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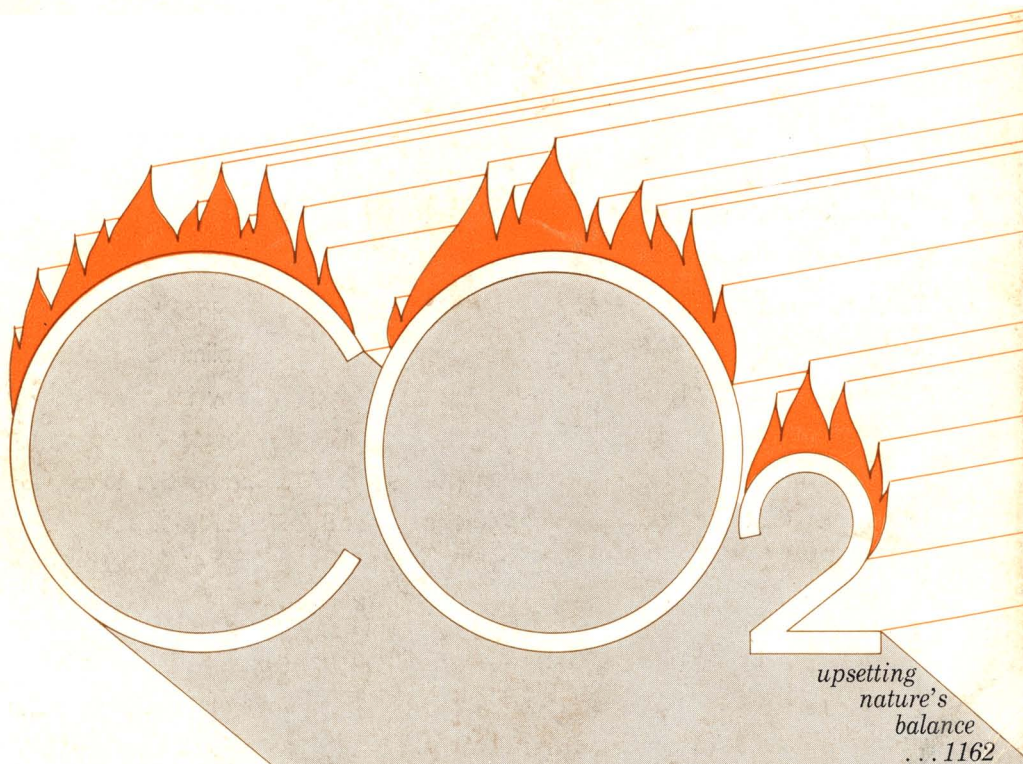
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Chemistry

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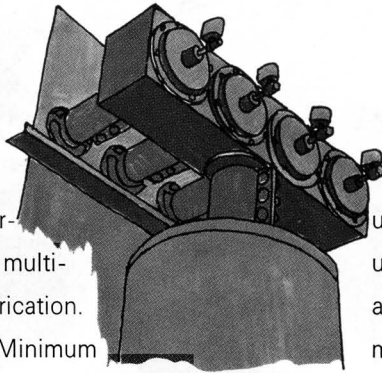


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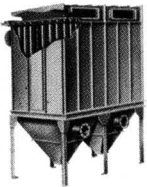
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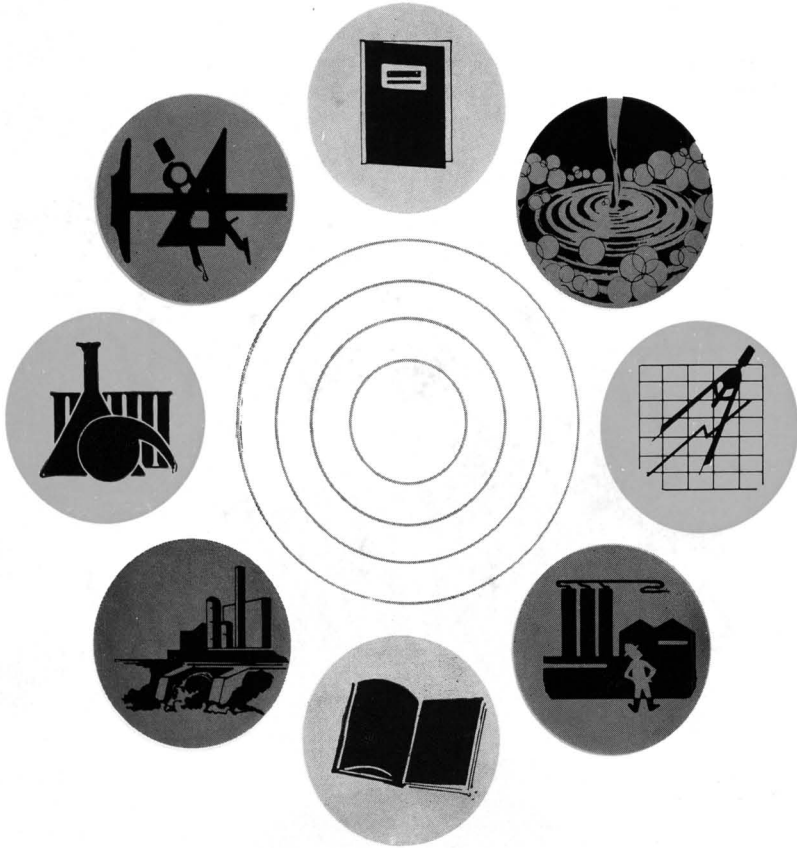
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Volume 3, Number 11

November 1969

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Published monthly by the American Chemical Society, from 20th and Northampton Sts., Easton, Pa. 18042. Executive Offices, Editorial Headquarters, and Subscription Service Department, 1155 Sixteenth St., N.W., Washington, D.C. 20036. Advertising Office: 600 Summer St., Stamford, Conn. 06904. Second class postage paid at Easton, Pa. 18042.

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Catalytic oxidation curbs solvent emissions 1159

White House and Congress at odds on solid waste program 1161

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The long-term effects of increasing CO₂ content of the atmosphere are outlined by E.K. Peterson of the Department of the Interior's Bureau of Land Management 1162

Oxidation ditches can provide small communities with efficient waste treatment at lower costs than conventional secondary plants, say J. C. Burchinal and C. R. Jenkins of West Virginia University 1170

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ห้องสมุด กรมวิทยาศาสตร์
6 H.A. 2513

Current research

- A dynamic model of photochemical smog** 1175
S. K. Friedlander and J. H. Seinfeld
This model may be useful in setting air quality standards for various air quality control regions throughout the U.S. Unlike previous diffusion models for photochemical smog with nonreacting pollutants, this model takes into account the reaction of the automobile exhaust pollutants, NO_x and unburned hydrocarbons, and further predicts the behavior of the reacting pollutant cloud. But the roles of oxides of sulfur and aerosols are not included.
- Double tracer techniques for studying air pollution** 1181
J. P. Friend and R. J. Charlson
Air pollutants such as NO_x from the automobile and SO₂ from the burning of fossil fuels are removed from the atmosphere at different rates, and their rates of removal from urban atmospheres are quite uncertain at this time. But the fate of these chemically reactive pollutants in typical pollution studies can be evaluated by considering the ratios of NO_x to CO, and SO₂ to CO₂ in existing data on tagged pollutant plumes.
- Parathion—Use of blood concentration to diagnose mortality of fish** 1183
D. I. Mount and H. W. Boyle
A diagnostic tool has been developed for correlating fish mortality with pesticide concentration in water samples. The data have been correlated for the organophosphorus pesticide parathion and bullheads. The applicability of the technique to other species of fish remains to be demonstrated, and further research is needed to determine if parathion occurs in higher concentration in muscle than in blood.
- Acidic dissociation constants of selected aquatic herbicides** 1186
N. H. Nelson and S. D. Faust
Aquatic herbicides are used to control vegetation in water supply reservoirs, and acidic dissociation constants are needed to understand the fate of herbicides and to evaluate treatment processes for their removal from water. Most literature values for dissociation constants disagree, but new values are presented for eight commonly used herbicides—2,4-D; 2,4,5-T; 2-CPA; 4-CPA; MCPA; MCPB; dalapon; and fenac.
- Distribution of Mn, Fe, P, Mg, K, Na, and Ca in the surface sediments of Lake Mendota, Wis.** 1189
J. J. Delfino, G. C. Bortleson, and G. F. Lee
Before accurate computation of nutrition or mineral balances in lakes can be made, it is necessary to know the chemical composition of the sediments with respect to water depth and location within the lake. For Lake Mendota (Wis.), there is a definite correlation for Mn, Fe, and P; a significant inverse correlation for Mg and K; but no significant trend for Ca and Na.
- Rapid direct-reading spectrographic determination of elements in industrial waste water** 1192
R. L. Steiner, J. B. Austin, and D. W. Lander
The metal content of industrial waste waters can be monitored for 14 elements in less than five minutes per sample. In particular, heavy metals—which are harmful to aquatic life and toxic to bacteria—now can be determined with a minimum of sample preparation by the direct-reading spectrographic analysis of both filterable and nonfilterable residues.
- Loss of weight, ⁶⁰Co, and ¹³⁷Cs from tree litter in three subsystems of a watershed** 1195
M. Witkamp and M. L. Frank
Leaf litter, the main medium for returning mineral elements from trees to soil and water, is of interest to those concerned with water quality and management of forests and waters. The loss of weight and minerals from three species of leaves—alder, sycamore, and oak—was evaluated using tracer technique with ⁶⁰Co and ¹³⁷Cs under several different conditions such as one year in a forest, pond, and brook.
- Rapid estimation of 7H-benz[de]anthracen-7-one and phenalen-1-one in organic extracts of airborne particulates from three hour sequential air samples** 1198
T. W. Stanley, M. J. Morgan, and J. E. Meeker
The direct spectrophotofluorometric procedure can be used in comprehensive air pollution studies and, specifically, for the rapid determination of the above two organics in particulates from polluted urban atmospheres. Coupled with the recent development for the separation of these organics by instant thin layer chromatography, the analysis of urban particulates now can be performed more rapidly than the earlier procedure.
- Influence of mineral nutrition on the sensitivity of tomato plants to hydrogen fluoride** 1201
D. C. MacLean, O. F. Roark, G. Folkerts, and R. E. Schneider
Often observed interactions between nutrition deficiency and fluoride exposure are indirect. But, in order to correlate direct effects between fluoride exposure and damage to vegetation, tomato plants were grown in sand cultures and nutrient solutions containing the essential elements Ca, Mg, and K. The growth, fluoride accumulation, foliar damage, flowering, and fruiting of these tomato plants exposed to HF are described.
- Communications**
- Instrument response time in an analytical system for continuous glucose measurement** 1205
C. R. Baillod and W. C. Boyle
The Technicon AutoAnalyzer can be used to measure glucose uptake rates by biological systems, but it has a response time limitation when used for continuous record of glucose concentration. The effect of instrument lag time on the recorded glucose concentration profile is illustrated for the case when the uptake rate is approximately zero order.
- Vanadium, copper, and aluminum in the lower atmosphere between California and Hawaii** 1207
G. L. Hoffman, R. A. Duce, and W. H. Zoller
Particulate matter can be transported via the atmosphere from the West Coast toward Hawaii. Analysis of atmospheric samples from Hawaii and onboard ship between these points reveals a nonmarine source for the metals Cu, V, and Al. Man-made pollution on the West Coast is offered as one explanation for the high Cu content.



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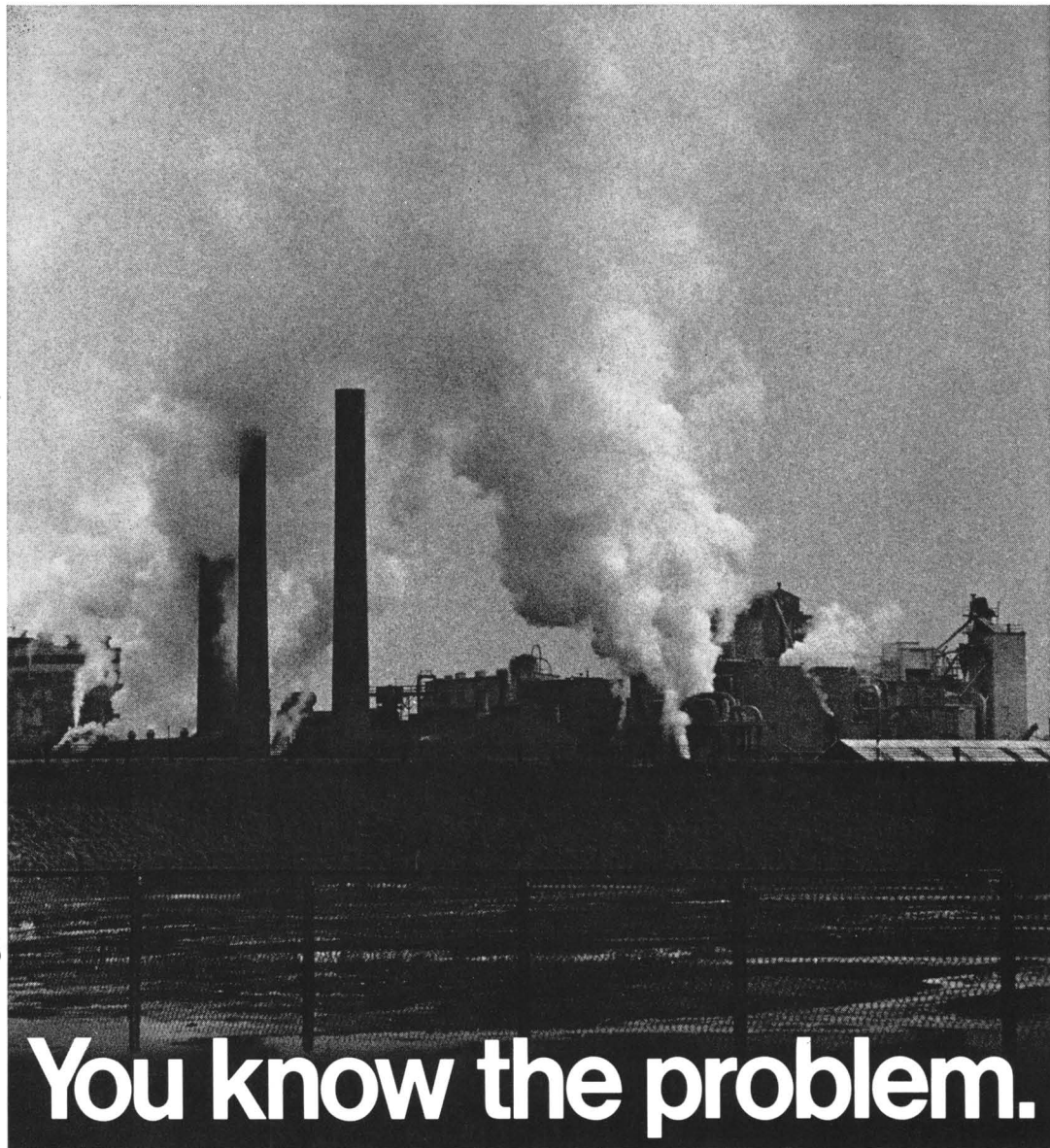
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WASHINGTON FWPCA will review exceptions in water standards

David D. Dominick, commissioner of the Federal Water Pollution Control Administration (FWPCA), gave further indications that the federal government is becoming impatient with progress toward water pollution control. At the 42nd annual conference of the Water Pollution Control Federation in Dallas last month, Dominick noted that he had directed the FWPCA staff to give highest priority to the resolution of exceptions in water quality standards. Although all states have submitted water quality standards that have been provisionally approved by the federal government, about half still have exceptions for dissolved oxygen, temperature, and other requirements. Dominick hopes to have the exceptions resolved by Jan. 1, 1970, but concedes that the target date may not be met partly because more research information may be needed and partly because state opposition may toughen.

House passes its public works appropriations bill

Last month, the House passed its appropriations bill for public works expenditure for fiscal year 1970, containing an appropriation of \$600 million for the construction of waste water treatment facilities, some \$400 million shy of the authorization in the Clean Water Restoration Act of 1966. A last minute amendment to increase the funding to the full authorization was defeated by a teller vote of 146 yeas to 148 nays. Thus, to date, only \$567 million out of an authorized \$2.3 billion has been appropriated.

Water Quality Improvement Act emerges from Senate

Also last month, the Senate passed S. 7, the omnibus water quality legislation which is stronger than that passed earlier by the House. As passed, S. 7 includes:

- Rules for dealing with oil spill catastrophes both from vessels and onshore and offshore facilities.
- Standards for marine sanitation devices.
- Requirement that federal licensees and permittees comply with water quality standards.
- Cleanup of hazardous substances other than oil.
- Training of a labor force for water pollution control.
- Establishment of an Office of Environmental Quality.
- Great Lakes demonstration program.

The next legislative step is a conference with House conferees. Regardless of the above House appropriation action, Sen. Edmund S. Muskie (D.-Me.) intends to press for full funding (\$1 billion) in the Senate.

Library of Congress adds Environmental Policy Division

Richard A. Carpenter has been appointed chief of the newly created Environmental Policy Division in the Legislative Reference Service (LRS) at the Library of Congress. His appointment was announced by L. Quincy Mumford, Librarian of Congress, and Lester S. Jayson, director of LRS. Established in response to increasing congressional concern for the quality and productivity of the physical environment, the new division will deal with natural resource management, agriculture and conservation, recreational resources planning, air and water pollution control, and other environmental issues. Other personnel on the 19 member division include Wallace D. Bowman, who serves as assistant chief, and two senior specialists—Walter W. Wilcox in agriculture, and John K. Rose in conservation.



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STATES **Florida keeps close watch on industrial polluters**

Florida's Department of Air and Water Pollution Control has a total of 67 cases of industrial pollution under close surveillance—62 of them violations of the state's water pollution code. According to industrial waste investigator Jose Fernandez DeCastro, 42 of the cases involve citations ordering industries to correct violations. Another 23 cases are in litigation (Florida's attorney general being the prosecutor) or under legal review. The industries involved include phosphate chemicals, pulp and paper, citrus, sugar, and metal plating. 71 citations for municipal sewage pollution violations also are on the Florida department's books.

Construction rules for Alaskan pipeline established by Hickel

Secretary of the Interior Walter J. Hickel has announced a stringent set of construction stipulations which will control the way in which a petroleum pipeline is built across federal lands in Alaska. The stipulations are intended to insure that the wildlife and ecology of the Arctic, along with the culture and opportunities of Alaska's native citizens, will be enhanced. The stipulations include: • Requirement that the contractor have a detailed contingency plan for controlling possible oil spills and leaks. • Conformity with federal water pollution standards already established for Alaska. • Assurance that Interior's Bureau of Land Management will have authority to inspect all phases of construction, to require realignment of the route to meet unforeseen environmental conditions, and to terminate all activities that do not conform with the stipulations.

Ohio's Rhodes sets deadlines for Lake Erie polluters

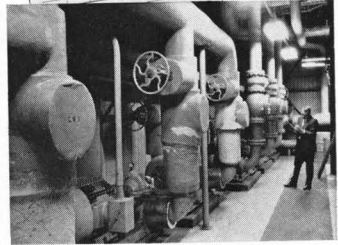
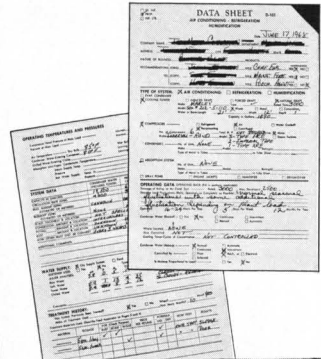
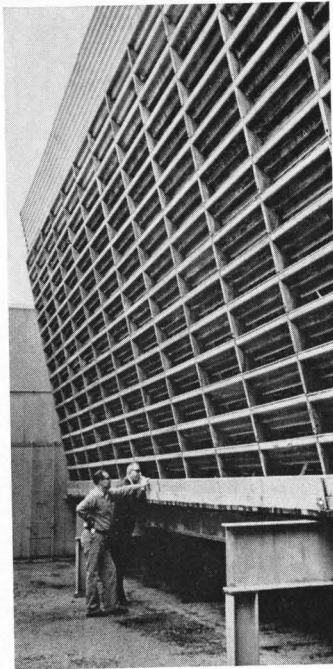
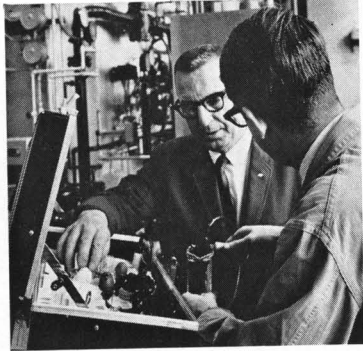
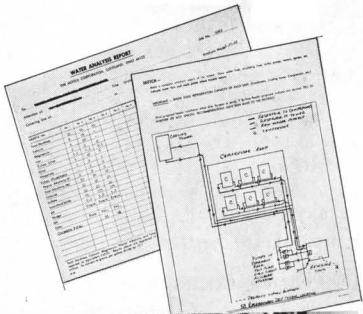
Governor James A. Rhodes of Ohio has designated Dec. 31, 1971, as the date on which the majority of Lake Erie polluters must complete improvements to their waste treatment facilities located in Ohio. Rhodes believes that some improvements will be seen long before that deadline because a large number of industries are going to complete their anti-pollution facilities as early as the end of 1969, and many others during 1970. But the governor's use of the words "majority of" could well imply that he thinks some firms will not meet the deadline. Nevertheless, Rhodes declares Lake Erie will be saved.

New Jersey code adds chapter on air pollution emergencies

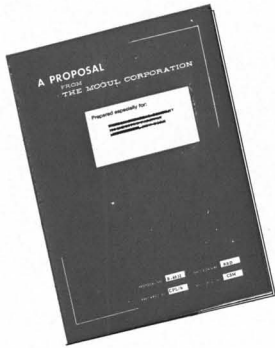
Chapter 12 of the New Jersey Air Pollution Control Code, which became effective Oct. 24, provides a framework for the governor to use emergency powers during periods of atmospheric stagnation, when air pollution is particularly hazardous to health. The new chapter establishes three stages of increasing danger—alert, warning, and emergency. Criteria that define the various stages are atmospheric concentrations of sulfur dioxide, carbon monoxide, and particulate matter, together with meteorological information. At each stage, the regulation requires that power generating facilities, steam plants, certain chemical plants, and refuse burning facilities reduce their emissions by specified amounts or, if necessary, cease operations altogether.



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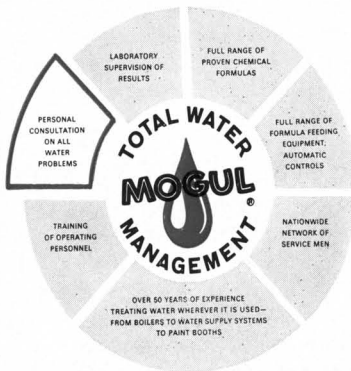
Division Technical Staff.

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FINDINGS OF SURVEY	RECOMMENDED PROGRAM	RESULTS
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Incomplete control of treatment and bleed-off	Mogul fully automatic failsafe cooling water control equipment	Failsafe control; reduced testing and supervision; improved treatment results
Pollution hazard	Use of a Mogul non-chromate, non-phosphate treatment	Program satisfies the most stringent pollution regulations
Excessive water costs — presently spending \$33.92 per day	Mogul treatment program allows operation with less bleed-off and less make-up	Important cost reduction—calculated savings of \$12.73 per day
Excessive chemical treatment costs — presently spending \$53.00 per day	New Mogul treatment concept with lower feed rate	Outstanding cost reduction—calculated savings of \$40.28 per day

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TECHNOLOGY Evaporators concentrate radioactive waste

Spray film evaporators are finding increasing use for handling radioactive wastes from nuclear power stations. The water technologies divisions of Aqua-Chem, Inc. (Milwaukee, Wis.), has just shipped two 7 g.p.m. units to the Duke Power Co. for its 874 megawatt nuclear station near Seneca (N.C.) which is scheduled for startup in 1971. Similar units of 12 g.p.m. capacity also have been ordered for Omaha Public Power's Fort Calhoun (Neb.) station and Commonwealth Edison's Zion (Ill.) nuclear plant. The units are used to concentrate the reactor coolant and miscellaneous wash water, to reduce the quantity of radioactive wastes requiring ultimate disposal.

