å radiation must first be considered. The electronic absorption spectrum of NO starts just below 2300 Å and extends well into the vacuum ultraviolet region; thus, in the region of 3000 to 4000 Å there is no photodissociation of NO or formation of electronically excited NO molecules.

The thermal oxidation of NO by molecular O_2—

$$2 NO + O_2 \rightarrow 2 NO_2 \qquad (32)$$
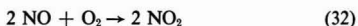
is slow $[k_{32}{}^{20°C} = 10.0 \times 10^3$ liter^2 mol^{-2} sec^{-1} (Greig and Hall, 1966)], but it is important because the thermal oxidation product, NO_2, on photolysis, serves as a source of oxygen atoms. In model systems, even though extreme caution is taken to remove all the NO_2 originally present in the NO, enough NO_2 is formed to initiate reactions between oxygen atoms and other components present.

NO_2 absorbs over most of the visible and ultraviolet spectrum. All of the evidence (Pitts et al., 1963; Sato and Cvetanovic, 1958; Noyes and Leighton, 1941) indicates that the photodissociation of NO_2 occurs at wavelengths shorter than 4047 Å by the process

$$NO_2 + h\nu \rightarrow NO\ (X^2\pi) + O\ (^3P) \qquad (33)$$
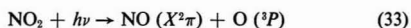
When NO_2 is present in low concentrations in air, the oxygen atom will react with O_2 to produce O_3, which in turn reacts with NO produced in the initial photodissociation to produce NO_2 and O_2. The net result will be a steady state in which small concentrations of O_3 and NO are present.

Bufalini and Stephens (1965) described the mechanism for the thermal oxidation of NO in the presence of ultraviolet light as

$$2 NO + O_2 \rightarrow 2 NO_2 \qquad (34)$$

$$NO_2 + h\nu \rightarrow NO + O \qquad (35)$$

$$O + NO_2 + M \rightarrow NO_3 + M \qquad (36)$$

$$O + NO_2 \rightarrow NO + O_2 \qquad (37)$$

$$O + NO + M \rightarrow NO_2 + M \qquad (38)$$

$$NO_3 + NO \rightarrow 2 NO_2 \qquad (39)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (40)$$

$$O_3 + NO \rightarrow O_2 + NO_2 \qquad (41)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (42)$$
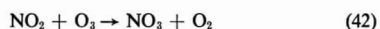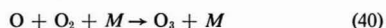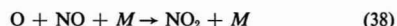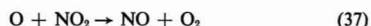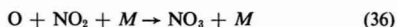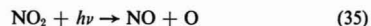
Thus, when SO_2 is photolyzed in the presence of NO_x the following reactions should be considered:

$$SO_2 + NO \rightarrow SO + NO_2 \qquad (43)$$

$$SO_2 + NO_2 \rightarrow SO_3 + NO \qquad (44)$$

$$SO_2 + O + M \rightarrow SO_3 + M \qquad (45)$$

$$SO_2 + O_3 \rightarrow SO_3 + O_2 \qquad (46)$$

$$SO_3 + O \rightarrow SO_2 + O_2 \qquad (47)$$

$$SO_4 + NO \rightarrow SO_3 + NO_2 \qquad (48)$$

$$SO_4 + NO_2 \rightarrow SO_3 + NO_3 \qquad (49)$$

$$SO_4 + O \rightarrow SO_3 + O_2 \qquad (50)$$

$$SO + O \rightarrow SO_2 \qquad (51)$$

$$SO + O_3 \rightarrow SO_2 + O_2 \qquad (52)$$

$$SO + NO_2 \rightarrow SO_2 + NO \qquad (53)$$
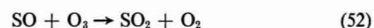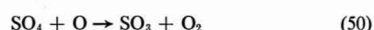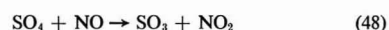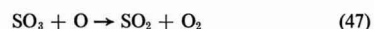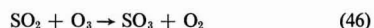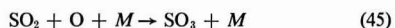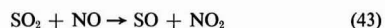
Jaffee and Klein (1966) report for Reaction 44 a specific rate constant of 3.7×10^{-3} liter mol^{-1} sec^{-1} in the dark, both components at high concentration and no O_2 present. Thus, Reaction 44 would not be an important reaction in the SO_2–NO_x system. From all indications, SO_2 in the presence of O_2 does not react with NO and NO_2 in the dark. If a reaction occurs, the rate constants must be extremely small.

There will be competition for the oxygen atom that is formed in the photodissociation of NO_2 by O_2, NO_2, and SO_2. The bimolecular oxygen atom–SO_3 reaction (Reaction 47) does not take place at room temperature (Kaufman, 1961). Although the rate constant for the oxygen atom–O_2 reaction is two to three orders of magnitude less than that for reaction of the oxygen atom with NO_2, NO, or SO_2, the oxygen atom–O_2 reaction will be the most effective in removing oxygen atoms since the concentration of O_2 is 10^5 to 10^6 times greater than that of the other components. However, depending on the ratio of concentrations of NO or NO_2 to SO_2, SO_2 could be an effective secondary competitor, at least with NO or NO_2, for the oxygen atom. The magnitude of the rate constants $k_{36} = 4.2 \times 10^{10}$ liter^2 mol^{-2} sec^{-1}, $k_{37} = 5.3 \times 10^9$ liter mol^{-1} sec^{-1}, $k_{38} = 2.3 \times 10^{10}$ liter^2 mol^{-2} (Schuck et al., 1966), and $k_{45} = 2.7 \times 10^9$ liter^2 mol^{-2} sec^{-1} (Mulcahy et al., 1967) indicates that the effectiveness of oxygen atom–SO_2 reaction increases as the SO_2/NO_x concentration increases.

When the SO_2/NO_x ratio is high, the SO_2 reaction will be of greater importance. At extremely low SO_2/NO_x ratios, the

SO$_2$ reaction would be of minor importance. Evidence for this is found in the work of Jaffee and Klein (1966). They report that with 3×10^{-4} mol liter^{-1} of NO$_2$ and up to 4×10^{-2} mol liter^{-1} of SO$_2$, the quantum yield for the disappearance of NO$_2$ decreases as SO$_2$ increases, an indication that SO$_2$ is indeed effectively competing with NO$_x$ for the oxygen atom. In photochemical smog, concentrations of 20 pphm of NO$_x$ and 20 pphm of SO$_2$ are typical. At an SO$_2$/NO$_x$ ratio of about 1, SO$_2$–O atom reaction rate will be less than NO$_x$–O atom rate by a factor of 10 to 20. However, the contradictory results obtained for SO$_2$–NO$_x$–air systems cannot be explained by differences in the SO$_2$/NO$_x$ ratio; they may be due to differences in the design of the experimental equipment.

Ozone may react with NO, NO$_2$, or SO$_2$. The work of Cadle (Magill et al., 1956) indicates that the SO$_2$–O$_3$ reaction cannot be important. They reacted 1 to 10% SO$_2$ with 1% O$_3$ (an extremely high value of O$_3$ as far as air concentrations are concerned) and 1% water vapor and found that less than 0.1% of the SO$_2$ had reacted in a 24-hr period. Further confirmation is the work of Dunham (1960), which indicates that few, if any, condensation nuclei H$_2$SO$_4$ are formed from the SO$_2$–O$_3$ reaction. The rate constants for the reaction of O$_3$ with NO and NO$_2$, $k_{41} = 2.8 \times 10^7$ liter mol^{-1} sec^{-1} (Ford et al., 1957) and $k_{42} = 4.3 \times 10^4$ liter mol^{-1} sec^{-1} (Johnston and Yost, 1949), signify the importance of the O$_3$–NO reaction in the SO$_2$–NO$_x$ photochemical system. Wilson et al. (1970) have observed that SO$_2$ is removed by a product of the reaction of NO$_2$ and O$_3$. Apparently NO$_3$ and (or) N$_2$O$_5$ react(s) with SO$_2$ to form SO$_3$ and NO$_2$.

Little is known about the reactions of SO$_4$ and SO. In fact, there is no evidence for the existence of SO$_4$. Some work is available on the reactions of SO with oxygen atoms (Rolfes et al., 1965; Sharma et al., 1967; Halstead and Thrush, 1964, 1966) and with NO$_2$ (Clyne et al., 1966).

Thus, for the reaction of SO$_2$ in the presence of NO$_x$ in O$_2$, all likely reactions that can be postulated except for the reactions of SO with oxygen atoms, ozone, or NO$_2$ and the atomic oxygen–SO$_3$ reaction will lead to enhancement of the formation of SO$_3$. If, indeed, the disappearance of SO$_2$ is retarded in the presence of NO, more than likely this would be caused by the effective deactivation of electronically excited SO$_2$ molecules by NO. More work is needed on this reaction system before a quantitative assessment can be given. The effect of the SO$_2$/NO$_x$ ratio over a wide range of concentrations should be ascertained; rate constants for SO$_2$ reactions and more information on aerosol formation are needed.

Photochemical Reactions of SO$_2$–Hydrocarbon System

Paraffins. Dainton and Ivin (1950) reported results of the gas-phase reactions of paraffinic hydrocarbons with SO$_2$, at high concentrations in the absence of O$_2$ ($\lambda >$ 2300 Å). The reactions of SO$_2$ with methane, ethane, propane, *n*-butane, isobutane, and *n*-pentane were investigated.

The investigators observed a pressure fall and formation of a mist, which on settling gave a colorless or pale yellow involatile oil with a disagreeable odor. Molecular weight determinations, and infrared and elemental analyses of the solid product from the *n*-butane–SO$_2$ reaction indicated the presence of C$_4$H$_{10}$SO$_2$ (sulfinic acid) mixed with some disulfinic and disulfonic acids. For the normal paraffins, the quantum yield increased as the number of carbon atoms increased. The quantum yield for the branched-chain isobutane was between the values for *n*-propane and *n*-butane.

Kinetic data for the *n*-butane–SO$_2$ reaction show that the rate of disappearance of SO$_2$ is first order with respect to

light intensity and is fractional order with respect to *n*-butane for *n*-butane pressures less than 200 mm. Butadiene and 1-butene retarded the reaction markedly. Dainton and Ivin (1950) postulated a mechanism involving the initial formation of a biradical,

$$\begin{array}{ccc}
R & & O \\
| & & \| \\
\cdot CH-CH_2-C \cdot \\
| & & \| \\
R & & O
\end{array}$$
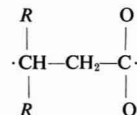
and the sulfinic acids were formed by enolization reactions.

Timmons (1969) irradiated a fixed pressure of SO$_2$ and varying amounts of *n*-butane, isobutane, propane, ethane, or methane at 3130 Å. The decrease in pressure, plus mass spectrometric and gas chromatographic analysis, indicated a stoichiometric ratio of one SO$_2$ molecule removed per molecule of hydrocarbon reacted when the concentration of SO$_2$ was much lower than the concentration of hydrocarbon. When the concentration of SO$_2$ was equal to or greater than the concentration of hydrocarbon, the ratio of SO$_2$ consumed to hydrocarbon consumed always exceeds unity. The quantum yields for hydrocarbon consumption were pressure dependent, ranging from 0.07 for isobutane to less than 0.01 for methane for equal initial concentrations of SO$_2$ and hydrocarbon. Sulfur-containing products, such as sulfinic acids, were observed but no oxygen-containing organic products were found. Only small amounts of other hydrocarbons were present. Timmons concluded that the interaction between excited SO$_2$ and hydrocarbon does not proceed via a free radical mechanism, since no hydrocarbon cracking was observed. However, Ogata et al. (1965) earlier postulated a free-radical mechanism for the photochemical reaction of SO$_2$ with *n*-hexane, which involves the simultaneous formation of alkyl radicals by reaction of the paraffin with excited singlet SO$_2$ and energy transfer by the excited SO$_2$ molecule.

The singlet–triplet energy separation of SO$_2$ is approximately 13 kcal/mol, and since the paraffinic hydrocarbon C—H bond dissociation energy is of the order of 100 kcal/mol, it is highly doubtful whether energy transfer by the excited singlet, forming SO$_2$ in the triplet state, could supply the necessary energy for alkyl radical formation.

Badcock et al. (1970) have suggested two alternate pathways for sulfinic acid formation. A true ^{3}SO$_2$ insertion in the C—H bond of the hydrocarbon-forming RSO$_2$H or an initial H-atom abstraction by ^{3}SO$_2$-forming SO$_2$H and R radical may occur. They conclude that their data and the results of previous studies seem to be most consistent with the H-atom abstraction mechanism. Of interest is the suggestion by Trotman-Dickenson (1955) that the reactions are probably molecular, involving a four-center activated complex.

$$\begin{array}{ccc}
C & \cdots & H \\
\vdots & & \vdots \\
O = S & \cdots & O
\end{array}$$
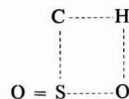
Johnston and der Jain (1960) irradiated mixtures containing 20 and 50 mm each of SO$_2$ and *n*-butane in the presence of dry air with natural sunlight as the ultraviolet source. The formation of aerosol was light when SO$_2$ and *n*-butane only were present at 20-mm pressure each but became heavy when air was also present. The liquid product was colorless when only SO$_2$ and *n*-butane were present but was light yellow when air was also present. When SO$_2$ and *n*-butane were increased

to 50 mm, the formation of aerosol was heavy within two min after the mixtures were placed in sunlight. Qualitative chemical tests indicated that the liquid product was a mixture of highly oxidized strong organic acids containing sulfur. These results led the authors to propose that the photochemical reactions of SO_2 with paraffinic hydrocarbons were important in air pollution because of the formation of aerosols.

More recently, Kopczynski and Altshuller (1962) investigated the photochemical reactions of paraffinic hydrocarbons with SO_2 using lower concentrations (50 to 1000 ppm). The reactions of n-butane, isobutane, and neopentane with SO_2 were studied in irradiations with either a mercury sunlamp or a mercury arc. Infrared spectra of the gaseous components were obtained before and after each irradiation. Formation of aerosol or liquid film was determined visually.

When high concentrations (12-mm each) of SO_2 and hydrocarbon were irradiated with either the sunlamp or mercury arc, appreciable quantities of condensate formed on the walls and a strong band at 5.7 μ, attributed to carbonyl, was present. This confirmed Johnston and der Jain's work at high concentrations. However, when the concentrations were decreased to 1-mm each, only a light condensate and a weak carbonyl band were present with the mercury arc and no detectable condensate or carbonyl was present with the sunlamp.

At concentrations in the 0.05 to 0.10-mm range, no film could be detected with either the mercury arc or sunlamp. The investigators concluded that reactions of SO_2 with saturated hydrocarbons do not contribute significantly to the formation of aerosols in air pollution situations.

Olefins

Dainton and Ivin (1950) found that irradiation of high concentrations of SO_2 and 1-butene produced an oil which, on further irradiation, formed a solid that resembled a polysulfone. Renzetti and Doyle's (1960) experiments in which butadiene or 1-pentene (3 ppm) was added to SO_2 (0.3 ppm) and irradiated with a medium pressure mercury arc indicated that production of aerosol was suppressed by the olefins. Kopczynski and Altshuller (1962) found no detectable condensate in the presence of SO_2 at corresponding concentrations.

Sidebottom et al. (1970) measured the quenching rate constants for reaction of $^3SO_2$ with ethylene, trichloroethylene, trifluoroethylene, propylene, cis-2-butene, and cyclopentene. They hypothesize that the quenching reaction proceeds through a highly polarized charge transfer-like intermediate formed between the $^3SO_2$ and the π-system of the olefin. This complex leads to an SO_2 addition to the olefinic bond, forming a diradical:

$$
\begin{array}{c}
O \qquad O\cdot \\
\diagdown\!\!\diagup \\
S \qquad\qquad R \\
\diagup \qquad\quad \diagdown \\
R\!-\!C\!-\!\!C \\
\diagup \qquad\quad \diagdown \\
R \qquad\qquad R
\end{array}
$$
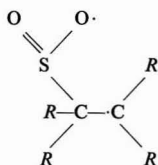
Previous published results on SO_2–olefin systems were rationalized in terms of alternate paths of decay of the intermediate triplet diradical.

Thus, all available evidence indicates that the reactions of SO_2 in the presence of hydrocarbons at levels that occur in a polluted atmosphere are not significant in the formation of aerosols. If O_3 is indeed formed as postulated in the photo-

oxidation of SO_2, its presence would be manifested by the formation of aldehydes and ketones, which are major products observed from gaseous olefin–ozone reactions.

Photochemical Reactions of the SO_2–NO_x–Hydrocarbon System

Prager et al. (1960) surveyed the formation of aerosols from different types of hydrocarbons mixed with NO_2 in the presence and absence of SO_2. Results are summarized in Tables II and III. Paraffinic hydrocarbons (n-butane and 2-methylpentane) gave little or no aerosol in the presence of NO_2 and SO_2. Monoolefins (ethylene, 1-butene, 2-butene, 1-pentene, 2-pentene, 1-hexene, 2-hexene, and 3-heptene) produced no appreciable amounts of particulates in the presence of only NO_2 but produced large quantities of aerosols when SO_2 was added to the hydrocarbon–NO_2 blend. The amount of aerosol produced increased as the number of carbon atoms in the monoolefin increased. Whereas, little particulate matter was produced during irradiation of straight-chain monoolefins and NO_2, aerosol formed slowly in irradiations of diolefins (1,3-butadiene and 1,5-hexadiene) and NO_2. The 1,5-hexadiene–NO_2 system produced a significantly larger number of aerosols than the 1,3-butadiene. In the presence of SO_2 and NO_2, the increase in aerosol was larger for the butadiene than for the hexadiene.

Little information is available on the acetylenic hydrocarbons. The work of Renzetti and Doyle (1960) indicates that 1-butyne forms no aerosol when irradiated in the presence of NO and forms only a small amount, if any, in the presence of NO and SO_2.

Irradiation of cyclic saturated hydrocarbons (cyclopropane and cyclohexane) in the presence of NO_2 produced little or no aerosol, whereas irradiation of cyclic olefins (cyclopentene, cyclohexene, and dicyclopentadiene) in the presence of NO_2 gave a large amount of aerosol whether SO_2 was present or not. The rate of aerosol production with cyclic olefins was much more rapid than the rate with straight-chain olefins; SO_2 did not significantly affect the rate of aerosol production or the amount of aerosol obtained (Prager et al., 1960).

Data on aerosol formation in aromatic systems are meager.

Table II. Effect of Irradiation on Aerosol Formation in Nitrogen Dioxide–Hydrocarbon Reactions[a]

(Reactant concn., ppm: olefin, 10; NO_2, 5; SO_2, 2)

| Hydrocarbon	Photometer reading incr.[b]	
	Olefin–NO_2	Olefin–NO_2–SO_2
Ethylene	0.1	2.2
1-Butene	0.05	2.85
2-Butene	0.05	3.0
2-Methylpropene	0.0	
1-Pentene	0.1	3.05
2-Pentene	0.0	3.0
3-Methyl-1-butene	0.1	
1-Hexene	0.05	3.35
2-Hexene	0.25	3.05
cis-3-Methyl-2-pentene	0.2	
3-Heptene	0.45	3.35
2,4,4-Trimethyl-1-pentene	3.3	3.3
n-Butane		0.1
2-Methylpentane		0.0

[a] Prager et al., 1960.
[b] Average of three determinations for straight-chain olefins. Reading before irradiation subtracted from readings during irradiation.

Early work by Renzetti and Doyle (1960) indicated that aromatics (benzene, toluene, ethyl benzene, and *p*-xylene) in the presence of NO alone formed no aerosol. These aromatic compounds in the presence of both NO and SO_2 formed significantly less aerosol than olefin–NO–SO_2 systems. The more recent work of Altshuller et al. (1966) and the Air Pollution Control District, Los Angeles County (1966) disagrees with the work of Renzetti and Doyle. Aerosol formation in the toluene–NO system and trimethyl benzene–NO system occurs to an extent comparable to the ethylene–NO_2–SO_2 system. Benzene and xylene in the presence of both NO_x and SO_2 form little aerosol whereas toluene in the presence of NO and SO_2 forms aerosol to an extent comparable to olefin–NO–SO_2 systems. A 1/1 mixture of toluene and xylene (NO_x and SO_2 present) produces a significantly greater quantity of aerosol than that found from the single aromatic compound. Under the proper conditions, the toluene–xylene mixture forms aerosol in excess of that formed from irradiated auto exhaust. Apparently, a large aerosol synergistic effect occurs in aromatic hydrocarbon–NO_x–SO_2 systems. A detailed investigation of aerosol formation from aromatic systems is needed.

Of interest here are the experiments of Stevenson et al. (1965) in which *trans*-2-butane was added to the cyclohexene–NO_2 system after aerosol was formed. Concentrations of *trans*-2-butene greater than 3 ppm caused a marked decrease in aerosol, whereas concentrations of 3 ppm or less increased the aerosol. Unfortunately, no cohydrocarbon irradiations were made in the presence of both SO_2 and NO_2.

The reactions taking place when NO_x is irradiated in the presence of hydrocarbons are summarized briefly in the following paragraphs. The summary is followed by discussion of the effect of mixtures of hydrocarbon and NO_x on the rate of disappearance of SO_2, the effect of SO_2 on the rate of consumption of hydrocarbon and rate of oxidant formation, and the effect of the ratio of reactants in the SO_2–NO_x–hydrocarbon system.

Table III. Aerosol Formation by Systems Containing Diolefins and Cyclic Hydrocarbons[a]

(Reactant concn., ppm: hydrocarbon, 10; NO_2, 5; SO_2, 2; O_3, 5)

	Photometer readings		
System	Trial 1	Trial 2	Trial 3
1,3-Butadiene, NO_2[b]	1.0	1.3	.
1,3-Butadiene, NO_2, SO_2[b]	3.2		
1,3-Butadiene, O_3[c]	0.25	0.0	0.0
1,5-Hexadiene, NO_2[b]	3.7	3.6	
1,5-Hexadiene, NO_2, SO_2[b]	3.9	3.95	
1,5-Hexadiene, O_3[c]	3.2	3.2	
Cyclopropane, NO_2[b]	0.3	0.0	
Cyclopentene, NO_2[b]	2.75	2.5	
Cyclohexane, NO_2[b]	0.0		
Cyclohexene, NO_2[b]	3.65	3.7	3.2
Cyclohexene, NO_2, SO_2[b]	3.5		
Cyclohexene, NO, SO_2[b]	3.75		
Dicyclopentadiene, NO_2[b]	4.35	4.35	
Dicyclopentadiene, NO_2, SO_2[b]	3.9		
Cyclopentene, O_3[c]	2.7		
Cyclohexene, O_3[c]	3.35		

[a] Prager et al. (1960).
[b] Irradiated.
[c] Dark.

When hydrocarbons are present with NO and ultraviolet light, the equilibrium

$$NO_2 + O_2 \overset{h\nu}{\rightleftarrows} NO + O_3 \tag{54}$$
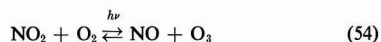
is disrupted. The NO is oxidized almost completely to NO_2 and ozone builds up with the disappearance of NO. The ozone does not appear until NO_2 is at its maximum value and a subsequent increase in O_3 occurs as NO_2 then decreases. A typical profile of the olefin–NO_2 reaction is shown in Figure 1 (Altshuller and Cohen, 1963). The major products in the photooxidation of hydrocarbons in the presence of NO include ozone (or oxidant), aldehydes, ketones, carbon monoxide, and organic nitrates. Small yields of epoxides, alcohols, esters, and peroxides have been obtained in some systems. Most of the products can be explained by an initial attack by either atomic oxygen or ozone, which produces hydrocarbon radicals, alkoxy radicals, and hydroperoxy radicals. Further fragmentations, rearrangements, and reactions of the radicals with other substituents produce the observed products.

Rate constants for the ozone–hydrocarbon reactions are generally lower than those for atomic oxygen–hydrocarbon reactions by a factor of 10^4 to 10^5. However, since ozone is present at a much higher concentration than atomic oxygen, it still is an important reactant for hydrocarbons. The available rate constant data show that the rate constants for the reactions of ozone with olefins are one to three orders of magnitude larger than those obtained for reactions of ozone with paraffinic hydrocarbons, acetylene, and aromatic hydrocarbons. Likewise, the atomic oxygen–olefin rate constants are larger than those obtained for the reaction of atomic oxygen with paraffinic hydrocarbons and aromatic hydrocarbons. For more detailed discussions of hydrocarbon–NO_x reactions, the reviews of Altshuller and Bufalini (1965, 1971) may be consulted.

Although Renzetti and Doyle's (1960) measurements of SO_2 concentration are uncertain because of difficulty in measuring such low concentrations, their data for different classes of hydrocarbons indicate a marked increase in the disappearance of SO_2 in the presence of hydrocarbons and NO over that observed in irradiation of SO_2–O_2 mixture.