	Trickling filter	Carbon treatment
Organic content of effluent	30 p.p.m.	5 p.p.m.
Percent removal of organics	80-90%	95%
Cost per thousand gallons	10¢	16¢

Carbon treatment cost competitive

Cost of activated carbon treatment to remove 95% of the organic matter in waste water is competitive with biological treatment, according to Walter J. Weber, Jr., of the University of Michigan. In a paper coauthored with FMC Corp.'s Charles B. Hopkins and Ralph Bloom, Jr., and presented at last month's meeting of the Water Pollution Control Federation (Dallas, Tex.), Weber stated that costs for chemical clarification and absorption (including amortization of capital costs) would run about 16 cents per thousand gallons. Conventional biological treatment can remove 80-90% of organic material at 10 cents per thousand gallons; however, the addition of tertiary treatment to achieve a removal efficiency equivalent to carbon treatment pushes the total cost to about 25 cents per thousand gallons.

Dual fuel evaluation goes into high gear

In a program aimed at testing the potential of the recently developed dual fuel system in reducing motor vehicle exhaust emissions, the General Services Administration (GSA) is converting 12 vehicles from its Los Angeles based motor pool for operation on compressed natural gas. Six of the vehicles will operate intermittently with natural gas and gasoline, and the rest will use natural gas only. GSA administrator R. L. Kunzig says successful tests of the compressed gas system could have tremendous impact on the agency's operations; GSA operates over 51,000 motor vehicles for the executive branch of the federal government. Pacific Lighting Corp., which is assisting GSA in the study, has just completed a two year study of the system on 33 of its own vehicles; the company says that, as a result of this study, it will convert substantially all of the 1100 service vehicles of subsidiary companies in southern and central California to the dual fuel system over the next 12 months.

Ultraviolet radiation purifies water supplies

Ultraviolet treatment of water supplies will replace the conventional chlorination process on three Norwegian cruise ships now abuilding at the Wartisalla shipyard (Helsinki, Finland). Ellner Division of Ecological Science Corp. (Miami, Fla.), which will supply the ultraviolet units for the ships, also has been awarded contracts for two similar units to be installed aboard offshore oil drilling rigs being built at Todd Shipyards (Houston, Tex.). Each Ellner unit consists of a purification chamber, an automatic monitoring system, and a proprietary control unit that is connected to the discharge side of the water supply tank. Product water is of uniform quality, free of pathogenic bacteria—without the odor associated with chemical treatment—regardless of the local source of water, according to the company.

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here.



Circle No. 10 on Readers' Service Card

environmental currents

INDUSTRY Power companies form joint environmental council

Electric utility companies, representing 80% of total U.S. generating capacity, have established an Electric Power Council on Environment. Council chairman W. C. Tallman says the group has three main objectives:

- To provide a means for organizations in the generating industry to coordinate their activities in the environmental field.
- To serve as a focal point for criticism and suggestions regarding the industry's stance on environmental matters.
- To stimulate research (the council has no budget of its own).

Scientists and conservationists outside the industry are not represented on the council—apparently a source of some dissension among its members—but, nevertheless, will be asked to work with standing committees on air and water pollution, land use, and aesthetics.

Noise control receives added emphasis

Regulations that came into effect this year under provisions of the Walsh-Healey Public Contracts Act spell out for certain suppliers of goods or services to the federal government permissible levels of noise in their places of work. Purpose of the regulations is to protect the hearing of employees. General Radio Co. (West Concord, Mass.), a manufacturer of sound level meters, is making available a plant noise survey form to simplify the recording of data needed to determine whether noise conditions are illegal under the act. Although noise conditions outside plants are not yet subject to legislative control, Consolidated Edison in New York City has established a special task force on noise control. One of its concerns is citizen fear of excessive noise from Con Ed's Astoria generating station, soon to be expanded in size.

U.S. firms take licenses on foreign ozone processes

Two U.S. firms have taken licenses on foreign ozone technology, and both see a significant role for ozone in waste water treatment:

- Ozonator Corp. (Batavia, N.Y.), has obtained rights to manufacture large ozonators under patents held by Mibis Co. (Stockholm, Sweden). The agreement allows Ozonator to extend its product line to generators with capacities in the hundreds of pounds per day range. Applications to waste treatment cited by the company are oxidation of such industrial wastes as phenols and cyanides, as well as tertiary treatment of sewage for odor removal.
- Crane Co. (New York, N.Y.) has just completed an agreement with La Companigne des Eaux et de l'Ozone (Paris, France), which makes Crane the exclusive distributor of the Otto ozonation process in the U.S. and its possessions. Crane's Cochrane Division and the Philadelphia Water Commission, under an FWPCA grant, currently are testing a microstrainer ozonation combination for treating storm water overflows.

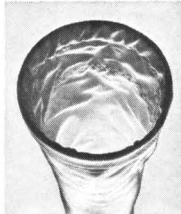


Interior's Train

Steel firms and Interior have on-again, off-again affair

Speaking at a joint seminar attended by officials of the steel and water industries in Washington, D.C., Undersecretary of the Interior Russell E. Train applauded the efforts of the steel men for initiating cooperative moves with the water people. Train said that the steel industry can help solve water supply problems by installing complete water treatment facilities in its plants and continuing to develop cheaper and better steels for tanks, pipes, and pumps. Train's complimentary remarks came hard on the heels of Secretary Hickel's recent order that several companies—including four steel firms—will be taken to court unless they take rapid action to control pollution (ES&T, June 1969, page 519).

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Better things for better living
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Circle No. 20 on Readers' Service Card

Pulp and paper makers are finding reverse osmosis and electro dialysis effective in their battle against water pollution

Membrane processes upgrade wastes

Noting that the current pressure for pollution control is here to stay, the nation's pulp and paper industry is continuing to work on its considerable water pollution problems. Spearheading the effort—in an industry which has more than its share of diverse company and technical associations—is the Pulp Manufacturers' Research League (PMRL) (Appleton, Wis.), a lightly budgeted (\$250,000 per year and 20 man staff) organization that has an impressive list of technical accomplishments to its credit. Recent work by the PMRL on three membrane processes—reverse osmosis, electro dialysis, and ultrafiltration—promises to make the job of compliance with state and federal water pollution regulations a good deal easier for pulp and paper manufacturers.

Pulping processes

The object of the pulp and paper industry is to make a profit out of wood by extracting from it the cellulose fiber which can be made into paper products. Most of pulping's water pollution problems (and, indeed, economic problems) arise because the wood in a tree contains only about 50% cellulose; the other half is composed mostly of lignin, a complex polymeric phenol that acts as the glue which holds the tree together. Chemical pulping processes are many and varied, but the purpose of all is to dissolve away the lignin and other non-cellulosic material to leave the fiber. The trouble—from the point of view of the industry—is that it has, in recent years, been increasingly restricted from diverting into the nearest waterway

wastes containing lignin and other by-products of the pulping process. Lignin colors the water, while sugars and acetic acid (other byproducts) impose an oxygen demand.

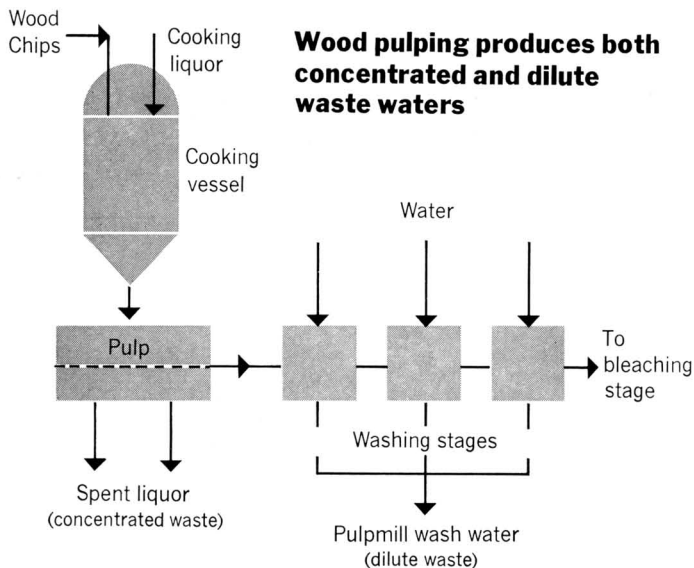
In its early years of existence, PMRL—which was founded in 1939—worked on conventional bio-oxidation sewage treatment methods and on ways to enhance the oxidizing capacity of the receiving stream by aeration. Experience led PMRL eventually to more complex treatments; the economics of these methods were such, however, that it became essential to recover part of the processing cost by recovering useful, and preferably salable, byproducts.

Concentrated wastes

The spent liquor leaving the cooking vessel (digester) contains from 8–18%



Wood pile. Only half of a tree can be used for paper making; the other half must be disposed of somehow



(typically 10–12%) of dissolved solids. Many mills evaporate off much of the water, usually to a solids content of about 50%. PMRL's torula yeast process, in successful use since 1948, desugars digester strength spent liquor by growing yeast in it. In Wisconsin, a healthy spent liquor byproducts industry has evolved in the past 15 years. This industry uses spent liquor concentrate from evaporators to make a whole range of salable products, from oil well drilling mud conditioners to linoleum cements. But the fact remains that less than half of all spent pulping liquors produced in the U.S. are converted into useful commodities.

A recent PMRL development that aims at recovering valuable products from concentrated pulping wastes is an ingenious modification of the electro-dialysis cell, which has been widely used for desalination. In electro-dialysis, an imposed electric current causes selective movement of charged ions out of the feed solution. Special ion-selective membranes are used to allow positively charged ions (cations) to move toward the cathode and negatively charged ions (anions) toward the anode. The PMRL modification, briefly described here, for a sodium bisulfite base spent liquor, has several compartments in the cell that carry sulfurous acid. A second set of compartments is fed with the spent liquor, which contains large amounts of the sodium salt of lignosulfonic acid, and lesser amounts of nonionizable sugars. Cation- and

anion-selective membranes are so arranged that sodium and bisulfite ions combine in a third set of compartments to form sodium bisulfite, which can be recycled as cooking liquor. The product is an aqueous mixture of sugars and lignosulfonic acid, which PMRL has discovered is an excellent adhesive for plywood and could be sold competitively against conventional polymeric adhesives.

The PMRL process, despite its inherently attractive concept, has several drawbacks in practice. As in all electro-dialysis applications, power costs are high (the potential across a stack of membranes can be more than 500 volts, and currents may be as high as 80 amps.—a 40 kW requirement). And because electrical neutrality does not prevail in all compartments, there may be trouble with hydrogen transfer balances. Nevertheless, PMRL is continuing to study the process at the semicommercial level. Its equipment supplier, Aqua-Chem, Inc. (Waukesha, Wis.), is to work on improved hardware, and the membrane manufacturer, Ionac Chemical Co. (Birmingham, N.J.), is developing newer and better membranes. Both heterogeneous (ion exchange resin impregnated) and homogeneous (ion exchange sites built in through sulfonation) membranes are being studied.

Dilute wastes

Although disposal of concentrated pulping wastes remains a big headache, PMRL's technical director Averill

J. Wiley says that dilute pulping wastes are the number one priority for PMRL's research. Dilute wastes arise largely from the washing stages in the process, where lignin adhering to the cellulose pulp is washed away. Several washing stages customarily are used, since the presence of lignin greatly increases the amount of bleaching required at a later step in the process. These dilute wastes (pulp mill wash waters) may contain as little as 1% dissolved solids, but this still is too much to discharge to a river, and PMRL work has emphasized concentration of water containing solids by reverse osmosis and ultrafiltration, so that nearly pure water can be recovered for reuse. Membranes made by Havens Industries (San Diego, Calif.), American Standard, Du Pont, and Gulf General Atomic have been tested for reverse osmosis applications. A Havens Industries mobile reverse osmosis unit currently is being tested at a number of mills in a demonstration program that is supported 70% by the Federal Water Pollution Control Administration and 30% by PMRL. Results to date look extremely promising: Wiley states that the demonstration unit has been able to reject 90% of solids and color, and 75–90% BOD from the typical mill's wash water. The purified water can be returned to the process, while the concentrated liquid can be treated in the same way as the digester strength wastes. The one remaining hurdle is low service life of reverse osmosis membranes, but Wiley is confident that this problem will be solved reasonably soon.

Ultrafiltration, too, can play a part in cleaning up the pulp and paper industry's water pollution. Its most likely use, according to PMRL's research associate George A. Dubey, is for pretreatment of dilute wastes before they are processed by reverse osmosis. Ultrafiltration can remove larger molecules which tend to block reverse osmosis membranes.

Outlook

While the membrane processes being studied at PMRL still lack widespread industrial application to demonstrate their usefulness, there seems little doubt that, eventually, they will be commercially practicable. Most pulp and paper manufacturers are eagerly looking for economically supportable ways to utilize the other half of the tree and to prevent their wastes from entering streams.

Particulate controls: A must to meet air quality standards

Industrial processes release more than 50% of today's particulate emissions

Particulate emissions make up about 10% of the U.S. air pollution burden. In 1966, stationary and mobile sources emitted 11.5 tons of particulates, industrial processes being the principal contributor.

Defined to include dusts, fumes, oils, smoke, and mists, particulate emissions can be controlled by a wide variety of available equipment. The key for controlling and reducing these emissions from industrial sources is primarily gas cleaning devices—for example, mechanical centrifugal cyclones, wet scrubbers, fabric filter devices, electrostatic precipitators, and direct flame and catalytic afterburners. But other control techniques—including plant relocation, plant shutdown, fuel substitution, and process changes—are possible alternatives, according to HEW's control technology document, "Control Techniques for Particulate Air Pollutants."

This document points out that the selection of gas cleaning equipment is far from an exact science and must be based on characteristics of particle and carrier gas, as well as on process, operation, construction, and economic factors. Particularly important in the proper selection of gas cleaning equipment is information on particle size gradation in the inlet gas stream. Particles larger than 50 microns in diameter may be removed satisfactorily in inertial and cyclone separators and simple low energy wet scrubbers, but particles smaller than 1 micron in diameter can be arrested effectively by electrostatic precipitators, high energy scrubbers, and fabric filters.

Whereas the most promising areas of improvement for small industrial sources might involve basic changes in plant operations, cleaner fuels, or some alternatively low cost procedure, control of industrial particulate from large sources invariably requires the purchase, installation, maintenance, and operation of gas cleaning equipment, all of which cost money.

The cost of gas cleaning equipment usually is greater for devices of high efficiency; however, the performance of competitively priced equipment may

differ considerably, the control technology document points out. Furthermore, of the many techniques used to control particulate air pollutants, none has emerged as an all inclusive answer to the problem.

In some industrial processes, efficient collection of particulates increases overall plant operating efficiency by recovering a portion of the product that would otherwise be lost to the atmosphere. For example, dust collectors used in cement plants, grain handling operations, and carbon black plants can recover valuable products.

Most of the high efficiency particulate control devices are being developed for use in steel mills, steam-electric generating stations, petroleum refineries, and chemical plants, to mention just a few.

Variety of industrial sources

The major sources of particulates in **iron and steel mills** are blast furnaces, steelmaking furnaces, and sintering plants. Normally, blast furnace gas cleaning systems reduce particulate loadings to less than 0.01 grain per standard cubic foot to prevent piling of the stoves where the gas is burned. Either low efficiency or high efficiency wet scrubbers and electrostatic precipitators normally are used in these systems. Of the three types of steel furnaces—open-hearth, basic oxygen, and electric—venturi scrubbers and electrostatic precipitators are used to control iron oxide emissions from open-hearth furnaces. Basic oxygen furnaces, which produce more particulates emissions than open-hearth furnaces, all are equipped with either high efficiency electrostatic precipitators or venturi scrubbers. But electric furnaces, which are used for alloy production and because of their flexibility, have particulate emissions of 3 grains per standard cubic foot. Baghouses are especially suited for particulate collection from these furnaces. In sintering plants, the major sources of dust are the combustion gases drawn through the bed and the exhaust gases from sinter grinding, screening, and cooling operations. Although most

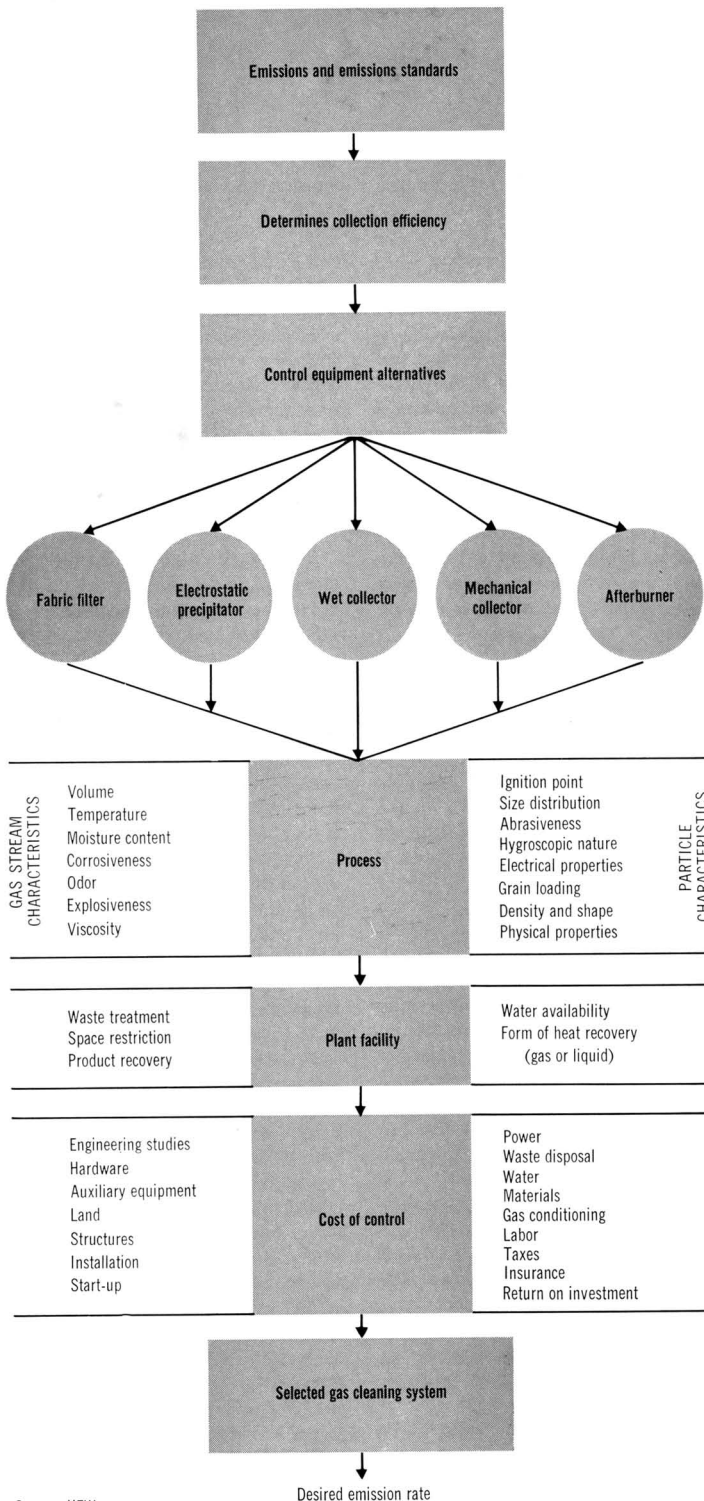
plants are equipped with cyclones, high efficiency baghouses and electrostatic precipitators offer promise of much better collection, but few have been applied to sintering machines.

Melting cupolas are the principal sources of particulate matter at **gray iron foundries**. The most effective control system incorporates an afterburner to eliminate combustibles and a fabric filter to collect inorganic dust and fumes. Even though baghouse control systems provide excellent particle collection, these systems have not gained wide acceptance in this industry primarily because of cost. Dry centrifugal collectors and scrubbers are used in many instances, and high efficiency scrubbers are reported to provide about the same performance as fabric filters but visible emissions are more pronounced.

At **petroleum refineries**, major sources of particulates are catalyst regenerators, air-blown asphalt stills, and sludge burners. Lesser sources include fired heaters, boilers, and emergency flares, according to the control technology document. Often, dust collectors, as well as carbon monoxide waste heat boilers, are used to control air pollution in modern fluidized catalytic crackers. These boilers are installed as common practice to use the fuel value of the clean gas stream exiting from the particulate collector. In typical installations, two stage or three stage cyclones are located in the regenerator vessels of the cracker units for catalyst recovery and reutilization. Electrostatic precipitators also may be used to collect fine particles from the regenerator exit gases, but, here, the efficiency of the precipitators is a function of the inlet dust loading from the regenerator and the desired emission rate to the atmosphere.

High efficiency precipitators, baghouses, and high energy scrubbers are among the stack cleaning devices that are available to collect the fine dust from the open burning or incineration of sludges, another major source of particulate matter at petroleum refineries. But incineration alone is not the solution for all forms of refin-

Criteria for selection of gas cleaning equipment



Source: HEW

ery waste sludges. Solvent extraction is another method, and the separated clean solids can be disposed of to normal landfill sites.

In the **Portland cement industry**, bag filters usually are the best control means for dust generated at the blast hold drilling operation at a quarry. Essentially combinations of multiple cyclones, baghouses frequently are used on rotary dryers in dry process cement plants, a major source of dust generation. Another larger source of emissions at cement plants is direct fired kilns for burning Portland cement clinker. More than 85% of these gas boring particles are smaller than 20 microns in diameter so that electrostatic precipitators are used widely to control particulate emissions from kilns. Fabric filters of silicized glass bags also have been installed on both wet and dry process kilns, and each control device is successful when adequately designed and properly maintained.

A major particulate source in **Kraft pulping** is the recovery furnace in which spent cooking liquors are burned to remove the organic materials dissolved from the wood to recover the inorganic cooking chemicals. Electrostatic precipitators of about 90% efficiency are used to recover particles emitted from these furnaces. Smelt tanks and lime kilns are other sources of particulates in this industry; venturi scrubbers are used on lime kilns, and water sprays or mesh demisters are used on smelt tanks.

At **asphalt batching plants**, which involve the mixing of hot dry sand, aggregate, and mineral dust with hot asphalt, centrifugal and baffled scrubbers have been used with success to control the fine dust which escapes the primary cyclone. The major source of particulates is the direct fired dryer used to dry and heat aggregates. Most dryers employ simple cyclone separators which collect from 70–90% of the dust entrained in the exit gases. Fabric filters—frequently more expensive than scrubbers—can be used to collect dry fines which may be usable in high grade asphaltic concrete mixes. In addition, fabric filters obviate the need for holding ponds and preclude water pollution problems.

Most modern **sulfuric acid plants** are equipped with high efficiency electrostatic precipitators or mesh eliminators to eliminate 99% of the acid mist generated. In fact, acid mists usually are controlled to a far greater extent

than gaseous sulfur dioxide releases. In the **production of phosphoric acid** by the burning of elemental phosphorus, electrostatic precipitators or high pressure drop mesh entrainment separators are used to collect acid mists from exhaust gases. But, in the wet process for the production of this acid, scrubbers frequently are used to control the large quantities of gaseous silicon tetrafluoride liberated.