It is impossible to ascertain the amount of increase with this

Figure 1. Concentration curves of ethylene and major products upon photooxidation with nitric oxide

type of hydrocarbon because the SO$_2$ concentration measurements are so uncertain. However, a series of experiments on the photooxidation of 2-methyl-2-butene in the presence of NO and SO$_2$ indicates that the increase in SO$_2$ disappearance is dependent on the ratio of reactants. When initial concentrations of SO$_2$ and NO are held constant at 0.1 and 1 ppm, respectively, and the olefin concentration is decreased from 3 ppm to 0.5 ppm, the rate of disappearance of SO$_2$ increases. The rate also increases if the olefin and NO concentrations are held constant at 3 ppm and 1 ppm, respectively, and the SO$_2$ concentration is decreased from 1 to 0.1 ppm. These results indicate that low concentrations of olefin can be quite effective in photooxidizing SO$_2$ in the presence of NO.

The effect of the ratio of reactants on the formation of aerosol was pointed out by Harkins and Nicksic (1965b). They found that light scattering was directly proportional to the concentration of SO$_2$ (0 to 16 ppm) when the concentration of propylene was 5 ppm and concentration of NO$_2$ was 2 ppm. These findings seem to contradict those of Renzetti and Doyle (1960), who observed that the rate of SO$_2$ consumption increased as SO$_2$ concentration was decreased from 1 to 0.1 ppm in the presence of 3 ppm olefin and 1 ppm NO. This implies that the formation of aerosol is proportional to the initial concentration of SO$_2$ but is not proportional to the rate of disappearance of SO$_2$. With the ratio of propylene to NO to SO$_2$ held constant at 5/2/0.5, respectively, but with the concentrations increased by factors of 2, 4, and 8, the amount of aerosol increased essentially linearly with increasing SO$_2$ concentrations at the higher concentration levels. The slope was less at the low concentration level.

In irradiations of mixtures of 2-pentene, NO$_2$, SO$_2$, and air with a residence time of 34 min, SO$_2$ disappeared rapidly, with equilibrium being reached in about 20 min. Aerosol formation was much slower; little light scattering was observed at 20 min, and maximum light scattering was measured at 90 min (Reckner and Scott, 1963).

The effect of concentration of NO on aerosol concentration is shown in Figure 2 (Harkins and Nicksic, 1965b). The main aerosol formation occurs shortly after conversion of NO to NO$_2$ is completed. Aerosol buildup continues until the ozone maximum is reached, then aerosol formation gradually decreases. At the ozone maximum, there is an increase in aerosol as NO concentration increases from 0.5 ppm NO to 1 ppm followed by a decrease as it goes from 1 ppm to 2.0 ppm.

Harkins and Nicksic (1965b) found that an increase in SO$_2$ concentration results in less hydrocarbon and less formaldehyde being formed in a given time. This effect must be slight, however, because in mixtures of 5-ppm propylene and 2-ppm NO the rate of propylene oxidation decreased only by a factor of 2 to 3 when SO$_2$ was increased from 2 ppm to 1000 ppm. This was later confirmed by Altshuller et al. (1968). They irradiated mixtures of 2-ppm propylene, 0.5-ppm NO, and 0 to 1.12-ppm SO$_2$. As the SO$_2$ was increased, no significant differences were apparent in the rates of disappearance of propylene and NO or in the yields of oxidant, peroxyacetyl nitrate, formaldehyde, and acetaldehyde. The sulfate levels increased with increasing SO$_2$. The amount of SO$_2$ consumed decreased from 60% at lower initial SO$_2$ concentration to 25% at the higher levels but only 15 to 35% of the SO$_2$ consumed could be accounted for as sulfate.

With the system 1-hexene (4.5 ppm)–NO$_2$ (1 ppm)–SO$_2$ (1 ppm), Ripperton et al. (1962) found a significant increase in the rate of SO$_2$ disappearance. Sixty to sixty-nine percent of the SO$_2$ was consumed as compared with 30% in the SO$_2$–O$_2$ system. Their work also shows that the formation of oxi-

dant is notably suppressed when SO$_2$ is added to the 1-hexene–NO$_2$ system.

Wilson and Levy (1968), however, found that with 1-butene (4 ppm)–NO (1 ppm)–SO$_2$ (0–0.75 ppm) in relatively dry conditions the presence of SO$_2$ resulted in a general slowing down of photochemical smog reactions; the rate of conversion of NO to NO$_2$, the rate of disappearance of NO$_2$, the rate of production of ozone, and the maximum reaction rate of 1-butene all decreased. The induction time for 1-butene increased. However, the maximum ozone concentration increased. Some of these effects are shown in Figures 3–7. (These figures are discussed in more detail later.) The maximum light-scattering signal, presumably aerosol, was low except with an SO$_2$ concentration of 0.75 ppm. The aerosol was not observed until after the NO$_2$ peak had been reached and the NO concentration had fallen to a low value. The rate of decay
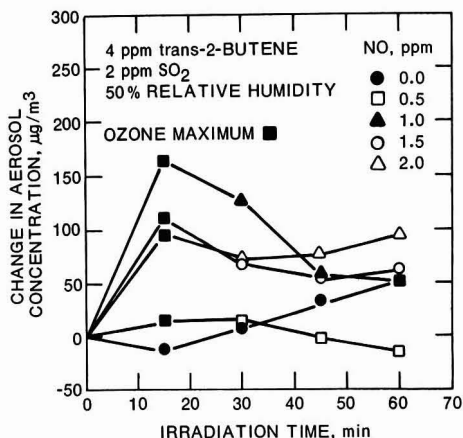
Figure 2. Effect of nitric oxide concentration on SO$_2$-induced aerosols
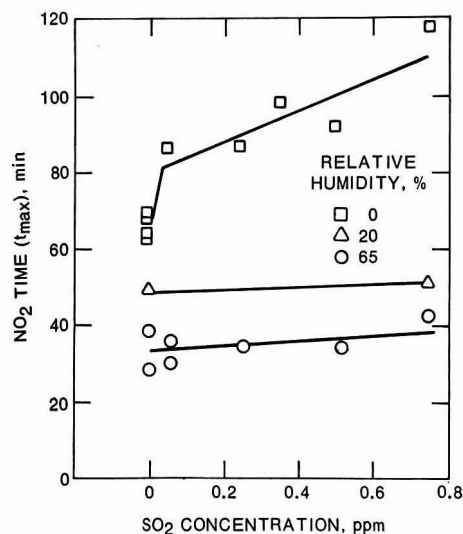
Figure 3. Time required to reach maximum NO$_2$ concentration vs. SO$_2$ concentration for the system 1-butene (4 ppm)–NO (1 ppm)–SO$_2$ (0–0.75 ppm)
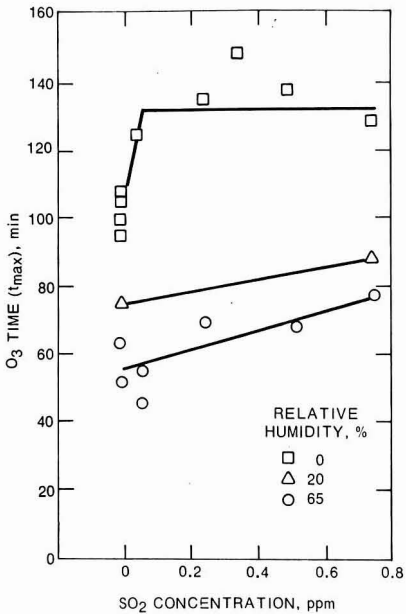
Figure 4. Time required to reach maximum O_3 concentration vs. SO_2 concentration for the system 1-butene (4 ppm)-NO (1 ppm)-SO_2(0-0.75 ppm)
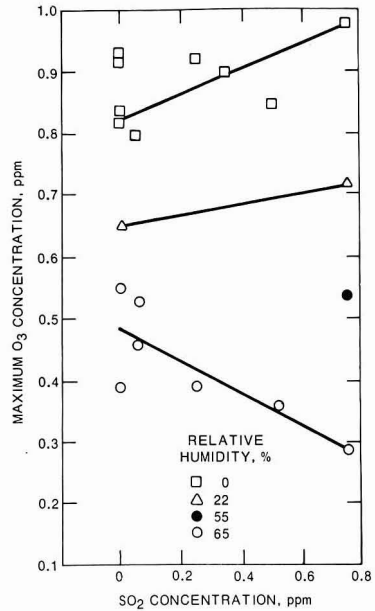

Figure 5. Maximum O_3 concentration vs. SO_2 concentration for the system 1-butene (4 ppm)-NO (1 ppm)-SO_2 (0-0.75 ppm)

of SO_2 greatly increased in the presence of 1-butene and NO. A typical reaction profile for the system 1-butene-NO-SO_2 in relatively dry conditions is shown in Figure 8.

Although the role of SO_2 in the photooxidation of hydrocarbon-NO systems is difficult to assess quantitatively, the literature provides some indications from which a rough qualitative picture might be formed.

Prager et al. (1960) found that when SO_2 was present at the start of photolysis of a 2-pentene-NO_2 system, the greatest amount of particulate matter was formed. The longer the reaction had proceeded before SO_2 was introduced, the less aerosol was formed. The addition of SO_2 10 min after the start of irradiation reduced light scattering to 10%; addition at 20 min reduced light scattering to 1%. In photolysis of

Figure 6. Half-times for reaction of 1-butene vs. SO_2 concentration for the system 1-butene (4 ppm)-NO (1 ppm)-SO_2 (0-0.75 ppm)
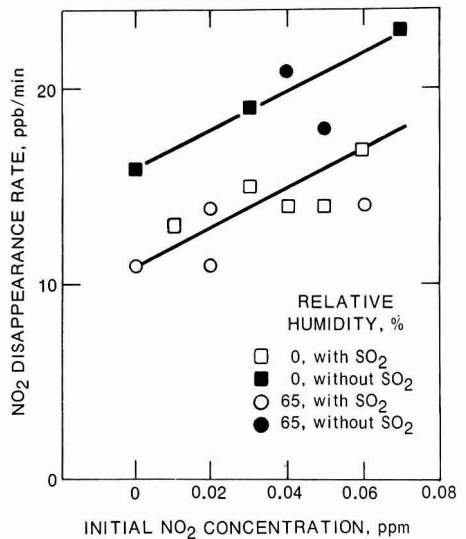
Figure 7. Maximum rate of NO_2 disappearance vs. initial NO_2 concentration for the system 1-butene (4 ppm)-NO (1 ppm)-SO_2 (0-0.75 ppm)
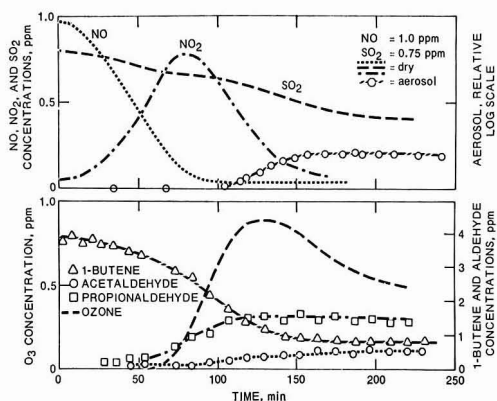
Figure 8. Typical smog profile for the system 1-butene (4 ppm)–NO (1 ppm)–SO$_2$ (0–0.75 ppm) in 200-liter smog chamber under dynamic conditions with no added water vapor

2-pentene and NO$_2$ (no SO$_2$), the NO$_2$ was reduced to 40% after 10 min and to about 10% after 20 min. The investigators concluded that the aerosol was produced by reaction of SO$_2$ and an intermediate in the olefin–NO$_2$ reaction.

Harkins and Nicksic (1965b) found that in the hydrocarbon–NO–SO$_2$ system the main aerosol formation occurred shortly after conversion of NO to NO$_2$ was complete. At this point, the NO$_2$ concentration was at its maximum and the production of oxygen atoms was also at a maximum. Buildup of particulates continued until the ozone maximum was reached, after which aerosol production gradually decreased and leveled off. When NO$_2$ was used instead of NO in photolysis, they obtained more intense light scattering without a delay or induction period. Prager et al. (1960) also found that in olefin–NO–SO$_2$ photooxidations little or no aerosol was formed until the NO was converted to NO$_2$ and that once ozone was produced, particulates accumulated rapidly. Thus, NO can be eliminated as an active species.

There are some indications that ozone is somehow involved in the formation of particulates. The reaction of O$_3$ with SO$_2$ produces no aerosol (Dunham, 1960). The reaction is too slow to be of any significance. Although straight-chain monoolefins and 1,3-butadiene formed few, or no particulates when reacted with O$_3$ in the dark, 1,5-hexadiene, cyclopentene, and cyclohexene formed a larger number from the reaction with O$_3$ in the dark (Prager et al., 1960). The oxidation of SO$_2$ occurred at a comparable rate when SO$_2$ was reacted with ozone and hydrocarbons in the dark (Harkins and Nicksic, 1965b). The rate depended strongly on ozone concentrations. It, therefore, seems that some intermediate in the O$_3$–hydro-

carbon reaction is effective in promoting the oxidation of SO$_2$ and in the formation of particulates in hydrocarbon–NO$_x$–SO$_2$ systems. Several authors have proposed that this intermediate might be an alkyl, alkoxy, peroxyalkyl, or peroxyacl radical and that such reactions as SO$_2$ addition or oxygen atom

$$R \cdot (RO \cdot, RO_2 \cdot) + SO_2 \rightarrow RSO_2 \ (ROSO_2, RO_2SO_2) \quad (55)$$

$$RO \cdot (RO_2 \cdot) + SO_2 \rightarrow R \cdot (RO \cdot) + SO_3 \quad (56)$$

transfer could account for the enhancement (Harkins and Nicksic, 1965b; Leighton, 1961).

Reactions of type 56 could account for an increase in formation of sulfuric acid aerosol, and reactions of type 55 could explain the formation of carbonaceous aerosols such as sulfenic or sulfonic acids. Most evidence indicates that the aerosols formed from irradiation of hydrocarbons (C > 4 or 5) in the presence of NO$_x$ and SO$_2$ do not contain carbon; the work of Prager et al. (1960) shows, however, that irradiations of hydrocarbons (olefins with C > 6) in the presence of NO$_2$ produce aerosols that are probably carbonaceous.

Several recent reports have described studies of alkyl radical additions to SO$_2$. Good and Thynne (1967) studied the reaction of SO$_2$ with methyl radicals generated from the photolysis of azomethane (λ > 3400 Å) and with ethyl radicals generated by the photolysis of diethyl ketone. The addition reaction of methyl radicals forming methylsulfonyl radicals was rapid at room temperature. The rate of this reaction was comparable with the rate of the three-body reaction of methyl radicals with oxygen. Table IV compares reactivities of methyl and ethyl radicals with SO$_2$ and O$_2$. The similarity in the rates of SO$_2$ and O$_2$ with CH$_3$ radicals, however, will be less at atmospheric conditions, where concentration of oxygen is 10^5 to 10^6 times greater than the concentration of SO$_2$. Thus, at CH$_3$ = 10^{-14} mol/cm^3, SO$_2$ = 10^{-11} mol/cm^3, O$_2$ = 10^{-5} mol/cm^3, and M = 10^{-5} mol/cm^3 (the CH$_3$ radical–O$_2$ reaction is a three-body process), log $R_{CH_3SO_2}$ = −15.3, and log $R_{CH_3O_2}$ = −7.8. Gall et al. (1969) have shown that photolysis of azomethane in SO$_2$ is much more complicated than Good and Thynne assumed and that their conclusions concerning the rate constants of methyl radical–SO$_2$ reactions must be reevaluated. Timmons (1969) investigated the alkyl radical addition to SO$_2$ using both CH$_3$ and CF$_3$ radicals. Scavenging of the CF$_3$ radicals by SO$_2$ is the slower process.

In summary, the rate of disappearance of SO$_2$ and the formation of aerosol increase when SO$_2$ is photolyzed in the presence of olefinic hydrocarbons and NO$_x$. However, the effect of SO$_2$ on the rate parameters in the hydrocarbon–NO$_x$ system has not been explained. Indications are that some intermediate in the ozone–hydrocarbon reaction is effective in promoting the oxidation of SO$_2$ and the formation of aerosols. Whether excited SO$_2$ is necessary for this reaction to be effective is not known.

Table IV. Comparison of Arrhenius Parameters, Velocity Constants, and Rates of Formation of RX at 25 °C for the Reaction: $R + X(+M) \rightarrow RX(+M)$[a]

R	X	log A mol^{-1} cm^3 sec^{-1}	E kcal mol^{-1}	log k(25 °C) mol^{-1} cm^3 sec^{-1}	log R_{RX}	Ref.
CH$_3$	SO$_2$	10.82	1.5	9.7	−11.3	Good and Thynne, 1967
C$_2$H$_5$	SO$_2$	11.0	3.1	8.6	−12.4	Good and Thynne, 1967
CH$_3$	O$_2$	16.18[b]	0	16.18[b]	−10.8	Hoare and Walsh, 1957
C$_2$H$_5$	O$_2$	10.7	0	10.7	−10.4	Jolley, 1957

[a] Good and Thynne, 1967.
[b] Units of k and A: mol^{-2} cm^6 sec^{-1}, calculated using [R] = 10^{-14}, [M] = 10^{-6}, [X] = 10^{-7}, mol cm^{-3}; R_{RX} in mol cm^{-3} sec^{-1}.

Photochemical Reactions of SO₂-CO System

At a recent meeting, Heicklen (1969) put forth an interesting mechanism for the role of carbon monoxide in photochemical smog. This mechanism involves the oxidation of CO by hydroxyl radicals and the subsequent formation of hydroperoxide radicals. The hydroperoxide radicals can then participate in the oxidation of nitric oxide. Subsequently, Westberg and Cohen (1970) analyzed the data of Schuck and Doyle (1959) and were able to reproduce the experimental curves by means of a computer. The computer calculations show that the rate of hydrocarbon disappearance is not significantly altered by the addition of 100 ppm of CO but that the yields of peroxyacetyl nitrate, ozone, and formaldehyde are greater. Bufalini et al. (1970) have found that the addition of CO to n-butane irradiated in the presence of nitric oxide enhances the rate of oxidation of nitric oxide. The mechanism put forth by Heicklen (1969) is apparently correct, and CO does facilitate the oxidation of nitric oxide. Whether the computer analysis of Westberg and Cohen (1970) is valid can be established only by experimentation. If experimental results verify that oxidant formation is enhanced by the presence of carbon monoxide, then it is entirely possible that the oxidation of SO₂, when it is present, is also affected. However, the photolysis of SO₂ and CO mixtures in the absence of O₂ is apparently quite low. Timmons (1969) found a quantum yield of 0.005 for CO₂ formation at 25°C with equal pressures of SO₂ and CO; he observed only a slight increase with increasing CO pressure. The quantum yield for CO₂ formation was low for all reactant pressures employed, and it decreased slightly with increasing temperature over the range of 25° to 150°C.

Effect of H₂O Concentration

The early work of Gerhard and Johnstone (1955) indicated that relative humidity had little effect on the photooxidation of SO₂ alone in air. They found that the rate of SO₂ disappearance was essentially constant for a series of runs with 10-ppm SO₂ and relative humidities of 32, 46, 71, and 91%. However, Renzetti and Doyle (1960) found that the quantum yield for sulfur dioxide consumption with SO₂ concentrations of 0.61 to 0.22 ppm in air of 50% RH decreased from 0.3 to 0.036 when SO₂ was photooxidized in a dry system and P_{SO_2} = 12.7 mm, P_{O_2} = 10.6 mm. They also found that humidity had a striking effect on light scattering. With a SO₂ concentration of 0.47 ppm, light scattering increased by a factor of 8 to 12 when the relative humidity was increased from 0 to 50%. Unfortunately, the rate of SO₂ consumption was not measured in this set of experiments.

Endow et al. (1963) obtained spectral data from aerosols generated from the 2-methyl-2-butene-NO₂-SO₂ system. These data indicated that the relative contributions of inorganic and organic components to the aerosol generated at 10 to 20% RH were different from those of aerosols generated at 50% RH. At 10 to 20% RH sulfuric acid was present in the collected material but the absorption attributable to inorganic nitrogen and particularly to unidentified components was much stronger.

Goetz and Pueschel (1967) investigated the system 1-octene (80 ppm)-NO₂ (60 ppm)-SO₂ (0, 2, 15, and 60 ppm) at relative humidities of 15 to 55%. Results, shown in Figure 9, indicate a notable increase in light scattering as SO₂ was increased from 2 to 60 ppm after an initial inhibiting effect at SO₂ = 2 ppm. The increase was most pronounced at lower humidities; at high humidities it was only moderate. The inhibiting effect of relatively low SO₂ concentrations (2 ppm) was greater at higher relative humidities. The data, plotted as a function of
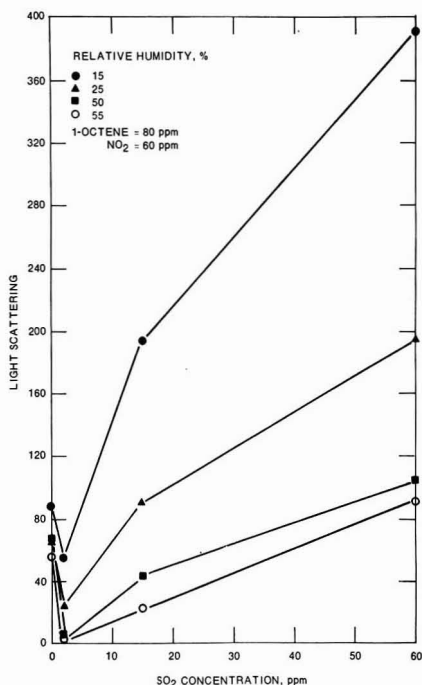
Figure 9. Light scattering as a function of SO₂ concentration for the 1-octene–NO₂–SO₂ system
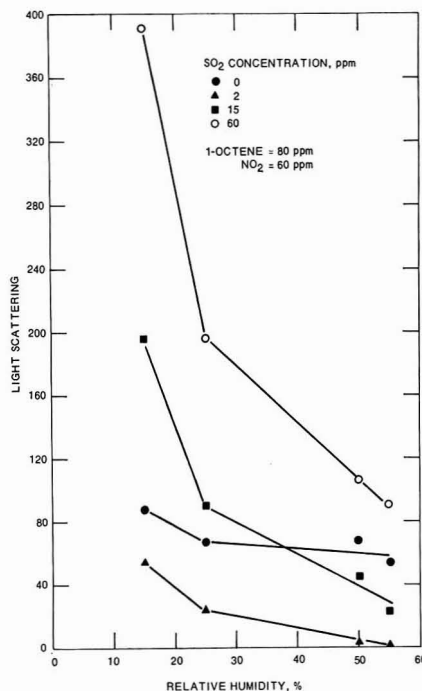
Figure 10. Light scattering as a function of relative humidity for the 1-octene–NO₂–SO₂ system

relative humidity in Figure 10, show that light scattering decreased as relative humidity increased, at all concentrations of SO_2 employed. The indicated behavior of hygroscopic particles exposed to increasing humidity is to adsorb moisture amounting to a few molecular layers at low relative humidities; to dissolve as humidity increases, becoming saturated droplets, and at the same time, undergoing an abrupt size increase; and thereafter, as humidity increases still further, to grow larger and more dilute (Orr et al., 1958). It is entirely possible that the aerosols produced by Goetz and Pueschel at high humidities grew to such a size that deposition on the walls of the photochemical chamber was occurring. No measurements were made, however, for sulfate on the reactor walls. The presence of inert nuclei did not affect the strong influence of humidity.

Figures 11–14, along with Figures 3–7, show the results of Wilson and Levy (1968) for the photooxidation of 1-butane (4 ppm)–NO (1 ppm)–SO_2 (0.75 ppm) at different relative humidities. The results obtained under dry conditions have been discussed. From Figures 3–7, the inhibiting influence of SO_2 on the 1-butene–NO reaction was less pronounced in the presence of H_2O. The maximum ozone concentration decreased as the relative humidity increased, but it decreased with increasing SO_2 concentration (0 to 0.75 ppm) at high relative humidity (65%). This was in contrast to results at lower humidities, where the maximum ozone concentration increased with increasing SO_2 concentrations.

Although SO_2 has an inhibiting effect on the 1-butene–NO reaction, Figures 11–13 show that H_2O has a general accelerating effect. The reaction time parameters in Figure 12 show a large increase in rate as humidity was increased from 0 to 22% and smaller increases between 22 and 65%. It should be pointed out that there has been some controversy in the past few years on the effect of water vapor on the olefin–NO reaction. Scott (Stephens and Price, 1969) and Dimitriades (1967) reported that the reaction is much slower in drier mixtures; however, Stephens and Price (1969) found no decrease in reactivity under dry conditions, and Bufalini and Altshuller (1969) found no difference in hydrocarbon consumption when the relative humidity was increased from 5 to 50%.

The effect of humidity on aerosol formation in Figure 14 is interesting. As the relative humidity increased, the amount of light scattering decreased until no aerosol appeared at 65% RH. This agrees with the work of Goetz and Pueschel (1967). However, as the relative humidity increased, the aerosol was observed earlier in the reaction. Since aerosol formation was first observed at the maximum NO_2 concentration, the earlier appearance of aerosol is attributed to the accelerating effect of H_2O on the time to reach the maximum concentration of NO_2. Wilson and Levy (1968) suggest that since the formation of peroxyacylnitrates shows this same dependence, the peroxyacyl radical may be important in aerosol formation. However, they have neglected the influence of water vapor on the coagulation and size of the condensation nuclei. A count of the condensation nuclei as well as the light scattering of the aerosol as the humidity was increased would have been more informative. There is strong evidence that water vapor concentration affects the coagulation rate and size of the aerosol (Hayakawa, 1964; Orr et al., 1958; Dalla-Vale et al., 1954).

Identity of Aerosols

Little work has been done on determining the chemical identity of aerosols. Part of the problem arises from the necessity of working with extremely small amounts of materials

and the limitations of the available analytical instruments.

The aerosol from the simple system SO_2 and O_2 has been identified as H_2SO_4. No tests have been reported on the chemical identity of aerosols obtained in the SO_2–NO_x system. More than likely, the aerosol is sulfate also. Nitrosyl hydrogen sulfate could possibly be formed as an aerosol, but this compound is so unstable in the presence of H_2O that if it were formed it would immediately be converted to H_2SO_4.
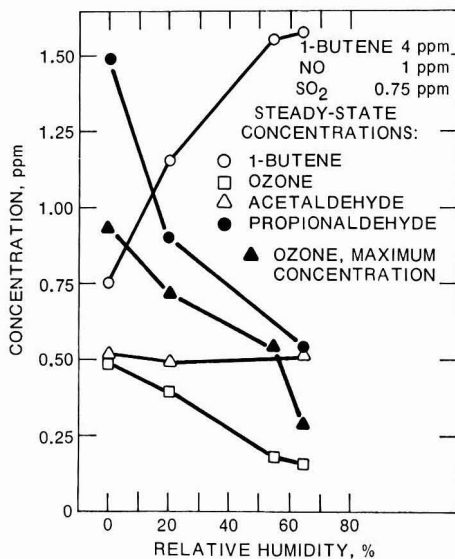
Figure 11. Effect of water vapor concentration on concentration parameters for the the 1-butene–NO–SO_2 system
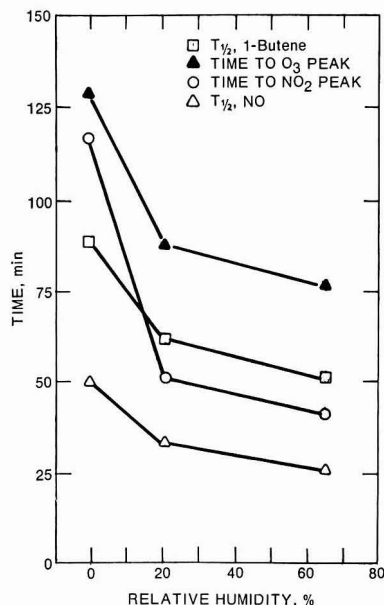
Figure 12. Effect of water vapor concentration on rate parameters for the 1-butene (4 ppm)–NO (1 ppm)–SO_2 (0.75 ppm) system
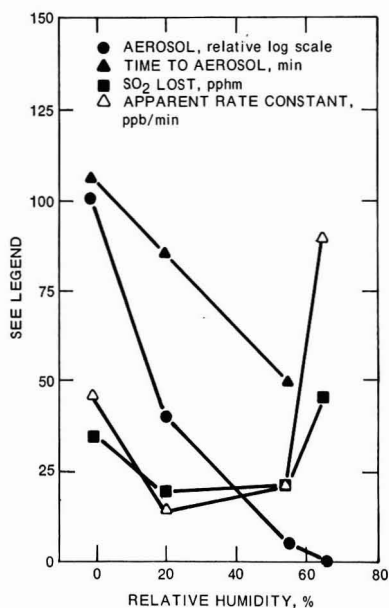
Figure 13. Effect of water vapor concentration on SO_2 parameters for the 1-butene (4 ppm)–NO (1 ppm)–SO_2 (0.75 ppm) system
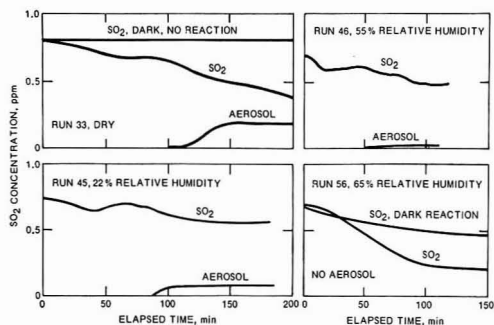

Figure 14. SO_2 decay curves and aerosol formation curves at various concentrations of water vapor

The dip in the early part of the SO_2 profiles for relative humidities of 0, 22, and 55% was due to interference of NO_2 with the SO_2 analysis (Wilson, 1971)

Prager et al. (1960) did not find enough nongaseous products from irradiations at low concentrations to permit identification but did obtain enough material for infrared analysis at higher concentrations (200 ppm hydrocarbon, 40 ppm NO_2, and 40 ppm SO_2). A CCl_4 solution of the particulates obtained from irradiation of 2-pentene–NO_2–SO_2 system gave a spectrum with C—H and carbonyl bands at 3.4 and 5.8 μ, respectively. Major peaks were also obtained at 6.9, 7.3, 7.8, and 8.8μ. Except for the 5.8μ peak, these peaks were the same as those obtained from a CCl_4 solution of a copolymer between 2-pentene and SO_2. The spectra from the cyclohexene–NO_2 system and the cyclohexene–NO_2–SO_2 system were similar except that the major peaks could be attributed to a nitrate ester. The smaller bands could be identified with a cyclohexene–SO_2 copolymer. Earlier work by Mader et al. (1952) supports the presence of carbonaceous aerosols. Microchemical tests on the ether-soluble aerosols confirmed the presence of various oxygenated organic functional groups, such as aldehydes, ketones, and organic acids. Infrared analysis backed up the chemical findings.

Infrared spectra, microchemical analysis, and spot tests on aerosols produced by irradiation of the lower olefins (3 ppm ethylene, propylene, or isobutylene) in the presence of 1 ppm NO_2 and 0.5 ppm SO_2 at 50% RH indicated that the principal constituent of the aerosol was sulfuric acid with a smaller concentration of nitrite-type material (Endow et al., 1963). Weight-loss studies of the aerosols indicated that considerable portion of the original aerosol sample may be material that either is volatile or decomposes to give volatile products. The work of Harkins and Nicksic (1965a) confirms the fact that aerosols produced by irradiation of the lower olefins in the presence of NO_x and SO_x are not of organic composition. To test for the formation of organic aerosols, 3 ppm of tagged propylene (the carbon atom on each side of the double band was labeled) or ethylene was irradiated with 2 ppm NO and 5 ppm SO_2. In every case, with or without SO_2, the total tracer count of the aerosol was, within experimental error, the same.

Thus, Harkins and Nicksic conclude that SO_2 does not provide condensation nuclei for the growth of organic aerosol.

When NH_3 is present in the gas-phase reactants, the aerosol formed from all the hydrocarbons investigated, except cyclohexene and α-pinene, has been identified as predominantly $(NH_4)_2SO_4$. Cyclohexene and α-pinene formed aerosols that contained carbonaceous material as well as $(NH_4)_2SO_4$ (Groblicki and Nebel, 1969).

Although this area of research in air pollution is beset with technical problems due to the extremely small amounts of material formed, more information is needed. Past work indicates that the aerosol formed from mixtures of the lower hydrocarbons with NO_x and SO_2 is predominantly sulfuric acid, whereas the higher olefinic hydrocarbons appear to produce carbonaceous aerosol also, possibly organic acids, sulfinic or sulfonic acids, nitrate-esters, etc. The chemical identity of these carbonaceous aerosols is of vast importance since photochemically formed aerosols are in the respirable-size range. Size distribution curves for aerosols formed from the irradiation of dilute auto exhaust indicate that most of the particles are less than 0.25 μ (Doyle and Renzetti, 1958).

Heterogeneous Reaction Systems

When foreign particles are present in a gas-phase photochemical system, the particles may act as nucleation centers. The nuclei can grow during the reaction to many times their original mass by the accumulation of certain reaction products, or they may serve as catalysts whereby an interaction between the reactants and the surface of the particle can cause an increase in the reaction rate and (or) the formation of an aerosol with a different composition.

The effect of nucleating particles on photochemical aerosol formation has been investigated by Goetz and Pueschel (1965, 1967).

Their results for the 1-octene–NO_2 system in the molar concentration range of 3×10^{-5} to 1.5×10^{-5} (50 to 100 times higher than in the atmosphere) can be summarized as follows:

The photochemical reaction produces products of relatively low volatility that tend to agglomerate and by so doing convert from the gaseous state into the aerocolloidal state by a process of autonucleation.

When monodisperse polystyrene latex nuclei (diam = 0.35 μ) are present in the system, the nuclei act as centers upon which the low-volatile products accumulate. Thus, the size of the nuclei increases substantially during the reaction. These

experiments showed that a 10-fold higher nuclei concentration will produce under the same conditions 10 times the mass of total accumulant and that the presence of nuclei will suppress the autonucleation process. Thus, fog formation by the condensation of water vapor on nuclei seems to occur by a different growth process since the growth of the nuclei for the same degree of supersaturation in fog formation is inversely proportional to their concentration.

In the absence of nucleating particles, the rate of autonucleation depends largely on the reactant concentration. Thus, if the reactant concentration is sufficiently high and the nuclei level is low, the formation of autonucleates will compete with the process whereby the low-volatile products accumulate on the nuclei. The latter process will be favored by lower reactant concentrations or higher concentrations of nuclei. Preliminary results from variation of NO_2 and nuclei levels indicated that there may be a preferential association of the NO_2 molecules with the nuclei which causes the surface to become catalytically active and accumulation thereon to accelerate.

There have been some indications that heterogeneous reactions of SO_2 with airborne particulates could be much more rapid than homogeneous gaseous reactions of SO_2 in air. Urone et al. (1968) found that SO_2 in the presence of powdered oxides of aluminum, calcium, chromium, iron, lead, and vanadium reacted within minutes even without ultraviolet irradiation. One of the most significant papers in this area of research is that of Goetz and Pueschel (1967). They surveyed the effect of SO_2 on the formation of aerosols, giving attention to the formation of "preferred reaction centers" as determined by the sequence in which the reactants enter the experimental system. They used the same concentrations of hydrocarbon (1-octene at 80 ppm) and NO_2 (60 ppm) under identical irradiation conditions for different concentrations of stable reaction centers (nuclei of pure water, tap water, and polystyrene latex) and SO_2 (0.03 to 60 ppm) at different relative humidity levels (15 to 70%). When no stable nuclei were present, 2 ppm of SO_2 caused a marked reduction in light scattering below the level observed when SO_2 was not present. This inhibiting effect of relatively small SO_2 concentrations was greater at higher relative humidities. Increasing the SO_2 concentration further reversed this inhibition. At low humidities with the SO_2 concentration increasing to the concentration of NO_2, the aerosol level increased up to five times that observed in the absence of SO_2; at high humidities the aerosol level never increased above about one and a half times the value observed without SO_2. In the presence of nuclei, aerosol formation followed the same pattern—i.e., inhibition in the presence of 2 ppm SO_2 and subsequent increase as SO_2 was further increased, and strong influence of water vapor.

Striking results were obtained when the sequence in which the reactants met was altered. In the absence of nuclei, the effect of altering of the sequence was negligible, but it became quite significant when nuclei were present. In the absence of SO_2, contact of the nuclei with NO_2 prior to contact with 1-octene always produced more light scattering than was produced when there was no prior contact. In the presence of SO_2, primary contact of the nuclei with SO_2 caused the least reduction in light scattering at low SO_2 concentrations but caused the largest growth of aerosol level at higher SO_2 concentrations. Thus, the presence of nuclei is a dominant factor in the formation and growth of aerosol.

Smith et al. (1969) studied reactions of SO_2 (no light source) with submicron particles of Fe_3O_4, Al_2O_3, lead oxides, and platinum. These particles were generated by an exploding-wire

technique and were allowed to interact with sulfur-35–labeled SO_2 at ppm concentrations. Sorption of SO_2 by Fe_3O_4 reached 3% at an initial SO_2 concentration of 6.2 ppm and 1.8×10^5 particles per cm^3, and sorption on Al_2O_3 particles was about 50% with an initial SO_2 concentration of 1 ppm. The lead oxides caused complete removal of gaseous SO_2 within five min after mixing. Preferential chemisorption was observed at low SO_2 concentrations, followed at higher concentrations by multilayered physical adsorption.

Heterogeneous reaction systems undoubtedly resemble atmospheric conditions more closely than do homogeneous systems. However, the interpretation of results obtained with such systems is a difficult task. The work reported to date strongly indicates that the presence of stable nuclei can be a dominant factor in the reaction system. The presence of reactive nuclei or particles of the transition metals should be even more influential because of the known catalytic activity of these metals.

Reactions of SO_2 in Solution

Early studies of SO_2 in solution have been reviewed by Urone and Schroeder (1969). The more recent work of Matteson et al. (1969) is discussed here. The kinetics of the oxidation of SO_2 in aqueous aerosols of $MnSO_4$ was investigated. Although the absorption rate of SO_2 ran as high as 20%, they were unable to detect H_2SO_4 in the aerosols by titrimetric analysis. This is attributed to most of SO_2 being utilized to form a manganese–SO_2 complex. The following mechanism was proposed:

$$SO_2 + Mn^{2+} \rightleftarrows Mn \cdot SO_2{}^{2+} \tag{57}$$

$$2\,Mn \cdot SO_2{}^{2+} + O_2 \rightleftarrows (Mn \cdot SO_2{}^{2+}) \cdot O_2 \rightleftarrows$$
$$2\,Mn \cdot SO_3{}^{2+} \tag{58}$$

$$Mn \cdot SO_3{}^{2+} + H_2O \rightleftarrows Mn^{2+} + HSO_4{}^- + H^+ \tag{59}$$

$$HSO_4{}^- + H^+ \rightleftarrows H_2SO_4 \tag{60}$$
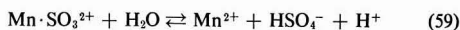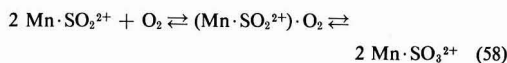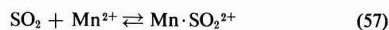
Rate constants for the rate of SO_2 disappearance (Reaction 57) and for the initial rate of acid formation (Reaction 59) were deduced to be

$$k_{57} = 2.3{-}2.5 \times 10^5 \text{ liter mol}^{-1} \text{ min}^{-1}$$

$$k_{59} = 33{-}38 \text{ liter}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

Although no humidity effect on the reaction could be established, the formation of acid below 95% RH was practically nil. The authors calculate that in a stagnant air mass at 95% RH and 10-ppm SO_2 and 1 μg $MnSO_4/m^3$, 35 μg H_2SO_4/m^3 will be formed after 24 hr.

Conclusions

Extrapolation of results obtained from laboratory experiments, even those specifically designed to simulate the atmosphere, to the actual environment cannot be done quantitatively. The atmosphere is essentially an "open" reaction system, in which not only do the gas-phase reactants and their interactions with oxygen and themselves define the presence of smog, but, also, the complex meteorological conditions determine the extent and duration of smog. Fluctuating reactant concentrations, temperatures, humidities, and light intensities have not often been applied to the laboratory situations.

In the real atmosphere, relative humidity changes are wide and rapid. Variations in relative humidity from 70–80% to 40–50% are common during the day but levels below 35–40%

seldom occur during summer days. SO_2 levels during the 8–4 p.m. period range from 0.07 ppm up to no more than 0.2–0.3 ppm. Altshuller (1970) points out that aerometric results during the summer months in Philadelphia provide a significant number of days with elevated oxidant and with average 8–4 p.m. SO_2 levels ranging from 0.01 to 0.3 ppm. The frequency of days with elevated oxidant concentration was not greater for SO_2 in the 0.1–0.05 ppm range than for SO_2 in the range around 0.2 ppm. He concludes that aerometric results do not support the significant effect of SO_2 on atmospheric oxidant suggested by Figures 4 and 5.

However, irrespective of the uncertain effect of SO_2 on smog parameters, there is abundant evidence that the photochemical mechanism provides an efficient means for converting SO_2 to particulate sulfur compounds.

Literature Cited

Air Pollution Control District, Los Angeles County, "Effectiveness of Organic Solvents in Photochemical Smog Formation," Solvent Project, Final Rept., 1966.
Altshuller, A. P., *J. Air Pollut. Contr. Ass.* **20,** 390 (1970).
Altshuller, A. P., Bufalini, J. J., ENVIRON. SCI. TECHNOL. **5,** 39 (1971).
Altshuller, A. P., Bufalini, J. J., *Photochem. Photobiol.* **4,** 97 (1965).
Altshuller, A. P., Cohen, R. R., presented at American Chemical Society Meeting, Division of Water, Air, and Waste Chemistry, New York, N.Y., Sept. 8–13, 1963.
Altshuller, A. P., Klosterman, D. L., Leach, P. W., Hindawi, I. J., Sigsby, J. E., Jr., *Int. J. Air Water Pollut.* **10,** 81 (1966).
Altshuller, A. P., Kopczynski, S. L., Lonneman, W. A., Becker, T. L., Wilson, D. L., ENVIRON. SCI. TECHNOL. **2,** 696 (1968).
Badcock, C. C., Sidebottom, H. W., Calvert, J. G., Reinhardt, G. W., Damon, E. K., scheduled for publication in *J. Amer. Chem. Soc.*, June 30, 1971.
Billings, C. E., Berger, A. W., Dennis, R., Driscoll, J., Lull, D., Warneck, P., "Study of Reactions of Sulfur in Stack Plumes," Contract no. PH-86-67-125, GCA Corp., Bedford, Mass., First Annual Rept., 1968.
Blacet, F. E., *Ind. Eng. Chem.* **44,** 1339 (1952).
Bufalini, J. J., Altshuller, A. P., ENVIRON. SCI. TECHNOL. **3,** 469 (1969).
Bufalini, J. J., Gay, B., Kopczynski, S. L., *ibid.* **5,** 333 (1971).
Bufalini, J. J., Stephens, E. R., *Int. J. Air Water Pollut.* **9,** 123 (1965).
Clyne, M. A. A., Halstead, C. J., Thrush, B. A., *Proc. Royal Soc. London, Ser. A* **295,** 355 (1966).
Dainton, F. S., Ivin, K. J., *Trans. Faraday Soc.* **46,** 374, 382 (1950).
DallaVale, J. M., Orr, C., Jr., Hinkle, B. L., *Brit. J. Appl. Physics* H-201, (1954).
Dimitriades, F., *J. Air. Pollut. Contr. Ass.* **17,** 460 (1967).
Doyle, G. J., Renzetti, N. A., *ibid.* **8,** 23 (1958).
Dunham, S. B., *Nature* **188,** 51 (1960).
Endow, N., Doyle, G. J., Jones, J. L., *J. Air Pollut. Contr. Ass.* **13,** 141 (1963).
Fajans, E., Goodeve, C. F., *Trans. Faraday Soc.* **32,** 511 (1936).
Ford, H. W., Doyle, G. J., Endow, N., *J. Chem. Phys.* **26,** 1336 (1957).
Gall, J. W., Slater, D. H., Calvert, J. G., presented at General Motors Research Laboratories Symposium on Chemical Reactions in Urban Atmospheres, GMC, Warren, Mich., Oct. 6 and 7, 1969.
Gerhard, E. R., Johnstone, H. F., *Ind. Eng. Chem.* **47,** 972 (1955).
Goetz, A., Pueschel, R. F., *Atmos. Environ.* **1,** 287 (1967).
Goetz, A., Pueschel, R. F., *J. Air Pollut. Contr. Ass.* **15,** 90 (1965).
Good, A., Thynne, J. C. J., *Trans. Faraday Soc.* **63,** 2708, 2720 (1967).
Greig, J. D., Hall, P. G., *ibid.* **62,** 652 (1966).
Groblicki, P. J., Nebel, G. J., presented at General Motors

Research Laboratories Symposium on Chemical Reactions in Urban Atmospheres, GMC, Warren, Mich., Oct. 6 and 7, 1969.
Hall, T. C., Jr., Ph.D. Thesis, University of California, Los Angeles, Calif., 1953.
Halstead, C. J., Thrush, B. A., *Nature* **204,** 992 (1964).
Halstead, C. J., Thrush, B. A., *Proc. Royal Soc. London, Ser. A* **295,** 363 (1966).
Harkins, J., Nicksic, S. W., *J. Air Pollut. Contr. Ass.* **15,** 218 (1965a).
Harkins, J., Nicksic, S. W., presented at American Chemical Society Meeting, Division of Petroleum Chemistry, Detroit, Mich., April 4–9, 1965b.
Hayakawa, Ichiy, *J. Air Pollut. Contr. Ass.* **14,** 339 (1964).
Heicklen, J., presented at General Motors Research Laboratories Symposuim on Chemical Reactions in Urban Atmospheres, GMC, Warren, Mich., Oct. 6 and 7, 1969.
Hoare, D. E., Walsh, A. D., *Trans. Faraday Soc.* **53,** 1102 (1957).
Jaffee, S., Klein, F. S., *Trans. Faraday Soc.* **62,** 2150 (1966).
Johnston, H. S., der Jain, K., *Science* **131,** 1523 (1960).
Johnston, H. S., Yost, P. M., *J. Chem. Phys.* **17,** 366 (1949).
Jolley, J. E., *J. Amer. Chem. Soc.* **79,** 1537 (1957).
Kaufman, F., *Progr. React. Kinet.* **1,** 3 (1961).
Kopczynski, S. L., Altshuller, A. P., *Int. J. Air Water Pollut.* **6,** 133 (1962).
Leighton, P. A., "Photochemistry of Air Pollution," Academic Press, New York, N.Y., 1961.
Mader, P. P., MacPhee, R. D., Lofberg, T. R., Larson, G. P., *Ind. Eng. Chem.* **44,** 1352 (1952).
Magill, P. L., Holden, F. R., Ackley, C., "Air Pollution Handbook," McGraw-Hill, New York, N.Y., 1956, pp 3–20.
Matteson, M. J., Stoober, W., Luther, H., *Ind. Eng. Chem. Fundam.* **8,** 677 (1969).
Mulcahy, M. F. R., Stevens, J. R., Ward, J. C., *J. Phys. Chem.* **71,** 2124 (1967).
Noyes, W. A., Leighton, P. A., "The Photochemistry of Gases," Reinhold, New York, N.Y., 1941, p 400.
Ogata, Y., Izawa, Y., Tsuda, T., *Tetrahedron* **21,** 1349 (1965).
Okuda, S., Rao, T. N., Slater, D. H., Calvert, J. G., *J. Phys. Chem.* **73,** 4412 (1969).
Orr, C., Jr., Hurd, F. K., Corbett, W. J., *J. Colloid Sci.* **13,** 472 (1958).
Pitts, J. N., Jr., Sharp, J. H., Chang, S. I., *J. Chem. Phys.* **39,** 238 (1963).
Prager, M. J., Stephens, E. R., Scott, W. E., *Ind. Eng. Chem.* **52,** 521 (1960).
Rao, T. N., Collier, S. S., Calvert, J. G., *J. Amer. Chem. Soc.* **91,** 1609 (1969a).
Rao, T. N., Collier, S. S., Calvert, J. G., *ibid.,* 1616 (1969b).
Reckner, L., Scott, W. E., presented at American Chemical Society Meeting, Division of Water, Air, and Waste Chemistry, New York, N.Y., Sept. 8–13, 1963.
Renzetti, N. A., Doyle, G. J., *Int. J. Air Pollut.* **2,** 327 (1960).
Ripperton, L. A., Decker, C. E., Page, W. W., presented at American Chemical Society Meeting, Division of Water, Air, and Waste Chemistry, Atlantic City, N.J., Sept. 13–17, 1962.
Rolfes, T. R., Reeves, R. R., Jr., Harteck, P., *J. Phys. Chem.* **69,** 849 (1965).
Sato, S., Cvetanovic, R. J., *Can. J. Chem.* **36,** 279, 970, 1668 (1958).
Schuck, E. A., Doyle, G. J., "Photooxidation of Hydrocarbons in Mixtures Containing Oxides of Nitrogen and Sulfur Dioxide," Rept. no. 29, Air Pollution Foundation, San Marino, Calif., 1959.
Schuck, E. A., Stephens, E. R., Schrock, R. R., presented at the 59th Annual Meeting of APCA, San Francisco, Calif., June 20–24, 1966.
Sethi, D. S., Allen, E. R., Cadle, R. D., abstracts of Fifth International Conference on Photochemistry, IBM Watson Research Center, Yorktown, N.Y., Sept. 2–5, 1969.
Sharma, A., Padur, J. P., Warneck, P., *J. Phys. Chem.* **71,** 1602 (1967).
Sidebottom, H. W., Badcock, C. C., Calvert, J. G., Rabe, B. R., Damon, E. K., scheduled for publication in *J. Amer. Chem. Soc.*, June 30, 1971.
Smith, B. M., Wagman, J., Fish, B. R., ENVIRON. SCI. TECH-

NOL. **3**, 558 (1969).
Stephens, Edgar R., Price, Monty A., *Atmos. Environ.* **3**, 573 (1969).
Stern, A. C., Ed., "Air Pollution," Vols I–III, 2nd ed., Academic Press, New York, N.Y., 1968.
Stevenson, H. J. R., Sanderson, D. E., Altshuller, A. P., *Int. J. Air Water Pollut.* **9**, 367 (1965).
Strickler, S. J., Howell, D. B., *J. Chem. Phys.* **49**, 1947 (1968).
Timmons, R. G., presented at General Motors Research Laboratories Symposium on Chemical Reactions in Urban Atmospheres, GMC, Warren, Mich., Oct. 6 and 7, 1969.
Trotman-Dickenson, A. F., "Gas Kinetics," Academic Press, New York, N.Y., 1955, p 249.
Urone, P., Lutsep, H., Noyes, C. M., Parcher, J. F., ENVIRON. SCI. TECHNOL. **2**, 611 (1968).