About 90% of the U.S. coke output, manufactured by distillation of certain coals, is used for the production of blast furnace iron, but satisfactory air pollution control equipment is not available for these **coking ovens**. Although a joint research effort by several steel companies has been underway for five years to develop new coke manufacturing technology, the potential commercial application of such technology still appears to be some time in the future.

Particulate matter—largely sublimed oxides, dust, and acid mists, along with sulfur dioxide gas—also is released from the **primary smelting of lead and zinc sulfides**. In this industry, the sulfide is converted to an oxide through roasting and subsequent reduction of the metal oxide through its metal state in a separate vessel. Baghouses usually are used to control oxide fumes; where the fumes are corrosive, electrostatic precipitators are used. In the production of metallic aluminum by the electrolytic reduction of alumina (by the Hall-Heroult process), wet scrubbers have long been used for collection of both particulates and corrosive gases. Wet scrubbers also are used to collect the gaseous contaminants from secondary aluminum recovery operations.

Principal sources of particulates in **soap and synthetic detergent manufacture** are the spray drying of products and the handling of dry raw material. Fabric filters are used widely to control dust generated from the handling of products and raw materials and from packaging operations.

Significant quantities of particulate matter are generated from reverberatory furnaces which are used to produce nearly all glass products and raw material in the **glass and glass fiber industry**. In the glass furnace, operators control emissions through furnace design, electric heating, and raw material controls rather than with any stack cleaning devices. Control of emissions with glass fiber filters is feasible, but particulates are extremely

difficult to handle. Although suitable control methods are not on hand in the manufacture of glass fiber, a combination of process changes in the industry and stack controls will be required to render exit gases acceptable in many communities, the control technology document points out.

In the **collection of carbon black**, a combination of cyclone and electrostatic precipitator is no longer satisfactory because it collects only about 60% of the particulates. In this case, the particulate matter is extremely fine, from 0.01–0.4 micron in size, and fluffy in nature.

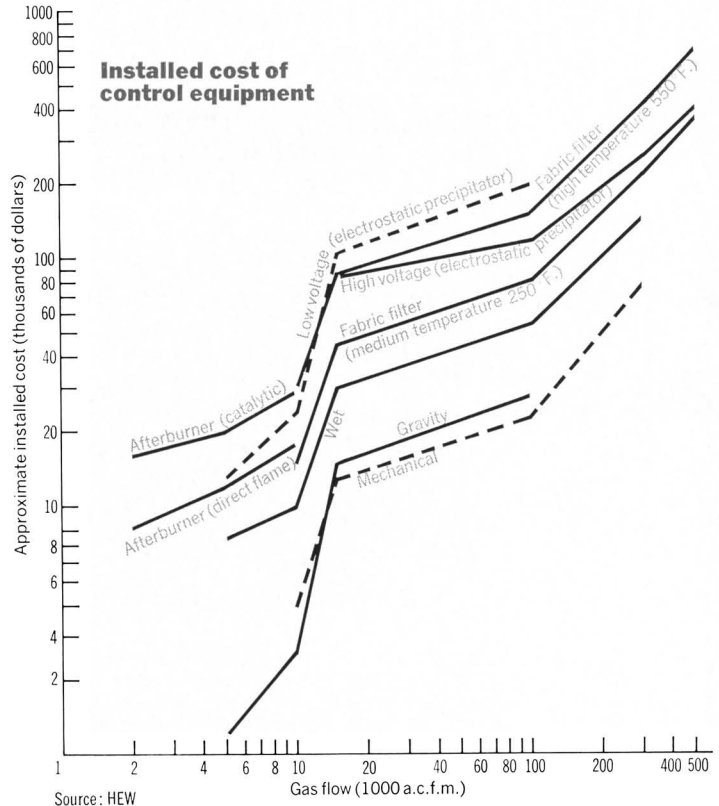
Most grinding operations in the **gypsum processing industry** are controlled with fabric filters. Before calcining, gypsum (the basic ingredient of plaster and wallboard) is dried in direct fired dryers to remove free moisture. Electrostatic precipitators, baghouses, or scrubbers are almost always used to remove this dust from exit gases. In addition, baghouses are used extensively to collect dust from various conveying and processing points in most modern gypsum plants. Often, a salable product is reclaimed.

Simple cyclones operating at temperatures from 400°–500° F. normally

are used in the control of particulate matter from **coffee processing roasters**, which produce the predominant source of oil aerosols and odors in this industry. The main aerosols and odorous gases may be incinerated in afterburners at temperatures ranging from 1200°–1400° F.

At **instant coffee plants**, particulate emissions are dependent on the type of firing, and the ash content (usually about 4% by weight of dry grounds). A common design for particulate control in these plants incorporates an underfeed stoker and auxiliary gas burners. Additionally, bean coffee cleaning and handling creates dust and chaff (a flaky membrane from the bean) which normally can be handled in simple cyclones.

High efficiency multiple cyclones are used in **cotton ginning** to collect coarse particles, and recently developed stainless steel in-line filters are effective for fine particles. The relative coarse materials are emitted from the ginning operation and relatively fine materials escape the associated lint cleaners. In addition, subsequent incineration of the trash produces a large portion of particulate emissions from uncontrolled ginning plants.



Monitor offers continuous TOC data

Last month, at the equipment exhibit at the Dallas (Tex.) meeting of the Water Pollution Control Federation, Automated Environmental Systems, Inc., (AES) unveiled its new total organic carbon (TOC) analyzer. The instrument is aimed at filling a conspicuous gap in present water monitoring technology—direct continuous measurement of organic content of effluent streams, a capacity beyond that of present carbon monitors. Key to this capability of the instrument is the use of an automated sample pretreatment technique to remove any inorganic carbon present, and the use of a fluidized bed oxidation reactor that can handle fairly high sample flow rates. Organic content of the sample stream is obtained by measuring the CO_2 output of the reactor with an infrared spectrometer.

AES' Frank Boucher points out that the system's ability to monitor organic carbon for long periods of unattended operation, plus optional configurations which allow total carbon analysis and homogenization of solids content of the sample, should open up wide applications in waste treatment systems, industrial effluent monitoring, and process control. Boucher adds that the model shown at Dallas reflects the

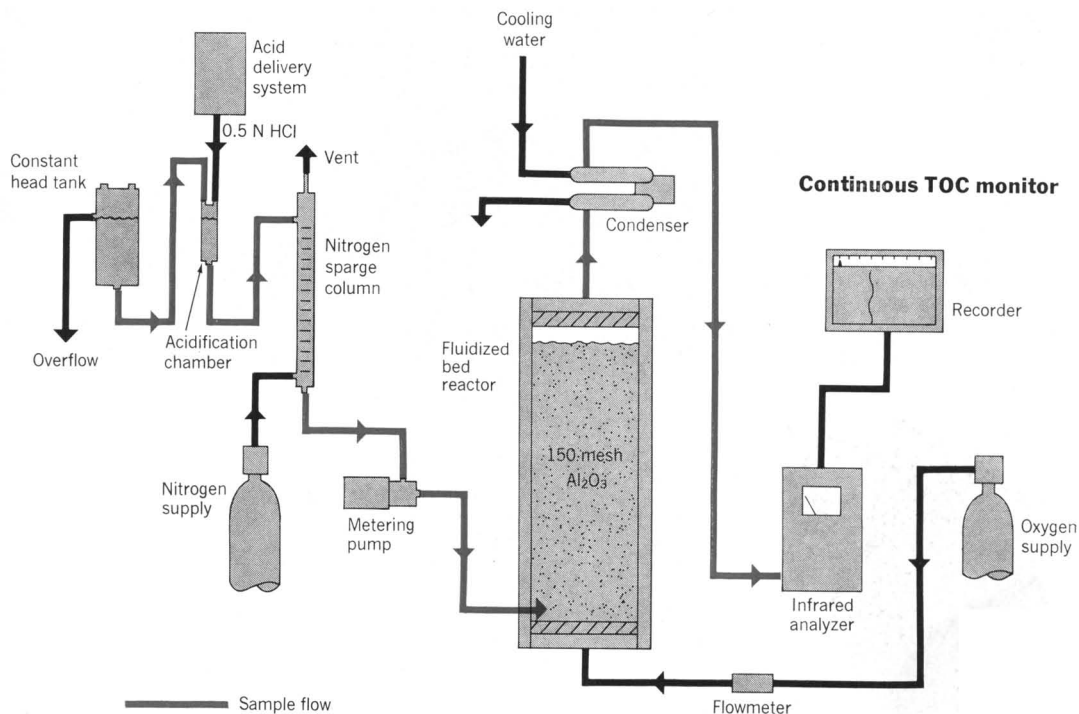
company's original modular design concept; later models may feature interchangeable, rack-mounted components. Price of the instrument will be within the range of present commercial carbon analyzers.

The major objective of carbon analysis is, of course, to measure the oxygen deficiency of effluent streams. Water chemists have long realized the limitations of the widely used five day biological oxygen demand (BOD) technique: It is cumbersome, time consuming, and of limited usefulness where inorganic carbon or slowly oxidizable organic compounds are present. Some manufacturers have approached the problem by considering total oxygen demand of the sample, and market instruments to measure the uptake of either oxygen or CO_2 during high temperature catalytic oxidation of the sample. These instruments offer more rapid analysis than the BOD method, but are not specific for organic carbon.

The new AES monitor achieves specificity for organic carbon by removing inorganic carbon in an automated sample pretreatment step. The effluent sample flows from a constant head tank to an acidification chamber, where it is treated with hydrochloric

acid to shift the carbonate equilibrium; the carbon dioxide thus generated is removed by sparging the sample with nitrogen.

The carbonate free sample then is delivered to the oxidation section of the analyzer. The oxidizer is essentially a fluid bed reactor, developed by Procecdyne Corp., which cooperated with AES on the development of the monitor. Procecdyne will manufacture the reactor units for the AES instrument. The reactor has a capacity for oxidizing up to 4000 mg./l. of total organic carbon at the design sample flow rate of 3 ml. per minute. The reactor bed consists of 150 mesh aluminum oxide particles that serve as a catalyst for the oxidation and as a heat transfer medium. Oxygen is supplied to the reactor at ten times the stoichiometric requirement to oxidize the maximum amount of total organic carbon which may be present; the oxygen and vaporized sample serve as the fluidizing gas for the reactor. Normal reactor temperature of 850° C. is maintained by external electric heating coils. A two-stage condenser cools the effluent gas stream of the reactor to less than 50° C. prior to entering a nondispersive infrared analyzer for CO_2 analysis.



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Cooperative effort. Federal, state, and local officials at the signing of the first contract for operators' training in Pennsylvania (l. to r.) Lyon—state water pollution control ad-

ministrator; Barber—FWPCA; Dominick—FWPCA; Mirring—Labor; Sen. Scott—Senate minority leader; Venn—HEW; and Baxter—Philadelphia's water commissioner

Plant operators train in most states

Training of more than 2000 operators in 33 states will meet some pressing domestic needs

Training of operators for waste water treatment plants at the state and local levels, where a major portion of the action in water pollution abatement is, appears to be taking on a new look. Recently, a national contract was signed for the training of nearly 1000 operators nationwide. In addition, key funding provisions for still more operator training in fiscal years 1970 and 1971 were retained in pending water enhancement legislation, S. 7, after full Senate consideration last month.

These training programs now offer opportunities to paraprofessionals (a term which the Department of Labor uses to include people with educational achievement at the third grade to high school graduate level). In one sense, disadvantaged persons—either unemployed or underemployed segments of the community and others with non-year-round employment—can receive training today and provide an urgently needed skill to fit into the mainstream of state and local community effort tomorrow.

Prior to the Department of the Interior's announcement of the national contract this April, behind-the-scenes operations and efforts led to the present mechanism for making funds available

to state and local officials. William D. Barber—who formerly headed the state and local manpower unit of the Federal Water Pollution Control Administration's (FWPCA) Manpower and Training Division—was able to cut the red tape and establish contact with other federal officials to pull off the task of making monies available to state and local officials for the training of paraprofessionals. "If necessary, FWPCA, within a week, can get the money out to state agencies and local municipalities for this training," Barber says. "And, really, the mechanism is the important thing that was established." Now, in his new position, Barber will be providing assistance to the office of the Secretary of the Interior on interagency and intergovernmental programs in the urban and environmental enhancement fields.

Need for operators

The need for waste treatment plant operators was demonstrated vividly in Boston. After construction of the Deer Island waste water treatment plant, its operation was delayed for several months simply due to the lack of adequately trained operators. Without more and better training programs, other delays in the opening of

plants are likely to take place throughout the U.S. For example, St. Louis needs approximately 100 operators at its new metropolitan treatment plant which will become fully operational late this year.

In 1967, the manpower study document (S. Doc. 49) amply stressed that, in the next five years, the U.S. would need to train 30,000 operators. Prior to the passage of the Manpower Development Act of 1967, practically no funds were available for the training of operators at the state and local level. But, through cooperative efforts of two federal departments—Labor and Health, Education, and Welfare (HEW)—during fiscal year 1969, more than \$2.5 million was committed to train more than 2000 operators in 33 states. And additional funds, totaling \$5 million for 1970 and \$7.5 million for 1971, have been earmarked for the operator training program in the Water Quality Improvement Act.

Manpower program

The position of waste water treatment plant operator offers job opportunities for groups of people who are traditionally at the lower stratum of the total work force, Barber observes. Many municipal and industrial water



Interior's Barber

Cooperative federal, state, and local training for plant operators^a

	NC ^b	CAMPS—69 funds	
		Institutional	OJT ^c
Ark.	20	20	—
Calif.	100	—	—
Colo.	20	—	—
Conn.	—	1	—
Fla.	60	—	—
<hr/>			
Ga.	—	—	115
Idaho	—	6	—
Ill.	80	—	—
Ind.	100	—	—
Iowa	20	—	—
<hr/>			
Ky.	40	—	—
La.	20	—	—
Me.	—	2	—
Md.	60	—	—
Mich.	60	—	—
<hr/>			
Miss.	—	—	75
Neb.	20	—	—
N.H.	—	1	20
N.Y.	40	—	—
N.C.	—	—	80
<hr/>			
N.D.	—	—	40
Ohio	20	—	—
Okla.	—	—	100
Ore.	40	20	—
Pa.	80	—	—
<hr/>			
P.R.	—	—	85
S.C.	—	—	80
Tenn.	—	—	100
Tex.	80	40	320
Va.	20	—	80
<hr/>			
Wash.	20	—	—
W. Va.	40	—	—
TOTALS	940	90	1095

^a As of Sept. 26, 1969

^b National contract

^c On job training

Funding level

National Contract	\$	813,969
CAMPS' Institutional		183,473
OJT		1,364,006

Source: FWPCA

pollution problems are prevalent in high density metropolitan areas, and here too are the labor pools of disadvantaged groups.

"The cooperative program accommodates the hiring of new personnel and the upgrading of existing personnel, upgrading skills being an integral facet of the training effort," Barber continues. "Other advantages also are realized through this system. For example, while the program immediately helps to alleviate the more critical manpower shortage, it increases mobility of operators so that personnel can be shifted to critical areas, and provides advancement opportunities for present employees," Barber elaborates. Operator programs already are functioning in Pennsylvania, Michigan, Illinois, Iowa, Oregon, Missouri, Colorado, and the District of Columbia. Barber emphasizes that this training effort was not the first or only program available for operators, but it is the first coordinated federal, state, and local effort and will serve as a springboard for expanded and improved programs.

He points out that training programs of the Water Pollution Control Federation, several states, and several universities are leaders in the field. However, all these projects are in need of additional resources, including money, materials, and trained instructors, to expand and improve their efforts. This new cooperative program offers them the resources to do a better job.

Established in 1967, and involving eight federal participants—Labor, HEW, Commerce, Office of Economic Opportunity, Housing and Urban Development, Agriculture, Interior, and Civil Service Commission—the Cooperative Area Manpower Program System (CAMPS) sought to identify manpower deficient areas and further serve

as a two-forked attack on some pressing domestic problems. In this case, the two aspects include manpower demands and availability of job opportunities for the disadvantaged. The personnel shortage in water pollution control and related environmental fields, such as air pollution and the like, was made apparent in CAMPS, planning guideline of early 1968. Further, the guideline noted that an important and specific component of this shortage existed in area plans of many states and localities.

The study, "Manpower Needs in Water Pollution Control Occupations"—the first such study in the U.S. which collected training deficiencies and needs for operators at the state and local levels—contained an inventory of every plant site in the state of Georgia. For the first time, the number and category of persons needing training became available, along with the first occupational analysis of operators, according to FWPCA's Barber, who notes that "the study was completed down at the grass roots level." In effect, state officials were telling federal officials which operators needed the training and where one job in a waste water treatment facility stops and another one begins, the FWPCA spokesman explains. These levels of occupational responsibility range from one of watching gages, cleaning pumps, and the like, to another of knowing how the pumps work and being able to repair them and so on, to a top position of plant manager, supervising all subordinates.

Progress

Barber notes that, under the national contract, approximately \$1000 each would be spent on training nearly 1000 operators. In cooperation with HEW's Area Manpower Institutes for Development of Staff program, FWPCA has trained the instructors in two week courses for this program in Oklahoma City, Chicago, Los Angeles, Portland, and Washington, D.C.

The 44 week curriculum involves three phases: A first three weeks of classroom work; a second 20 weeks spent six hours per day on job training, and two hours instructional; and a last phase of 21 weeks on job training with remedial training as needed.

Barber and his former FWPCA unit have been nominated for a special governmental service award for their efforts in this program.

Reynolds' aluminum reclamation programs set pace for U.S. industrial solid waste management efforts

Aluminum scraps find second life

Recover, recycle, and reuse are the new 3R's that the public and business must learn if Congress passes S. 2005, the Resource Recovery Act of 1969. As this new schooling is accepted and becomes standard operating procedure in today's economy, the U.S. will begin to manage some of its solid wastes, accelerate conservation of its natural resources, and learn that such operations are economically viable.

Reynolds Metals Co. (Richmond, Va.), the second largest aluminum company in the U.S.—but first in the reclamation field—has two test programs in operation today. Reynolds has found that aluminum reclamation is economically feasible, even at today's price. Its second redemption center in Los Angeles (Calif.) started operation this June, but an earlier one in Miami (Fla.) opened in Jan. 1967. Already, Sen. Edmund S. Muskie (D.-Me.) has commended the company on its reclamation efforts.

"The first Reynolds all aluminum beverage can went on the market just five years ago," says Paul Murphy, vice president of Reynolds' packaging division. "In 1969, 2.7 billion cans will be produced, and some experts say that, by 1973, this figure will reach 9 billion cans."

"The potential reclamation value of these cans is enormous," Murphy elaborates. "At 10 cents a pound, the present production rate of 225 million cans—or 11,500,000 pounds—would bring in \$1,125,000 monthly. No one expects 100% return of these cans, but these figures show that even as small a return as 10% would bring in a substantial amount of money."

Aluminum cans and ends are the fastest growing segment in the packaging materials industry, according to the recent report, "The Role of Packaging in Solid Waste Management

1966 to 1976." Prepared by Midwest Research Institute (MRI) for the Bureau of Solid Waste Management (ES&T, August 1969, page 705), the report notes that, in 1966, 329 million pounds of aluminum were consumed in the manufacture of aluminum cans and ends (primary ingot price is 27 cents per pound) and by 1976, 1400 million pounds of this metal will be used for this purpose. In other terms, the 10 year growth figure for aluminum cans and ends is 15.6% per year, considerably more than the overall 1.6% per year growth figure for all packaging materials in the U.S. in the decade 1966-76.

Wasted metal

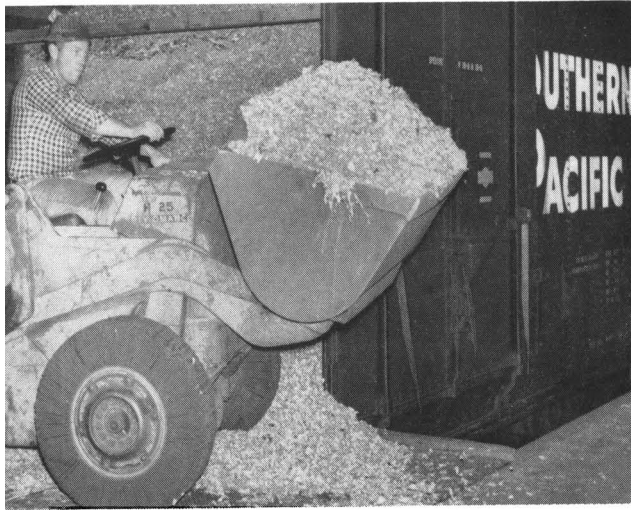
Annually, the U.S. disposes of 48 billion metal cans—a statistic that includes both steel and aluminum cans—according to the President's Science Advisory Committee 1965 report, "Restoring the Quality of Our Environment." At this rate, each person disposes of 250 cans each year.

Aluminum cans are newcomers to the market. On a weight basis, about 90% of all metal packaging material is steel; aluminum accounts for most of the remaining 10%. MRI notes that, in 1966, aluminum accounted for only 4.6% of the total base boxes of can metal shipped. A base box is the unit of measure used in can sheet stock; about 500 12 ounce cans can be made from one base box. Used primarily for beverages such as beer, soft drinks, and the like, aluminum cans are lightweight—weighing from 39-45 pounds per base box compared with 55 pounds per base box for the lightest steel cans. Although aluminum cans cost more than steel ones, the weight differential and subsequent shipping cost savings offset their higher price, according to the MRI report.

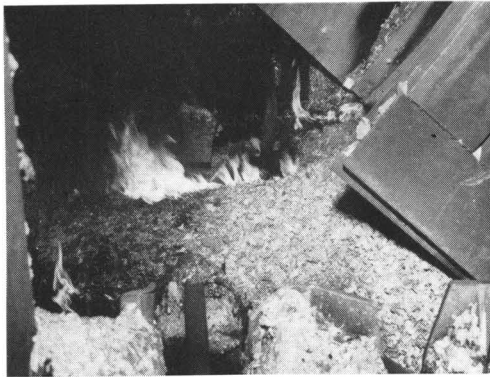


David P. Reynolds

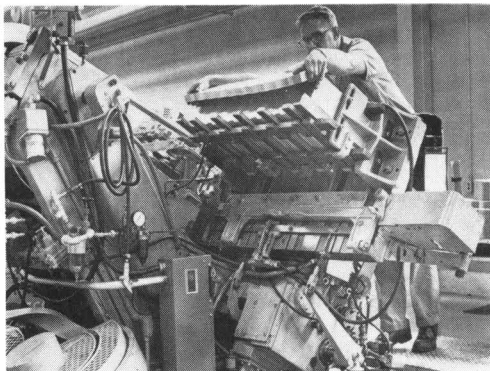
"We are very happy with the progress of our recycling and can reclamation program," says David P. Reynolds, executive vice president of Reynolds Metals Co. "We are now picking up all aluminum cans at the rate of better than half a million a month. Equally as gratifying is the response this program has brought from all parts of the nation. Both national and regional publications have praised our program editorially and we have also received many complimentary letters from legislative and community leaders throughout the nation."



First R—Recover. With redemption centers in L.A. and Miami, Reynolds ships shredded aluminum by railroad to reclamation plants



Second R—Recycle. At the Bellwood plant, aluminum is fed into a furnace for casting as secondary ingots



Third R—Reuse. Recycled aluminum reenters the economy in many ways (above, in the manufacture of new cans)

Value of scrap materials per ton

Aluminum	\$200
Steel	20
Waste paper	16

Plant operation

In a Reynolds test program, waste aluminum and steel cans are separated magnetically at the Los Angeles redemption center; the aluminum ones are shredded to remove moisture. After shipment to the company's Bellwood reclamation plant (Richmond, Va.), the shredded aluminum is melted at 1200° F. and cast into secondary ingots. Then, these secondary ingots are available for reuse in other aluminum applications, depending on the alloy content of the metal.

By July, Reynolds recycled 60,000 pounds of shredded aluminum cans at its Bellwood plant. Another reclamation plant (Florence, Ala.) is beginning to recycle aluminum scrap generated in Reynolds' can manufacturing operation, but not shredded waste aluminum cans from its redemption centers, according to a company spokesman.

Other companies produce aluminum can stock for a number of can manufacturers. In general, these manufacturers use the aluminum for can ends on steel cans, making their products easy to open. But such cans are not recovered at either of Reynolds' redemption centers.

According to MRI's report, 52 million tons of packaging materials were produced and used in the U.S. in 1966, and only 10% of this material was reused or recycled back into industrial raw material channels.

With the exception of corrugated paper board—of which about 20% is reused—and minute quantities of steel and aluminum cans, most other packaging materials never enter reuse channels, but this practice hopefully will change in the future.

Catalytic oxidation controls emissions

Low temperature technique handles a wide variety of solvents and vapors

A major air pollution problem facing many industrial firms, particularly in the chemical processing and allied industries, is that of oxidizable gaseous emissions. These types of emissions are a major component of the complex mix of materials loosely defined as smog, and sources of these emissions have become the subject of increasing legislative concern. The types of industries facing this problem run the gamut from high volume operations, such as basic organic chemicals and petrochemicals, to smaller industrial segments that use substantial amounts of organic solvents, such as paint, varnish, and metal coatings makers, dry cleaning plants, and metal finishing firms.

In spite of the prevalence of the problem, the means of coping with these types of vapors are rather limited. Absorption on activated carbon is one method, but the relatively high cost of this form of control makes it useful primarily for recovery of potentially valuable byproduct emissions. Lacking this economic incentive, most plants faced with the problem fall back on some type of oxidation—thermal or catalytic—of the emissions to carbon dioxide, water, and other innocuous byproducts.

Thermal, or direct flame, incinerators are in fairly common use; less common, but drawing more attention, is catalytic incineration. There are, as yet, relatively few commercial catalytic systems available, but the field is a fairly large potential market for pollution control equipment (ES&T, January 1969, page 30).

The main advantage of catalytic incineration over direct combustion technique is lower cost. Catalytic incinerators operate at lower temperatures—500°–900° C., compared with 1100°–1500° C. for thermal incinerators—and use substantially less fuel. Because of the lower operating temperatures, materials of construction do not need to be as heat resistant, reducing installation and construction costs. In addition, since it has a faster reaction time, a catalytic sys-



Headquarters. Catalysis is a key abatement technique at Johnson Wax's Racine (Wis.) complex, site of the company's corporate offices and research facility

tem usually is smaller and lighter, further reducing capital costs.

Although the major potential for catalytic oxidation units is in the basic processing industries, the technique can solve knotty problems in the manufacture of consumer products as well. For instance, during the development of self-polishing floor waxes, workers at S. C. Johnson & Son (Racine, Wis.), noted that certain acrylate monomers, vital to the manufacturing process, gave off an offensive odor. Design work on the production unit to be built at Racine indicated that the large volume of these vapors would create a problem, particularly since the plant was to be located in a mixed industrial-residential area.

Before full-scale production of the new product could get underway, the company had to launch a full-scale research project to find a way to control the exhaust vapors. Conventional methods, such as steam stripping columns, proved impractical. A catalytic oxidation system, developed by Oxy-Catalyst, Inc. (West Chester, Pa.), was tested; the results confirmed that catalytic oxidation could handle the odorous gases, and a full-scale unit was installed.

Successful operation of this prototype prompted the selection of another such system for use at a major expansion at Waxdale (Wis.), where

Johnson is in the final stages of consolidating all its raw ingredient processing, wax manufacturing, and container filling operations.

In both of the catalytic oxidation units at Johnson, the effluent exhaust odor is diluted with air at a 400:1 dilution ratio as it enters the catalytic unit. Diluent air is drawn by a suction fan from outside the building; a second blower fan mixes the air with the vapor stream which is preheated by a natural gas burner. At startup, the units require maximum fuel consumption, but, as the normal operating temperature of 450° C. is reached, the gas valve is throttled back to reduce burner fuel consumption. By contrast, a thermal incinerator would require a preheat temperature of 1000° C. or more, and a much higher fuel consumption.

The Racine unit, because of its rooftop location, does not require an exhaust stack; the Waxdale unit, at ground level, requires only an 8 inch metal stack. A more significant difference between the two units is in the type of catalyst support. In the original Racine installation, the catalyst bed is comprised of brick-sized porcelain units coated with the catalyst. The catalyst support for the newer unit uses a honeycomb configuration, developed by Oxy-Catalyst, inserted in a stainless steel cartridge.

Solid waste problem gains recognition

Senate subcommittee hearings open with administration officials testifying

One environmental round between legislative and executive officials of the federal government this Congressional season centers on the nation's mounting solid waste management problem. At the beginning of hearings by the Senate Subcommittee on Air and Water Pollution on proposed legislation S. 2005—the Resource Recovery Act of 1969—legislators felt the need for continuing federal leadership in this field. Administration officials opposed specific attention to solid waste, pointed out the need for comprehensive planning for all environmental programs, and indicated that the coordination of existing federal authorities should be handled by the new Environmental Quality Council (EQC) (ES&T, July 1969, page 611). But when the star witness—George Romney, Secretary of Housing and Urban Development (HUD) and chairman of EQC's new solid waste committee—failed to testify, little additional insight was available on the administration's plans or views for this mounting problem.

The bipartisan subcommittee plans to invite industrial witnesses to testify on S. 2005 at some later date. Perhaps, they will garner more support for the proposed legislation (which is a continuation of the existing legislation that expires next June). Some stimulation of the private sector also will lead to additional help with this problem.

Different views

"The problem of solid waste has been growing, and there is little evidence that state and local governments are doing anything at all or are stimulated or motivated to do anything about the mounting problem," says Sen. Edmund S. Muskie (D-Me.). The subcommittee chairman asked, "At what point does some level of government begin to make the investment necessary to roll the tide of waste back?"

The administration's lead-off witness—Robert H. Finch, Secretary of Health, Education, and Welfare (HEW)—testified, "I do not believe that the solution . . . (to the mounting discharge of man-made wastes to the environment) . . . lies in passing more federal legislation." Finch opposed



Chairman. Sen. Muskie expresses need for federal leadership

categorical solid waste planning grants, as well as construction grants for disposal facilities, because such planning cannot be separated from other environmental planning. Finch is looking for a comprehensive systematic approach to all environmental quality problems and believes that this can best be accomplished under the guise of the EQC.

Hubert B. Heffner, deputy director of the Office of Science and Technology (OST), stressed that the planning grants provisions of the proposed legislation should be part of a more comprehensive program designed to attack the whole of a community's environmental problem. One of our problems today is the multiplicity of overlapping authorities, such as water pollution planning in the Federal Water Pollution Control Administration (FWPCA), land use planning in HUD, and air resource planning in HEW, and so on.

The types of solid wastes are domestic, mining, manufacturing, agricultural, and industrial. Approximately \$4.5 billion is spent each year on solid wastes; of this total, \$3.4 billion is spent on collection of domestic

wastes, and another \$700 million on its disposal.

Communities are anxious to do something about the solid waste problem, according to John L. Buckley, technical assistant at OST. He noted that the demand for urban systems engineering grants under HUD's 701 grant authority—a relatively new, small program which was intended to help communities improve their performance in all fields of systems engineering—has included more requests for grants to improve solid waste management than for all other areas combined. Buckley also pointed out that EQC's principal objective is to focus existing competence and authorities of the various federal agencies to fully and effectively address this solid waste problem.

Other support

But subcommittee members, as well as the public, wonder how long we can wait. Two recent reports stress the need for continuing federal effort in this field. Sen. Muskie noted that the subcommittee waited one and one half years for the first report—"Solid Waste Management," by Rolf Eliassen, a technical consultant to OST—before introducing S. 2005. The first recommendation of the Eliassen report calls for an expanded research, development, and demonstration program in solid waste management, and adds that such a program should be adopted by the federal government.

The second report—"Policies for Solid Waste Management," from the National Academy of Engineering-National Academy of Sciences-National Research Council—makes the following three recommendations:

- Establishment of a solid waste management information center.
- Research, development, and larger full-scale demonstrations in metropolitan areas.
- Improvement of management information, planning, and manpower programs.

Some critics are beginning to wonder whether the federal government plans to preempt the field of environment with its EQC. The same critics feel the need for more state and local concern with environmental programs.

The case of the \$750,000 waste water plant that never had to be built!

Waste water from a midwestern manufacturer's plant was polluting a stream. The state board of health threatened immediate action unless pollution was eliminated.

The company investigated the cost of waste water treatment facilities, and found that a plant that would handle their total effluent would cost at least \$750,000.

They called in Calgon to make a survey. Calgon engineers did a thorough job (today, we call this the Calgon Water Audit™) and found that the primary cause of contamination came from a process requiring the spraying of a clay slurry. Their findings indicated that the process could be improved to the point that the amount of clay slurry to be disposed of would be reduced by 85%.

Changing the process would cost only \$80,000 and the effluent would now meet required standards. The proposed

\$750,000 waste water plant would never have to be built.

A Calgon Water Audit is the key to evaluating what it will take to bring your plant into conformity with water quality standards. A Water Audit will not only tell you exactly what the plant effluent contains, but will also tell you how to minimize the amount of water to be treated. It will give you costs; it will tell you how much time you have to comply with regulations; and it will show you how big (if any) a waste treatment plant you will need.

Calgon Corporation has been dealing with waste water problems since 1945. We know how to get the job done — at the least cost to you. For further information on how you can benefit from this unique service, write or phone Calgon Corporation, Calgon Center, Pittsburgh, Pennsylvania 15230.



SUBSIDIARY OF MERCK & CO., INC.

Carbon dioxide affects global ecology

Continued increases in atmospheric carbon dioxide will change worldwide weather and plant growth

Managers of renewable land resources in most nations of the world recognize the principles of sustained yield—harvesting on an annual or periodic basis only what is replenished during the same period. Sustained yield may be applied to soil nutrients used in growing crops; to forests; to water, both surface and subsurface; to forage for domestic and wild animals; and to fish and wildlife. Natural resource managers are attempting to make long-range plans—for as long as 150 years in the case of forests.

Worldwide, there is growing acceptance of the principles of sustained yield and the desirability of achieving a balance between harvest and growth of the renewable land resources. Weather is a major factor governing these resources. But will weather remain constant, or will it change appreciably by the year 2000 or 2050?

What is the situation concerning the air resources? Are they renewable? There has been worldwide concern over pollution of the atmosphere with radioactive materials, and local concern over pollution of the cities' air with carbon monoxide, hydrocarbons, sulfur compounds, smoke, dust, and many other irritating, malodorous, and poisonous byproducts of combustion. It appears both technically and economically feasible to control these emissions, and we are beginning to move in that direction. In this sense, the quality of our air is renewable.

Other changes in the air, however, cannot be reversed so readily. Man's activities are changing the carbon dioxide and oxygen content of the entire atmosphere; these changes may, in turn, affect weather and the growth of plants. Oxygen and carbon dioxide,

plus water and nitrogen, are the basic building blocks for all life processes, and, therefore, the foundation for man's sustained yield programs—both plant and animal.

Both oxygen and carbon dioxide are, of course, colorless, odorless, and non-poisonous, and neither is a pollutant in the ordinary sense of the word. Through photosynthesis, plants use light energy to convert carbon dioxide and water into carbohydrates and release oxygen into the atmosphere. When plant materials decompose, or burn, or are consumed by animals, the process is reversed. Oxygen is used to convert carbohydrates into energy plus carbon dioxide and water. These are the basic steps in the complex carbon cycle.

Under normal conditions, the amounts of CO₂ and O₂ in the atmosphere remain approximately in equilibrium on a year-to-year basis. In 1963, Helmut Leith reported that the annual use of carbon in photosynthesis is about 150 billion tons per year, roughly equally divided between land plants and marine plants. This is about one fifth of the amount present in atmospheric CO₂. This is matched by the annual release from oxidation of organic matter.

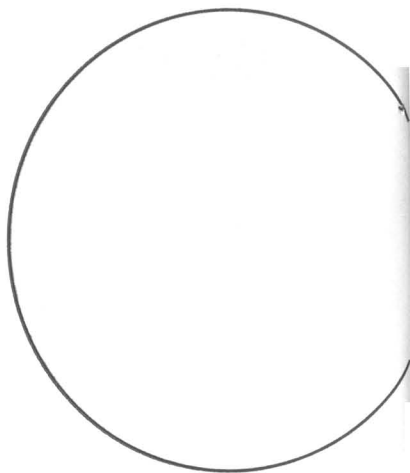
The atmosphere today contains about 21% O₂ and about 0.032% CO₂ by volume. However, man's activities—mainly land clearing, the burning of fossil fuels, and making cement from limestone—are artificially reducing the O₂ content and increasing the CO₂ content of the air. The burning of fossil fuels is primarily responsible, but the other two factors should not be ignored.

The long-term effects of these

changes in atmospheric gases upon world weather and upon man's environment are of vital interest to everyone, since worldwide temperatures may rise or fall in response to the amount of CO₂. Changes that have occurred within the past century are barely discernible. They have attracted little attention. One reason is that the study of such phenomena involves several sciences, whereas our scientific efforts are focused primarily by individual disciplines. Perhaps, changes in the atmosphere and world weather will be obvious to all by the year 2000.

The temperature of the earth has changed—from periods when most of the earth's surface had a tropical climate, to severe glacial epochs—many times during its several billion year history. For at least nine tenths of the past one billion years, the earth was warmer than it is today. These warm periods have been interrupted at intervals of roughly 250 million years by severe glacial periods of a few million years duration. Today, the earth is in a warming trend following such a glacial epoch—the Pleistocene. In "Early Man," E. C. Howell reports that the annual mean temperature of Paris about 20,000 years ago was probably 11° F. colder than it is now.

What are the prospects for the year 2000 and beyond? Are the increases



in atmospheric CO_2 and decreases in O_2 desirable or undesirable? How will they affect world temperatures? Are they irreversible, or can they be modified to an optimum level for human welfare? Complete answers to these questions are not yet available. However, sufficient scientific information has been accumulated to support reasoned projections.

Origin of present CO_2 - O_2 ratio

Carbon dioxide and oxygen percentages in the atmosphere have varied considerably throughout geologic time. In 1965, the Environmental Pollution Panel of the President's Science Advisory Committee concluded that, over the past four billion years, at least 40,000 times the quantity of CO_2 now present in the air entered the atmosphere from volcanoes. Nearly three fourths of it combined with calcium, magnesium, and other elements during the weathering of silicate rocks to form carbonates. The most rapid combination occurs in steep, mountainous areas with igneous rocks and high precipitation; rivers then carry the dissolved carbonates to the seas. The carbonates in the upper layers of the oceans probably have long been at the saturation point. Thus, any additional input from the rivers is precipitated (frequently with the aid of such marine organisms as those that form coral

reefs) and is deposited on the floor of shallow seas as limestone (calcium carbonate) or dolomite (calcium magnesium carbonate).

The other one fourth of the CO_2 emitted by volcanoes during the earth's history was converted by plants to carbohydrates and other organic compounds that became buried in sediment and, thus, preserved from oxidation. A small fraction of this organic matter was concentrated into what we call fossil fuels. During the carboniferous period, for example, the atmosphere contained more CO_2 and water vapor and less O_2 than at present, and the earth was warmer. One possible indication of the relationship between atmospheric CO_2 and temperature is the Russian announcement, as reported in news articles, that the temperature near the surface of the plant Venus is very hot—over 720°F .—and its atmosphere contains more than 75% CO_2 .

It is evident that most of the O_2 now in the earth's atmosphere displaced the original CO_2 as the result of photosynthesis by plants and the burying of organic carbon in sediment during the past three billion years that life has existed on earth. In "The Origin of Life on Earth," H. C. Urey, V. A. Sokalov, et al. state that the amount of O_2 before photosynthesis began was negligible. Organic matter

is being buried in sediment today, but the amount is estimated to be only one billion tons per year.

Insulating properties of CO_2

The temperature of the earth rises when the amount of CO_2 in the atmosphere rises because this gas absorbs and traps heat and prevents a portion of it from radiating back into space. Visible rays from the sun penetrate the atmosphere, but CO_2 absorbs and reflects back portions of the infrared radiations from the earth, particularly in the wave lengths from 12-18 microns. Water vapor and ozone also have these characteristics. However, there is such a small percentage of ozone in the atmosphere that its worldwide effect on temperature, except in the upper regions of the stratosphere, probably can be ignored.

The amount of water vapor in the atmosphere is highly variable in time and place; also, it is concentrated within a few thousand feet of the earth. Carbon dioxide, on the other hand, is uniformly distributed up to at least 50 miles. Where there is sufficient water vapor to form clouds, the portion of light energy from the sun that reaches the earth is reduced. Since the amount of water vapor is highly variable, and since it tends both to increase and decrease temperature, depending upon cloud formation, its total effect upon worldwide temperature is difficult to measure. Other components of the atmosphere—nitrogen (78%), oxygen (21%), and argon (0.9%)—do not possess the insulating properties of carbon dioxide.

The insulating properties of CO_2 and water vapor do not necessarily lead to the conclusion that increases in these gases will warm the earth. Many complex relationships must be evaluated over a period of years before positive proof can be established.

Global temperature

The possibility of a worldwide increase in temperature due to the additional CO_2 from the burning of fossil fuels was first posed in 1899 by the American geologist, T. C. Chamberlain. In 1956, G. N. Plass, a physicist, calculated that if the CO_2 content of the atmosphere were to double to 0.062%, the worldwide mean sur-

Buildup. *Atmospheric CO_2 is increasing at a measureable rate. Between 1958-62, the increase amounted to 3.7 p.p.m., or 1.13%*



face temperature would rise 6.5° F. If the CO₂ content were decreased by half, he predicted that the mean temperature would fall 6.8° F., and ice sheets would begin to flow over the continents.

In 1963, Möller calculated that a 25% increase in atmospheric CO₂ would increase the average temperature by 1.1°-7° F., depending upon the amount of additional water vapor present in the atmosphere that resulted from the increased temperature.

In 1967, S. Manabe and R. T. Wetherald of Environmental Science Services Administration (ESSA) calculated that increasing atmospheric CO₂ from 300 p.p.m. to 600 p.p.m. would increase surface temperatures by 4.25° F., assuming average cloudiness, and 5.25° F., assuming no clouds. Their calculations are based upon a constant relative humidity.

The President's Science Advisory Committee Environmental Pollution Panel in 1965 projected a 25% increase in the CO₂ content of the atmosphere by the year 2000 as compared to 1950. They concluded: "This may be sufficient to produce measurable and perhaps marked changes in climate, and will almost certainly cause significant changes in the temperature and other properties of the stratosphere. At present, it is impossible to predict these effects quantitatively, but recent advances in mathematical modeling of the atmosphere, using large computers, may allow useful predictions within the next two or three years."

Atmospheric CO₂ has been increas-

ing since 1860. In 1961, in the *Journal of the Royal Meteorological Society*, G. S. Callender estimated the increase has been from 282 p.p.m. in 1860 to 325 p.p.m. in 1955, or from 0.027% to 0.032%, a relative increase of 15%. Beginning in 1958, C. D. Keeling, of Scripps Institute of Oceanography, made precise measurements of atmospheric CO₂. These data show clearly that, from 1958-1962, the CO₂ content increased by 1.13%, or 3.7 p.p.m. This represents about half of the CO₂ resulting from the burning of fossil fuels during the same period. The other half evidently was absorbed by surface waters of the oceans and by the biosphere, mostly the former.

J. M. Mitchell, Jr., of ESSA, has determined that worldwide mean temperatures also have risen since 1860. The rise was 0.9° F. between 1885-1940. The rise was greatest between 40°-70° N. latitude, where the average winter temperature rose 2.8° F. This has been accompanied by a warming of the northern hemisphere oceans—in the North Atlantic, about 3.6° F. Between 1940-1960, additional warming occurred in northern Europe and North America, but, for the world as a whole, there was a slight lowering (0.2° F.) in mean annual temperature. Although complete data are not available yet, the preliminary indications are that the cooling trend has continued since 1960. This leads to the conclusion that other factors such as cyclic variations in the radiant energy available from the sun (as yet, not accurately measured), or dust and smoke from volcanoes and man's activ-

ities, or contrails from jet planes, also are influencing weather trends. (According to Manabe and Wetherald, a 15% increase in CO₂ would cause only a 0.6° F. temperature increase, other factors being equal.)

Volcanoes, dust, and smoke

Mitchell contends that there is a consistent tendency for major volcanic eruptions to be followed by five year average temperatures on the order of 0.1° F. lower in the hemisphere in which the eruption occurred. The decrease is most noticeable in the first two years and is not distinguishable after five years, presumably because all the dust has settled out of the atmosphere. The worldwide cooling in the 1950's possibly was due in part to the Mt. Spurr (Alaska) eruption in 1953 and the Bezymyannaya (Kamchatka, U.S.S.R.) eruption in 1956.

The President's message to the Congress on conservation in March 1968 estimated that the total smoke and dust emission to the atmosphere from automobiles and industries in the U.S. is 130 million tons per year. Other combustion, including smoke from jet planes, forest fires, and trash burning, contributes another 30 million tons or more a year. If we assume that 20% of the smoke and dust originates in the U.S., we have an annual input to the atmosphere today of about 800 million tons of dust and smoke particles. This is about one eighth of a cubic mile—equivalent to a small volcano. The portion that reaches the stratosphere and is suspended for several months could produce a slight



Ignored. Long-term effects of man's activities on the global CO₂ balance have attracted little attention as yet



cooling effect on worldwide temperature. This is because the very small particles in the atmosphere reflect sunlight, giving the earth more of a halo appearance as seen from space.

Thus, there may be a possibility of introducing controlled quantities of reflective particles into orbit around the earth to counteract the warming effects of the added CO₂.

Fossil fuel

Roughly one third of our estimated recoverable reserves of fossil fuels is petroleum; the other two thirds is coal. These reserves have the potential for adding an additional 185% more CO₂ to the atmosphere than was present in 1950 (assuming 50% of the increase will continue to be absorbed by the oceans and biosphere). This would increase the CO₂ content of the atmosphere to .092%, or 925 p.p.m., and decrease the O₂ content by less than 1% to 20.94%. These reserves undoubtedly will increase as new fossil fuel discoveries are made and new techniques of recovery developed.

The National Air Pollution Control Administration (NAPCA) predicts that the greatest average yearly increases in rates of CO₂ emissions in the U.S. will be about 4% per year, and will occur between 1965-1985. Afterwards, NAPCA predicts that the rate of increase in fossil fuel consumption will diminish and the use of nuclear power will provide the needed energy increment.

Population pressures

The predicted relative decrease in

fossil fuel consumption in the U.S. may not apply elsewhere. World population may increase from 4 billion in 1975 to 6.3 billion in 2000. Hundreds of millions of Asians and Africans may aspire in the next century to attain the same degree of comfort, convenience, and mobility that the Western world now enjoys. This will require vast quantities of energy. Will it all come from clean sources, such as water power, solar energy, geothermal steam, and nuclear energy? Probably not. Chances are much of it will come from the cheapest and most readily available source—fossil fuels.

In 1960, the U.S. had 5½% of the world population and burned 34% of the fossil fuel. The total world consumption of fossil fuels probably will continue to accelerate, even if that in the U.S. tapers off. Assuming an annual increase in worldwide fossil fuel consumption of 5% by the year 2000, the CO₂ emissions from fossil fuel will be 59% of the amount of CO₂ in the atmosphere in 1950. If half of this added CO₂ is absorbed by the oceans, the amount in the atmosphere would increase 30% to about 415 p.p.m. In the absence of effective action on a global scale to curtail fossil fuel consumption, the CO₂ will increase still another 30% by the year 2020 to 540 p.p.m. This is double the amount present in 1860, when mankind began to burn fossil fuels in appreciable quantities. According to the calculations of Manabe and Wetherald, such an increase in atmospheric CO₂ would increase world temperatures about 4° F. as compared to 1860.