Urone, P., Schroeder, W. H., *ibid.* **3**, 436 (1969).
Walsh, A. D., *J. Chem. Soc.*, 2266 (1953).
Westberg, K., Cohen, N., submitted for publication to *Int. J. Chem. Kinet.* (1971).
Wilson, W. E., Jr., Battelle Memorial Institute, Columbus, Ohio, private communication, 1971.
Wilson, W. E., Jr., Levy, A., "A Study of Sulfur Dioxide in Photochemical Smog," American Petroleum Institute, Project S-11, Battelle Memorial Institute, Columbus, Ohio, 1968.
Wilson, W. E., Jr., Levy, A., Wimmer, D. B., presented at 63rd Annual Meeting, Air Pollution Control Association, St. Louis, Mo., June 10–14, 1970.

Uranium Concentrations in Surface Air at Rural and Urban Localities within New York State

Peter McEachern,[1] **Willard G. Myers, and Frederick A. White**

Division of Bio-Environmental Engineering, Dept. of Nuclear Science, Rensselaer Polytechnic Institute, Troy, N.Y. 12181

■ This investigation measured the concentration of uranium in surface air at urban and rural locations within New York State by both mass spectrometric and fission track analysis. Average uranium concentrations ranged from 0.10 to 1.47 ng/m³ (0.035–0.47 fCi/m³), with each area indicating that a significant correlation exists between the uranium concentration and the density of total suspended particulates. Present levels of uranium in the air environment are attributed primarily to naturally occurring uranium sources and nonnuclear industrial activity. In the immediate vicinity of a nuclear fuel reprocessing plant, a slight excess uranium has been detected by observing the degree of U^{235} enrichment. However, at all locations sampled, the uranium concentration is substantially below presently established standards.

A n investigation was undertaken to determine uranium concentrations in surface air within selected regions of New York State. Reasons for conducting this study may be cited specifically. Firstly, limited information on "background" atmospheric levels of uranium can be found in the literature. Secondly, the projected rapid increase of nuclear-generated power and associated industry has raised questions regarding possible increases over existing uranium levels in the environment. Consequently, it is important both to determine present atmospheric uranium levels to which future concentrations may be compared and to consider trace uranium concentrations that may be assigned to natural and nonnuclear industrial sources. Further, in view of the present concern of the toxicity of heavy metallic elements

in the environment, it is desirable to know the levels of this element presently found in ambient air.

Continuous monitoring of the atmosphere by both federal and state health agencies for gross radioactivity has yielded substantial data relative to concentration changes in alpha-particle emitting nuclides. However, due to a lack in analytical sensitivity, data on the contribution from uranium isotopes are rarely provided. Periodic environmental measurements in the immediate vicinity of AEC-operated nuclear facilities have allowed estimation of the uranium contribution to the relatively high ambient alpha activity in the local air (HEW, 1970). Recent studies on the release of radioactivity from nuclear and fossil-fuel power plants (Eisenbud and Petrow, 1964; Martin et al., 1969) and a nuclear fuel reprocessing plant (Cochran et al., 1970) have also allowed determination of the magnitude of these sources of atmospheric uranium. In addition, study of uranium concentration in the atmosphere over the Atlantic Ocean from Belgium to Antarctica and at a site in the United Kingdom has been reported (Hamilton, 1970).

On the basis of the uranium concentrations found in the above studies, it was evident that analytical techniques having high uranium sensitivity had to be applied to determine background levels in areas removed from large sources of airborne uranium. Two such methods were employed in this study—mass spectrometry and fission track analysis.

Experimental

Air samples, provided by the New York State Dept. of Environmental Conservation, were taken at selected sites across New York State, representing localities from the highly industrialized to rural. One site included an important nuclear facility. Figures 1 and 2 show their geographical locations within New York. Samples 1 through 11 were collected on 8 × 10-in., glass-fiber filters (Mine Safety Appliances, Type 1106–BH) with a 99.98–99.995% removal efficiency for

---

[1] Present address: Florida State Dept. of Air and Water Pollution Control, Winter Haven, Fla. 33880.
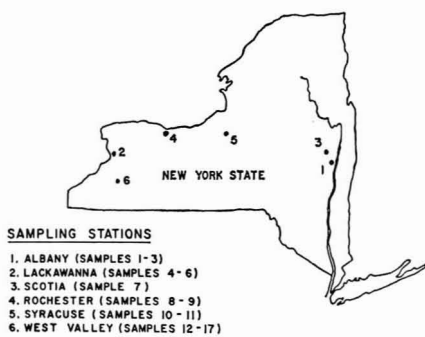
Figure 1. Location of sampling stations within New York State where uranium concentrations in surface air were determined

SAMPLING STATIONS

1. ALBANY (SAMPLES 1-3)
2. LACKAWANNA (SAMPLES 4-6)
3. SCOTIA (SAMPLE 7)
4. ROCHESTER (SAMPLES 8-9)
5. SYRACUSE (SAMPLES 10-11)
6. WEST VALLEY (SAMPLES 12-17)

Figure 2. Sampling stations around the West Valley Nuclear Fuel Reprocessing Plant, showing wind direction and frequency from air stack during the period, Dec. 26, 1968 to Jan. 2, 1969

particles larger than 0.3 μ. These 24-hr samples were collected on high-volume samplers which filtered a minimum of 2500 m³ of air. Samples 12 through 17 were collected on 2-in. diam, glass-fiber filters (Gelman, Type E) with a removal efficiency of greater than 98% for particles larger than 0.05 μ. These samples were obtained from a low flow rate, air sampler, which filtered between 180 and 400 m³ of air over a one week period.

The filter papers were first weighed to determine the total suspended particulate levels at each sampling station during the sampling period. For the uranium analysis, an area of 8 in.² was cut from the 8 × 10 in. filter papers for both the mass spectrometer and fission track assay. The relatively low volume of air filtered through the 2-in. diam filter-paper samples necessitated the use of the whole paper for analysis. Of the six samples collected on these filters, two were analyzed by mass spectrometry, the remaining by fission track analysis. Dissolution of the filter-paper samples was accomplished by gently boiling them for 20 min in a mixture containing 20 ml double distilled, concd nitric acid (J. T. Baker), 20 ml deionized, double distilled water, and 1 ml reagent-grade concd hydrofluoric acid in a Teflon beaker. After digestion, the solution was evaporated to a few drops in a dust-free evaporation chamber. Blank filter papers were treated in a similar manner.

Fission Track Analysis. Since the total quantity of uranium in the samples was expected to be quite small, an ether extraction procedure was employed both to concentrate and separate the uranium from other material dissolved during the filter-paper digestion. The removal of extraneous dissolved solids was particularly important to the fission track analysis since their recrystallization on the detector surface could prevent penetration of the fission fragments and subsequent track registration. The extraction also separated the uranium from any thorium which may have been present. Knowledge of the uranium extraction efficiency for the ether extraction procedure was necessary for samples to be analyzed by fission track counting. To obtain consistent results, only a single extraction was performed on these samples. The efficiency for this single extraction was determined separately by use of the mass spectrometer and isotopic dilution procedure (White, 1968). The procedure followed from here on is similar to that described elsewhere (Carpenter and Cheek, 1970). Since the tracks produced in the detector by thermal neutron irradiation were essentially those from fissioned U²³⁵ atoms, final assignment of total uranium concentration in the air at some locations depended on the mass spectrometrically determined U²³⁸/U²³⁵ isotopic ratio.
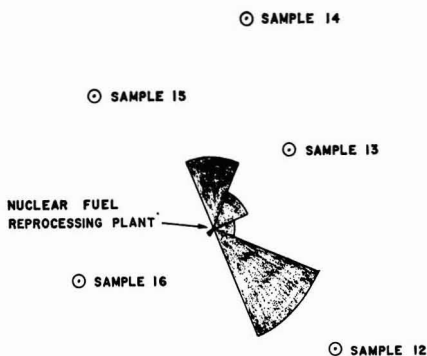
Mass Spectrometric Analysis. An enriched U²³⁵ isotopic spike (NBS U930) was added, prior to the ether extraction, to the samples to be quantitatively analyzed by mass spectrometry. Ten microliter portions of the extracted solutions were transferred to rhenium, "canoe," configuration, thermal ionization filaments and inserted within the source chamber of a four-stage mass spectrometer (White and Forman, 1967) for subsequent isotopic analysis. The averages of the recorded isotopic ratios for each sample were used in the appropriate isotopic dilution equation to determine the quantity of uranium present. Mass discrimination corrections were determined using NBS U500 (U²³⁸/U²³⁵ = 1.000) and applied to the measured ratios. After subtracting background, the atmospheric uranium concentrations were calculated from knowledge of filter-paper area and total air volume sampled.

A number of the unspiked sample solutions prepared for the fission track analysis were mass spectrometrically analyzed to determine uranium isotopic abundances. This additional analysis was performed on those samples for which there was reason to suspect the presence of U²³⁵-enriched uranium in the air environment, as well as to assure a natural uranium isotopic abundance at those areas removed from nuclear industrial activity.

The presence of appreciable quantities of plutonium-239 in the air sampled would introduce errors in the fission track analysis due to its high thermal neutron fission cross section. Although the low background levels of plutonium in ambient air ($\sim$10⁻¹⁵–10⁻¹⁶ gram Pu²³⁹/m³, Shleien et al., 1970) can be neglected in most fission track analyses, the high concentrations in spent nuclear fuel warranted concern over the air samples collected around the West Valley reprocessing plant. Consequently, when these samples were mass spectrometrically

analyzed for their U^{238}/U^{235} isotopic ratios, the mass-239 position was scanned as well.

Results and Discussion

A summary of the results of this investigation is listed in Tables I and II. The correlation between concentrations determined by the two analytical methods was good, considering their wide procedural differences and the small quantities of uranium handled. Random results indicated that neither method was discriminating for nor against the uranium contained in the air samples.

The mass spectrometric analysis of the samples surrounding the nuclear fuel reprocessing plant indicated only traces of plutonium-239 present ($\sim$1% of the uranium ion beam), and since both uranium-235 and plutonium-239 have similar thermal ionization potentials and fission cross sections, the fission tracks contributed by plutonium were considered negligible. With the ether extraction removing any thorium present, the resulting fission tracks produced could safely be assumed to come essentially from the uranium contained in the sample.

The uranium concentrations listed in Table I are considered to be correct to within ±30%. Limiting factors were found to be the volume of air sampled, plus the range of total uranium background contributed by the filters—a consequence of inconsistency in paper density. The 8 × 10-in. papers averaged 1.1×10^{-8} gram U/in.^{2}, while the 2-in. diam ones were found to contain on the average 4.3×10^{-8} gram U/in.^{2} The relatively high uranium content of the 2-in. diam filters, plus the low volume of air filtered by samples 14 and 17 prevented precise assignment of uranium levels for these locations. The concentrations shown for these sites are listed as being less than the background determined for the blank filter papers.

Little can be concluded from a direct comparison of total uranium concentrations at the various locations due to differences in sampling date and local industrial activity. Even at the same sampling station, significant variations are noted; an apparent function of meteorological conditions and day of the week influences. A more meaningful method of correlating uranium concentrations to a specific area would be to compare the concentration of uranium (U) to the total suspended particulates (TSP) for that area. The U/TSP ratios listed in Table I definitely normalize most of the above influential factors and appear to establish a direct relationship between ambient uranium levels in the air and type of activity near each site. This uranium fingerprint may be particularly important in an area where the nuclear industry plans to enter or expand.

Lackawanna, a heavily industrialized suburb of Buffalo, had the highest total uranium concentration of all the sites surveyed in this study. The nature of the local industry (steel and chemicals) would account for the relatively low U/TSP ratio, which averaged 3.5×10^{-6}. The Albany samples were taken near the site of a very extensive construction project (South Mall), so that the average 5.25×10^{-6} U/TSP ratio found here may have been reflecting the comparatively high uranium content of soils and cement in the filtered particles. The Scotia sample, taken at a rural airport, showed a U/TSP ratio similar to that of nearby Albany and would most likely represent present background levels of uranium in rural New York localities. The Syracuse and Rochester areas had U/TSP ratios different from those above, indicating a characteristic combination of industrial and natural sources of uranium. No major nuclear industrial activity (reactors, reprocessing or fabrication plants, uranium separations, etc.) is presently being conducted near any of the above sampling stations.

The uranium concentrations in the air surrounding the nuclear fuel reprocessing plant situated in a rural area 3.5 miles northwest of West Valley, N.Y., were found to be lower than the urban areas sampled in this study. However, from the high U/TSP ratios found and the uranium isotopic analysis data (Table II), it was evident that the plant was contributing U^{235}-enriched uranium to the local environment. Comparing concentrations upwind of the plant with those found downwind indicates a doubling of the uranium levels in the surface air at a distance of 1–2 miles away. Reasonable correlation between measured isotopic ratios and wind direction and duration data (Figure 2) can be seen. The uranium concentrations

Table I. Summary and Comparison of Uranium Concentrations in Atmospheric Samples

Sample no., location, site	Sample date and day	Uranium concn (ng/m³)			Total suspended particulates in air (μg/m³)	Gram U/gram TSP[a] (×10⁻⁶)
		Fission track analysis	Mass spec. analysis	Av		
1. Albany (1)	6/6/69 (Fri.)	0.41	0.35	0.38	117	3.22
2. Albany (1)	6/12/69 (Thurs.)	0.61	0.78	0.69	99	7.00
3. Albany (1)	6/18/69 (Wed.)	0.42	0.64	0.53	96	5.52
4. Lackawanna (1)	6/30/68 (Sun.)	1.21	1.72	1.47	337	4.35
5. Lackawanna (2)	6/30/68 (Sun.)	0.84	1.15	0.99	341	2.91
6. Lackawanna (2)	7/3/68 (Wed.)	0.49	0.63	0.56	170	3.28
7. Scotia (1)	7/8/69 (Tues.)	0.19	0.03	0.11	19	5.57
8. Rochester (1)	4/14/70 (Tues.)	0.39	0.25	0.32	202	1.58
9. Rochester (1)	4/8/70 (Wed.)	0.58	0.39	0.49	246	1.97
10. Syracuse (1)	11/14/68 (Thurs.)	0.40	0.81	0.60	235	2.57
11. Syracuse (1)	11/2/68 (Sun.)	0.72	0.80	0.76	212	3.59
12. W. Valley (NW)	12/26/68 to	0.22	. . .	0.22	27	8.15
13. W. Valley (N)	1/2/69	0.26	. . .	0.26	27	9.55
14. W. Valley (NE)	(Thurs.	. . .	<0.42	. . .	27	. . .
15. W. Valley (SE)	to	0.36	. . .	0.36	27	13.30
16. W. Valley (SW)	Thurs.)	0.17	. . .	0.17	27	6.10
17. W. Valley (SW)	1/2–9/69	. . .	<0.44	. . .	27	. . .

[a] Total suspended particulates.

Table II. Background Isotopic Ratios Determined by Mass Spectrometric Analysis

Sample no., location	Isotopic ratio U^{238}/U^{235}
7. Scotia	131
12. West Valley (NW)	66
13. West Valley (N)	45
15. West Valley (SE)	81
16. West Valley (SW)	105
Natural Uranium	**137.8**

in the air environments sampled in this study were found to be substantially below the New York State maximum permissible natural uranium concentrations of 6 and 9 $\mu g/m^3$ (soluble and insoluble compounds, respectively) for uncontrolled areas. A comparison of the data with other environmental measurements shows good agreement with several filters collected in New York City during January and February 1965 where subsequent analyses indicated an average uranium concentration of 0.4 ng/m^3 (Welford and Baird, 1967). As anticipated, the average levels found in this investigation were above those (2.2–4.1 pg U/m^3) measured over the Atlantic Ocean in 1959 and at Sutton, England (62 pg U/m^3) in 1967–68 (Hamilton, 1970), but well below those measured at or near obvious industrial sources of atmospheric uranium. For example, a concentration of 13.3 ng U/m^3 (35 times higher than the highest level measured around the West Valley nuclear fuel reprocessing plant) was recorded at a point 3.7 miles downwind from the 1400 MWe coal-fired (1.1 ppm U) power plant at Widows Creek, Ala. (Martin et al., 1969). Although the output from this plant is not representative of that from most coal-fired power generating stations, it does identify a major source of airborne uranium contributed by the nonnuclear industry. On the other hand, these levels are much less than the 90 and 300 ng U/m^3 levels found near gaseous diffusion plants at Paducah, Ky., and Piketon, Ohio, respectively; and the 6900 ng U/m^3 ambient concentrations near a nuclear fuel fabrication plant at Fernald, Ohio (HEW, 1970). Other measurements (Cochran, 1970) taken at the West Valley nuclear fuel reprocessing plant in 1969 were able only to establish the uranium-238 levels to be less than 6 ng U/m^3 (2×10^{-15} $\mu Ci/cc$).

Conclusions

The combination of fission track and mass spectrometric analyses offers a sensitive and precise method for detecting and monitoring trace quantities of uranium in the air environment, particularly those originating from nuclear industrial activity. However, with the exception of a few isolated areas, present concentrations of uranium in surface air are due almost exclusively to natural and nonnuclear industrial sources. Inasmuch as nuclear power represents only 1.5% of the total amount generated in the U.S. at present, it is reasonable to expect larger contribution from this source if the industry grows at expected rates.

Based on the uranium concentrations found in the air environments sampled in this study, there does not appear to be any imminent danger to individuals who inhale these levels. However, uranium levels in the air can be expected to increase and should, therefore, receive the same attention afforded to other heavy metallic elements.

Literature Cited

Carpenter, B. S., Cheek, C. H., *Anal. Chem.* **42**, 121 (1970).
Cochran, J. A., Smith, D. G., Magno, P. J., Shleien, B., "An Investigation of Air Borne Radioactive Effluent from an Operating Nuclear Fuel Reprocessing Plant," HEW, BRH/NERHL 70-3, (1970).
Eisenbud, M., Petrow, H. G., *Science* **144**, 288 (1964).
Hamilton, E. I., *Health Phys.* **19**, 511 (1970).
HEW, "Radiological Health Data and Reports," Vol 11, nos. 3 and 4 (1970).
Martin, J. E., Harward, E. D., Oakley, D. T., "Comparison of Radioactivity from Fossil Fuel and Nuclear Power Plants," HEW, Bureau of Radiological Health, November 1969.
Shleien, B., Cochran, J. A., Magno, P. J., ENVIRON. SCI. TECH. **4**, 598 (1970).
Welford, G. A., Baird, R., *Health Phys.* **13**, 1321 (1967).
White, F. A., "Mass Spectrometry in Science and Technology," Wiley, New York, N.Y., 1968, p 297.
White, F. A., Forman, L., *Rev. Sci. Instrum.* **38**, 355 (1967).

Evaluation of Rat Eradication Programs

James W. Gentry

Dept. of Chemical Engineering, University of Maryland, College Park, Md. 20742

■ The formulation and development of a mathematical model for eradication programs of rat populations with several options are presented. A numerical algorithm especially suitable for the numerical solution of integral-differential equation with integral boundary conditions, which arise directly from the model, is developed. The model is applied to three different eradication strategies: an alternate poisoning–sterilization strategy; a strategy where the female offspring of a treated female are sterile, and where the female must be treated only once; and finally, a strategy where the female offspring of a female treated during a specific time period of her reproductive cycle are sterile.

I t has been suggested that the population of rats in a city could be controlled by sterilizing the male rats; by treating the females with an androgen such that the female offspring show male characteristics and are sterile (Young, 1964); by an extensive eradication program; and by cutting down the available food supply by more tidy modes of living. There appears to have been little effort to quantify the probable effects of these eradication programs, and, indeed, the principal arguments have been primarily subjective and largely dominated by conjectures (Ardrey, 1966). In this paper a model is developed to allow the evaluation of any proposed control option and to illustrate those parameters which must be accurately estimated for the rat population in the cities.

The most promising approach seems treatment of the female rat with androgen. The female offspring of the rat are sterile, showing male characteristics (Phoenix et al., 1959; Tedford and Young, 1960). This phenomenon had been previously noted by Dahtchakoff (1938a, 1938b, 1947).

The problem remains as to whether the treated female has sterile female offspring for the rest of her life after one treatment or whether the treatment must be repeated during each pregnancy. Diamond (1960) has indicated for guinea pigs the success of a one time treatment; however, the preponderance of the literature would indicate that continual treatment is required (Young, 1964).

In this paper both policies are considered and evaluated. Also, the use of a combined poisoning and sterilization treatment is evaluated.

Model

The mathematical model consists of a series of simultaneous integral equations which describes the change in the number of rats having an age s with time being the independent variable. The rate of death of the rats is taken as the sum of the rate due to natural causes, the increase in the rate caused by the administration of poison, and the increase in rate due to overcrowding.

The mathematical formulation of this model has the form

$$\frac{\partial n(s, t)}{\partial t} + \frac{\partial n(s, t)}{\partial s} = - [\lambda(s, t) + \phi(s, t, t_0)] \times$$

$$n(s, t) - \gamma(s, t)\, n(s, t) \int_0^\infty n(p, t)\, \Gamma(p)dp \quad (1a)$$

where t is the time variable and s is the age of the rats. The term $\lambda(s, t)$ is the death rate of rats due to natural causes. In the results which follow, the "natural death rate" is assumed to be a function of age only. In general, the death rate could be a function of time. For example, it is possible that the death rate will show a seasonal variation being higher in the winter. The function $\phi(s, t, t_0)$ accounts for the increase in the death rate due to distribution of poison. It seems prudent to assume that this increase is a strong function of age, since the young inexperienced animals are more likely to eat poisoned bait than the mature animals. The model is specifically designed to evaluate different strategies of control, especially the periodic distributions of poison and androgen. Consequently, the mortality rate of the rats is a function of age, time, and the time when the poison was distributed (t_0). It is assumed that the death rate due to natural causes and due to poisoning is proportional to the number of rats with age s. The third factor is the increase in deaths due to overcrowding. It seems reasonable that the death rate increase should be proportional to the number of rats of age s and to a multiplier which is a function of the total number of rats of all ages. The term

$$\gamma(s, t) \int_0^\infty n(p, t)\, \Gamma(p)dp$$

represents a versatile functional form. The term $\gamma(s, t)$ corresponds to the death rate due to overcrowding. Again the possibility that more mature rats fare better in adverse and overcrowded conditions is accounted for. The integral is a summation over all ages. $\Gamma(p)$ accounts for the fact that rats of different ages may require more living space or food. The basic idea is that there is a critical population number. Consequently, as the total population increases, the death rate increases. The γ and Γ factors allow the increase in death rates to differ for different age groups and to depend on the age distribution of the rats. This model was chosen in order to have a general form. The left-hand side of Equation 1a represents the change in population with time. This effect is the sum of two terms. The first term $\partial n(s, t)/\partial t$ represents the change in the rat population with time. The second term represents the change in population due to the aging of the rats. If the population were stable, that is the number of rats of age s did not change with time, then $\partial n(s, t)/\partial t$ would equal zero. The term $\partial n(s, t)/\partial s$ represents the influx of rats of age $s - \delta s$ obtaining an age s and the outflux of rats of age s obtaining the age $s + \delta s$. The term δs represents a small incremental change in s. For a stable population, the influx of rats into the age s just balances the outflux of rats growing

older plus those that die within the time interval. This term is what Richards (1970) describes as "recruits."