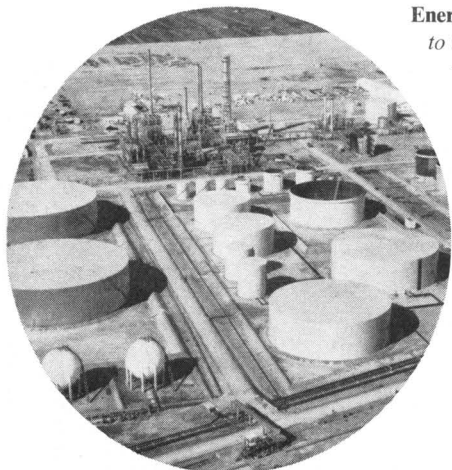
Effects on plant growth

Recent experiments in greenhouses at Michigan State University, and earlier work in Europe, have demonstrated that, under favorable conditions of temperature, sunlight, water, and soil nutrients, the availability of CO₂ to a large extent limits the rate of plant growth. The present normal atmosphere level of 0.032%—325 p.p.m.—is much below the optimum level. When the percentage is increased under controlled conditions, plants grow more rapidly.

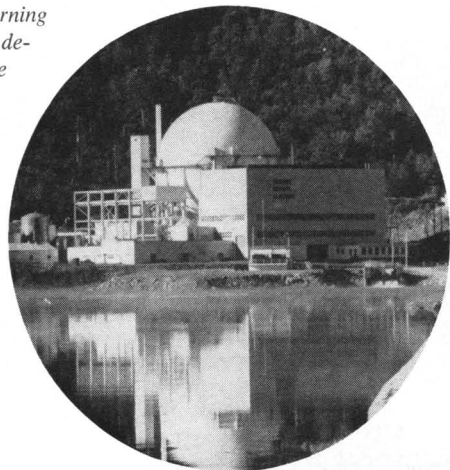
The Michigan State University experiments with lettuce and tomatoes, using from 800-2000 p.p.m. CO₂ during daylight hours, increased the dry weight 115%. Fruit size increased and quality was enhanced; reproduction improved; tomatoes had higher vitamin C and sugar content; and plants were more resistant to some fungi, virus diseases, and insects. The most significant yield increases yet reported for CO₂ enrichment of greenhouse atmospheres were for cucumbers and kohlrabi in hydroponic cultures—more than 800%. Large-scale use of CO₂ to enrich greenhouse atmospheres was begun in 1960.

The upper limits of plant response have not been established yet, but there are reports of plants that have responded favorably to levels of CO₂ ranging from 20,000-30,000 p.p.m. By comparison, the human safety limit for prolonged exposure is about 5000 p.p.m. CO₂—15 times present levels.

What effect the 15% worldwide increase in CO₂ since 1860 is having on plant growth under natural conditions



Energy. *The U.S. is turning to nuclear power, but developing nations are likely to rely on fossil fuels for some time to come*



is unknown. Probably, it is not appreciable so far. However, if the CO₂ content increases 30% by the year 2000 and another 30% by 2020, an accompanying increase in worldwide plant growth rate and production of about 5% by 2000 and 10% by 2020 may occur. These percentages are based upon the assumption that the rate of plant production will increase in proportion to the increases in CO₂, according to the Michigan State findings, discounted by 50%—an assumption not supported by actual measurements. However, experiments to verify this should not be difficult.

Since forests are responsible for about two thirds of the world's photosynthesis by land plants (one third of the world total) and, since some species of forest trees may live for 100 years or more, some of the additional carbon extracted from the atmosphere as the result of accelerated growth may be stored for several decades in the form of cellulose and lignin in trunks, branches, and roots of living trees. A few years after the trees die, however, the CO₂ is returned to the atmosphere and equilibrium reestablished. With the exception of forests, and here for only a few decades, I expect that the increased growth rate of land and marine plants will be balanced by the increased rate of decay of plant material. A net reduction in atmospheric CO₂ would occur if the total volume of living plants should increase. However, man's land-clearing activities worldwide make this unlikely.

Oceans and Ice Ages

The world's oceans contain about 50 times as much carbon as the atmosphere. A 1952 publication entitled "The Physical and Economical Foundation of Natural Resources," by the House Interior and Insular Affairs Committee, assured the nation that the oceans had almost unlimited capacity to absorb CO₂. However, since 1952, it has become apparent that several hundred years must elapse before the buffering effect of the oceans becomes fully effective. Most of the carbon in the seas is in the form of carbonate and bicarbonate ions that do not readily exchange with the atmosphere. The surface waters of the oceans (the top 200 feet) do contain substantial quantities of dissolved CO₂ in equilibrium with atmospheric CO₂. This gas is more soluble at lower temperatures than at higher ones. Consequently, atmospheric CO₂ is being ab-

Paracutin. Melting of icecaps would redistribute weight on earth's crust and could trigger an increase in earthquakes and volcanic eruptions

sorbed in the Arctic regions and, subsequently, released in the tropics.

If the oceans turned over annually, as do most inland lakes, most of the CO₂ added to the atmosphere from burning fossil fuels probably would be rapidly dissolved. However, the turnover rate is much slower. Plass estimated it to be as much as 10,000 years for the deeper parts. He and others subscribe to the theory that fluctuations in CO₂ content of the atmosphere account in a large degree for alternating ice ages and warm periods that the earth has experienced in the past. Relatively frequent pulsations in global temperature, in roughly 10,000 year cycles, have been attributed to the turnover rate for deep ocean waters; however, more recent information provided by Kilho Park, at Oregon State University School of Oceanography, using radioactive carbon dating techniques, places the turnover rate of the Pacific Ocean at about 1000 years.

If the earth continues to warm, all glaciers will recede and the Antarctic and Greenland ice caps will begin to melt. The Antarctic ice cap covers 6.7 million square miles, or 4.3 billion acres—almost twice the size of the 50 states. The ice averages over one mile thick. The Antarctic, Greenland, and other ice caps contain roughly 7.2 million cubic miles or 26 quadrillion tons of ice—the equivalent of about 200 feet of water from the top of all the oceans. During the Pleistocene Epoch, the ice sheets were much larger—enough to reduce the sea level about 400 feet.

The President's Science Advisory Committee reports there is no possi-



bility our present ice caps would melt suddenly. There is no evidence that they have begun to melt. Sea level has been constant for about 5000 years. However, if present trends in CO₂ buildup continue, there should be measurable melting by the year 2000. Between 400-4000 years might be required to melt the ice caps. If a melting period of 1000 years is assumed, the sea level would rise on the average of about two feet in 10 years.

The melting of the ice caps would also cause a tremendous redistribution of weight and pressure exerted on the earth's crust. Such a drastic change could trigger earthquakes and increase volcanic activity, resulting in more CO₂ in the atmosphere from volcanoes. However, more atmospheric CO₂ probably would be ab-





sorbed by the oceans because the additional fresh water from the melting ice caps would dilute the seawater; so the net effect would be most difficult to assess.

As the atmospheric temperature rises, the temperature of surface ocean waters in temperate and tropical regions could be expected to rise by an equal amount; but the temperature of the ocean waters in the polar areas would tend to remain the same for several centuries due to the melting of the ice caps and resulting icebergs.

Perhaps the long time period (from the human point of view) necessary to enable deeper ocean waters to absorb additional atmospheric CO_2 could be speeded up by the artificial injection of air into deep ocean waters (or better yet, the CO_2 emissions from fossil fuel

power plants). The feasibility of such a process, if investigated, has not been reported.

Can atmospheric CO_2 be reduced?

Any addition of CO_2 to the atmosphere (and the seas) through the burning of fossil fuels and limestone is cumulative. A technique to reduce the CO_2 content of the air or speed up its absorption by ocean waters, while theoretically possible, is not now economically feasible, and prospects of discovering a feasible process in the future are remote. By the use of nuclear power, atmospheric CO_2 could be converted to elemental carbon or carbohydrates and O_2 as outlined in the schematic chemical reaction: $\text{Energy} + \text{CO}_2 + \text{H}_2\text{O} = \text{Fuel} + \text{O}_2$. Possibly, the same energy could be used to create limestone artificially. However, either process probably would require more power and heat than was generated by the burning of fossil fuels in the first place, depending upon the efficiency of the system. Also, it would be necessary to preserve hundreds of billions of tons of this carbon fuel or limestone from future oxidation—probably in stockpiles.

A substantial increase in forest areas and cubic volume of wood in the forests would reduce the CO_2 content, but possibilities are very limited. About 2.7 billion acres of new, growing forest (120% of the area of the 50 states) would be required to absorb the CO_2 generated by fossil fuel combustion at the rate prevailing in 1962.

Processes are available to preserve the status quo as far as future CO_2 in the atmosphere is concerned. These

would substitute water power, geothermal steam, direct solar energy, and nuclear power—mostly nuclear—for power derived from the burning of fossil fuels.

Basic facts

From the foregoing it is apparent that:

- Needed research concerning increases in atmospheric CO_2 is in its infancy.

- There are no programs to control the amount of CO_2 released to the atmosphere, and no plans for such programs have been announced.

- The percentage of atmospheric CO_2 is increasing due to the burning of fossil fuels. It has increased about 15% since 1860. This increase is accompanied by an equivalent decrease in atmospheric O_2 .

- If not offset by other factors, this CO_2 increase will further increase global temperatures.

- CO_2 added to the atmosphere and oceans is removed by natural processes over a time scale of millions of years. Thus, because of the lack of a feasible artificial method of restoring atmospheric CO_2 levels that existed in 1860, CO_2 may, in an unorthodox sense, be considered a nonrenewable resource.

- The known reserves of fossil fuels, if burned, would add to the atmosphere 3.7 times more CO_2 than now is present. Some of this added CO_2 would be absorbed by the oceans.

- Burning all known fossil fuel reserves would reduce the oxygen content of the atmosphere only 0.06%, from 21% to 20.94%. This O_2 could be restored only through natural processes over geologic time. Thus, O_2 is a nonrenewable resource also, in the same sense as CO_2 . However, a reduction in atmospheric O_2 of less than 1% would not appreciably effect humans, or other animal life or plants, or the overall balance of nature. Poisoning of a substantial portion of marine life or the massive destruction of forests on a global scale could have an adverse effect upon the O_2 supply, but probably not before the earth was so hot due to added CO_2 that many present life forms could not exist.

Using these facts, we can point to some possibilities. By the year 2000, atmospheric CO_2 may increase by 20-60% above 1950 levels. This amount may bring about a global increase in average temperature from $1^\circ\text{-}5^\circ\text{ F}$. One unknown factor is the exact per-



Photosynthesis. *At present rates of fossil fuel consumption, 2.7 billion acres of new forests would be required to absorb the CO_2 being generated*

centage of CO₂ that will be absorbed by the oceans. There also is the possible multiplier effect: Increased temperature would increase evaporation and result in more water vapor in the atmosphere. This, in turn, would tend to increase temperature even more, but it could result in more cloudiness which would have the opposite effect. Also, as water temperature rises, the ocean water would have less capacity for holding CO₂, possibly adding more CO₂ to the atmosphere. Another unknown which acts to reduce temperature is the amount of dust and smoke in the atmosphere. Also unknown are possible variations in insolation.

By the year 2020, 75% of the world's 1965 known reserves of petroleum and 50% of the coal could be burned. This could increase the

Let's look at the western U.S. as an example. Certainly, the temperature increase would not occur uniformly. Some localized areas could become colder. But an average increase of 3° F. would be the equivalent of a 1°-4° southerly shift in latitude. The largest shift in latitude equivalent might be along the Pacific Coast, due to the warmer ocean waters and the prevailing westerly winds. If average changes in weather prevail, temperatures at Astoria (Ore.), on the mouth of the Columbia River, would be comparable to present temperatures at Crescent City (Calif.), near the Oregon border. Other possibilities are:

- The southwest states would be hotter, probably by more than 3° F., and drier.
- The flow of the Colorado River

- The rate of plant growth in the Pacific northwest would increase 10% due to the added CO₂, and another 10% due to increased temperatures.

On the other hand, a pessimistic projection could assume that, by the year 2020, the world's population would not taper off but continue to grow, and fossil fuel consumption would increase proportionately. In this case, temperatures would be 9° F. above 1950 levels. What are now the temperate zones would be well on the way toward tropical or subtropical climates by 2050, a mere 80 years away.

Some possible effects of this projection are that:

- Most areas would get more rainfall, and snow would be rare in the contiguous 48 states, except on higher

Imbalance. *The carbon cycle—perhaps the most fundamental and most sensitive of all life systems—is being subjected to*



unprecedented stresses as a result of our rapid exploitation of mineral resources and consumption of fossil fuels

atmospheric CO₂ by 30-100% above 1950 levels and bring about a global temperature increase from 2°-10° F.

Speculative projections

Let us now make some speculations. An optimistic projection could be based on the assumption that, by the year 2020, the total amount of noxious fumes, dust, and smoke now admitted to the atmosphere would be reduced from present levels. That is, the burning of fossil fuels would taper off rapidly and be supplanted by nuclear energy as a power source. If so, the amount of CO₂ in the atmosphere would increase only 60% over 1950 levels and result in a further increase in global temperatures of about 3° F.

What would be some of the ecological consequences of such an increase?

would diminish and the southwest water shortage would become much more acute.

- Forest fire hazards would increase and forests at the lower elevations in the Rocky Mountains and east of the Cascades and Sierras would recede.

- Coast redwoods would grow luxuriantly along the entire Oregon coast.

- Most of the glaciers in the North Cascades and Glacier National Park would be melted. There would be less of a winter snow pack in the Cascades, Sierras, and Rockies, necessitating a major increase in storage reservoirs.

- Marine life would be markedly changed. Maintaining runs of salmon and steelhead and other subarctic species in the Columbia River system would become increasingly difficult.

mountains.

- Ocean levels would rise four feet.

- There would be major increases in earthquakes and volcanic activity resulting in even more atmospheric CO₂, and violent storms.

- The Arctic Ocean would be ice free for at least six months each year, causing major shifts in weather patterns in the northern hemisphere.

- The present tropics would be hotter, more humid, and less habitable, but the present temperate latitude would be warmer and more habitable.

The total effect upon the stable earth systems and the cycles upon which life depends would be extreme, unprecedented in rapidity, but difficult to speculate about because of lack of knowledge concerning the complex interrelationships.

Conclusions

These alternative projections to the year 2020 and beyond could be reasonably accurate if preliminary research findings prove to be a firm estimate of the rate of absorption of CO₂ by the oceans and the amount of heat trapped by CO₂ and water vapor in the atmosphere. If they prove to be substantially correct, whenever the optimum CO₂ level (from the standpoint of human welfare) over the centuries is reached (if it has not already been reached), additional CO₂ input through the burning of fossil fuels should cease. Other energy sources should be substituted. In fact, atmospheric CO₂ could prove to have such an effect upon the environment that it will be a major limiting factor for several centuries upon both industrial development and world population.

The carbon cycle probably is the most sensitive of the fundamental systems that control life on earth. Changes in the carbon cycle cause compensating changes in the hydrologic cycle, the nitrogen cycle, and the oxygen cycle. Through rapid exploitation of fossil fuels, mankind is inadvertently triggering major changes in the carbon cycle unprecedented in rapidity in known geologic history.

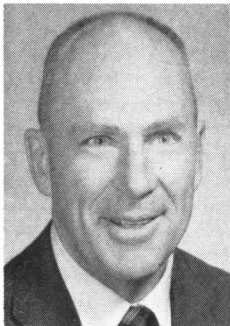
These changes may drastically affect world weather and global ecology within the next 30-80 years. We should avoid being misled because such other factors as dust, sun spots, or changes in local weather patterns may temporarily offset the long term, and perhaps irreversible, effects of CO₂.

A full-fledged research program to determine with certainty the long-term effects of atmospheric CO₂ is essential to mankind's future welfare. The U.S., as the leading consumer of fossil fuels, should shoulder a major share of the effort. The mineral fuels industry and natural resource oriented foundations should be major participants.

More scientists and interested individuals in environmental ecology and atmospheric sciences, and the related sciences of oceanography, geology, physics, plant physiology, forestry, agriculture, economics, demography, and land and water resources planning should become more fully aware of the interrelated basic principles and the consequences of the rising CO₂ content of the atmosphere and add to the available knowledge where possible. Also essential is machinery to gain worldwide acceptance of the facts revealed by research and worldwide intergovernmental action to achieve the desired results.

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Compact unit offers equivalent of secondary treatment, at lower costs than conventional processes

Ditches provide efficient treatment

West Virginia, like many other states, has a large number of small communities that have little or no facilities for treating municipal wastes. Most have declining population under 5000, have little or no industrial base, and are economically depressed. These communities are competing for industrial investment, and often are thwarted in their efforts by a lack of such community facilities as satisfactory waste treatment. A municipal waste treatment plant is actually an investment in the future. In addition, the increased national need for high quality water and the adoption of the Water Pollution Control Act of 1965 have made waste treatment a more urgent consideration for many communities throughout the nation.

Conventional treatment methods—involving a number of steps such as grit removal, sedimentation, aeration, biological treatment, digestion, and chlorination—result in high per capita construction costs for small communities. Where land costs are not prohibitive, oxidation ponds or sewage lagoons provide adequate treatment at lower costs, but in mountainous regions, large land areas required for oxidation ponds are nonexistent. Oxidation ditches do not require large land areas, and may be constructed at a cost intermediate to lagoons or ponds and conventional processes.

We have recently evaluated an oxidation ditch built at Cameron (W.Va.) for construction and operating costs, chemical and bacteriological effectiveness, and other factors pertinent to the treatment of municipal wastes.

Design criteria

When the oxidation ditch was first proposed for Cameron in 1962, the West Virginia State Health Department had no guidelines or regulations covering this method of waste treatment.

Consulting engineers for the city proposed a design which was subsequently approved by both the West Virginia State Health Department and the city government. The plant was constructed and, after correcting some minor problems, placed in operation in Sept. 1965.

Design of the oxidation ditch was based on published criteria and information from Lakeside Engineering Corp. (Chicago, Ill.). Design engineers for the project were A. R. Todd and Assoc.—now Cerrone and Vaughn—Wheeling, (W.Va.). Briefly, the design was based on a population of 2400 (present population of Cameron is 1652) and an average flow of 240,000 gallons per day (g.p.d.). The five day, 20° C. biological oxygen demand (BOD) of 435 pounds per day allows for 0.17 pound per capita per day and 27 pounds per day for a small dairy plant at Cameron.

The oxidation ditch volume—32,200 cubic feet—is based on 74 cubic feet per pound of BOD load. The rotor length required for entraining 2.32 pounds of oxygen for each pound of BOD, at an oxygen transfer rate of 2.83 pounds per hour per foot of rotor length, was 14.88 feet. However, the length of rotor needed to maintain a ditch velocity of one foot per second is 15.1 feet, so two 8 foot rotors were used. These computations were based on a 27½ inch diameter cage rotor at 75 revolutions per minute, at a 6 inch immersion depth.

With the water surface width of the ditch fixed at 16 feet, a design depth of 4 feet, a bottom width of 9 feet, and a 7:8 slope on the ditch bank, the required ditch length was 620 feet along the center line. The final settling tank was designed for an overflow rate of 600 gallons per square foot per day and a three hour detention time. The sludge drying bed was de-

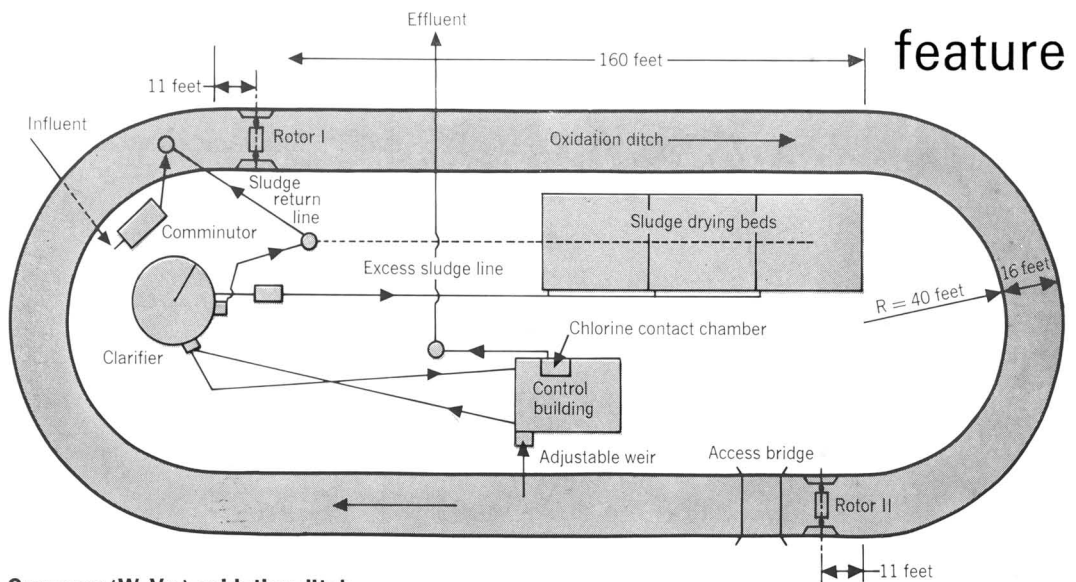
signed for 1.0 square foot per population equivalent, or 2560 square feet.

The design also provides for a comminutor, chlorine contact chamber, a small laboratory, recirculating pumps, chlorinator, and miscellaneous items. A pump station and grit removal equipment some distance from the treatment plant also were installed.

The sequence of flow through the treatment plant begins with the comminutor and bar screen, which receive the sewage from the pumping station. From the comminutor, the sewage enters the ditch just upstream from one of the two cage rotors. It circulates around the ditch at about one foot per second. The average detention time in the ditch is 24 hours, at the design flow. Half way around the ditch a submerged line picks up the liquid, carries it to an adjustable weir; the liquid flows over the weir and into a sump to be pumped to the clarifier. This weir can be used to control depth of flow in the ditch. From the clarifier, the effluent flows to the chlorine contact chamber and on to the receiving stream. A bypass is provided around the chlorine contact chamber and the ditch itself, for emergency purposes. The sludge from the clarifier is either returned to the ditch or wasted to the sludge drying beds.

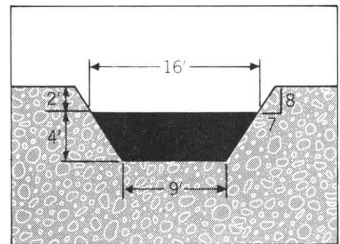
Treatment evaluation

From Sept. 1965-Aug. 1967, we sampled the influent sewage, ditch contents, and the treatment plant effluent to evaluate the efficiency of the unit. We found that flow was a major factor affecting the operation of the plant. Average daily flow varied in 1966 from 69,400 g.p.d.-438,000 g.p.d. One reason for the wide variation is that a portion of the Cameron sanitary sewage collection system is combined with storm sewers. During the first year's operation, breaks in an interceptor line



Cameron (W. Va.) oxidation ditch

Efficiency. Compactness of oxidation ditches make them efficient units for communities with small populations.



laid in the bed of a stream occurred and were repaired. Since periods of low flow at the plant occur only when the stream with the interceptor sewer is dry, we suspect that there is still some infiltration into the interceptor sewer.

Removal of both suspended solids and BOD were quite high during the low flow period of September and October. The range of BOD removal was 86-98%, and removal of suspended solids varied much the same as total suspended solids, and ranged from 49-97%. The volatile portion of total suspended solids was fairly constant for both influent and effluent solids. Consequently, removal of suspended volatile solids varied much the same as total suspended solids, and ranged from 19-97%.