In the development that follows, the simplified equations are

$$\frac{\partial n(s, t)}{\partial t} + \frac{\partial n(s, t)}{\partial s} = -[\lambda(s) + \phi(s, t, t_0)] n(s, t) -$$

$$\gamma(s) \left| \int_{a^*}^{b^*} n(p, t)\, dp \right| n(s, t) \quad (1b)$$

This simplified model assumes that the normal death rate is a function of age alone, that there is no seasonal or periodic variation with time. It further assumes that the increase in the death rate due to overcrowding shows no time dependence. The integral $\int_{a^*}^{b^*} n(p, t)\, dp$ represents the total adult rat population. The limits of integration a^* and b^* represent the age of youthful maturity and the maximum age of the rat. The value of b^* was chosen as three years and the age of maturity a^* was chosen as two months. Both values are consistent with the known data for the Norway rat. No effort was made to distinguish between the requirements of rats of different ages.

The birth rate is assumed to be equal to the summation of the product of the adult rats and their production rate. The production rate is the product of the average reproduction number $\zeta(s)$ and the fraction of the total population of female rats that is fertile $\Lambda(s, t, t_0)$. The fraction of fertile females may be altered by the method of control and is, consequently, a function of time (t) and the time the control program was started (t_0). The term $\zeta(s)$ is obtained by dividing the average litter size by the time required for a reproduction cycle. This quotient is then multiplied by the fraction of the population that is female. This value was taken to be 0.50. With these assumptions, the mathematical form of the boundary conditions becomes

$$n(0, t) = \int_0^\infty n(p, t)\, \zeta(p)\, \Lambda(p, t, t_0) dp \quad (2)$$

where

$$\Lambda(s, t, t_0) = B(s) \exp^{-\alpha(t - t_0)} \quad (3)$$

where α is a numerical constant that is proportional to the amount of bait. B is a constant less than one, which accounts for the fact that not all females are fertile and that all fertile females are not pregnant during any given reproduction cycle. If no control program were applied, $B(s)$ would be the average value of the fraction of female rats of ages s that is pregnant during each reproduction cycle.

The model above must be modified somewhat if the treated females produce sterile offspring. In this paper two cases are considered, one where the treated females are permanently affected and, secondly, where the females are only temporarily affected. In this case two population numbers are required $n(s, t)$ (the number of fertile rodents of age s at time t) and $\bar{n}(s, t)$ (the number of sterile rodents of age s at time t). The corresponding equations are

$$\frac{\partial n(s, t)}{\partial t} + \frac{\partial n(s, t)}{\partial s} = -[\lambda(s)\, n(s, t)] -$$

$$\gamma(s)\, n(s, t) \int_{a^*}^{b^*} [n(p, t) + \bar{n}(p, t)]\, dp \quad (4a)$$

$$\frac{\partial \bar{n}(s, t)}{\partial t} + \frac{\partial \bar{n}(s, t)}{\partial s} = [-\bar{\lambda}(s)\, \bar{n}(s, t)] -$$

$$\bar{\gamma}(s)\, \bar{n}(s, t) \int_{a^*}^{b^*} [n(p, t) + \bar{n}(p, t)]\, dp \quad (4b)$$

with the boundary conditions

$$n(0, t) = \int_0^\infty n(p, t)\, \bar{\zeta}(p)\, \psi(p, t, t_0)\, dp \quad (5a)$$

$$\bar{n}(0, t) = \int_0^\infty n(p, t)\, \bar{\zeta}(p)\, [1 - \psi(p, t, t_0)]\, dp \quad (5b)$$

where $[1 - \psi(p, t, t_0)]$ represents the fraction of the female population that has been treated. The term $\bar{\zeta}(p)$ is linearly related to $\zeta(p)$. In fact, $\bar{\zeta}(p) = \Lambda(s, t, t_0)\, \zeta(p)$.

To use the more precise Equation 1a rather than 1b creates no additional computational difficulty. There are, however, insufficient data available to define more than the first generation model as presented below. Consequently, seasonal variations in mortality rates are neglected.

It seems reasonable to assume that the death rate is a function of living space and food supply per rodent. The simplest plausible assumption is that the death rate is inversely proportional to these averages or that

$$\gamma^*(s) = \frac{K_1(s)S}{\displaystyle\int_0^\infty A(p)\, n(p, t) dp} + \frac{K_2(s)F}{\displaystyle\int_0^\infty B(p)\, n(p, t)\, dp} +$$

$$K_3 G \left[\int_0^\infty A(p) n(p, t) dp, \int_0^\infty B(p) n(p, t) dt \right] \quad (6)$$

Where G indicates the synergistic effect of the two population-limiting criteria. It is assumed here that $G \equiv 0$, or that overcrowding and lack of food supply can be treated separately. If it is further assumed that a rodent which requires more food, requires proportionally more living space, therefore, one has

$$\gamma^*(s) = \frac{\displaystyle\int_0^\infty \Gamma(p)\, n(p, t) dp}{K_1(s) + K_2(s)F}$$

$$= \gamma(s) \int_0^\infty \Gamma(p)\, n(p, t) dp \quad (7)$$

with $\Gamma(p) \equiv A(p) \equiv B(p)$. This term appears in Equations 1a,b. Physically these assumptions are tantamount to assuming that an incremental mortality rate is directly proportional to the total adult rat population.

Mathematical Solution

The mathematical solution utilizes three basic methods in the numerical solutions of the equations described in the previous section. The method of Crank and Nicolson (1947), the method of quasilinearization (Bellman et al., 1961), and the modified Gentry algorithm for solution of block-band matrices (Gentry, 1970b).

The method of Crank-Nicolson is an efficient method of solution of parabolic differential equations with a small computing error. (Ames, 1965; Wilkes, 1970). For convenience, the time interval is designated Δt and the age interval ΔS. The term $n^i(j)$ represents the number concentration at an age j and at a time step i. To illustrate the method, γ and ϕ are made identically zero in Equation 1a. This restriction on γ and Φ applies only to the discussion of the Crank-Nicolson method and quasilinearization and is not applicable to the results given later.

The differential equation

$$\frac{\partial n}{\partial t} + \frac{\partial n}{\partial s}\frac{ds}{dt} = -\lambda(s)\,n(s) \qquad (8a)$$

has the difference form

$$\frac{n^{i+1}(j) - n^i(j)}{\Delta t} + \frac{\Delta s}{\Delta t}[n^i(j) - n^i(j-1)]\tau +$$

$$\frac{\Delta s}{\Delta t}[n^i(j) - n^{i+1}(j-1)](1-\tau) =$$

$$-\lambda(j)[n^{i+1}(j)\cdot(1-\tau) + n^i(j)\cdot\tau] \quad (8b)$$

If $\tau = \frac{1}{2}$ the method is known as the Crank-Nicolson method and is unconditionally stable for linear equations. (Young and Frank, 1963; Crandall, 1955).

The second mathematical feature which is incorporated into the model is quasilinearization. Quasilinearization assumes that the nonlinear terms can be expanded into a Taylor's series of the dependent variables (Bellman et al., 1961; Lee, 1968a, 1968b). For example, the last term in Equation 4a can be expanded as

$$\gamma(s)\,n(s,t)\int_{a^*}^{b^*}[n(p,t) + \bar{n}(p,t)]\,dp =$$

$$\gamma(s)\,n(s,t)\,\Sigma_n(t) = \gamma(s)\,n(s,t_0)\,\Sigma_n(t_0)\times$$

$$\left[1 + \frac{n(s,t) - n(s,t_0)}{n(s,t_0)} + \frac{\Sigma_n(t) - \Sigma_n(t_0)}{\Sigma_n(t_0)}\right] =$$

$$\gamma(s)\,n(s,t_0)\,\Sigma_n(t_0)\,[1 + \Delta_s + (\Delta^* + \bar{\Delta}^*)] \quad (9)$$

Since in the Crank-Nicolson approximation t is equal to $\frac{1}{2}$, the last term in Equation 4a is approximated by

$$\gamma(s)\ n(s,\,t_0)\,\Sigma_n(t_0)\left|1 + \frac{\Delta_s}{2} + \frac{(\Delta^* + \bar{\Delta}^*)}{2}\right| \quad (10)$$

The writing of the differential equation in difference form involves the usual difference equations. There is only one unusual definition. The first difference interval corresponds to the last age group. This is necessary to order the coefficient matrix for the Δ, Δ^* in the form suitable for the algorithm used here (Gentry, 1970a).

After the Crank-Nicolson approximation and the application of quasilinearization, the resulting set of equations is:

$$a_i\Delta_i + b_i\Delta_{i+1} + c_i\Delta^* + d_i\bar{\Delta}^* = e_i$$
$$\bar{a}_i\bar{\Delta}_i + \bar{b}_i\bar{\Delta}_{i+1} + \bar{c}_i\Delta^* + \bar{d}_i\bar{\Delta}^* = \bar{e}_i$$
$$\Sigma f_i\Delta_i = \Delta^*$$
$$\Sigma \bar{f}_i\bar{\Delta}_i = \bar{\Delta}^* \quad (11)$$

With the boundary conditions

$$a_n\Delta_n + \Sigma b_{nj}\Delta_j + d_n\bar{\Delta}^* + c_n\Delta^* = e_n$$
$$\bar{a}_n\bar{\Delta}_n + \Sigma \bar{b}_{nj}\bar{\Delta}_j + \bar{d}_n\bar{\Delta}^* + \bar{c}_n\Delta^* = \bar{e}_n \quad (12)$$

The equations above can be solved by the Gentry algorithm or equivalent methods.

In the application of the model, functional relationships for the following biological parameters need to be established. The mortality rate as a function of age, the reproduction rate as a function of age, the fraction of the female population which is pregnant during a reproductive cycle, the mortality rate due to overcrowding or perhaps storage of food, the rapidity with which the rats learn that they are being poisoned as function of age, and the fraction that never learns that it is being poisoned.

The numerical experiments that follow can be easily up-

dated as more data become available for the life cycle of the wild rat. The reproduction rates were derived from data by Asdell (1964). The mortality data were derived from the data for human population (Chiang, 1968). It assumed that reproduction occurs at a uniform rate over the time period of the reproduction cycle rather than in discrete litters. This approximation approaches the actual reproduction cycle if there is no seasonal variation in the reproduction rate and if there is a sufficiently large population of rats that fluctuations in the birth rate caused by a single rat are negligible. It seems likely that for a typical urban environment where the rats may number more than 100,000 this is a reasonable assumption. The numerical values of the variables used in the model are discussed below.

The mortality rate due to natural causes was taken as a step function of age. The mortality rate λ is given as a function of time (Table I).

The values of mortality chosen have the following features: the highest mortality rates occur for the very young and the old; there is a period corresponding to the teenage period in humans where the mortality rate is low; and no rat lives longer than three years.

All of the above assumptions seem reasonable except the assumption that all rats die after they reach three years. This condition of a maximum attainable age is required for a closure of the mathematical solution. The choice of this age is arbitrary. Three years was selected since this is given as the upper limit of the age of the Norway rat. The values selected for the mortality rate do not alter the mathematical algorithm nor do they impose additional conditions in order to obtain a numerical solution.

The reproduction rate is defined as the average litter size divided by the length of the reproduction cycle in months. The litter size is a function of female size and age. In the model used for this paper, only the effect of age on litter size was considered. The average litter size as a function of age as determined by the mathematical model is given in Table II.

The fraction of rats that are pregnant during any given time interval is related to the type of treatment that is administered. For an untreated population, 65% of the female rats with an age greater than nine months was assumed to be pregnant during a cycle. For rats with an age less than eight months, the fraction that was assumed to be pregnant during the reproduction cycle was given by $\{0.65 - [0.09 \cdot (9 - \text{age})]\}$. Thus the average reproduction rate for female rats two months old is given by the fraction that is pregnant (0.02) times the average litter size (2.00). Therefore, the monthly reproduction rate of rats between one and two months in age is 0.04.

It was assumed that the increase in the mortality rate owing to overcrowding is proportional to the total population. Again it was assumed that the young and the old were more

Table I. Mortality as a Function of Age

Age, months	λ (Mortality rate due to natural causes)	Fraction of rats dying per month
0–1	0.4	0.330
1–2	0.145	0.135
2–8	0.0072	0.007
8–29	0.105	0.100
29–36	1.0	0.732
36+	0.0	1.000

adversely affected. The mortality rate in rats under three months and over 30 months in age is 1.1 times greater than for the bulk of the population. For rats older than 33 months, the increase in mortality was assumed to be 1.21 times the normal rate. The numerical value of γ determined the steady-state population. Presumably an increase in the food supply would mean a decrease in the mortality rate. In the development below two different values of γ were evaluated. One value of γ was chosen to be sufficiently large that the steady-state population decreases from the initial population. A population showed this trend is labeled a "contracting" population. In the second case the value of γ was sufficiently small that the steady-state population tended to increase above the initial population. A population having this characteristic is an expanding population. The same conclusions regarding control options appear to be valid for both expanding and decreasing populations.

The mortality rate due to the administration of poison is given by the equation

$$\phi = A_1 |Q + (1 - Q) \exp [-A_2 (t - t_0)]| \qquad (13)$$

where Q is given by

$$Q = \left| \left[A_3 + \frac{37 - \text{age}}{36} \right] \middle/ 1 + A_3 \right|^2 \qquad (14)$$

The number A_1 is the fraction of rats that would be poisoned if the rats were unable to distinguish that they were being poisoned. Q is the fraction that has not learned to distinguish poison. For rats older than one month, the value of Q increases with increasing values of A_3. The term A_2 determines how rapidly the rats learn that they are being poisoned. In the combined androgen–poison strategy, the rats do not distinguish the androgen. It is assumed that during the cycle, poison is distributed rather than androgen. For a brief time all the rats are inexperienced and vulnerable to the poison. The rapidity with which they learn to avoid the poison is determined by A_2. In the calculations given below A_2 has the value 0.75/month. The value of A_3 was taken as 0.05. In Table III, the fraction of rats that learns to avoid the poison as a function of age and the duration of time that passed since the last poison was administered is presented.

The three control strategies are:

A Sterilization Strategy. In this strategy the females that are treated have offspring that are permanently sterile. It is assumed that only one application is required during the lifetime of the rat. The model assumes that the rats are unable to recognize this treatment; consequently they do not learn to avoid the treated bait.

An Alternating Poison–Sterilization Treatment. This control program consists of a cycle program with two phases. During the poisoning phase, only poisoned bait is distributed.

During the sterilization cycle, only the androgen is being distributed. Since the rats learn to detect poison, the poison option is most effective during the initial stages of the phase. The sterilization stage is the same as in the first option, but has the disadvantage in that it has no effect during the poisoning episode. The possible advantage of this method lies in that it utilizes a poisoning strategy at its peak efficiency, and simultaneously employs a sterilization strategy, albeit with a reduced efficiency.

A Second Pure Sterilization Strategy. This procedure differs in that the androgen must be distributed during a specified time period of the reproduction cycle. Furthermore, the treatment must be repeated for each cycle.

In Table IV, the effect an alternating poisoning–sterilization cycle is illustrated for different cycle lengths. In addition, the two limiting strategies of a continuous poisoning episode and a continuous sterilization treatment are presented. The treatment cycle consists of a sterilization period followed by a poisoning period of the same time duration. The time intervals in the difference equation were arbitrarily chosen as 0.2 month and calculations were determined over a period of 10 years.

In the second column of Table IV, the mean age of the rat population is listed. For the alternating strategies, the mean age fluctuates between two values, both of which are given. As the mean age decreases, total population increases at a faster rate.

In the third column the fraction of newborn rats which are sterile is given. This number fluctuates for the alternating strategy. The limiting value is given by the pure sterilization strategy. For short-cycle period, this fraction approaches a constant value.

The fourth column gives the normalized adult rate population ($s > 2$). This is the ratio of the adult population of rats

Table III. Fraction of Rats Avoiding Poisoned Bait

Duration of poison episode, months	Age of rat		
	10 Months	20 Months	30 Months
0.5	0.140	0.238	0.298
1.0	0.278	0.403	0.501
1.5	0.303	0.514	0.640
2.0	0.349	0.592	0.736
2.5	0.381	0.645	0.802
3.0	0.402	0.682	0.848
5.0	0.439	0.745	0.925

Table IV. Effect of Alternating Poison-Androgen Strategy
(Fraction of Rats Treated per Month = 0.02)

Cycle length, months	Av age, months	Fraction sterile	Population, ratio
2	6.19	0.13	0.860
4	6.18	0.11–0.14	0.86 –0.875
8	6.13–6.16	0.07–0.14	0.870–0.895
12	6.09–6.14	0.05–0.14	0.878–0.914
16	6.04–6.14	0.02–0.14	0.873–0.933
Poison	5.93	0	0.962
Sterilization	6.18	0.143	0.890

Table II. Litter Size as a Function of Age

Age, months	Litter size
0–1	0.00
1–2	2.00
2–5	2.25
5–6	2.70
16–22	$1.80 + [(22 - \text{age}) (0.1)]$
23	0.90
24+	0.00

after treatment to the adult population if there were no treatment. For alternating strategies there is no limiting value but rather a limiting cycle. As is apparent the values for cycles of two and four months are lower than either of the pure strategies.

The most noteworthy consequence of this calculation is that the most efficient procedure (where the total mature population shows the greatest reduction) is a combination of poisoning and treatment with androgen.

The case where once-treated females produce litters of sterile females is considered next. The fraction of untreated females which receive treatment during a month is 0.5, 1, 2, 3, 5, 7, 10, and 18.5%. In Table V the fraction sterile, the average age, and the reduced ratio of adult rats to adult rats if there were no treatments are presented.

The resulting numerical experiments show that the age of the rat population increases as the population contracts. All the above experiments were conducted for a contracting population. The primary interest in this program concerns the reduction of adult rats. An extrapolation yields the result that approximately 18.5% of the rats must be reached per month to exterminate the population. A treatment of this extent would require the controlling agency to distribute baited food equal to 23% of the total food available for the rats. This result from the extrapolation was confirmed by a subsequent numerical experiment.

Next, the problem of controlling a rat population by treating the females during a specified time period in its reproductive cycle is considered. This time period corresponds to the 10 days prior to conception and to the 10 days after conception. The data are presented in terms of the fraction of females which is treated in the interval. The results are given in Table VI for a "contracting" population and for an "expanding" population where the number increases from the initial value.

The question we wish to determine is whether the control strategy is altered by a "contracting" or "expanding" population. If there were differences, it might be desirable to have two different strategies—one for when the population is expanding as in the aftermath of a plague or food shortage. When a large numerical value of γ is chosen, the death rate due to overcrowding increases, and the total population necessary for a stable population is less than the initial population. If γ is made smaller the population increases. The importance of this analysis is to determine if it is necessary that a population be limited by territory or food supply in order to invoke a particular control program. It has not been shown that the rat populations in urban centers in the United States are limited by territory or food supply.

An examination of Table VI indicates that the equilibrium population ratio is independent of the value of $\gamma(s, t)$ the limiting population term. Furthermore, the ratio of the equilibrium values is exactly 5/1. One would anticipate this conclusion because at equilibrium one has

$$\frac{\partial n_s}{\partial t} + \frac{\partial n_s}{\partial s} = -\lambda_s - \lambda n_s \int n(p)dp$$

or

$$\frac{\partial n_s}{\partial s} = -\lambda_s n_s - \gamma_s n_s \, \Sigma_n \tag{15}$$

Since one would anticipate $\partial n/\partial s + \lambda_s n_s$ to be proportional to a constant times n_s, one has

Table V. Effect of Androgen on Rat Population

(Female Rat Requires Single Treatment)

Fraction treated per month (5)	Av age, months	Fraction newborn sterile, %	Population ratio
0.0	5.91	0.0	1.000
0.5	5.98	3.8	0.973
1.0	6.06	7.4	0.945
2.0	6.18	14.3	0.890
3.0	6.37	20.8	0.835
5.0	6.71	36.2	0.726
7.0	7.10	43.0	0.620
10.0	7.78	56.0	0.465
18.5	10.24	80.3	0.078
			(and decreasing)

Table VI. Effect of Androgen on Rat Population

(Female Rat Requires Treatment in Each Reproduction Cycle)

Contracting			Expanding		
Fraction newborn sterile, %	Av age, months	Population ratio	Fraction newborn sterile, %	Av age, months	Population ratio
0.0	5.91	1.000	0.0	5.91	1.000
10.0	6.11	0.928	10.0	6.11	0.925
30.0	6.63	0.754	30.0	6.63	0.753
60.0	8.05	0.410	60.0	8.05	0.410
70.5	9.00	0.247	90.0	13.36	0.000
90.0	13.35	0.000			

$$\frac{\frac{\partial n_s}{\partial s} + \gamma_s \Sigma n_s}{n_s} = -\gamma_s \Sigma_n = e \tag{16}$$

Thus one would expect Σ_n to be inversely proportional to γ_s. Similarly one would not expect a difference for different levels of sterilization, since this affects only the reproduction rate and not the mortality. Consequently, the control strategy adopted is independent of whether the population is growing or decreasing. Numerical calculations confirm this analysis.

In evaluating the efficiency of a program, one needs more information than is currently available on the feeding habits of wild rats and the dose requirement for sterilization. However, these studies suggest that a treatment for which one treatment of the female results in all of her subsequent offspring being sterile in combination with a poison distribution program shows the possibility of substantially reducing the rat population.

Conclusion

A model for the effect of population of several different types of controls has been developed. A mathematical program is developed to test the effectiveness of these programs. Incorporated into the model is an improved algorithm for more rapid numerical calculations. The model was used to consider three possible strategies. From the numerical experiments one can conclude that a policy of alternating poison and androgen is more effective, secondly that one must treat approximately 15% of the rats per month to eliminate the population. This would correspond to providing nearly 18% of the current food supply as bait. If one must treat the rats during each reproduction cycle with androgen

which is now the case, one must succeed in treating more than 75% of the rats in order to eradicate the population.

Literature Cited

Ames, W. F., "Nonlinear Partial Differential Equations in Engineering," Academic Press, New York, N.Y., 1965, p 315.
Ardrey, R., "The Territorial Imperative," Atheneum, New York, N.Y., 1966, p 1.
Asdell, S. A., "Patterns of Mammalian Reproduction," 2nd ed., Comstock, Ithaca, N.Y., 1964, p 324.
Bellman, R., Juncosa, M., Kalaba, R., Rand Corp. Rept. no. P–2200, Santa Monica, Calif., 1961.
Chiang, C. L., "Introduction to Stochastic Processes in Biostatistics," Wiley, New York, N. Y., 1968, p 266.
Crandall, S. H., *Quart. Appl. Math.* 13, 318 (1955).
Crank, J., Nicolson, P., *Proc. Cambridge Phil. Soc.* 43, 50 (1947).
Dahtchakoff, V., *Compt. Rend. Acad. Sci.* 206, 945 (1938a).
Dahtchakoff, V., *Compt. Rend. Soc. Biol.* 127, 1255 (1938b).
Dahtchakoff, V., *ibid.* 141, 114 (1947).
Diamond, M., *Proc. Amer. Soc. Zool. Anat. Rec.* 137, 349 (1960).

Gentry, J. W., *Can. J. Chem. Eng.* 48, 451 (1970a).
Gentry, J. W., *Ind. Eng. Chem. Fundam.* 9, 671 (1970b).
Lee, E. S., *AIChE J.,* 14, 490 (1968a).
Lee, E. S., *ibid.* 14, 908 (1968b).
Phoenix, E. H., Goy, R. W., Gerall, A. A., Young, W. C., *Endocrinology* 65, 369 (1959).
Richards, C. E., *Analog Comput. Ed. Users Group Trans.* 2, 203 (1970).
Tedford, M. D., Young, W. C., *Abstr. Proc. Amer. Ass. Anat. Rec.* 136, 325 (1960).
Wilkes, J. O., *AIChE J.* 16, 501 (1970).
Young, W. C., "The Hormones and Mating Behavior," in "Sex and Internal Secretions," Vol II, Williams and Wilkins, Baltimore, Md., 1964, p 1173.
Young, D. M., Frank, T. G., *Int. Comput. Cent. Bull.* 2 (1963).