One of the rotors was inoperative during April, and there was deposition of solids due to the reduction in velocity. In May, when the rotor was placed back in operation, the solids were washed out of the system, and overall removal of total and volatile suspended solids was considerably reduced. In the conventional activated sludge process, reduction of suspended solids and BOD ranges from 85-95% and 80-95%, respectively.

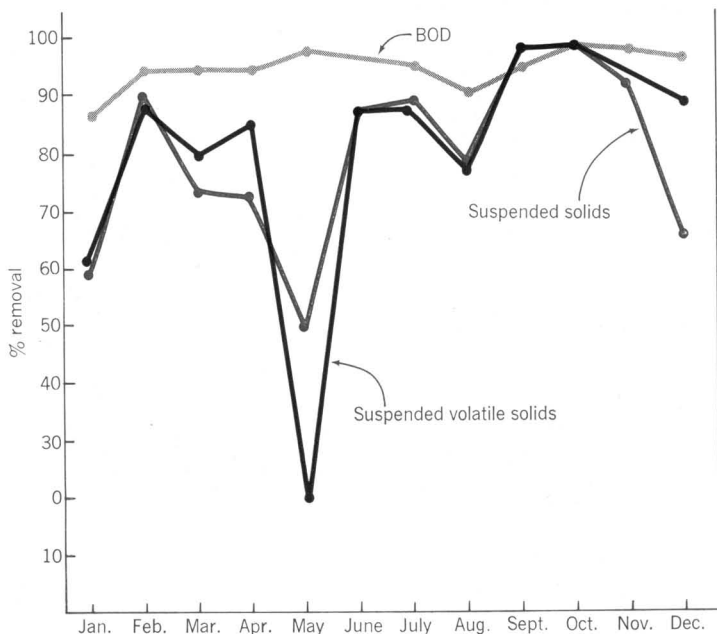
Sludge was not removed during the study period. Solids were allowed to accumulate in the ditch in order to build up the mixed liquor suspended solids (MLSS) and evaluate treatment at high solids loadings. A maximum monthly average of 9941 mg./l. MLSS occurred in October, concurrent with maximum BOD and suspended solids removal. Sludge accumulated in the ditch when flow rates were below the design value and solids concentration dropped sharply with increased flow, apparently a result of wash out. A large sedimentation basin would have retained much of the sludge that was lost during the six months of the year when flow through the plant was greater than the design flow.

F. Cavallos collected data on coliform removal during the 1966-67 study period. The samples for the coliform studies were taken from the effluent line just prior to the addition of chlorine; chlorination effectively reduced the coliform count to near zero. The presence of coliforms prior to chlorination points out the desirability of including disinfection in the operation of the oxidation ditch, especially when the receiving stream may not have

natural flow during a portion of the year.

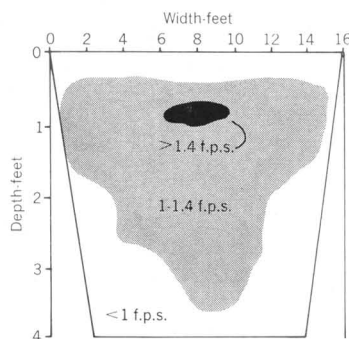
A number of other environmental and operational factors were evaluated. The pH was consistently near 7.0, and ranged between 7.0-7.6 for influent, ditch contents, and effluent. Dissolved oxygen, while often zero in the influent, ranged from 5.2-9.0 mg./l. for ditch contents with consistently similar values for the effluent. There was normally about a 74% reduction in alkyl-benzene sulfonate (ABS) content with a range of effluent concentration of 0.14-0.30 mg./l. The degree of nitrification was high; only at low flow did the ammonia nitrogen concentration reach 13.0 mg./l. and in the effluent ranged between 6.7-47 mg./l. In general, there was some reduction in phosphate through the plant, although this was highly variable. In one month, the average effluent concentration was greater than that of the influent samples, thus indicating a release of phosphates. Phosphate concentrations in the effluent ranged from 3.0-20 mg./l.

The rotors were not housed, and while ice built up around the rotors in winter, it did not interfere with



Removal of solids and BOD

Velocity distribution in a typical cross section



operation. Temperature of the ditch contents ranged from 4°-22.2° C.

Velocity studies

H. T. Shih made a velocity distribution study of the ditch to estimate if the critical velocity for keeping organic solids in suspension was maintained. Theoretically, for organic particles with a specific gravity of 1.008, a critical velocity of 0.136 feet per second (f.p.s.) is needed. But since such particles vary in size and specific gravity, Shih assumed that the ditch velocity should be near 1.0 f.p.s.

To study the actual velocities, a series of cross sections was laid out and vertical velocity gradients were measured at 2 foot intervals along the inside edge of the 16 foot ditch. Velocities were measured for each point at the surface and at various depths.

Most of the measurements were made with the rotor operating at its design immersion of 6 inches, but measurements also were made at immersions of 4 inches and 8½ inches, and with only one rotor operating.

With the rotor at the normal operating depth of 6 inches, the velocity distribution was largely between 1.0-1.5 f.p.s., except at the surface and in the bottom 20% of the ditch depth. When compared with the calculated critical velocity 0.136 f.p.s., this seems more than adequate to keep organic solids in suspension. However, some bottom deposits were found; also, at the ends of the ditch, velocity increased

at the inner bank due to centrifugal forces and transverse currents which were generated within the curving flow.

Rotor immersion depth was the most important factor affecting the velocity distribution—at deeper immersion the velocity increased. Since an increase or decrease in immersion caused extremes in velocity, the 6 inch immersion was more desirable.

With only one rotor operating, there were extreme variations in velocity, especially at sections farther removed from the operating rotor. Greater vertical variation occurred at any particular section, and as the overall velocity in the ditch became less, the possibility of solids deposition was more likely. Under these conditions, sludge was observed to accumulate.

Capital cost studies

It should be remembered that the oxidation ditch provides the equivalent of secondary treatment, since efficiency of BOD removal is generally above 90%. In order to determine whether the oxidation ditch was an economical method for secondary treatment, R. W. Wheeler made a capital cost study. He sent a questionnaire to all known consulting engineers who had designed oxidation ditches, and converted the cost data to cost per population equivalent. Regression analysis was used to determine the best linear fit, and the data further adjusted for plant location and Apr. 1966 cost levels.

The regression analysis indicated

that the capital costs per 1000 population equivalent for oxidation ditches ranged between \$29-68. Average cost was \$45 per capita, based on the national cost index for Apr. 1966. The costs increase with a decrease in population. A study of activated sludge plant costs, adjusted to the same date, give a range of \$50-114 per capita at the 1000 population equivalent level, with an average of \$76.

Construction costs per gallon of flow for oxidation ditches range from \$0.35 for a population equivalent of 5,000 to \$0.83 for a population equivalent of 250. This compares with \$0.53-2.37 per gallon of flow, at the same population equivalents, for extended aeration package treatment plants.

Operating costs

The operating costs of the Cameron treatment plant include operator salaries, power costs, treatment chemicals, and miscellaneous items such as repairs, soap and towels, gasoline for the power mower, and other incidentals. Power measurements were made on all sewage pumps, the comminutor, the chlorine water and sludge pump, and all auxiliaries. Unit annual operating cost was \$104.50 per million gallons of raw sewage treated. This may also be expressed as \$5.48 per capita per year based on actual population (\$3.35 based on design population).

Compared with the operating costs of two extended aeration plants and two contact stabilization plants in

Ohio, the operating costs of the oxidation ditch represented a savings of 46.6% and 71.8%, respectively.

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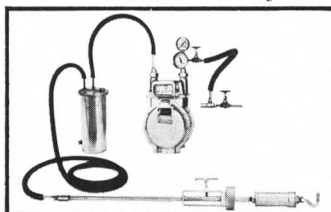
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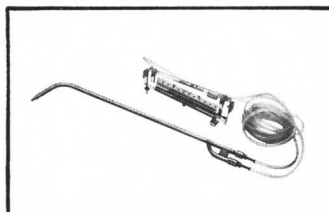
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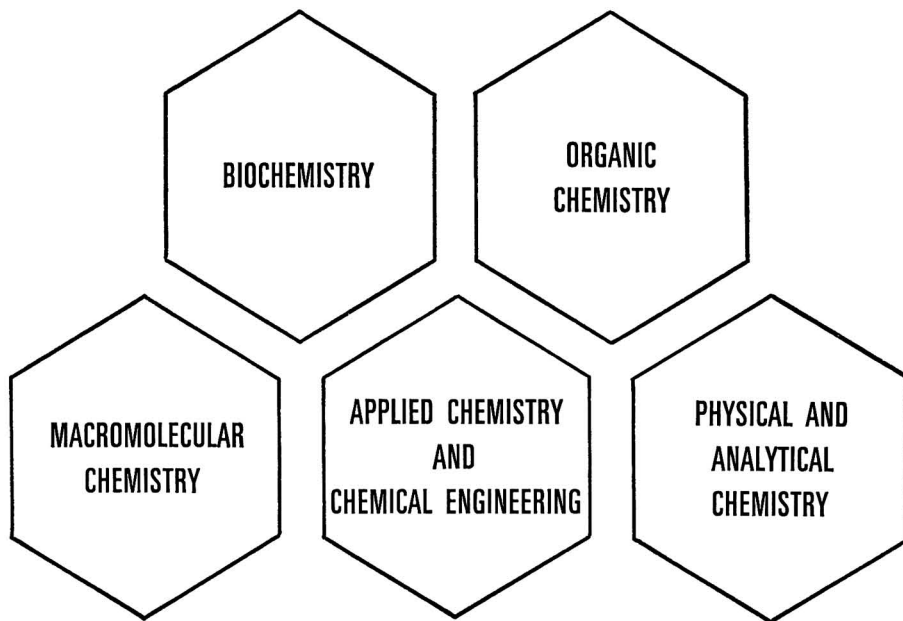
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A Dynamic Model of Photochemical Smog

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■ A simplified kinetic scheme is proposed as a model for the photochemical smog reactions. Calculations based on the model lead to concentration dependences on time, similar in form to the experimental results for laboratory reaction chambers. To take into account the effect of atmospheric mixing processes on the chemical reactions, the Lagrangian similarity hypothesis for the diffusion of nonreactive components is extended to reacting species. This leads to a set of ordinary differential equations for the reactive species, of the type describing a chemical reactor of variable volume. As a preliminary example of the application of the model, a calculation is made for a single bimolecular reaction.

The United States is currently being divided into about 100 air quality control regions, each one incorporating two or more communities having a common air pollution problem. These regions will have the responsibility for the development of local air quality standards. A major emphasis will be placed on diffusion modeling in the delineation of the regions (Sec'y., HEW, 1968); forecasting the effects of variations in the strength and location of pollutant sources will also depend on the existence of reliable methods for predicting the spread and behavior of pollutant clouds.

The object of this paper is to formulate a general dynamic model for photochemical smog. Unlike previous diffusion models, which have been concerned almost exclusively with nonreacting pollutants, the formulation of the model takes into account both the chemical reaction and turbulent mixing aspects of the photochemical smog problem. The need for such a model has been pointed out by Hilst (1967). The considerable quantities of source inventory information and pollutant concentration data currently being gathered in many urban areas makes the validation of a model a practical possibility. In addition, the factors which most heavily influence smog formation can be determined by a sensitivity analysis of the model. Finally, a model will enable one to pose and answer questions relating to the control of smog formation.

In the first part of the paper, a simplified kinetic mechanism is presented for the formation of photochemical smog from NO and unburned hydrocarbons. In the second part, diffusion models based on the general equation of conservation of species are discussed. The dynamic model is a combination of the transport and chemical kinetic equations, and predicts the behavior of a reacting pollutant cloud. The roles of oxides of sulfur and aerosols are not considered in the present study.

Photochemical Reactions in the Urban Atmosphere

Photochemical smog is produced by reactions involving NO and unburned hydrocarbons, introduced into the atmosphere in automobile emissions. The smog formation process is characterized by the oxidation of NO to NO₂, the oxidation of unsaturated and aromatic hydrocarbons to aldehydes and ketones, and the formation of O₃ and peroxyacyl nitrates (PAN's). Considerable progress has been made in recent years towards understanding the principal reactions in smog formation (Leighton, 1961; Wayne, 1962; Altshuller and Bufalini, 1965; Stephens, 1966, 1969; Haagen-Smit and Wayne, 1967).

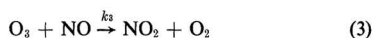
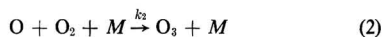
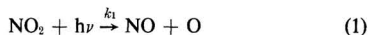
In developing a chemical reaction scheme which can be combined with a diffusion model to simulate atmospheric processes, the following points should be kept in mind. The details of the hydrocarbon oxidation process are not known, even for the relatively well defined laboratory systems which have been studied. The complexity of the chemical mixtures present in urban air makes a detailed understanding of the atmospheric processes very difficult. Moreover, the theory of turbulent diffusion with simultaneous chemical reaction is not well understood for homogeneous turbulence, much less for multicomponent reactions in the atmosphere. Finally, the role of the smog aerosol particles in the chemical reaction processes and as condensation centers is not known. For these reasons, it will be useful to begin with a simplified kinetic model which, while not involving a large number of chemical species whose concentrations cannot be measured, permits simulation of the behavior of an irradiated mixture of automobile exhaust.

The study of reaction mechanisms for smog formation should include the following steps. First, the compilation of published mechanisms for the photochemical smog reactions and integration of the rate equations for a constant volume batch reactor to produce curves of concentration *vs.* time for the key constituents; second, the compilation of published experimental data on the irradiation of mixtures typical of automobile exhaust and air, and comparison of the results generated in the first step with the experimental observations; and third, the derivation of new kinetic models to incorporate effects or information which might be lacking in current proposed mechanisms. Following this procedure, a simplified kinetic mechanism for the smog formation process has been developed which possesses the features common to most mechanisms currently proposed.

Simplified Kinetic Model

It has been established that absorption by NO₂ of the ultraviolet portions of sunlight (3000–4000Å) results in the follow-

ing set of reactions in air (Ford and Endow, 1957; Blacet, Hall, and Leighton, 1962; Pitts, Sharp, and Chan, 1964; Stephens, 1966):

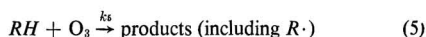
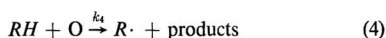


where $k_1 = \Phi k_a$, with k_a the rate of absorption of ultraviolet by NO_2 (per unit of NO_2 concentration), Φ the ratio of molecules dissociating to molecules absorbing (the quantum yield), and M a third body.

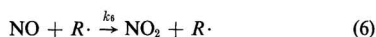
When a reactive hydrocarbon is added to the system, many additional reactions take place producing such characteristic products as formaldehyde, acetaldehyde, acrolein, PAN, and alkyl nitrites. Olefins and aromatics are most reactive, but saturates (paraffins and naphthenes), although less reactive than either unsaturates or aromatics, may also play a significant role. It is generally agreed that hydrocarbon oxidation plays a key role in the conversion of NO to NO_2 . However, current mechanisms advanced to explain the conversion of NO to NO_2 in the presence of hydrocarbons predict rates of hydrocarbon consumption two to ten times less than observed (Schuck, Doyle, and Endow, 1960; Leighton, 1961, p. 264).

A number of detailed mechanisms have been suggested for the hydrocarbon photooxidation process (Haagen-Smit and Wayne, 1967). While all are considered highly speculative, they have in common a chain-like behavior:

(1) In the initiation step, hydrocarbon molecules react with atomic oxygen to give oxygen-containing free radicals and other products. In later stages, hydrocarbons also react with ozone to give a variety of products. If we represent any free radical species by $R\cdot$, then these two reactions can be written:



(2) The propagation and branching steps which follow may or may not involve the nitrogen oxides:

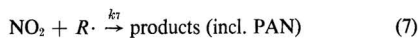


where a reaction of this type occurs for many different radical species $R\cdot$ with different values of k_6 . $R\cdot$ indicates that another free radical species is a product of the reaction.

(3) The radicals are lost by chain terminating steps. As suggested by Haagen-Smit and Wayne, these may be of three main types:

(a) Reaction of two free radicals (unlikely at atmospheric concentrations)

(b) The reaction of a free radical with NO or NO_2 . In the latter case, one product is PAN



(c) The collision of a radical with the surface of a particle (which may contribute to particle growth).

The rate constants k_4 , k_5 , k_6 , and k_7 depend on the particular hydrocarbon species present. The proposed kinetic model consists of reactions 1-7. Summarizing, the following assumptions have been made in this mechanism:

1. The principal initiation step is reaction 4.

2. Reaction 6 embodies all the propagation steps. (Actually considerable branching, which is not represented in reaction 6, takes place. This will be accounted for shortly.)

3. The principal termination step is reaction 7.

If it is assumed that O and O_3 are in a pseudo-steady state (Stephens, 1966):

$$[\text{O}] = \frac{k_1[\text{NO}_2]}{k_2 + k_4[\text{RH}]} \quad (8)$$

$$[\text{O}_3] = \frac{k_2[\text{O}]}{k_3[\text{NO}] + k_4[\text{RH}]} \quad (9)$$

From the orders of magnitude of k_2 , k_3 , k_4 , k_5 , one can make the further assumptions that

$$k_2 \gg k_4[\text{RH}]$$

$$k_3[\text{NO}] \gg k_5[\text{RH}]$$

Then,

$$[\text{O}] = \frac{k_1}{k_2}[\text{NO}_2] = \gamma[\text{NO}_2] \quad (10)$$

$$[\text{O}_3] = \frac{k_1[\text{NO}_2]}{k_3[\text{NO}]} = \beta \frac{[\text{NO}_2]}{[\text{NO}]} \quad (11)$$

A consequence of assumptions 4 and 5 is that $r_1 = r_2 = r_3$, the usual pseudo-steady state attained among NO_2 , NO , O_3 , and O in the absence of organic vapors. If we assume, in addition, that all the free radicals are in a pseudo-steady state, then

$$k_4[\text{O}][\text{RH}] + \epsilon k_6[R\cdot][\text{NO}] = k_6[R\cdot][\text{NO}] + k_7[\text{NO}_2][R\cdot]$$

where ϵ is the number of free radicals generated as a result of propagation and branching in reaction 6. This yields

$$[R\cdot] = \frac{k_4[\text{O}][\text{RH}]}{k_7[\text{NO}_2] - (\epsilon - 1)k_6[\text{NO}]} \quad (12)$$

Finally, if it is assumed that:

$k_4/(k_7[\text{NO}_2] - (\epsilon - 1)k_6[\text{NO}])$ is approximately constant, the free radical concentration is

$$[R\cdot] = k_4'[\text{RH}][\text{O}] \quad (13)$$

The rate equations are then

$$\frac{d[\text{NO}_2]}{dt} = r_6 - r_7 \quad (14)$$

$$\frac{d[\text{NO}]}{dt} = -r_6 \quad (15)$$

$$\frac{d[\text{RH}]}{dt} = -r_4 - r_5 \quad (16)$$

which, in terms of $[\text{NO}_2]$, $[\text{NO}]$, and $[\text{RH}]$ become

$$\frac{d[\text{NO}_2]}{dt} = [\text{NO}_2][\text{RH}] \{ \alpha [\text{NO}] - \lambda [\text{NO}_2] \} \quad (17)$$

$$\frac{d[\text{NO}]}{dt} = -\alpha [\text{NO}_2][\text{NO}][\text{RH}] \quad (18)$$

$$\frac{d[\text{RH}]}{dt} = -[\text{NO}_2][\text{RH}] \{ \theta + \mu/[\text{NO}] \} \quad (19)$$

where

$$\alpha = \gamma k_6 k_4' \quad (20)$$

$$\lambda = \gamma k_7 k_4' \quad (21)$$

$$\theta = \gamma k_4 \quad (22)$$

$$\mu = \beta k_5 \quad (23)$$

With specific initial concentrations, Eqs. 17-19 can be

integrated numerically, to give the results shown in Figures 1 and 2. The parameter values $\alpha = 0.1 \text{ p.p.m.}^{-2} \text{ min.}^{-1}$, $\theta = 1.83 \times 10^{-3} \text{ p.p.m.}^{-1} \text{ min.}^{-1}$, $\mu = 2.45 \times 10^{-4} \text{ min.}^{-1}$ and $\lambda = 0.02 \text{ p.p.m.}^{-2} \text{ min.}^{-1}$ were used. These were based on rate coefficients given by Leighton (1961), but were adjusted to simulate the experimental observations. Figure 1 represents the dynamics for $[\text{NO}_2]_0 = 0.2 \text{ p.p.m.}$, $[\text{NO}]_0 = 1.0 \text{ p.p.m.}$, and $[\text{RH}]_0 = 2.0 \text{ p.p.m.}$ Figure 2 represents the case of $[\text{NO}_2]_0 = 0.2 \text{ p.p.m.}$, $[\text{NO}]_0 = 0.68 \text{ p.p.m.}$ and $[\text{RH}]_0 = 1.15 \text{ p.p.m.}$ The shapes of the curves are in general agreement with those found in irradiation chamber experiments.

General Equation of Diffusion and Chemical Reaction

The calculations of the previous section apply to a constant volume, batch chemical reactor. In the formation of smog over an urban basin area, the transport and reaction of the gaseous pollutants are further influenced by the rate of introduction of each species into the atmosphere, the locations of the sources of pollution in the city, the wind speed and turbulent mixing, and the temperature and intensity of the solar radiation. The spatial and time history of all chemical contaminants could, in principle, be obtained by solving the equation of conservation of mass for each species

$$\frac{\partial c_i}{\partial t} + \vec{u} \cdot \nabla c_i = \nabla \cdot D_i \nabla c_i + r_i \quad (i = 1, 2, \dots, n) \quad (24)$$

where c_i = concentration of species i , \vec{u} = wind velocity vector, D_i = molecular diffusivity for species i in the atmosphere, and r_i = rate of generation of species i by homogeneous chemical reaction. (Molecular diffusion cross coefficients have been neglected.)

In the case of a turbulent flow with a surface source whose strength is a function only of time and distance in the wind direction, x , these equations become

$$\frac{\partial C_i}{\partial t} + \bar{u}(z) \frac{\partial C_i}{\partial x} = \frac{\partial}{\partial z} \left[\epsilon_z \frac{\partial C_i}{\partial z} \right] + \bar{r}_i \quad (25)$$

with the usual simplifying assumptions, including the neglect of diffusion in the wind direction compared with convective transport (Sutton, 1953). Atmospheric transport models have generally been concerned with inert species (such as CO) for which $r_i = 0$. Solutions based on different assumptions concerning the wind speed and eddy diffusivity are reviewed by Sutton.