Model Ecosystem for the Evaluation of Pesticide Biodegradability and Ecological Magnification

Robert L. Metcalf, Gurcharan K. Sangha, and Inder P. Kapoor

Departments of Zoology and Entomology, University of Illinois, Urbana-Champaign, Ill. 61801

■ A small laboratory "model ecosystem" has been developed to study the biodegradability of pesticides, and evaluated with radiolabeled DDT, DDE, DDD, and methoxychlor. The model ecosystem has a terrestrial–aquatic interface and a seven-element food chain. It simulates the application of pesticides to crop plants and the eventual contamination of the aquatic environment. When used with 5 mg of ^{14}C-labeled DDT applied at an equivalent rate of about 1 lb per acre, the radiolabeled DDT was accumulated in mosquito larvae, snails, and fish as DDE, DDD, and DDT and concentrated from 10,000- to 100,000-fold. ^{14}C-DDE was concentrated 30,000- to 50,000-fold and stored with little metabolism, while ^{3}H methoxychlor was readily metabolized to mono- and di-OH derivatives and was stored at comparatively low levels. The model ecosystem approach has considerable value for studying the biodegradability and ecological fate not only of new candidate pesticides, but also of industrial chemicals.

E nvironmental pollution by stable lipid-partitioning substances such as DDT, dieldrin, polychlorbiphenyls, and dimethyl mercury has caused successive waves of concern by ecologists as the extent of their global distribution is revealed. We are slowly learning that such substances may accumulate to almost unbelievable levels—10^3 to 10^6-fold—in the lipids of carnivors at the upper ends of food chains. It appears that the presence of such stable contaminants in reservoirs such as the Great Lakes is virtually irreversible and may cause immense damage to important food chains and to fish and game.

There is an urgent need to develop persistent, yet biodegradable, pesticides that will remain effective for relatively long periods on household surfaces, in plants, animals, and the soil; yet when ingested by all sorts of living organisms from microorganisms to man will be decomposed by enzymatic processes to readily eliminable, water soluble fragments.

The threat of environmental catastrophes has demonstrated that we can no longer afford to learn about environmental behavior of new pesticides through one to two decades of wide-scale use. We need a realistic laboratory method for screening proposed new pesticides for their environmental fate. The use of radiolabeled compounds in such a model ecosystem would provide both qualitative and quantitative information about the metabolism of the compound in various plants and animals and should ideally provide for simulation of a simple environmental situation as a multi-componented laboratory organism.

We report here the evaluation of such a simple "model ecosystem" which has yielded valuable information about the biodegradability of numerous pesticides. The methodology described is capable of almost infinite variation and extrapolation and is essential in the study of new pesticides as a result of recent U.S. Department of Agriculture regulations providing for detailed information of potential effects on environmental pollution, as a registration requirement for new products (USDA, 1969).

Experimental

Radiolabeled Compounds. The ^{14}C-DDT used in the evaluation of the model ecosystem was supplied by the Radio-chemical Centre (Amersham, England). The compound was labeled in the aryl rings and had a specific activity of 5.48 mCi/mmol. The compound had been stored for several years in benzene solution, and thin-layer chromatography (TLC) with silicic acid and petroleum ether bp 60° to 68°C (Skelly-solve B) showed it to contain approximately 69.5% DDT; 1.13% DDE, or 2,2-*bis*-(*p*-chlorophenyl)-1,1-dichloroethylene; and 5.8% TDE or DDD, or 2,2-*bis*-(*p*-chlorophenyl)-1,1-dichloroethane, together with 18.7% of more polar compounds such as *p,p*-dichlorobenzophenone. Since these latter impurities were desired as labeled compounds, approximately 50 mg of the labeled DDT was passed through a preparative column of silica gel and eluted with hexane. Pure fractions were collected and contained ^{14}C-labeled DDT, DDE, and DDD, all of which were +99% pure upon TLC in two systems: (*a*) petroleum ether bp 60° to 80°C, and (*b*) ether–petroleum ether, 1:9; and which cochromatographed with authentic samples of the pure compounds using fluorescent silicic acid (E. Merck G_F254). The R_f values for DDT and its degradation products are shown in Table I.

^{3}H-ring substituted methoxychlor was prepared by tritiation of methoxychlor as described by Hilton and O'Brien (1964) and purified by column chromatography to a purity of +99% as evaluated by TLC on silicic acid using (*a*) ether–petroleum ether (60° to 80°C), 3:1; or (*b*) petroleum ether, chloroform, methanol, 3:2:1. The ^{3}H-methoxychlor had a specific activity of 4.81 mCi/mmol.

Radioautographs of TLC plates were made using Eastman no-screen x-ray film and the plates were evaluated quantitatively by scraping 1-cm sections or fluorescent spots into scintillation vials. These were counted with use of "cocktail D" (100 g naphthalene and 5 g PPO in dioxane to make 1 liter) or for ^{3}H-labeled compounds in "^{3}H cocktail" (200 g naphthalene, 10 g PPO, and 0.25 g POPOP in dioxane to make 1 liter). Tritium-labeled compounds in biological fluids were assayed by the Schöniger oxygen flask combustion technique (Kelly *et al.*, 1961) as described by Kapoor *et al.* (1970). This method uniformly gave 99 to 100% recoveries.

Model compounds for TLC cochromatography were prepared as described by Kapoor *et al.* (1970) and were detected

on TLC plates by (*a*) quenching of fluorescence, (*b*) spraying with 0.5% diphenylamine plus zinc chloride in acetone and heating to 110° for 10 min, followed by exposure to ultra-violet light to give pink spots with ethylene derivatives and black or bluish spots with dichloro- or trichloroethanes, or (*c*) for methoxychlor derivatives by exposure to ultraviolet light which produced yellow to orange spots from *p*-hydroxylated metabolites.

The general methods for preparation and evaluation of radiolabeled samples have been described in detail by Kapoor *et al.* (1970).

Model Ecosystem Methodology. The basic units are glass aquaria 10 × 12 × 20 in. with 180 in.^{2} of surface. They contain 15 kg of washed white quartz sand molded into a sloping soil/air/water interface (Figure 1). The terrestrial end of the sand shelf is flattened for about 6 to 7 in. in width to accommodate growing plants. The aquaria contain 7 liters of "standard reference water" (Freeman, 1953) containing the following concentrations of salts, in ppm: $MgSO_4$, 36.4; K_2SO_4, 0.135; $CaCl_2$, 14.0; $NaHCO_3$, 25; NH_4NO_3, 3.0; K_2HPO_4, 0.78; $CaCO_3$, 57.5; $NaSiO_3$, 23.6; and $FeCl_3$, 0.81, adjusted to pH 7.9. This standard water has provided satisfactory mineral nutrition for the growth of the *Sorghum halpense* plants in the aerial portion of the chamber and for the *Oedogonium cardiacum* algae in the aquatic portion. It is also satisfactory for the growth and development of plankton, *Physa* snails, cladocera, mosquitoes, and fish. The use of pure sand and water culture is not only much more reproducible than soil but also eliminates a large amount of organic material which had uncertain effects and interfered with extraction and determination of radiolabeled products.

The model ecosystems containing 10 snails, algae, and a few milliliters of old aquarium water are aerated continuously by air bubbles from a Silent Giant aquarium pump. A Plexiglas cover (11 × 12 in.) covers the aquatic portion of the chambers and greatly reduces the rate of evaporation of the water. The individual aquarium units are housed in an environmental plant-growth chamber (Percival P-80) which is operated at 80°F ± 1° on a 12-hr diurnal cycle of 5000 ft candles.

Rearing Plants and Animals. A major part of the technology of the model ecosystems has dealt with the selection of a series of food chains of organisms compatible with the conditions in the aquarium. These, of necessity, must be readily reared and available throughout the year.

Sorghum halpense (Pioneer 846) was selected after many trials, as a thoroughly satisfactory plant for growth in the semiaquatic environment of the terrestrial end of the chamber. It combines uniform and rapid growth, palatability for the salt marsh caterpillar (the second element in the food chain), good germination and growth in the sand culture, and ease of treatment with the radiolabeled pesticide. Fifty seeds are planted in five rows along the flattened terrestrial end of the chamber. The seeds germinate in about three to four days, and, after 20 days, the plants are about 4 in. high and satisfactory for treatment with the radiolabeled pesticide.

Estigmene acrea, the salt marsh caterpillar, was selected as the key terrestrial insect because of its omnivorous and voracious nature and the considerable amount of information available in our laboratory about its ability to metabolize a variety of pesticides (Metcalf *et al.*, 1968; Kapoor *et al.*, 1970). To ensure its year-round availability, a synthetic diet modified from that of Searle and MacFarlane (1968) was used in paper cups with five to ten larvae. The eggs of the caterpillars are placed on top of 15 g of the diet, and the larvae transferred weekly to fresh diet, requiring about four weeks to

Table I. R_f Values for Model DDT Metabolites on Thin-Layer Chromatography

Compound	mp, °C	R_f on silicic acid with petroleum ether
2,2-*bis*-(*p*-Chlorophenyl) acetic acid	162	0.0
4,4'-Dichlorobenzophenone	146	0.06
2,2-*bis*-(*p*-Chlorophenyl)-2-hydroxy-1,1,1-trichloroethane	79	0.11
2,2-*bis*-(*p*-Chlorophenyl)-1,1-dichloroethane	110	0.17
2,2-*bis*-(*p*-Chlorophenyl)-1-chloroethane	54	0.33
2,2-*bis*-(*p*-Chlorophenyl)-1,1,1-trichloroethane	109	0.34
2,2-*bis*-(*p*-Chlorophenyl)-1,1-dichloroethylene	82	0.53
2,2-*bis*-(*p*-Chlorophenyl)-1-chloroethylene	67	0.50
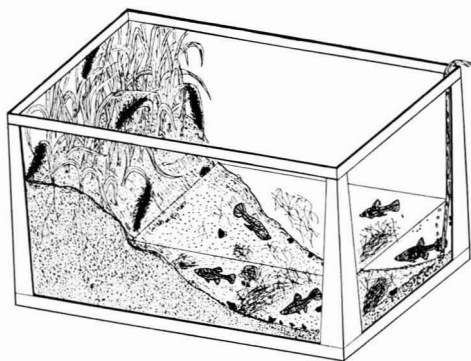
Figure 1. Schematic drawing of model ecosystem for studying pesticide biodegradability and ecological magnification

reach maturity. Ten early fifth instar larvae (27 to 33 days old) are placed on the treated sorghum plants and the 4 in. open end of the aquarium covered with copper screen to confine the insects. The larvae generally consume most of the treated plant surface within three to four days and their feces, leaf frass, and the larvae themselves contaminate the moist sand and water, and begin the distribution of the radiolabeled metabolic products throughout the model ecosystem. If the larvae are killed by the pesticide treatment as has occurred with carbofuran (2,2-dimethyl-2,3-dihydrobenzofuranyl-7 N-methylcarbamate) and aldicarb (2-methylthio-2-methylpropionaldehyde oximyl N-methylcarbamate) new groups of larvae are added at intervals until the sorghum is consumed. The time interval for consumption is noted as evidence of the rate of environmental degradability.

Daphnia magna, the water flea, was selected as the intermediate plankton organism because of its size and ease of rearing on a 0.5% infusion of powdered sheep manure in the "standard reference water" (Frear and Boyd, 1967). The Daphnia are extremely sensitive to pesticides in the ppt to ppb range (Frear and Boyd, 1967) and serve as a valuable indicator organism for the presence of toxic metabolites. Approximately 30 Daphnia are added to the model ecosystem at the beginning of the experiment, and if they are killed by the treatment, the aquarium is reinfested at intervals until the culture survives. This again provides useful ecosystem information.

Culex pipiens quinquefasciatus, mosquito larvae, are added to the model ecosystem after 26 days using 300 larvae. This species was chosen because of ease in rearing and a background of 20 years of evaluation in our laboratory of its response to thousands of insecticidal compounds. If the larvae do not survive, reinfestation can be accomplished at intervals as with Daphnia. However, none of the 10 insecticides studied to date have killed the larvae in the ecosystem procedure. After the larvae have remained in the model ecosystem for four days, 50 are removed for tissue analysis of their radioactive contaminants as described below.

FISH. The food chains are completed after 30 days by the addition of three Gambusia affinis mosquito fish which readily devour all the remaining mosquito larvae and the Daphnia. After three days in the system, these are sampled for radioactivity as described below.

Operation of Model Ecosystem. After sand and water are equilibrated for a day, the sorghum seeds are planted and 10 Physa snails, about 30 Daphnia magna, a few strands of

Oedogonium cardiacum algae, and a few milliliters of old aquarium water containing a plankton culture are added. At about 20 days, when the Sorghum plants are approximately 4 in. high, they are treated quantitatively with 5.0 mg of radio-labeled pesticide (ca. 15 to 25 μmol). This is applied from about 1% acetone solution using a capillary pipet so that the compound contaminates only the leaves. This rate of application for the 6-in. wide plant area is approximately 1 lb per acre, and thus simulates a rate of treatment commonly used in pesticide applications.

The experiment is terminated after 33 days, when weighed samples of the organisms were examined for radioactivity. The samples are homogenized in water and extracted with equal volumes of diethyl ether. Both layers are examined by TLC to determine the qualitative and quantitative nature of the radiolabeled products, with use of radioautography and scintillation counting of serial sections. The water partitioning radioactivity is hydrolyzed by heating with $0.1M$ HCl to free metabolites conjugated as aglycones, phosphates, or sulfates. Samples of sand are counted for radioactivity together with duplicate 1-ml aliquots of water taken from the aquarium at 1, 3, 7, 14, and 28 days after treatment of the sorghum.

FOOD CHAINS. The food-chain pathways for the radio-labeled pesticide in the model ecosystem are:

(1) Sorghum → Estigmene (larva)
(2) Estigmene (excreta) → Oedogonium (algae)
(3) Oedogonium → Physa (snail)
(4) Estigmene (excreta) → Diatoms
(5) Diatoms → Plankton
(6) Plankton → Culex (larva)
(7) Culex → Gambusia (fish)

Among the diatoms identified are Navicula, Coscinodiscus, Diploness, and Diatomella. The plankton species include Daphnia; the protozoans Nuclearia, Coleps, Vorticella, Paramecium; and the rotifers Asplanchnopus, Notomatta, Euclaris, and Scaridium.

Results and Discussion

During the past two years, more than 10 insecticides radio-labeled with ^{14}C or ^{3}H have been evaluated by the model ecosystem technique as described. Many of these are new insecticidal carbamates and the results obtained will be described elsewhere. The purpose of this paper is to describe and evaluate the proposed methodology and to demonstrate the results obtained with DDT and its derivatives which are persistent and essentially nonbiodegradable and with methoxychlor which is persistent and biodegradable.

Reproducibility. The ultimate purpose of the model ecosystem is to be used as a single living unit for in-depth studies of environmental biodegradability. The question of reproducibility of results is of considerable importance as even this simple ecosystem is substantially more complex than any single experimental animal or groups of animals. This factor has been evaluated by two complete individual evaluations of the behavior of ^{14}C-labeled DDT in the model ecosystem with the results shown in Table II. The two studies gave remarkably similar results, both as to distribution and accumulation of total radioactivity in the components of the system and as to the quantitative biodegradability of DDT to DDE, DDD, and polar metabolites. Both experiments clearly demonstrate why DDT is an environmentally undesirable compound because of its stability and high lipid/water partitioning and because of its metabolic conversion to DDE and DDD which have

Table II. Comparison of ^{14}C Distribution in Two Replicates of DDT in Model Ecosystem

	Water		Snail		Fish	
	I	II	I	II	I	II
Total ^{14}C, ppm	0.002	0.004	17.2	22.9	20.8	54.2
DDT, %	5.3	5.4	29.0	33.4	28.3	34.3
DDE, %	7.8	6.5	41.0	52.3	57.5	53.9
DDD, %	13.4	3.0	15.5	7.2	13.2	9.9
Polar compounds, %	68.5	79.8	9.8	4.3	1.0	1.6

Table III. Distribution and Metabolism of Radiolabeled DDT, DDE, DDD, and Methoxychlor in a Model Ecosystem

	Concentration, ppm			
Pesticide	H_2O	Snail	Mosquito, dry wt	Fish
DDT–total ^{14}C	0.004	22.9	8.9	54.2
DDT	0.00022	7.6	1.8	18.6
DDE	0.00026	12.0	5.2	29.2
DDD	0.00012	1.6	0.4	5.3
Polar metabolites	0.0032	0.98	1.5	0.85
DDE–total ^{14}C	0.008	121.6	168.9	149.8
DDE	0.0053	103.5	159.5	145.0
Polar metabolites	0.0027	18.1	9.4	4.8
DDD–total ^{14}C	0.006	5.6	5.8	39.1
DDD	0.0004	3.3	3.43	33.4
DDD ethylene	...	0.24	...	2.08
Unknown I	...	0.14	...	1.54
Unknown II	...	0.87	...	...
Polar metabolites	0.0056	1.1	...	2.0
Methoxychlor–total ^3H	0.0016	15.7	0.48	0.33
Methoxychlor	0.00011	13.2	...	0.17
Methoxychlor ethylene	...	0.7	...	...
Mono-OH-ethane	0.00013	1.0	...	...
Di-OH-ethane	0.00003	...	...	...
Di-OH-ethylene	0.00003	...	...	...
Unknowns	0.00009	...	...	...
Polar metabolites	0.00125	0.8	...	0.16

environmental behavior very similar to the parent compound. These findings are analyzed more completely in the following discussion.

The data shown in Table II demonstrate that DDT is concentrated and stored in the tissues of the *Gambusia* fish which is at the top of the food chains in the model ecosystem to approximately 10,000-fold in Experiment I and 13,000-fold in Experiment II, over the concentration of ^{14}C in the water phase of 100 to 200 ppt, which is approaching the true solubility of DDT in water (Gunther *et al.*, 1968). The pure *p,p'*-DDT has been substantially converted to *p,p'*-DDE, which is clearly the predominant stable metabolite, accounting for about half of the ^{14}C radioactivity in both the fish and snails. Typical radioautographs from the TLC resolution of these compounds are shown in Figure 2.

Comparative Environmental Behavior of DDT, DDD, and DDE. It has been demonstrated repeatedly that DDT is biologically dehydrochlorinated to form DDE and, more recently, that under anerobic conditions it may undergo reductive dechlorination to form DDD (Peterson and Robison, 1964). However, little is known of the relative environmental stabilities of these three compounds or of their comparative food-chain effects. DDD is well known, from the Clear Lake, Calif., experience, to undergo ecological magnification in food-chain organisms in a manner very similar to DDT (Hunt and Bischoff, 1960). The model ecosystem approach with ^{14}C-labeled compounds provides a convenient method for investigation of this problem. Conversely, if the model ecosystem method is valid, the results of such evaluations should conform closely to data accumulating from environmental studies and should indicate the expected effects on environmental quality from the employment of these compounds.

Table III presents the comparative results of the model

Figure 2. Radioautographs of TLC plates with extracts of fish, snails, and mosquito larvae from model ecosystems containing ^{14}C-DDT, DDE, and DDD

ecosystem study of pure DDT, DDE, and DDD. The results in Table III show the route of conversion of DDT to DDE which is the predominately stable and persistent contaminant in the ecosystem. One month after the application of ^{14}C-DDT to the sorghum, 52% of the radioactivity in snails, 58% in mosquito larvae, and 54% in fish was DDE. In *Gambusia* fish, DDE was present at a concentration of 110,000 times that in water and DDT at 84,000 times that in the water, although the fish were present in the system for only three days. Substantial amounts of DDD were present in all three organisms reaching approximately 10% of the total ^{14}C in *Gambusia*. This, together with the relatively large percentage of polar metabolites in the water, 80%, shows that DDT is not by any means nonbiodegradable. However, its principal disadvantage environmentally would seem to be its conversion to DDE, which is relatively nonbiodegradable (Table III). In the DDT experiment, the snails contained about 3% of a metabolite R_f 0.05 which is probably *p,p'*-dichlorobenzophenone. The polar metabolite fraction is probably *p,p'*-dichlorodiphenylacetic acid, R_f 0.0.

The conclusions about the environmental fate of DDT are amplified by the experiment summarized in Table III, where ^{14}C-DDE was the starting contaminant in the model ecosystem. Although a substantial proportion of polar metabolites (34%) was found in the water phase after 30 days, these were minimal in the organisms (7% in snail, 6% in mosquito larvae, and 4% in fish), and no ^{14}C-labeled compounds other than DDE were identified in any of the organisms. The environmental stability of DDE is demonstrated by the radioautograph of snail extracts in Figure 2. Thus, it is apparent that DDE is a highly persistent lipid-partitioning metabolite of DDT which is responsible for the major portion of the adverse environ-

mental effects of concentration and storage in animal tissues following the use of DDT.
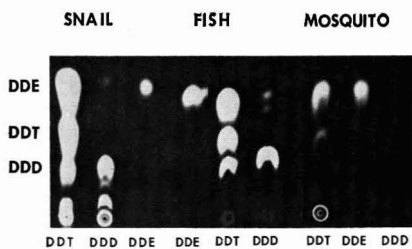
The data shown in Table III, where ^{14}C-DDD was the starting contaminant of the model ecosystem, show that DDD, like DDT and DDE, is a stable lipid-partitioning compound. However, DDD is more biodegradable than either DDT or DDE as shown by the appreciable amounts of polar metabolites and other compounds present in snail and fish (Figure 2). In *Gambusia*, in addition to about 5% polar metabolites, there were nearly equal quantities of two compounds with solubility characteristics similar to DDE—i.e., R_f 0.53 [probably 2,2-*bis*-(*p*-chlorophenyl)-1-chloroethylene] and R_f 0.47, identity unknown. The snail contained a much higher proportion of polar metabolites (20%), presumably resulting from the much longer exposure to the radiotracer over the 30-day period. In addition, there were traces of the same two metabolites, R_f 0.53 and R_f 0.47, and substantial amounts of two compounds with R_f values less than DDD, R_f 0.11, 11% [possibly 2,2-*bis*-(*p*-chlorophenyl)-2-hydroxy-1,1-dichloroethane] and R_f 0.05, 5% (probably *p,p'*-dichlorobenzophenone). (Figure 2.)

The overall picture of DDT contamination of the terrestrial-aquatic model ecosystem as revealed by the data of Table III is remarkably similar to that now being demonstrated in nature. For example, in Lake Michigan following widespread terrestrial applications of DDT to the watershed for the control of the gypsy moth, bark beetle, Japanese beetle, etc., recent studies show DDT in the water at 0.000002 ppm yet present in lake trout and coho salmon at 3 to 10 ppm (Johnson and Pecor, 1969). Thus, the simple model ecosystem studies described here have given a clear picture of the accumulation of DDT and its stable lipid-partitioning metabolites in food-chain organisms. Some 20 years have been required to demonstrate this phenomenon in the Lake Michigan ecosystem. The model ecosystem studies have also shown rather clearly the metabolic and degradative pathways which have produced the ecosystem phenomena.

Environmental Behavior of Methoxychlor. A comparison study has been made of the model ecosystem behavior of ^{3}H-methoxychlor, or 2,2-*bis*-(*p*-methoxyphenyl)-1,1,1-trichloroethane. This compound is a persistent, biodegradable pesticide because of its ready *o*-demethylation to various phenols as described in detail by Kapoor *et al.* (1970). The results obtained in the model system with methoxychlor are shown in Table III. The relatively large number of methoxychlor degradation products found demonstrates substantial degradation. The amounts of methoxychlor and derivatives found in fish were of the order of 0.01 those found with DDT, and half the radioactivity in the fish was as polar metabolites suggesting a rapid turnover of the xenobiotic. In the snail *Physa*, however, methoxychlor was stored to substantial levels and it appears that this snail is unable to metabolize methoxychlor rapidly. These results, together with other studies in progress, suggest that methoxychlor is environmentally degradable and will not be stored in high concentrations in most organisms.

The rate of leaching of the radiolabeled compounds into the aquatic phase of the ecosystem was evaluated. Whereas DDT, DDE, and DDD rose to maximum values over the four weeks, methoxychlor reached an earlier peak and declined.

Conclusion

Several years of study of the model ecosystem with a variety of radiolabeled insecticides have shown that this relatively simple method can be used to investigate the biodegradability and ecological fate of candidate new compounds. The results obtained with DDT after one month in the food chains of the model system show remarkable approximation to conditions observed after many years in nature. The model ecosystem technique is precise and permits the observation and study of metabolic transformations of the pesticide in the various elements of the system. The method gives a good estimation of the potential toxicity of the degradation products of the pesticide to a variety of organisms. The system seems to be especially suitable for computer modeling and for study of the effects of small changes in molecular properties upon environmental biodegradability. We believe it has utility in the screening of candidate pesticides for potentially disadvantageous environmental effects.