The solution of even a moderate number of simultaneous, nonlinear, partial differential equations of the type Eq. 24 or 25 represents a formidable task for even the largest of modern computers, if, indeed, a solution can be obtained at all. It is thus desirable to simplify the problem, taking care to retain the essential aspects of the physical situation. These simplifying considerations fall into two categories: First, the identification of the principal reacting species from among the large number of reactants, intermediates, and products actually present (this has already been done in a previous section); second, the identification of meteorological situations in which the general conservation equation can be simplified. This can be done as follows:

Consider the case of an instantaneous point source at height h above ground level, from which a particle of contaminant is released into the turbulent atmospheric surface layer. If the experiment is repeated many times, the mean position of the particle at any time t is $\bar{x}(t)$, $\bar{y}(t) = 0$, $\bar{z}(t)$ where $\bar{x}(t)$ is measured in the direction downwind from the source and $\bar{z}(t)$ is the height above ground level. According to the Lagrangian

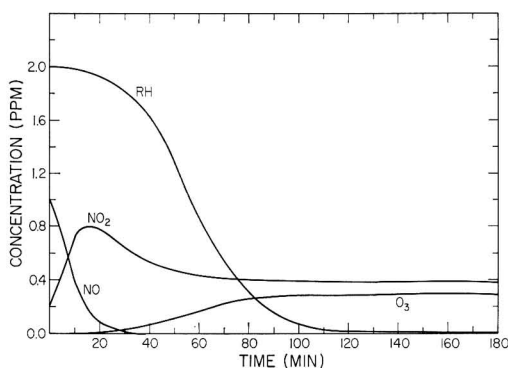


Figure 1. Pollutant concentrations vs. time, based on simplified kinetic model for photochemical smog reactions—constant volume batch reactor. $C_{\text{NO}_2}(0) = 0.2$, $C_{\text{NO}}(0) = 1.0$, $C_{\text{RH}}(0) = 2.0 \text{ p.p.m.}$

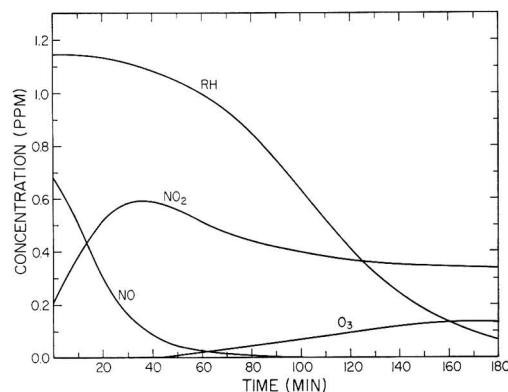


Figure 2. Pollutant concentrations vs. time, based on simplified kinetic model for photochemical smog reactions—constant volume batch reactor. $C_{\text{NO}_2}(0) = 0.2$, $C_{\text{NO}}(0) = 0.68$, $C_{\text{RH}}(0) = 1.15 \text{ p.p.m.}$

similarity hypothesis (Batchelor, 1964; Gifford, 1962; Cermak, 1963), the average concentration at any point in the cloud is given by the relation

$$C_i = \frac{Q_i}{\bar{z}^3} \Psi \left(\frac{x - \bar{x}}{\bar{z}}, \frac{y}{\bar{z}}, \frac{z - \bar{z}}{\bar{z}} \right) = \frac{Q_i}{\bar{z}^3} \Psi(\eta_x, \eta_y, \eta_z) \quad (26)$$

where Q_i is the strength of the instantaneous point source. The relation is expected to hold for t of order h/u_* or greater where u_* is the friction velocity.

Let us assume that the same form can be used in the case of a reacting pollutant but with Q a function of time. This assumption appears reasonable if the chemical reaction processes are slow compared with the mixing processes, so that Q is a slowly varying function of time. A more quantitative criterion can be obtained by an examination of the equation of conservation of species:

$$\frac{\partial C_i}{\partial t} + \vec{u}_R \cdot \nabla C_i = - \nabla \cdot \overline{c_i' \vec{u}'} + \bar{r}_i \quad (27)$$

where the velocity \vec{u}_R is measured relative to the velocity of the average cloud position, and all distances are measured relative to cloud center. Now the following similarity forms are assumed:

$$\vec{u}_R = \frac{d\bar{z}}{dt} \vec{F}(\eta_x, \eta_y, \eta_z)$$

$$\overline{c_i' u_i'} = C_i \frac{d\bar{z}}{dt} \bar{G}_i(\eta_x, \eta_y, \eta_z) \quad (28)$$

$$\bar{r}_i = \frac{1}{\bar{z}^3} \frac{dQ_i}{dt} f_i(\eta_x, \eta_y, \eta_z, t)$$

The function f_i depends not only on η_x, η_y, η_z but also on the time. Substitution in Eq. 27 gives

$$\frac{1}{\bar{z}} \frac{dQ_i}{dt} (\Psi - f_i) - 3\Psi - \bar{\eta} \cdot \nabla_{\bar{\eta}} \Psi + \bar{F} \cdot \nabla_{\bar{\eta}} \Psi + \nabla_{\bar{\eta}} \cdot \bar{G} = 0 \quad (29)$$

Approximate similarity exists if

$$\left| \frac{\frac{1}{\bar{z}} \frac{dQ_i}{dt}}{\frac{1}{\bar{z}} \frac{d\bar{z}}{dt}} \right| \ll 1 \quad (30)$$

and the functions dependent on η_x, η_y, η_z are of order unity. Eq. 30 shows that, for the similarity solution to apply, the fractional rate of change of material in the cloud due to chemical reaction must be small compared with the fractional rate of expansion of the cloud. There may be other circumstances under which the similarity hypothesis applies to reacting systems; at this time it can be considered as an *ad hoc* assumption to be tested further theoretically and experimentally.

The Variable Volume Batch Reactor (VVBR)

The similarity form for C_i must also be consistent with the integral relations

$$\frac{dQ_i}{dt} = \iiint \bar{r}_i dx dy dz \quad (31)$$

The generation rate for component i can be written in terms of the chemical reaction rates for the p reactions involving i as follows:

$$r_i = \sum_{j=1}^p \nu_{ij} J_j \quad (32)$$

where J_j is the rate of the j th reaction and ν_{ij} is the stoichiometric coefficient for component i in the j th reaction. Chemical reaction rates can often be expressed in the form

$$J_i = k_i \prod_{j=1}^n C_j^{\alpha_{ij}} \quad (33)$$

where α_{ij} is the order of reaction of species j in the i th chemical reaction. This applies, for example, to the reaction scheme given by Eqs. 17 through 19. Substituting Eqs. 32 and 33 in Eq. 31, and neglecting the fluctuating reaction terms in comparison with the mean terms gives:

$$\frac{1}{\bar{z}^3} \frac{dQ_i}{dt} = \sum_j \nu_{ij} A_j k_j \prod_k \left[\frac{Q_k}{\bar{z}^3} \right]^{\alpha_{jk}} \quad (34)$$

where the constants A_i are given by

$$A_i = \iiint \prod_{j=1}^n \Psi^{\alpha_{ij}} d\eta_x d\eta_y d\eta_z \quad (35)$$

Hence the similarity form is consistent with Eq. 31 and chemical reaction rates of the form Eq. 33.

In this way the diffusion and chemical reaction effects are

partially uncoupled. The set of nonlinear, coupled, second order partial differential equations (Eq. 25) has been reduced to a set of nonlinear, coupled, first order ordinary differential equations suitable for numerical computations. Eq. 34 corresponds to the kinetic expression for a variable volume batch reactor (VVBR) and is related to chemical reactor models often studied in chemical engineering (Denbigh, 1965). The term Q_i/\bar{z}^3 is equivalent to the concentration of component i in the reactor and \bar{z}^3 to the reactor volume.

The diffusional aspect of the problem appears in the rate at which the reactor volume expands with time; *i.e.*, the dependence of \bar{z}^3 on t . This is the information necessary to find Q_i as a function of time. In the general case, for both neutral and diabatic surface layers, Gifford (1962) has proposed the following relation for the average vertical velocity

$$\frac{d\bar{z}}{dt} = bu_* \phi(\zeta) \quad (36)$$

where $\zeta = \bar{z}/L$ and the function $\phi(\zeta)$ has been tabulated. The Monin-Obukhov length, L , is given by

$$L = \frac{-u_*^3}{k(g/T)(q/\rho C_p)}$$

where k is von Karman's constant, g the acceleration of gravity, T the average absolute temperature, q the heat flux in the z direction, ρ the air density, and C_p the specific heat at constant pressure. L is positive under stable conditions (q negative) and infinite under adiabatic conditions ($q = 0$).

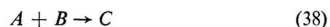
The concentration at ground level is given by the relation

$$C_{20} = \frac{Q_i \Psi(0, 0, -1)}{\bar{z}^3} = \frac{aQ_i}{\bar{z}^3} \quad (37)$$

Since \bar{z} , the mean position of the cloud above ground, increases monotonically with time as the cloud expands, the concentration at ground level of a nonreacting species decreases continuously as the cloud expands. For a species generated by a chemical reaction, such as NO_2 or O_3 in the case of photochemical smog, Q increases with time for at least some portion of the cloud trajectory. In this case, a maximum in ground level concentration can be expected.

Application to a Bimolecular Reaction

As an example, it is instructive to consider a single irreversible bimolecular reaction



since an analytical solution can be obtained by means of the similarity hypothesis. Eq. 34 takes the form

$$\frac{dQ_c}{dt} = \frac{Ak}{\bar{z}^3} (Q_{bo} - Q_c)(Q_{ao} - Q_c) \quad (39)$$

Substituting Eq. 35 gives

$$\zeta^3 \phi(\zeta) \frac{d(Q_c/Q_{ao})}{d\zeta} = \frac{AkQ_{ao}}{bu_* L^2} \left(\sigma - \frac{Q_c}{Q_{ao}} \right) \left(1 - \frac{Q_c}{Q_{ao}} \right) \quad (40)$$

where $\sigma = Q_{bo}/Q_{ao}$.

The amount of product appearing at any location corresponding to ζ downwind thus depends on the ratio of reactants released, Q_{bo}/Q_{ao} and on the Damkohler number $\tau_{MECH}/\tau_{CHEM} = (L/uu_*)/(L^3/kQ_{ao}) = kQ_{ao}/uu_* L^2$. The Damkohler parameter includes the effects of the following meteorological variables:

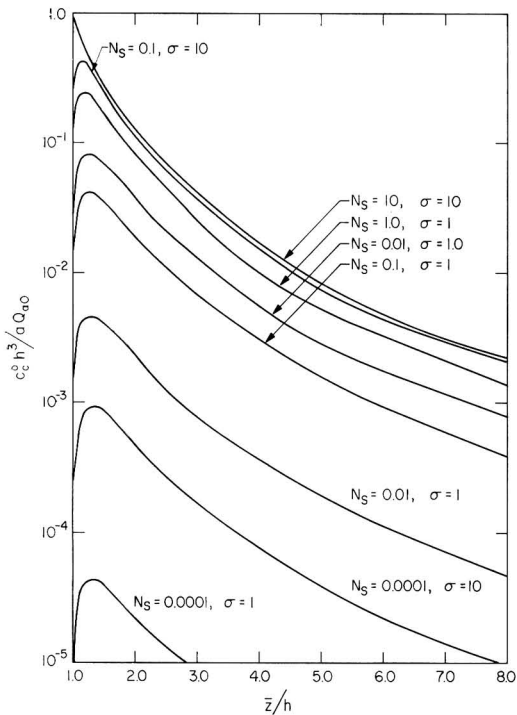


Figure 3. Dimensionless ground level concentration as a function of the mean position of the cloud above ground level

(1) solar radiation and temperature through k , (2) wind conditions through u_* , and (3) stability through L .

An analytical solution can be obtained for neutral conditions when $\phi(z) = \phi(0) = 1$. The solution which satisfies the initial condition $Q_c = 0$ at $\bar{z} = h$ is

$$Q_c = Q_{ao} \frac{\left\{ 1 - \exp \left[-\frac{A}{2b} N_s (\sigma - 1) (1 - h^2/\bar{z}^2) \right] \right\}}{\left\{ 1 - \frac{1}{\sigma} \exp \left[-\frac{A}{2b} N_s (\sigma - 1) (1 - h^2/\bar{z}^2) \right] \right\}} \quad (41)$$

where

$$N_s = \frac{k Q_{ao}}{u_* h^2} \quad (42)$$

The results of calculations based on Eq. 41 are shown in Figs. 3, 4, and 5. Figure 3 shows that the dimensionless ground level concentration of product reaches a maximum near the source and then rapidly decays. For given values of σ , the ratio of reactant source strengths, highest ground level concentrations are obtained for large values of N_s , corresponding to high chemical reaction rates and low friction velocities.

In Figs. 4 and 5, it is shown that the condition $\left| \frac{1}{Q_t} \frac{dQ_t}{dt} \right| \frac{1}{\bar{z}} \frac{d\bar{z}}{dt} \ll 1$ is best satisfied for large values of \bar{z}/h , consistent with the asymptotic nature of the original similarity hypothesis on which the analysis is based. The ratio $\left| \frac{1}{Q_t} \frac{dQ_t}{dt} \right| \frac{1}{\bar{z}} \frac{d\bar{z}}{dt}$ is greatest near the source and then falls rapidly, since the chemical reaction rates are particularly sensitive to the reactant concentrations.

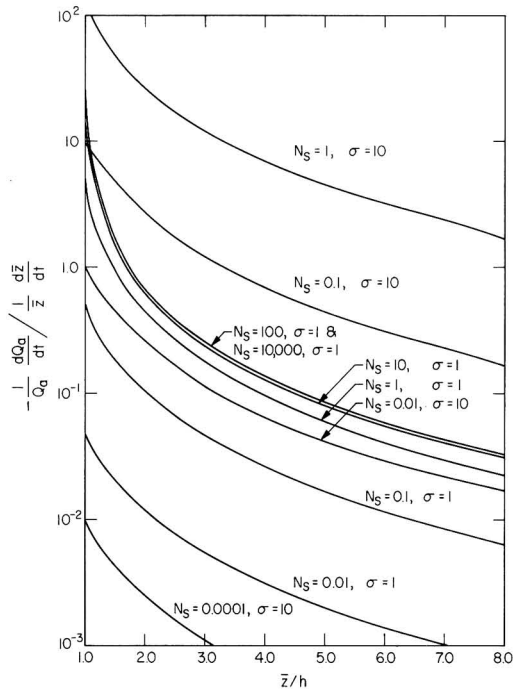


Figure 4. Ratio, fractional rate of change of mass of reactant A to fractional rate of expansion of cloud, as a function of mean position of the cloud above ground level

The total quantity of product generated by the chemical reaction as $z \rightarrow \infty$ can be calculated from Eq. 41 and is:

$$Q_{co} = Q_{ao} \frac{\left\{ 1 - \exp \left[-\frac{A}{2b} N_s (\sigma - 1) \right] \right\}}{\left\{ 1 - \frac{1}{\sigma} \exp \left[-\frac{A}{2b} N_s (\sigma - 1) \right] \right\}} \quad (43)$$

Q_{co} is always less than Q_{ao} , the maximum amount of product which would be produced in a fixed volume batch reactor ($Q_{ao} < Q_{bo}$). The reduction results from the quenching effect of the rapid expansion of the VVBR ($\bar{z}^3 \sim t^3$). This seems an important result: Not only is the concentration of the product of the chemical reaction reduced by the mixing process, but so also is the maximum attainable total quantity of product. The extent of the reduction depends on the dimensionless group N_s : small values of N_s , corresponding to low reaction rates (small k) and large mixing rates (high u_*), lead to small values of Q_{co} .

From this kind of analysis, it is possible to develop simple criteria for atmospheric contaminant levels in a reacting system. For example, if σ^{-1} and $N_s \ll 1$, Eq. (43) can be written approximately as

$$\frac{Q_{co}}{Q_{ao}} = \frac{Ak Q_{bo}}{2bu_* h^2} \quad (44)$$

Now assume that Q_{ao} and Q_{bo} represent the total amounts of pollutants A and B , emitted by a source into an air basin with inversion height H . As the cloud expands to the inversion height, the total amount of product generated, Q_{co} , will be mixed into the volume HS , where S is the effective area covered by the cloud. This leads to the following result for the average concentration of product, Q_{co}/HS , after expansion

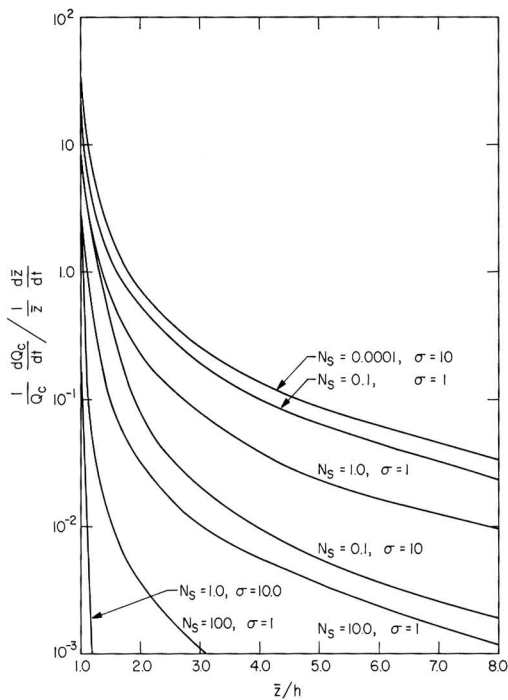


Figure 5. Ratio, fractional rate of change of mass of product C to fractional rate of expansion of cloud, as a function of mean position of the cloud above ground level

sion to the inversion height:

$$\frac{(Q_{co})HSu_*H}{k} = \frac{AQ_{ao}Q_{bo}}{2bh^2S} \quad (45)$$

When pollutant emissions and the effective area covered by the cloud are constant, the right hand side of Eq. 45 is a constant, independent of meteorological conditions. Eq. 45 is then similar in form to a correlation proposed by Schuck, Pitts, and Wan (1966) for oxidant concentration in the Los Angeles basin. The Schuck, *et al.*, expression was empirically derived, based on only two sets of experimental data. The theoretical calculation given above is based on the bimolecular reaction model which is highly oversimplified, so far as smog is concerned. Hence it cannot be claimed that the correlation is well established either on experimental or theoretical grounds. It will be interesting to see whether further studies support this observation.

Application to Smog Control

A more realistic calculation, so far as smog formation is concerned, would incorporate a kinetic model, such as Eqs. 17-19, with the VVBR Eq. 34. In practical application, this model would be employed with a grid of sources of the type described by Frenkiel (1957) for Los Angeles.

The ultimate objective of urban atmosphere modeling is the effective control of pollutant concentrations. In the terminology of control theory, the state of the system is the pollutant concentrations and temperature. The nonmanipulative input variables are sunlight intensity, wind speed and direction, geographical factors, etc. Variables in the system which can be selected to achieve some desired goal are termed the control variables. In this case, the control variables include, for example, traffic flow, the NO/hydrocarbon ratio in auto-

mobile exhaust, new routes for proposed freeways, and rush hour times. Thus, a control policy is likely to be a feedforward control, depending only on the initial state of the system and time. A feedback control would be possible if, for example, automobiles were classified according to their pollutant emissivity and the classes progressively excluded from the traffic system as pollutant concentrations rose.

Once a model has been determined, various control problems can be posed. Typical performance indices might be the integral average pollutant concentrations at a particular location over several hours, or the maximum pollutant concentration during the day. The problem is to determine the control policy that minimizes the performance index.

Nomenclature

- A_i = dimensionless constant defined in Eq. 35
 - a = dimensionless constant defined in Eq. 37
 - b = universal constant defined in Eq. 36
 - c_i = instantaneous concentration of species i
 - C_i = average concentration of species i
 - c_i' = fluctuating concentration of species i
 - C_p = specific heat at constant pressure
 - D_i = molecular diffusivity for species i
 - $\vec{F}(\eta_x, \eta_y, \eta_z)$ = dimensionless velocity defined in Eq. 28
 - $f_i(\eta_x, \eta_y, \eta_z, t)$ = dimensionless reaction rate defined in Eq. 28
 - $\vec{G}(\eta_x, \eta_y, \eta_z)$ = dimensionless function defined in Eq. 28
 - H = inversion height
 - h = source height
 - J_j = rate of j th chemical reaction
 - k = von Karman constant
 - k_i = reaction rate constant
 - L = Monin-Obukhov length
 - M = third body
 - N_s = dimensionless group defined in Eq. 42
 - n = number of chemical species
 - Q_i = moles of species i in cloud
 - q = heat flux in z -direction
 - r_i = generation rate of species i
 - S = effective area covered by the cloud
 - t = time
 - T = average absolute temperature
 - \vec{u} = wind velocity vector
 - \vec{u}' = fluctuating velocity vector
 - u_* = friction velocity
 - \vec{u}_* = velocity vector relative to cloud center
 - x, y, z = coordinate position in atmospheric surface layer
 - $\bar{x}, \bar{y}, \bar{z}$ = coordinate of the average position of the particle in the atmospheric surface layer
- Greek Letters**
- α = parameter defined in Eq. 20
 - α_{ij} = order of reaction of species j in i th chemical reaction
 - ϵ = number of radicals generated per radical consumed
 - ϵ_z = eddy diffusivity of material
 - ζ = z/L
 - η_x, η_y, η_z = dimensionless coordinates defined in Eq. 26
 - θ = parameter defined in Eq. 22
 - λ = parameter defined in Eq. 21
 - μ = parameter defined in Eq. 23
 - ν_{ij} = stoichiometric coefficient of component i in reaction j
 - ρ = air density
 - σ = Q_{bo}/Q_{ao}

τ	= characteristic time
ϕ	= universal function defined in Eq. 36
Φ	= quantum yield
Ψ	= probability density function

Superscript

-	= average value
0	= ground level concentration

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Received for review June 20, 1969. Accepted August 13, 1969. This research was supported in part by PHS Grant AP00580. The figures are based on calculations by Mr. Francis Lai, Research Assistant in Chemical Engineering. Some of the analysis stems from the authors' association with Meteorology Research, Inc., Altadena, Calif. Helpful comments by Dr. E. R. Stephens, University of California Statewide Air Pollution Research Center, are appreciated.

Double Tracer Techniques for Studying Air Pollution

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■ The technique of studying the relative behavior of concentrations of two materials emitted from the same source can yield valuable information concerning the importance of removal factors. For NO_x and CO emitted in automobile exhausts in Los Angeles, there may now exist sufficient data to determine whether NO_x is significantly removed compared to CO (which is thought to be quite well conserved) within the urban region. It may be possible to investigate SO_2 removal by comparing its concentrations to CO_2 concentrations or to the C^{14} contents of CO_2 .

Traditional meteorological approaches to the prediction of diffusion of pollutants from sources almost always are based on the assumption that the pollutant or tracer is conserved. This sort of model is appropriate for any material which is sufficiently inert or long-lived. However, real air pollution problems involve materials which are chemically reactive or, in the case of aerosols, may be removed by

mechanical processes (sedimentation, washout) or radioactive decay. The latter two have been studied (Junge, 1963a) theoretically and experimentally in some detail. Chemical reactivity remains as an important problem.

In general, it is possible to describe the transport of material in the atmosphere as follows:

$$\frac{\partial c}{\partial t} = Q + A + D - L$$

with source terms, Q ; advection terms, A ; diffusion terms, D ; and loss terms, L . Since chemical reactions proceed at rates that are concentration-dependent, difficulty in solving this equation will exist if L has an important relative magnitude. Further, since such losses occur both in the atmosphere and on surfaces via more than one chemical mechanism, the *a priori* prediction of the importance of L appears difficult. The purpose of this note is to propose an experimental approach to answer the following questions. Is L of important magnitude? If so, how close to sources in space or time does the assumption of conservation hold? The knowledge so gained will have relevance to detailed studies via numerical models of atmospheric diffusion and transport.

Double Tracer Technique

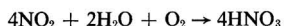
Consider a plume containing two materials emitting into the atmosphere. With reference to the above differential equation, there will be no knowledge of L gained by study of the comparative behavior of the two materials, if they are conserved or obey identical removal mechanisms. On the other hand, if one material is conserved (*i.e.*, relatively long-lived) and the other not, then study of the behavior of the relative concentrations of the two materials will give the answers to the two questions posed in the previous section.

While it is possible to add conservative tracers to a plume (SF_6 , Kr^{85} , fluorescent particles, etc.), existing sources of pollution emit both reactive and relatively inert materials. Examples of this are NO_x and CO from automobile exhaust, or SO_2 and CO_2 from burning of fossil fuels such as coal and heavy oil. Study of these double tracer systems is warranted in part because they exist in actual urban atmospheres, and in part because situations can be found where a single case of sources of each pair is dominant; *e.g.*, virtually all NO_x and CO come from automobiles in cities such as Los Angeles, and a relationship between the concentrations at the source has been shown to exist (State of California, 1966). Similarly, CO_2 might be related to SO_2 in New York City if the fossil fuel component (which is presumably related to SO_2) can be adequately distinguished from CO_2 from other sources, such as incinerators and natural sources. In these cases, CO and CO_2 are assumed to be conserved, while NO_x and SO_2 may be removed by either atmospheric reactions or interactions with surface materials.