Literature Cited

Frear, D. E. H., Boyd, J. E., *J. Econ. Entomol.* **60,** 1228 (1967).
Freeman, L., *Sewage Ind. Wastes* **25,** 845, 1331 (1953).
Gunther, F. A., Westlake, W. E., Jaglan, P. S., *Residue Revs.* **20,** 1 (1968).
Hilton, B. D., O'Brien, R. D., *J. Agr. Food Chem.* **12,** 236 (1964).
Hunt, G., Bischoff, A. I., *Calif. Fish Game* **46,** 91 (1960).
Johnson, H. E., Pecor, D., Trans. 34th N. American Wildlife, Natural Resources Conference, 1969.
Kapoor, I. P., Metcalf, R. L., Nystrom, R. F., Sangha, G. K., *J. Agr. Food Chem.* **18,** 1145 (1970).
Kelly, R. G., Peets, E. A., Gordon, S., Buyske, D. A., *Anal. Biochem.* **2,** 267 (1961).
Metcalf, R. L., Fukuto, T. R., Borck, K., El-Aziz, S., Munoz, R., Cassil, C. C., *J. Agr. Food Chem.* **16,** 300 (1968).
Peterson, J. E., Robison, W. H., *Toxicol. Appl. Pharmacol.* **6,** 321 (1964).
Searle, N. W., MacFarlane, J., *Ann. Entomol. Soc. Amer.* **61,** 949 (1968).
U.S. Department of Agriculture, C-72, "Data Requirements with Respect to Pesticides in the Environment," 1969.

COMMUNICATION

Accumulation of DDT by *Daphnia magna*

Donald G. Crosby and Richard K. Tucker[1]

Dept. of Environmental Toxicology, University of California, Davis, Calif. 95616

■ *Daphnia magna*, an important link in the aquatic food chain, accumulates the insecticide DDT in 16,000 to 23,000-fold quantities from dilute suspension in water within 24 hr. Uptake is principally through the carapace and initially is rapid. Final body levels may reach several thousand milligrams per kilogram.

With the increasing use of synthetic pesticides in agriculture, public health, forestry, and wildlife management, continuing concern has been expressed over the possibility of biological magnification of chemical residues in members of food chains (Hunt, 1966). Aquatic food chains have received particular attention, and there is no doubt that mollusks, fish, and other aquatic animals accumulate considerable quantities of certain compounds (Bridges et al., 1963, 1964; Newsom, 1967).

The planktonic Entomostraca generally are considered to be among the first animal links in the aquatic food chain, and *Daphnia* have been shown to represent an important part of this group (Gerking, 1962). Although there is field evidence for the concentration of chlorinated hydrocarbon insecticides by the genus (Keith, 1965), exact laboratory methods for the study and measurement of this phenomenon have not been reported previously.

The insecticide DDT [1,1,1-trichloro-2,2-bis(4'-chlorophenyl) ethane] has been found widely distributed in surface water. The present communication describes the laboratory measurement of DDT uptake by *D. magna* and the distribution of the compound during the experiments.

Materials and Methods

Pure *p,p'*-DDT was prepared by repeated recrystallization

[1] Present address: U.S. Dept. of the Interior, Fish and Wildlife Service, Denver, Colo.

of the technical product from ethanol until a constant melting point of 108°C was obtained. Solvents were carefully distilled immediately prior to use.

A laboratory strain on *D. magna* Straus was cultured as previously described (Crosby *et al.*, 1966). Groups of 24 first-instar organisms were starved for two and one-half hr and then transferred to 100-ml beakers containing 25 ml of deep-well water of the composition employed previously. An acetone solution (50 μl) containing the desired quantity of DDT was injected below the surface of the water, and the beakers were maintained at 21.1° ± 0.05°C for 26 hr. At the end of this period, those daphnids unable to swim more than 1 cm vertically toward light were considered to be immobile; those which showed no movement of appendages, eye, or heart under repeated microscopic (40×) observation were counted as dead.

The organisms and deposited carapaces were removed by centrifugation, washed carefully with water, and separated by hand. The water was extracted with several consecutive portions of petroleum ether, and a separate extraction of all test glassware was made with petroleum ether. Daphnids, carapaces, and extracts were analyzed separately by the gas chromatographic procedure of Crosby and Archer (1966).

Groups of 10 first-instar *Daphnia* were removed from their culture medium after starving, dried briefly by careful application of filter paper, and weighed immediately on a Cahn microbalance. From a series of measurements, the average weight of an individual was determined to be 9 ± 1 μg, although the weight declined rapidly on exposure of the animals to air.

Results and Discussion

It is apparent that *D. magna* accumulates DDT from its environment. For example, exposure to an insecticide level of about 8 ppb in water for a 24-hr period resulted in a 16,000-fold concentration, while exposure to water containing 50 ppb resulted in a 23,000-fold concentration (Table I).

At the latter level, 25 first-instar, 9-microgram organisms

Table I. Uptake of DDT by *Daphnia magna*

DDT level in water, ng/ml[a]	Total added DDT, ng	DDT in whole *Daphnia*			% Effect	
		Ng	% Of initial dose	Mg/kg[b,c]	Dead	Immobile
0.0	0	0	...	...	0	0
8.0	400	28.8	7 2	128	<4	64
16.0	800	60	7.5	266	12	86
50.0	2,500	260	10.4	1150	44	99+
100	5,000	285	5.0	1260	72	99+
200	10,000	530	5.3	2364	89	99+
1100	55,000	990	1.8	4280	99+	99+

[a] Nanograms per milliliter is equivalent to parts per billion in water.
[b] Calculated for *Daphnia* weight of 9 μg.
[c] Milligrams per kilogram is equivalent to parts per million in *Daphnia*.

swimming in 50 ml of water took up a total of 260 ng of DDT in 26 hr, or 10.4% of the entire amount added to their container. This quantity represented 1150 mg of DDT per kg of body weight.

A lower initial level in the water (8 ppb) resulted in a total uptake of 28.8 ng of DDT, or 7.2% of the available amount (a body level of 128 mg per kg). As shown in Table II, smaller proportions also were recovered from the carapaces shed by those organisms which moulted during the test period and from the walls of the beakers in which the experiments were conducted.

As expected, more than half of the initial dose of DDT was recovered from the water. Injection of the acetone solution had caused dispersion of the insecticide in the form of minute particles of a wide range of sizes. The filter-feeding *Daphnia* could be expected to ingest only a limited range of particle sizes, the smaller particles probably remaining in suspension during the course of the experiment and the larger ones settling to the bottom. Although the distribution of particle sizes appeared to be quite reproducible, changes in dispersion technique may change this distribution with resultant variation in the amount of DDT ingested.

Ingestion probably represents a relatively unimportant route by which *Daphnia* are exposed to suspended chemicals. Exposure of heat-killed daphnids resulted in an uptake of about half as much DDT as was accumulated by the living organisms (Table III). The close correlation of this amount with that found in moulted carapaces suggests that a significant proportion of the accumulated insecticide is dissolved or adsorbed externally by the exoskeleton. The process appears to be rapid, as the DDT level in the living *Daphnia* reached about 75% of its final value within one hr. Absorption through the presently undefined respiratory system may represent another important route of exposure.

Approximately 25% of the added DDT remained unaccountable. Although mechanical errors, incomplete extraction, and metabolic decomposition undoubtedly contributed, the greatest loss appeared to be due to the evaporative codistillation of DDT with water. Consistent with the data of Acree, et al. (1963), about 20% of a control DDT suspension disappeared on standing at room temperature overnight, although a volume change of only 6 ml (or 25%) was observed. Consequently, the initial concentration of 8 ppb was reduced to 6 ppb by the end of a 24-hr test unless precautions were taken to minimize volatilization.

The DDT concentration which causes paralysis of half of a test group of *Daphnia* (IC_{50}) has been shown to be 5.5 ppb

Table II. Distribution of Dispersed DDT[a]

	Recovery	
Source	Ng	% Of initial dose
Untreated water + *Daphnia*	0.0	—
Whole (washed) *Daphnia*	28.8	7.2
Daphnia carapaces ("shells")	14.4	3.6
Glass container	18.0	4.5
Water from *Daphnia*	235	58.8
Total recovered	296.2	74.1
Unrecovered	103.8	25.9
Treated water (no *Daphnia*)	316	79.0

[a] Initial level 8 ng/ml; initial dose 400 ng.

Table III. Uptake of DDT by *Daphnia magna*

	Recovery		
Source	Ng	% Of initial dose	Mg/kg
Dead *Daphnia*	14.3	3.6	64
Moulted carapaces	14.4	3.6	...
Live *Daphnia* (1-hr exposure)	21.1	5.3	94
Live *Daphnia* (26-hr exposure)	28.8	7.2	128

(Crosby et al., 1966). Most of the organisms used in the present tests became immobile within 26 hr but recovered when removed from the presence of the insecticide. With increasing DDT concentration, the proportion of individuals which could be revived declined (Table I), providing a median subacute lethal level of about 1170 mg per kg. No death or immobilization was observed among untreated controls.

The body burden of DDT in *Daphnia* was found to be roughly proportional to the logarithm of the DDT content of the medium (Figure 1). DDT levels in natural waters vary widely, but a concentration of 10 μg per liter (10 ppb) does not appear unusual (Faust and Suffet, 1966; Keith, 1965). Although it is doubtful that acute intoxication would result in most fish species exposed to this level dispersed in water according to the usual laboratory procedure (Henderson et al., 1959), ingestion of only 10 mg of *Daphnia* previously exposed for a day to the medium would provide an acute oral dose of about 1.5 mg per kg in a 1-gram fish. DDT levels of 3 mg per kg in the food of cutthroat trout were near the level of acute toxicity (Allison et al., 1964); the *Daphnia* exposed to 8 ppb of DDT in our experiments would provide fish food at 128 mg of DDT per kg.

The biological magnification of pesticides through food chains obviously requires much additional quantitative chemical and biochemical investigation. However, because of its high degree of volatility with water vapor, ready adsorption to solid surfaces, and tendency to separate from suspensions in water, aquatic experiments with DDT must be conducted and interpreted with extreme caution.

Figure 1. DDT Uptake by Daphnia magna

Literature Cited

Acree, F., Jr., Beroza, M., Bowman, M. C., *J.*, *Agric. Food Chem.* **11**, 278 (1963).
Allison, D., Kallman, B. J., Cope, O. B., Valin, C. V., "Some Chronic Effects of DDT on Cutthroat Trout," U.S. Fish and Wildlife Service, Res. Rept. 64, 1964.
Bridges, W. R., Kallman, B. J., Andrews, A. K., "C¹⁴-DDT in a Microenvironment at Denver," Fish and Wildlife Circ. 199, U.S. Dept. of the Interior, Washington, D.C., 1964, p 30.
Bridges, W. R., Kallman, B. J., Andrews, A. K., *Trans. Amer. Fish. Soc.* **92**, 421 (1963).
Crosby, D. G., Archer, T. E., *Bull. Environ. Contam. Toxicol.* **1**, 16 (1966).
Crosby, D. G., Tucker, R. K., Aharonson, N., *Food Cosmet. Toxicol.* **4**, 503 (1966).
Faust, S. D., Suffet, I. H., *Residue Rev.* **15**, 44 (1966).
Gerking, S. D., *Ecol. Monogr.* **32**, 31 (1962).
Henderson, C., Pickering, Q. M., Tarzwell, C. M., *Trans. Amer. Fish. Soc.* **88**, 23 (1959).
Hunt, E. G., "Scientific Aspects of Pest Control," National Academy of Sciences-National Research Council, Washington, D.C., 1966, pp 251–62.
Keith, J. O., U.S. Dept. of the Interior, Fish and Wildlife Service, Denver, Colo., personal communication, 1965.
Newsom, L. D., *Annu. Rev. Entomol.* **12**, 257 (1967).

CORRESPONDENCE

Sludge Dewatering by High-Rate Freezing at Small Temperature Differences

SIR: The recent communication by C. T. Chen, D. U. Updegraff, and L. W. Ross, "Sludge Dewatering by High-Rate Freezing at Small Temperature Differences" [ENVIRON. SCI. TECHNOL. **4**, 1145 (1970)] concludes that sludge dewatering by freezing deserves renewed attention.

The authors note that others (Bruce et al., 1953; Clements et al., 1950; Katz and Mason, 1970) have obtained good dewatering of sludges after conditioning by a freeze–thaw sequence, but that "freezing as a means of dewatering does not appear economical because the long times and high ΔT required would lead to high equipment and operating costs." Chen, Updegraff, and Ross claim that relatively rapid freezing of sludge in thin films produces the desired improvement in dewaterability of sludge provided chemicals, specifically aluminum sulfate, are added before freezing.

There are several impressions left by the authors which should be clarified. The impression is given in the quotation above that "long times" are required to freeze sludge. The long freezing times used by the cited authors were a process necessity and not some limitation caused by the fact that they used thicker sludge layers. The sludge did not show the desired improvement in dewatering rate on thawing unless the sludge was frozen slowly and completely.

The authors apparently worked with samples too small to permit them to carry out tests comparing the filtration rate of sludge conditioned by a freeze–thaw sequence with that of untreated sludge. Instead, they filtered the sludge, presumably according to some uniform procedure, and measured its final moisture content. Higher solids contents were obtained with the freeze-conditioned sludge, and from this result, the authors inferred that filtration rate would also be increased. I feel that this conclusion is not justified. Increased solids might be related to quite modest increases in filtering rate, whereas the desired effect is an increase in rate of orders of magnitude. With our current state of knowledge, there is no substitute for an actual filtration rate test.

If it is presumed that the desired improvement in filtration rate does take place, the process can be reexamined to see if these higher freezing rates do indeed make freeze–thaw conditioning more feasible. The highest rate observed was an $^1/_8$-in. layer of ice frozen in five min. It is a relatively simple task to convert this into freezing rate per unit of freezing surface area. Assuming the sludge has the same density as water,

$$\frac{^1/_8\ \text{in.}}{^5/_{60}\ \text{hr}} \cdot \frac{\text{ft}}{12\ \text{in.}} \cdot \frac{62.4\ \text{lb}}{\text{ft}^3} = \frac{7.8\ \text{lb}}{\text{hr ft}^2}$$

If the sludge were a waste activated sludge thickened to about 3.0% dry solids, this is equivalent to a dry solids production rate of 0.23 lb/hr/ft² of heat transfer surface.

This production rate should be compared to the area utilization rate of vacuum filtration. A chemically conditioned activated sludge can generally be filtered at a dry solids rate of 1.5 lb/hr/ft² of filtering surface. This is a surface utilization rate approximately seven times higher than for freezing.

The above comparison is fair only if the nature of the surfaces were comparable. Rapid freezing machines are often in the form of a drum of a belt and thus are no more efficient users of floor space than rotary vacuum filters. One only has to recall the large filter rooms at the Milwaukee and the Chicago municipal waste treatment plants to be awed at the thought of a building covering seven times the floor area.

There are other problems in developing a practical freeze–thaw sludge conditioning process than are noted here. However, the need for a large freezing surface area per unit of sludge processed is one of the most serious stumbling blocks. Freezing equipment is needed which will have a far higher freezing surface per unit of floor area than belt or drum freezing machines.

Freeze–thaw conditioning of activated sludges has been investigated recently by Rex-Chainbelt, Inc. and the Milwaukee Sewerage Commission, with the assistance of an FWQA grant. One phase of the study was a consideration of continuous freezing on a steel belt. Their conclusions were the same as this writer's. The results of their work will be published in an FWQA report within a few months.

Joseph B. Farrell

Advanced Waste Treatment Research Laboratory
Federal Water Quality Administration, EPA
Cincinnati, Ohio 45226

Literature Cited

Bruce, A., Clements, G. S., Stephenson, R. J., *Surveyor* **112**, 849 and 850 (1953).
Clements, G. S., Stephenson, R. J., Regan, C. J., *J. Inst. Sewage Purif.*, Part 4, 318 (1950).
Katz, W. G., Mason, D. G., *Water Sewage Works* **117**, 110 (1970).

industry trends

JBF Scientific Corp. (Burlington, Mass.) has been awarded $98,000 by EPA to study the feasibility of dredging or sealing in place mercury-contaminated sediments. Initial stages of the JBF proposal call for laboratory studies with follow-up field trials. Jarrell-Ash (Waltham, Mass.), a subsidiary of Fisher Scientific Corp., is under subcontract to JBF to develop advanced analytical techniques for mercury analysis.

Dravo Corp. (Pittsburgh, Pa.) will engineer and construct a complete chemical recovery system designed to reduce malodorous emissions for Lincoln Pulp and Paper Co.'s Lincoln, Me., kraft mill operations. Scheduled to begin early this year, the project is expected to take 15 months to complete.

Pollution Research Institute of America has been formed and will be headquartered in Miami, Fla., according to Fred C. Muntwyler, president of Wire Sales Co., Inc. Principals of the new company are Muntwyler and Rudy Sarroino, who has been working on pollution technology with Wire Sales. The new company holds various patents, including formulas for phosphate-free detergents and low nicotine-content cigarettes, several nonpolluting industrial aluminum cleaning compounds, and various environmentally related industrial processes. Sarroino will head up the new company and chemist George T. Lewis will be in charge of the Industrial Division.

Pollution Control Industries, Inc., will install its Marine Sanitation System on the ocean-going ferry operating between Cape May, N.J., and Lewes, Del. The project, sponsored by the Environmental Protection Agency, is designed to demonstrate a physico-chemical sanitation system with pollution reduction capabilities equivalent to high-level secondary treatment, says Pollution Control Industries. BOD and suspended solids will be reduced to less than 50 mg per liter and coliform density will be less than 240 MPN.

Dravo Corp. has been awarded a $4 million turnkey contract to design, supply, and construct a complete secondary waste water treatment facility for Packaging Corp. of America's Filer City, Mich., pulp and paper mill. The system will include collection facilities, primary clarifier, aeration basins, secondary clarifiers, thickener, and centrifuges. A final incineration stage will dispose of sludge. The facility will remove about 45,000 lb of oxygen-demanding wastes per day. Construction will be complete by 1972, according to Dravo.

Westinghouse Electric has received a $3 million contract from Dominion Foundries and Steel, Ltd. (Dofasco) of Hamilton, Ontario, for the design and construction of a hot mill industrial filtration water plant. The installation will use a deep bed, ultrahigh-rate filtration system to remove impurities from hot mill waste water. The Dofasco installation will be the largest ultrahigh-rate system in Canada, according to Westinghouse.

PPG Industries' Barberton, Ohio, chemical complex has begun using its new $315,000 water treatment plant to clean up process wastes from its chlorine, pigments, organic chemicals, and development departments. Although wastes from the plant contained no toxic materials, according to PPG, high suspended solids content gave a milky color to the discharge, and high water temperatures often gave rise to foggy conditions along the Hudson Run Creek into which the waste was released. Cleanup of the creek bed, to remove existing deposits, will begin this summer, says PPG.

Sealectro Corp. (Mamaroneck, N.Y.) will conduct research into corrosion-resistant coatings for the inner surfaces of desalination tanks under a contract with the Office of Saline Water. Sealectro will use its Sealectrocoat plasma gun process to coat tank surfaces with polytetrafluoroethylene (PTFE). The gun eliminates the need for several curing steps required by more conventional coating processes.
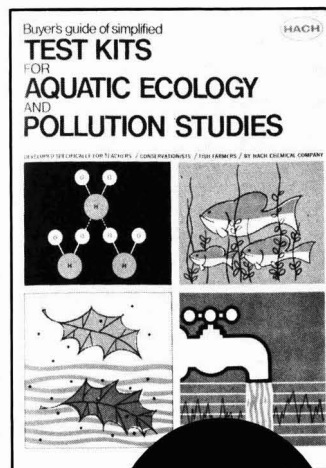
new products

Wet scrubber

Hydro-Filter wet scrubber and air pollution control device is primarily used for incinerators in apartment houses, commercial buildings, light manufacturing plants, and efficient material recovery in industrial processes. Vari-Systems, Inc.　　**61**

Noise control kit

Demonstration kit designed by a leading noise control engineer to show people how to reduce noise. Effectiveness of various noise control methods can be shown audibly with this kit. Howard Engineering Co.　　**62**

Metallic pollutants

Digital atomic absorption spectrophotometer determines the concentration of metallic pollutants in the parts per billion range. Typical metallic elements determined include arsenic, barium, calcium, cadmium, chromium, copper, iron, manganese, mercury, nickel, lead, tantalum, vanadium, and zinc. Perkin-Elmer Corp.　　**63**

Refrigerated pollution sampler

Unit will take 24 (450 ml) individual samples and hold them at low temperature until they can be studied. Prevents varying BOD count. Sigmamotor, Inc.　　**65**

Arsenic analysis

Mercury analysis kit contains additional chemicals and procedure necessary also to determine arsenic content. Determination of arsenic to 1.0 ppb by generating arsine and burning this in a hydrogen/argon flame. Utopia Instrument Co.　　**66**

Temperature conductivity meter

The Environmeter, designed for use in freshwater streams, rivers, and lakes, is useful for ecology students or environmental scientists making temperature studies of natural waters. Beckman Instruments, Inc.　　**67**

Coal dust filter

Cassette-type filter measures respirable coal dust in mines. Provides accurate monitoring system for mine environments. Bendix Corp.　　**68**

Gas chromatograph

Ideal instrument for separating gases or liquids in process analysis, schools, laboratories, and all cases where a portable, compact unit is desired. Matheson Gas Products　　**69**

Auto exhaust monitor

Portable, easy to use instrument designed to provide automotive service centers with a fast accurate way to measure CO in automobile exhausts. Simplifies setting carburetor to manufacturers specifications for CO emissions. National Environmental Instruments, Inc.　　**70**

Shredder and conveyor

Conveyor flattens and forcefeeds material into the shredder. Shredder chews up paper waste into easily baleable pieces. Ideal for use anywhere waste removal is a problem. Maren Engineering Corp.　　**71**

No-pollutant floor care

Waterless system of floor maintenance eliminates water pollution from disposal of waste water. Does away with water washoffs, rinses, and runoffs that usually go into sewage systems. Cello Chemical Co.　　**72**

Chlorine solutions

Chlorine and sodium hypochlorite users can safely and economically produce these chemicals on site. The PEP-CLOR system is applicable for chlorination of cooling water systems, plant effluent waste water, disinfection in municipal waste treatment plants, metallurgical oxidation, and removing organic and sulfur compounds from both gas and liquid streams. Pacific Engineering and Production Co. of Nevada　　**64**

Corrosion guard

Monolithic plastic linings and FRP piping protect process equipment against corrosive attack by liquids containing acids and chrome compounds. Applicable for water treatment plants. Ceilcote Co.　　**73**
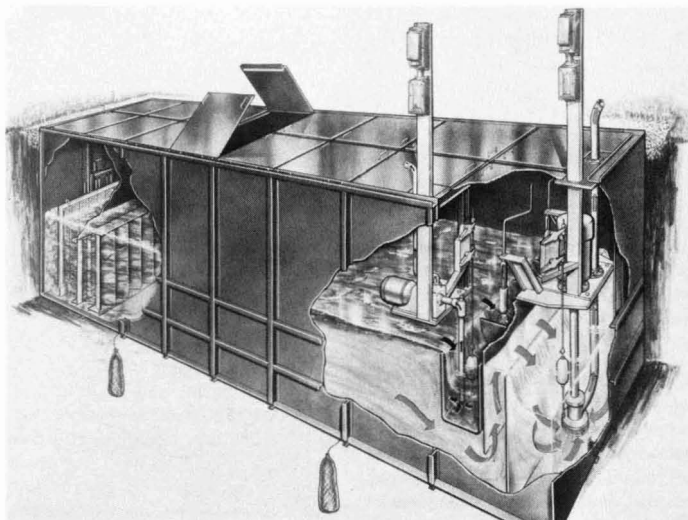
Oil/water separator

The Hydro-Gard Oil/Water Separator is built to API design specifications for the separation of oil from ground and process water before the flow is discharged into sewers and streams. Ready to install and operate when delivered. Inland Environmental **74**

Thermal oxidizer

A/R gas-fired thermal oxidizer is applicable in food processing, metal lithographing, metal decorating, wire enameling, to name a few. Can handle a varying volume of effluent and particulate matter and converts hydrocarbon emissions in the form of smoke, vapors, fumes, odors, and rich or dilute offgases to water vapors and CO_2. Alkar Engineering Corp. **75**
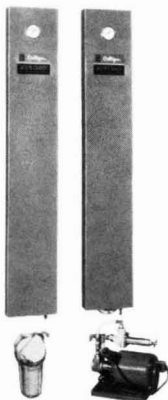
Reverse osmosis

Aqua Cleer reverse osmosis water treatment systems handle 20 to 200 gal per day. Units remove 90–95% of the total dissolved solids from water. Also provides filtration to remove colloidal suspensions and bacteria. Culligan International Co. **77**

Pressure pipe

High-density polyethylene pressure pipe can be used in municipal sewage and industrial effluent collection systems; river, lake, and salt water crossings; and fresh and salt water intakes and outfalls. M. L. Sheldon Plastics Corp. **76**

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

new literature

Bacterial pollution. Reprinted from *Scientific American*, the description offers a simple, cookbook approach to the analysis of bacterial pollution in water. Membrane filters "strain" microscopic life from water. Millipore Corp. **91**

Ecology catalog. Listing of instruments and apparatus used in environmental investigation and control. Specifications and prices shown for more than 2000 products that help provide improved testing techniques and control procedures for all environmental studies. Horizon Ecology Co. **92**

Corrosion. Brochure, "Corrosion in Cooling Waters," discusses the chemistry of corrosion, metal and water factors in corrosion, and how chemicals fight corrosion. Includes table illustrating corrosion inhibitors for cooling water treatment—type, systems where used, and special features. Drew Chemical Corp. **93**

Water instruments. Brochure lists devices used in field and laboratory water pollution control programs by government, public health, and industrial organizations. Accessory instrumentation completes this compilation which has technical data references for further information. Kahl Scientific Instrument Corp. **94**

Hydrology. Quarterly publication contains articles of interest to those concerned with the hydro arts and sciences. "Hydromike" articles are both technical and light-hearted. Leupold & Stevens, Inc. **95**

Particle sizing. Manual tells how to measure and plot aerodynamic particle-size distribution and enumerate particles in any size range. Also discusses plotting of settling velocity spectra of aerosols. AIR, Inc. **96**

pH Analyzers. Bulletin provides detailed operational information for two recently introduced analyzers—both designed for continuous pH measurement in industrial process applications. Beckman Instruments, Inc. **97**

Mg compounds. Brochure discusses magnesium oxide, magnesium hydroxide, mangesium chloride, and Epsom salt. Includes environmental considerations for these products plus health hazards and handling precautions. Dow Chemical Co. **98**

Film effluents. Publication presents an evaluation of photographic chemicals used in film processing, a discussion of sewer codes and stream standards, and suggested methods of reducing outflow. Eastman Kodak Co. **99**
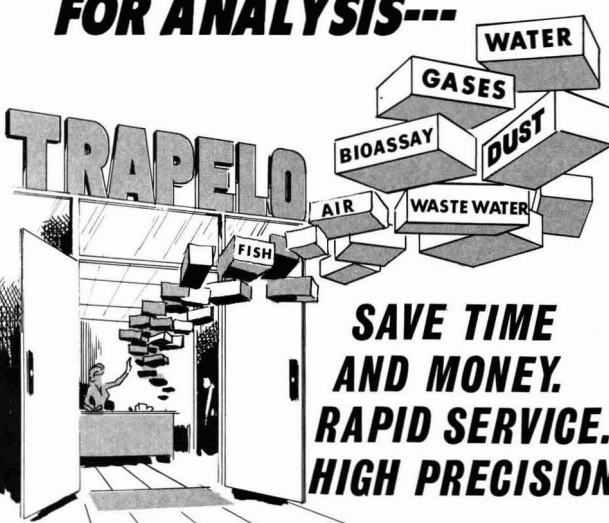
Protective coating guide. 114-Page guide discusses protective coatings for pollution control facilities and equipment. Reference for maintenance and plant engineers, engineering design companies, and all personnel involved with preventing corrosion in pollution control facilities. Carboline Co. **100**

Gas scrubber. Bulletin 15B describes an advanced-design scrubber for handling gases containing submicron particulate matter. Lists data on collection efficiencies for different gases and pollutants. Koertrol Corp. **101**

Pollution charges. Reprint, "Pollution Control—Whose Responsibility?," considers assigning pollution

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

SOLID WASTES

A new publication of the American Chemical Society puts the nation's solid waste problems in perspective.

A 96-page book entitled "SOLID WASTES" contains 26 articles that first appeared in Environmental Science & Technology.

Among the topics covered are:
- Incineration
- Pyrolysis of plastics
- Electricity from waste
- Federal government programs
- Fly ash utilization
- Auto hulk disposal

and many others

The book can only be obtained from the Society and is not available in any bookstore. It costs just $2.00.

Order from:

Special Issues Sales – E
American Chemical Society
1155 16th St., N. W.
Washington, D. C. 20036

---

charges to individual plant cost centers for improving industrial plant effluent quality. Nalco Chemical Co. **102**

Paper and pollution. Report discusses the effect of household paper products on the environment and the steps taken by paper companies to protect the environment. Scott Paper Co. **103**

Wet scrubbing. Catalog features venturi scrubber systems for fume control, particulate matter and chemical removal, gas cooling, gas–liquid absorption or blending, and vapor condensation in process industries. Graham Mfg. Co., Inc. **104**

Peaking generation. Brochure describes the application of gas turbines to meet critical peak generation requirements. Includes response to environmental objectives. Commonwealth Associates Inc. **105**

Pollution data. Description of computer interface system to collect and control data from pollution monitoring stations. Princeton Applied Research Corp. **106**

Fume incineration. How direct-flame fume incineration with heat recovery can cut fuel cost as much as 80% is described in bulletin. Applicable in food processing, printing, chemical processing and manufacturing, oil refining, sewage plants, scrap salvaging, and others. Air Preheater Co., Inc. **107**

Awards. Booklet lists the Sports Foundation, Inc. Gold Medal Awards to eight American companies for achievement in water pollution control and related water conservation or development. Limited number available. Sports Foundation, Inc., 717 N. Michigan Ave., Chicago, Ill. 60611 (Write direct)

Stop pollution. "Seventy-one things you can do to stop pollution" does list what homeowners, communities, businessmen, and public officials can do to ease the burden of pollution in the U.S. Keep America Beautiful, Inc., 99 Park Ave., New York, N.Y. 10016 (Write direct)

Jobless engineers. "AIChE Pollution Solutions," a situations wanted bulletin, lists chemical engineers who are seeking jobs, and are qualified for pollution control work. AIChE, 345 E. 47th St., New York, N.Y. 10017 (Write direct)

---

bookshelf

Where Have All the Flowers Gone?
iii + 121 pages. Arrow Co., 3385 S. Bannock, Englewood, Colo. 80110. 1970. $2.95, paper.

Published as a reference guide and sourcebook to ecological literature, this book includes books, children's books, magazine articles, and films. Totally, it contains more than 600 selections on some of the crucial problems in the U.S. today. "One of our major objectives," say the publishers, "is in the area of environmental education, for we feel that an informed, ecologically aware public is virtually necessary if our planet is to be preserved." ■

Industrial Discharge Permits Required Under Enforcement Act of 1899. Community and Regional Development Group, Chamber of Commerce of the U.S., 1615 H St., N.W., Washington, D.C. 20006. 1970. $1.00

Prepared by the Community and Regional Development Group, U.S. Chamber of Commerce, this book is a businessman's guide to implementation of the permit system governing industrial waste water discharges. Contains pertinent data on the permit system and a question-and-answer section. ■

Marine Ecology, Vol. I: Environmental Factors, Part 1. ix + 681 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1970. $34.50, hard cover.

Neither a compendium nor an encyclopedia, this book is intended as a systematic exposition summarizing and evaluating information obtained thus far on living systems in the sea and surrounding areas. Intended reading for investigators, engineers, teachers, students, administrators, and businessmen who are professionally concerned with life in the marine environment. ■

New and Improved Oil Burner Equipment Workshop. 156 pages. National Oil Fuel Institute, Inc., 60 E. 42nd St., New York, N.Y. 10017. 1970. $3.00, paper.

Information on oil burner development and the impact of air pollution

regulations is contained in the proceedings of the Third New and Approved Oil Burner Equipment Workshop. This technical workshop demonstrated the concepts and equipment under development. ■

The Water Encyclopedia. David Keith Todd, Ed. x + 559 pages. Water Information Center, Water Research Bldg., Manhasset Isle, Port Washington, N.Y. 11050. 1970. $27.50, hard cover.

Contents of "The Water Encyclopedia" include climate and precipitation, hydrology, water use, surface water, groundwater, water resources management, agencies and organizations, constants and conversion factors, and water quality and pollution control. For use as a basic reference, this book is designed to provide quick access to more than 200,000 facts never before put together in one publication. ■

Water Supply and Wastewater Disposal in Developing Countries. M. B. Pescod and D. A. Okun, Eds. 309 pages. Asian Institute of Technology, Henri Dunant St., P.O. Box 2754, Bangkok, Thailand. 1971. $5.00, paper.

A Water Supply and Sanitation seminar was held in Thailand and more than 400 participants from all over the world attended. Experts in the field presented over 37 papers concentrating on aspects of water supply and waste water disposal in developing countries. ■

Microbial Ecology. Martin Alexander. x + 511 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1971. $12.95, hard cover.

Ecology has been the subject of a large surge of interest in the last few years. The field of microbial ecology has expanded rapidly during this same period—microorganisms play a critical role in environments subject to pollution. Professor Alexander hopes to acquaint the reader with one or more applied fields, such as pollution, medicine, public health, food production, and other areas. ■

Technological Trends in the United States Electric-Power Industry. 126 pages. Interdevelopment, Inc., 176 Second Ave., Waltham, Mass. 02154. 1971. $270.

Since the production of electrical power has undergone a dynamic growth since the first supply to the public in 1882, Interdevelopment has conducted a survey to identify technological trends. The resulting report discusses environmental considerations including pollutant emissions, water pollution, emission control, and influence on technology and economics. ■

Law, Pollution and the Environment: A View of Pollution Control in Texas. 154 pages. State Bar of Texas, Austin, Tex. 78711. 1970. $20, hard cover.

The State Bar of Texas has published this comprehensive survey and analysis of the pollution laws of Texas and other states. As stated in the preface, the work "explores in depth the relationship between public good and private rights, the limitations created by traditional jurisdictional and constitutional concepts, and the respective roles of agencies and courts in the control of the environment." ■

Defending the Environment: A Strategy for Citizen Action. Joseph L. Sax. xix + 252 pages. Alfred A. Knopf Co., 501 Madison Ave., New York, N.Y. 10022. 1971. $6.95, hard cover.

Professor Sax, an expert on environmental law, makes clear why it is necessary and possible for citizens to reassert their right to determine the fate of their own environment. He demonstrates how this can be done by carrying the battle into the courtrooms of the nation and restoring democracy to environmental disputes. ■

Methods of Study in Soil Ecology. J. Phillipson, Ed. 303 pages. Unipub, Inc., P.O. Box 433, New York, N.Y. 10016. 1970. $17, hard cover.

Published as the proceedings of a UNESCO conference, this book relates the interchange of ideas among scientists from around the world. The

contents include general problems in soil ecology, various aspects of soil ecosystems, and soil ecology in the next decade, to name a few. ∎

Air Pollution Aspects of Emission Sources: Municipal Incineration—A Biography with Abstracts. Environmental Protection Agency. vii + 95 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1971. $1.00, paper.

Municipal incineration contributes to the overall air pollution level in the U.S. To aid efforts to improve air quality, the Air Pollution Control Office compiled this bibliography pertaining to the problem and its solution. Approximately 320 abstracts cover the 14 topic categories of the book. All documents are on file with the Environmental Protection Agency. ∎

Conservation in the United States: A Documentary History. 5 vols. Van Nostrand Reinhold Co., 450 W. 33rd St., New York, N.Y. 10001. 1971. $150.

As the first complete reference library documenting the historical development of conservation policies in water, air, land, minerals, and recreation, these books present guidelines to roles of the individual, school, and industry in conserving our natural resources. Described by the publishers, the set is "the most comprehensive study ever compiled on the history of conservation policies in the United States." ∎

Solid Wastes—An Environmental Science & Technology Reprint Book. 87 pages. Special Issues Sales, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. 1971. $2.00, paper.

A collection of 25 articles that originally appeared in ENVIRONMENTAL SCIENCE & TECHNOLOGY, this book covers all the major aspects of what has become a serious social problem. Topics discussed include incineration, pyrolysis of plastics, electricity from wastes, federal government programs, fly ash utilization, auto hulk disposal, and others. This publication can only be obtained from the American Chemical Society. ∎

Circle No. 13 on Readers' Service Card

Environmental Improvement Exposition at ACS meeting

Plan to be at the society's first exhibit
of pollution control equipment and dozen
sessions on hot environmental topics

Displays. *Ten exhibitors are ready to kickoff the ACS effort*

Next month, the first Environmental Improvement Exposition opens to attendees of the 162nd National ACS meeting in Washington, D.C. The exposition is sponsored jointly by the American Chemical Society and the Chemical Society of Washington. The exposition runs for three days—Tuesday, September 14 through Thursday, September 16. It will feature the products and services related to environmental improvement from the following companies. In addition, the 162nd national meeting will feature a dozen sessions on various environmental topics (see box). The meeting runs a full week.

Exhibitors	Booth No.
Ventron Corp.	304
Environmental Protection Agency	306
Guardian Chemical Corp.	318
Pollution Equipment News	320
Resource Control, Inc.	325
Scott Research Labs, Inc.	317
Technicon Industrial Systems	305
Tri-Pak	319
The VirTis Co.	307
Water Pollution Control Federation	303

Cahn will display instruments for measuring magnetic susceptibility, density, surface tension, and particle sizing. It will also show a new magnetic susceptibility system as well as balances including the Electrobalance.
Cahn Division/Ventron Corp.
Paramount, Calif.

Guardian will show three environmental products: Deselex, a new detergent base to replace phosphate; Polycomplex A-11, an oil spill dispersant; and Polycomplex R for cleaning and purifying air contaminated with particulate matter and gases.
Guardian Chemical Corp.
Hauppauge, N.Y.

Copies of the publication will be available.
Pollution Equipment News
Pittsburgh, Pa.

Resources Control will show water pollution control treatment processes for removal of metals, cyanides, oxygen demand, and color; an air pollution control wave generator for improving the efficiency of electrostatic precipitators; and analytical devices for measuring NO_2.
Resources Control, Inc.
West Haven, Conn.

Scott Research Labs will display a chemiluminescence monitor and a total heated hydrocarbon analyzer which can be used in studies on automotive pollutants.
Scott Research Laboratories, Inc.
Plumsteadville, Pa.

Technicon will exhibit a range of analytical instruments for measuring air and water pollutants.
Technicon Industrial Systems
Tarrytown, N.Y.

Tri-Pak, a division of Industrial Services of America, Inc., plants to exhibit solid waste handling equipment.
Tri-Pak
Louisville, Ky.

VirTis will show an aerosol photometer for measuring the extent of aerosol formation in photochemical reactions; devices for checking filter leaks; and devices for monitoring cleanrooms.
The VirTis Co.
Gardiner, N.Y.

Meeting sessions on environmental topics

	M 9/13	T 9/14	W 9/15	T 9/16	F 9/17
Bioassay techniques and environmental chemistry	■	■	■		
Herbicides and pesticides—policies and perspectives	■				
Pollution control in fuel combustion, mining, and processing	■				
Guidelines for environmental studies of pesticide chemicals	■				
Applications of continuous culture theory to biological waste-treatment processes	■				
Polymers for desalination			■	■	
Geochemical cycle of trace elements in the environment				■	
The scientist in the age of environmental consciousness				■	
Boron in the aquatic environment					■
The responsibility of pesticide scientists in the scientific community and society					■
Ozone applications in waste treatment					■
New solid waste disposal process					■

meeting guide

August 16–18
Marine Technology Society
Seventh Annual Conference & Exposition
Washington, D.C.
Includes sessions on coastal zone management, waste management, and pollution control. Contact: Mrs. Gene Court, Marine Technology Society, 1730 M St., N.W., Washington, D.C. 20036

August 17–19
Chicago Association of Commerce and Industry
Midwest Environmental Pollution Control Conference and Exhibition
Chicago, Ill.
Deals with waste disposal, noise pollution, industry and municipal water problems, water treatment, and air pollution. Write: Lloyd Norris, Director, Management Development and Communications, CACI, 130 S. Michigan, Chicago, Ill. 60603

August 23–27
Engineering Foundation
Solid Waste Disposal—Incineration Research Conference
Deerfield, Mass.
Discusses the place of incineration at the present time, 1980, and 2000, and its relation to landfill problems, compaction, composting, and their relative costs. Fee: $160. Contact: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

August 29 and 30
American Medical Association
31st Annual Congress on Occupational Health
Grand Teton National Park, Wyo.
Includes sessions on pest control, atomic power, CO effects, and other environmental topics. Contact: Louis R. Skiera, Assistant Director, American Medical Assoc., 535 N. Dearborn St., Chicago, Ill. 60610

August 29–September 1
American Institute of Chemical Engineers
AIChE 70th National Meeting
Atlantic City, N.J.
Includes papers on solid waste, air and water pollution, and the Pollution Solution groups. Write: W.B. Patterson, Sun Oil Co., 1608 Walnut St., Philadelphia, Pa. 19103

August 29–September 3
American Institute of Biological Sciences
22nd Annual AIBS Meeting
Fort Collins, Colo.
Discussions include topics environmental in nature. Contact: AIBS, 3900 Wisconsin Ave., N.W., Washington, D.C. 20016

August 30–September 2
Southwestern Radiological Health Laboratory (EPA) and the University of Nevada
Tritium Symposium
Las Vegas, Nev.
Technical sessions include tritium and ecology including biological effects. Contact: Tritium Symposium Committee, Southwestern Radiological Health Laboratory, P.O. Box 15027, Las Vegas, Nev. 89114

August 30–September 3
Gordon Research Conferences
Environmental Sciences: Air
New Hampton, N.H.
Write: Director, Gordon Research Conferences, Colby Junior College, New London, N.H. 03257

September 8
National Association of Secondary Material Industries, Inc.
Eco-Technic Factors in Expanding Recycling Workshop
Chicago, Ill.
Program will deal with economic and technological aspects of recycling. Contact: NASMI Eco-Technic Workshop, 330 Madison Ave., New York, N.Y. 10017

September 10 and 11
Washington Dept. of Natural Resources
Western Council on Underwater Reserves and Parks Meeting
San Juan Islands
Coastal states will discuss use, management, and regulation of underwater land. Contact: Bert L. Cole, Commissioner of Public Lands, Dept. of Natural Resources, State of Washington, Olympia, Wash. 98501

September 10–12
Virginia Polytechnic Institute
Pollution and Conservation of the Seventh Continent, Antarctica
Blacksburg, Va.
Colloquium will deal mainly with U.S. bases and operations in preparation for forthcoming Australian and U.N. meetings. Contact: Bruce C. Parker, Botany Dept., VPI, Blacksburg, Va. 24061

September 12–17
American Chemical Society
162nd Annual Meeting
Washington, D.C.
Features of the meeting will include numerous symposia on environmental subjects and an environmental improvement exposition. Contact: Meetings and Expositions Office, ACS, 1155 16th St., N.W., Washington, D.C. 20036

September 13–15
Technical Association of the Pulp and Paper Industry (TAPPI)
26th Annual Plastics-Paper Conference
Chicago, Ill.
Covers environmental problems ranging from air pollution and solid waste disposal to reclamation of materials. Contact: M. J. Williams, TAPPI, 360 Lexington Ave., New York, N.Y. 10017

September 15–17
Technical Association of the Pulp and Paper Industry (TAPPI)
Secondary Fibers and the Future
San Francisco, Calif.
Conference will deal with the need to develop new products from recycled paper fibers. Contact: H.O. Teeple, TAPPI, 360 Lexington Ave., New York, N.Y. 10017

September 23 and 24
Western Michigan University
Annual Meeting of the Paper Technology Foundation
Richland, Mich.
Write: Paul W. Bartholomew, Executive Secretary, Paper Technology Foundation, Inc., Western Michigan University, Kalamazoo, Mich. 49001

September 28–30

American Society for Metals, Canadian Welding Society, Inc., and others

Canadian Welding Metalworking Exposition Conference

Toronto, Ontario

Pollution Control Center will be featured. Write: Ronald J. Seman, American Society for Metals, Metals Park, Ohio 44073 or W. G. F. Winship, Suite 302, 130 Merton St., Toronto, Ontario

September 29–October 1

Western Canada Water and Sewage Conference

23rd Annual Convention and Operators' School

Edmonton, Alberta

Contact: D. A. Shillabeer, P. Eng., Western Canada Water and Sewage Conference, c/o Division of Pollution Control, Milner Bldg., 10040 104th St., Edmonton 14, Alberta

October 3–8

Water Pollution Control Federation

44th Annual Conference

San Francisco, Calif.

Contact: R. A. Canham, WPCF, 3900 Wisconsin Ave., N.W., Washington, D.C. 20016

October 16–20

The Institute of Sanitation Management

1971 National Environmental Sanitation and Maintenance Exposition and Conference

Los Angeles, Calif.

Sessions on all aspects of environmental sanitation and management. Contact: National Environmental Sanitation and Maintenance Management Conference, 1710 Drew St., Clearwater, Fla. 33515

October 18–22

Society for Applied Spectroscopy

Tenth Annual Meeting

St. Louis, Mo.

Papers on spectroscopy in environmental control included. Contact: Joan E. Westermeyer, Titanium Pigment Division, National Lead Co., Carondelet Sta., St. Louis, Mo. 63111

October 19–21

Disposables Association

International Disposables Exposition and Assembly

Philadelphia, Pa.

Includes waste management sessions. Write: The Disposables Association, 10 E. 40th St., New York, N.Y. 10016

October 21 and 22

American Institute of Chemical Engineers

26th Annual Technical Meeting and Exposition

Galveston, Tex.

Contact: AIChE, United Engineering Center, 345 E. 47th St., New York, N.Y. 10017

October 23–26

American Institute of Biological Sciences

Second National Biological Congress

Miami Beach, Fla.

Theme "Man and Environment II." Contact: American Institute of Biological Sciences, 3900 Wisconsin Ave., N.W., Washington, D.C. 20016

October 27–30

Federation of Societies for Paint Technology

Annual Meeting

Detroit, Mich.

Includes seminars on waste disposal. Contact: Federation of Societies for Paint Technology, 121 S. Broad St., Philadelphia, Pa. 19107

Courses

August 23 and 24 and September 21–23

University of Wisconsin Extension

Short Courses on Sanitary Landfill Site Selection and New Technology for Solid Waste Management, respectively

Madison, Wis.

Fees: $70 and $100, respectively. Contact: Warren K. Porter, Program Director, 733 University Extension, Department of Engineering, University of Wisconsin, 432 N. Lake St., Madison, Wis. 53706

September 30 and October 1

University of California

Theory and Design of Advanced Waste Treatment Processes

San Francisco, Calif.

Course is intended for engineers, scientists, managers, consultants, and government personnel. Fee: $150. For details, write: Continuing Education in Engineering, University Extension, University of California, 2223 Fulton St., Berkeley, Calif. 94720

professional consulting services directory

professional consulting services directory

professional consulting services directory

INDEX TO ADVERTISERS IN THIS ISSUE

ENVIRONMENTAL SCIENCE & TECHNOLOGY
READER SERVICE

If you would like to receive any of the material made available by advertisers in this issue, circle the numbers on one of the attached cards corresponding to the number shown beneath each advertisement. The New Product and New Literature Digests also have corresponding numbers for each item. This is a free service provided by ES&T.

AUGUST 1971
VALID THROUGH OCTOBER 31, 1971

ADVERTISED PRODUCTS:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
46	47	48	49	50	51	52	53	54	55	56	57	58	59	60

NEW PRODUCTS, NEW LITERATURE:

61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
106	107	108	109	110	111	112	113	114	115	116	117	118	119	120

Name _____

Position _____

Affiliation _____

Address _____

_____ Zip _____

NATURE OF BUSINESS: ☐ Industrial Firm ☐ Academic ☐ Government ☐ Other _____

FIRST CLASS
Permit No. 25682
Philadelphia,
Pa. 19101

BUSINESS REPLY MAIL
No Postage Stamp Necessary If Mailed in the United States

POSTAGE WILL BE PAID BY—

**ENVIRONMENTAL
Science & Technology**

P. O. BOX 8639
PHILADELPHIA, PA. 19101

ENVIRONMENTAL
SCIENCE & TECHNOLOGY
READER SERVICE

If you would like to receive any of the material made available by advertisers in this issue, circle the numbers on one of the attached cards corresponding to the number shown beneath each advertisement. The New Product and New Literature Digests also have corresponding numbers for each item. This is a free service provided by ES&T.

AUGUST 1971

VALID THROUGH
OCTOBER 31, 1971

ADVERTISED PRODUCTS:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
46	47	48	49	50	51	52	53	54	55	56	57	58	59	60

NEW PRODUCTS, NEW LITERATURE:

61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
106	107	108	109	110	111	112	113	114	115	116	117	118	119	120

Name _____

Position _____

Affiliation _____

Address _____

_____ Zip _____

NATURE OF
BUSINESS:
☐ Industrial Firm   ☐ Academic   ☐ Government
☐ Other _____