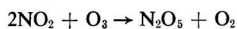
It is reasonably certain that CO and CO_2 are insignificantly removed from the atmosphere for distances of the order of 10 km. Considerations pertinent to this concept are presented by Junge (1963b). On a local scale, fluctuations of CO_2 concentration are governed by assimilation by vegetation and variations in atmospheric turbulent eddy motions. From Huber's (1952) study, it is estimated that changes of CO_2 concentration up to 20 p.p.m. per hour would be normal. Clark and Faoro (1966) showed that fluctuations of CO_2 concentrations in urban atmospheres are contributed to significantly by the diurnal cycle in plant assimilation. Thus, for travel distances of 10 km, it may be expected that fluctuations of the order of 10% in CO_2 concentrations would be normal.

The sink for atmospheric CO is generally not known. Estimates by Junge (1963b) indicate that the global scale characteristic removal time is of the order of 0.3 year or more. If the removal occurs by means of gas phase reactions, then CO is conserved for small scale motions of the atmosphere.

The rates of removal of oxides of nitrogen and SO_2 from urban atmospheres are quite uncertain. The ultimate fate of most NO_2 is probably oxidation to nitrate in solution via the overall reaction



(Haagen-Smit and Wayne, 1968). In regions where O_3 concentrations are high, the reactions



may also occur (Haagen-Smit and Wayne, 1968).

Although there is little established information on removal mechanisms, it may be anticipated from the known chemical properties of the molecules that significant amounts of reaction could occur over spatial scales of the order of 1–10 km. It thus seems reasonable that simultaneous observation of the reactive and conserved species from a single class of sources will permit

the determination of the importance of removal by chemical reaction (L) relative to the meteorological processes (Q , A , and D). Observations of multiple tracers leading to removal-rate information have been possible in studies of world-wide radioactive fallout (U.S.A.E.C., 1965). In such measurements, the background concentration and its variation must obviously be considered. For example, CO_2 concentration can be expected to vary ± 15 p.p.m. in a random fashion; other larger excursions should represent reliable concentration information. Within a few km of sources, 100 to 500 p.p.m. above background are frequently measured. The limits of concentrations of CO_2 accuracy of estimating dilution therefore range from $\pm 15\%$ to $\pm 3\%$, which represent sufficient accuracy for many problems.

In the case of NO_x and CO, the necessary observation and data reduction procedures are straightforward and involve established methods of measurement. Essentially, a parcel of air should be traced as it progresses away from a source region. This could be achieved with either a moving monitoring system or systems located at a number of stationary sites. In fact, coincident meteorological and chemical data may already exist which would permit such an analysis. In the case of CO_2 and SO_2 , the problem of distinguishing the fossil fuel component of CO_2 from extraneous emission might be solved in either of two ways. The data can be so stratified that only periods of extraordinarily high CO_2 , say (CO_2) > 500 p.p.m., are used. In such cases, variations of natural sources would contribute little to the observed events. Since fossil fuels contain no C^{14} , it seems possible to identify the components of the existing abundance of CO_2 due to natural sources and combustion of nonfossil carbon (which do contain C^{14}).

CO_2 may be a very important tracer to consider in development of large scale modeling of megalopolitan areas. Slade (1967) has made a preliminary attempt at modeling, using estimated CO_2 emissions in the eastern seaboard region. Verification of such CO_2 diffusion models would be quite impossible by any method other than that involving C^{14} content.

Conclusion

The use of two or more materials emanating from a single class of sources should provide needed information concerning the importance of chemical sinks for reactive materials in the planetary boundary layer. Perhaps in time this method could be extended to combinations of pollutants other than those mentioned. One result might be that the reaction of materials like NO_2 with surfaces is so rapid that it is safe to assume zero concentration at the boundary. No such simplifying assumption seems forthcoming for reactions occurring only in the atmosphere.

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Received for review September 18, 1968. Accepted July 30, 1969.

Parathion—Use of Blood Concentration to Diagnose Mortality of Fish

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■ Catfish, *Ictalurus nebulosus* (Le Sueur), were exposed to various concentrations of technical grade parathion dissolved in water for time periods of up to 30 days. Analyses of the blood revealed that the concentration of parathion in the blood and in the water is closely related, and can be used to predict death due to acute toxicity. Several methods of chemical analyses, including infrared spectra, demonstrate that the material is unaltered parathion and not paraoxon. The presence of unaltered parathion in the blood suggests that the metabolism of parathion in cold-blooded vertebrates, such as fish, should be studied further to determine if there is a significant accumulation in such animals.

Synthetic pesticides are frequently blamed for mortalities of aquatic animals, even though no proof is found. The high toxicity and widespread use of pesticides are important reasons for such accusations, but fish kills are common, and there is an urgent need to determine their specific causes. Most of the larger kills are a result of short-term, high-concentration exposures, because chronic effects are expressed over long periods of time, and usually only a few mortalities occur at any one time. Examination of bottom fauna in the affected waters is often disappointing because the sensitivities of different aquatic animals vary greatly; a pollutant that kills fish may not kill insects at the same concentration, or vice versa. Chemical analyses of water are often uninformative, because the water mass containing the pollutant does not move at the same rate as the dead fish; thus, the pollutant is difficult to locate and sample. Methods are needed for diagnosing the cause of fish kills, and the research herein reported was for this purpose.

Several methods for diagnosing the cause of fish mortalities have been published (Mount, 1964; Mount, Vigor, *et al.*, 1966; Brungs and Mount, 1966). These are based on the measurement of the concentration of a chemical in a particular tissue and on experimental exposures that have demonstrated a threshold concentration, above which death results. Nicholson (1967) summarized the literature and supported the use of cholinesterase inhibition as a method of detecting death or adverse effects in fish due to organophosphates.

This paper proposes the measurement of blood concentration of parathion as a diagnostic tool to detect fish mortality caused by acute exposures to parathion dissolved in water. It further demonstrates conclusively that parathion is not readily and completely metabolized in the fish's body.

Biological Methods

A test system similar to the one described by Mount, Vigor, *et al.* (1966) was used for this study. Test chambers measuring 30 × 30 × 180 cm. were made of Type 304 stainless steel. The drain was adjusted to maintain approximately 100 liters of

test water. Six such chambers were fed test water by a proportional diluter (Mount and Brungs, 1967) that delivered five concentrations and a control. All water lines, valves, and tanks were made of glass, PVC plastic, stainless steel, or concrete.

The water, originating from a limestone spring, was circulated through two 1.2-hectare (1/2-acre) earthen ponds, and was then pumped to a 750,000-liter concrete reservoir having a detention time of 30–60 days. Sufficient deionized water was added to give a final water of 200 mg. per liter of EDTA hardness (as CaCO₃). It then flowed by gravity through a headbox and to the test system. Moderate quantities of plankton were present and Secchi disk readings were 5 to 7 meters. Temperature was 22° ± 1°C.

Brown bullheads, *Ictalurus nebulosus*, Le Sueur, were netted in October 1966, from a 1500-hectare lake, and were maintained in spring water until March 1967, when testing began. Two fish were placed in each tank initially; when these died, two others were added. Finally, the concentrations were reduced and three fish were maintained at each of five sublethal concentrations for 30 days. The same two control fish were used throughout the test period.

Technical grade parathion (80% active) was used; for the lethal exposures, 11.4 grams of parathion was added to 0.125 gram of Triton X-100 (Rohm and Haas) and made up to 10 ml. with acetone. A technical grade was intentionally used to simulate actual practice. For sublethal exposures, the Triton concentration was maintained, but the parathion was reduced. The stock was added at the rate of 4.5 μl. to 1940 ml. of water to give the highest concentration, and other concentrations were made automatically by dilution. The highest concentration of Triton was 26 μg. per liter, approximately 1/200 of the acutely lethal concentration. A circulating pump was used to mix the stock with the water in the M-1 cell of the diluter (Mount and Brungs, 1967).

Average dissolved oxygen concentrations were 4 mg. per liter, and a minimum of 3 mg. per liter occurred several times. Bullheads can live at less than 1 mg. per liter of dissolved oxygen. Average pH was 7.5 to 7.6, acidity was 10 to 15 mg. per liter and alkalinity was 150 to 170 mg. per liter, both as CaCO₃. Water flow through each test chamber was 200 ml. per minute and the fish, weighing 75 to 150 grams, were fed commercial trout food. A total of 44 fish was used during the test period. Water concentrations, as measured in composite water samples, are given in Table I.

Chemical Methods

Water Samples. Volumes of 50 ml. of water from the test chambers were extracted with 25 and 15 ml. of redistilled hexane. After concentration to convenient small volumes in 5-ml. graduated conical tubes, the extracts were subjected to gas chromatography on a single column (1/8-inch times 3-foot glass, 5% Dow 11 silicone grease on 60- to 80-mesh Chromosorb-W) gas chromatograph with dual detectors. The detectors were Varian Aerograph electron-capture and phosphorus

Table I. Analyses of Water from Test Chambers for Parathion

Nominal concn., mg./l.	Dates								
	2/15	2/16	2/20-24	2/27-3/3	3/13-17	3/20-24	3/27-31	4/3-7	4/10-14
	Observed concentrations, mg./l.								
2.0	1.5	1.8	1.8				
1.5	1.4	1.5				
1.0	0.7	0.61	0.78	0.7	0.77				
0.5	0.28	0.29	0.33	0.33	0.41				
0.25	0.13	0.15	0.16	0.17	0.23	0.22	0.19	0.12	0.16
0.12	0.07	0.07	0.08	0.08	0.09	0.09	0.09	0.06	0.06
0.06						0.05	0.05	0.03	0.04
0.03						0.02	0.03	0.02	0.02
0.015						0.009	0.008	0.004	0.007

flame ionization; signals were recorded on a Westronics 1 m.v. dual channel recorder. Identification was made by comparing the retention time of the sample peak with the retention time of a parathion reference standard. The identification was confirmed by the ratio of peak heights shown by the two detectors and also by the "p-values" of Bowman and Beroza (1965). The peak height ratio is empirical for the instrument.

Blood Samples. Blood samples were quick-frozen immediately after being taken; no preservative was used. The blood was alternately frozen and thawed 5 times to break down the cells (Billaudelle and Bruner, 1959). Aliquots of 2 to 3 grams of blood were extracted once with 15-ml. and once with 10-ml. portions of hexane, and analyzed in the manner described above for water samples.

It is difficult to get a quantitative recovery of phosphorus pesticides from blood by direct extraction with a solvent. Krueger and O'Brien (1959) failed to extract malathion from tissue homogenates with chloroform in neutral or acid tissue, but recovered 90 to 95% of known amounts using a trichloroacetic acid precipitation of the protein. Protein binding was suggested as the reason for the low recoveries.

Blood samples that were alternately frozen and thawed, then extracted with hexane, gave comparable recoveries to those that were precipitated with trichloroacetic acid and gave more reproducible results for a number of samples; also, the extensive cleanup necessary with the trichloroacetic acid precipitation was not required. Two samples of blood from exposed fish gave a 10 and 14% higher recovery, respectively, by hexane extraction over trichloroacetic acid precipitation. Table II shows typical recoveries using both the hexane extraction after alternate freeze-thawing and the trichloroacetic acid precipitation of blood samples with added parathion.

A single sample of blood with sodium citrate added as a preservative and extracted with hexane after freeze-thawing gave only 24% of the total parathion recovered when using trichloroacetic acid precipitation, and it appears that precipitation of the protein becomes necessary when a preservative is added to the blood.

With the gas chromatographic conditions used, parathion had a retention time of 3 minutes, while paraoxon had a retention time of 4.5 minutes and was completely separated from parathion. Paraoxon could have been detected easily at a concentration of 0.5 p.p.m., if present, but none was detected in any of the blood samples, including one containing 82 p.p.m. of parathion.

Final proof of the presence of unaltered parathion was obtained by infrared spectroscopy (Figure 1). A sufficient quantity of blood to contain at least 25 µg. of parathion was

Table II. Comparison of Per Cent Recovery for Two Extraction Methods

Sample ^a	% Recovery	
	Hexane extraction after freeze-thawing	Trichloroacetic acid precipitation
1	78	63
2	77	68
3	83	88

^a 5 p.p.m. concentration used.

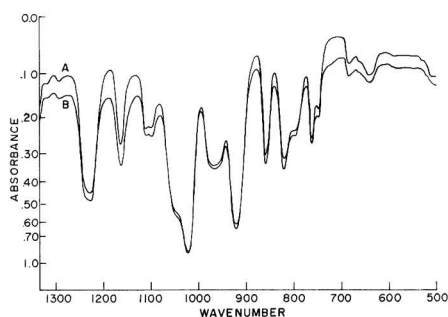


Figure 1. Infrared spectra of parathion

A. Parathion standard, 98.6%
B. Parathion sample from fish blood

extracted as described above, purified by thin-layer chromatography with an alumina-10% ether-in-hexane system, and subjected to infrared spectroscopy using a 1.5-mm. KBr disk and a 4 × lens-type beam condenser.

Results

The analytical results of the blood analyses for parathion are given in Figure 2. Only three live fish had values equal to those of the killed fish. This is three out of 42, or approximately 7%. The close relationship of water concentration to blood concentration is expected; the sharp dividing line between living exposed and killed fish exists because all 25 fish that died did so within 11 days, and no mortality from chronic exposure occurred. At least seven of the fish in the higher three concentrations of the 30-day sublethal exposure showed severe symptoms of intoxication for three of the four weeks of exposure, including kinked or disjointed vertebral column, convulsions, and hemorrhaging. These fish surely represented

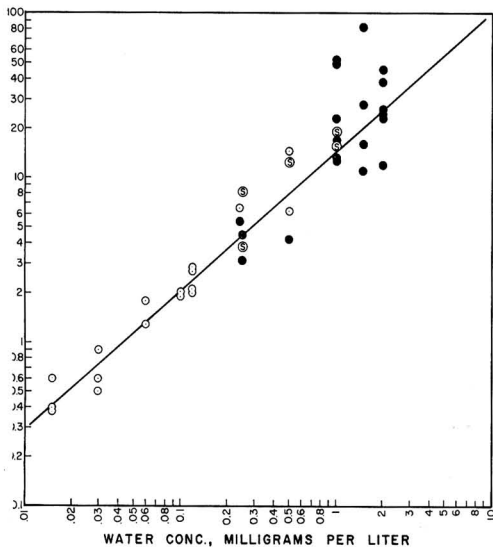


Figure 2. Relationship of concentration of parathion in the blood to concentration in water

- Dead
- ⊗ Dead with disease symptoms
- Alive

; maximum concentration that could be tolerated by the living fish of this species. Of the three living exposed fish having blood concentrations higher than some of the killed fish, one was exposed to 0.24 mg. per liter of parathion in the water for 28 days and was convulsing when bled; the other two had been exposed to 0.5 mg. per liter for 14 and 17 days, respectively, and also were convulsing when bled. Both concentrations were lethal to some fish.

The highest concentration found in the blood was 82 $\mu\text{g.}$ per gram in a fish exposed two days to 1.5 mg. per liter. Four other fish had concentrations ranging from 38 to 53 $\mu\text{g.}$ per gram. The fish exposed for 30 days, only those in the 0.015 mg. per liter concentration appeared normal. Those in 0.03 mg. per liter had tremors at times. Those in 0.06 mg. per liter ate normally, even though they convulsed and had kinked vertebral columns.

Discussion

The data demonstrate that bullhead mortalities caused by

acute exposure to parathion can be diagnosed by measurement of unaltered parathion in the circulating blood. Applicability to other species remains to be demonstrated. The presence of unaltered parathion, established by positive chemical identification, suggests that the present concept of "degradable" or "soft" insecticides should be used carefully. Actively feeding bullheads carrying approximately 2 $\mu\text{g.}$ per gram of parathion in their blood would be catchable fish in contaminated areas. Bullheads are sensitive to parathion; further tests should be made to reveal the expected concentrations in blood and especially the edible portion of more tolerant fish. The use of a chemical measurement of parathion in the body of the animal is superior to a less specific measure such as the use of cholinesterase, because many substances may depress that enzyme system. The specificity of a chemical identification provides much more useful data for regulatory agencies and reduces the chance of placing blame on the wrong pollutant or discharge.

Research is needed to determine if parathion occurs in higher concentrations in muscle than in blood, as is the case with chlorinated hydrocarbons, and the biological half-life should be determined. Mulla, Keith, *et al.* (1966) found indications that parathion is stored in mosquito fish, but concluded that the residue is lost quickly. Apparently, fish do not concentrate parathion in their bodies over the concentration in water to the extent that occurs with chlorinated hydrocarbons.

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Received for review September 25, 1968. Accepted July 23, 1969. Mention of brand names does not imply endorsement of products by the Federal Water Pollution Control Administration of the U.S. Department of the Interior.

Acidic Dissociation Constants of Selected Aquatic Herbicides

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■ Many aquatic herbicides are organic acids for which the acidic dissociation constant is not known, or for which a discrepancy of values has been reported in the literature. Herein, the pK values are reported for 2,4-D (2.73, $I = 0.05$), 2,4,5-T (2.88, $I = 0.03$), 2-CPA (2.92, $I = 0.05$), 4-CPA, (2.95, $I = 0.05$), MCPA (3.05, $I = 0.03$), MCPB (4.80, $I = 0.05$), fenac (3.70, $I = 0.05$), and dalapon (1.84, $I = 0.05$). These values evolved from potentiometric titrations wherein the physical conditions were held constant and the work was performed by one operator. An accurate acidic dissociation constant is needed for calculation of the distribution of the undissociated acid and anion species of an aquatic herbicide under given conditions of pH and ionic strength. This may be useful in ascertaining the availability of the molecule to enter into biologically-mediated oxidation-reduction reactions or into such chemical and physical reactions as dissolution, ion exchange, coagulation, and adsorption.

The advent of organic pesticides some 30 years ago has led to their purposeful application to and incidental pollution of surface waters. Some pesticides—namely, the aquatic herbicides—are effective for control of vegetation in water supply reservoirs. Many aquatic herbicides are organic acids: 2,4-D (2,4-dichlorophenoxyacetic acid), 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), 2-CPA (2-chlorophenoxyacetic acid), 4-CPA (4-chlorophenoxyacetic acid), MCPA (2-methyl-4-chlorophenoxyacetic acid), MCPB [4-(2-methyl-4-chlorophenoxy)butyric acid], dalapon (2,2-dichloropropionic acid), and fenac (2,3,6-trichlorophenylacetic acid).

In order to understand the fate of these herbicides, or to evaluate treatment processes for their removal from water, an acidic dissociation constant should be available. Knowledge of the distribution of the undissociated acid and anion species of an aquatic herbicide with pH can be useful in ascertaining the availability of the molecule to enter into biologically-mediated oxidation-reduction reactions, or into such chemical or physical reactions as dissolution, ion exchange, coagulation, and adsorption.

An examination of the literature revealed disagreement on values for dissociation constants of most of the aforementioned acidic herbicides, especially 2,4-D. In addition, only one value has been reported for dalapon and fenac. This work was undertaken, therefore, to determine the constants of the eight compounds by potentiometric titration under the same physical conditions and by one investigator.

Reagents

Herbicides. Dalapon, a liquid, was supplied in an an-

alytical reference grade. The seven solid herbicides were purified by conventional dissolution-crystallization procedures. The general technique involved dissolution in acetone, addition of carbon, filtration, heating of filtrate, continuous addition of benzene until the initial volume of acetone was replaced, cooling of benzene solution, collection of crystals by filtration, washing of crystals with benzene, and drying of crystals. Purity of the crystals was judged by color, *i.e.*, white crystals as compared to various off-white colors—yellow, brown, etc.—of the original solid, a narrow melting range as compared to literature values, and a melting point as compared to literature values.

Sodium Hydroxide Titrant. The usual precautions were observed in preparation and standardization of 0.10N NaOH. Sodium carbonate and carbon dioxide were eliminated from the NaOH by conventional techniques. Sodasorb traps were placed in the automatic titration and reservoir system to prevent encroachment by carbon dioxide. Standardization of the sodium hydroxide was against potassium acid phthalate (National Bureau of Standards).

Ionic Strength Control. Sodium perchlorate was used for ionic strength control, with the exception of potassium chloride in the 2,4-D system.

Equipment and Experimental Procedure

Conventional potentiometric techniques and procedures were utilized with special precautions and equipment. A Beckman expanded-scale pH meter was used with glass and saturated calomel electrodes. This instrument was standardized and linearized against the National Bureau of Standards' buffer solutions of 0.05M $\text{KH}_2\text{C}_2\text{O}_4$ (pH = 4.01, $I = 0.0533$) and of 0.025M KH_2PO_4 and 0.025M Na_2HPO_4 (pH = 6.86, $I = 0.10$) (Bates, 1959). The temperature was monitored constantly and maintained within $25^\circ \pm 0.1^\circ\text{C}$. by an E. H. Sargent thermoelectric temperature-regulating magnetic stirrer. Titrations were performed under an atmosphere of nitrogen that was run through sodasorb and distilled water. This technique prevented evaporation of the acid solutions during the titration.

The experimental procedure consisted of direct weighing of the purified herbicide to an approximate concentration of 0.2 to 1.25 mmoles in a final volume of 500 ml. This aqueous mixture was heated to dissolve the free acid herbicide and to exclude any carbon dioxide. Subsequently, the solution was cooled to room temperature under a stream of nitrogen. Each compound was titrated at two ionic strengths, and each titration was repeated six to eight times.

Stoichiometry of Titration

The following outline obtained the necessary data for calculation of the acidic dissociation constants:

a. Plot pH *vs.* ml. of NaOH to yield the typical S-shaped titration curve of an acid.

b. Plot the $\Delta\text{pH}/\Delta\text{ml.}$ *vs.* average ml. of titrant to yield the first derivative curve which, in turn, reveals the equivalence point or point of inflection of the titration curve.

c. In the S-shaped curve, choose a point about halfway to

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the equivalence point, where a well-buffered region exists. In this region, the concentration of the undissociated acid is approximately equal to the concentration of the anion, and the pH change is small with each addition of NaOH. Consequently, there is less chance for error in the pH reading. The chosen point yields values for $[H_3O^+]$, V , and v for insertion into the equation

$$K = \frac{[H_3O^+] \left([H_3O^+] + \frac{Mv}{V} \right)}{\frac{M}{V} (V_0 - v) - [H_3O^+]} \quad (1)$$

This equation yields the classical or concentration acidic dissociation constant, which varies with ionic strength. Equation 1 is a straightforward derivation from the law of electroneutrality and appropriate substitutions. The $[OH^-]$ was assumed to be small and negligible in the portion of the titration curve from which the calculation of K was made.

d. The $[H_3O^+]$ in Equation 1 was calculated from

$$[H_3O^+] = \frac{(H_3O^+)}{f_{H^+}} \quad (2)$$

and

$$pH = -\log (H_3O^+) \quad (3)$$

A value for f_{H^+} was taken from an activity coefficient-ionic strength plot, as published by Rieman *et al.* (1951).

e. A theoretical titration error at the equivalence point was calculated from

$$\frac{V_e - V_0}{V_0} \times 100 = \text{per cent titration error} \quad (4)$$

Experimental Results

The classical K values as calculated from Equation 1 are listed in Table I for several ionic strength values. A theoretical error value is offered also, as an indication of the experimental error in the potentiometric technique.

Discussion

The purpose of this investigation was to determine the acidic dissociation constants of six aquatic herbicides for

Table I. Acidic Dissociation Constants at Various Ionic Strengths

Compound	I	K^a	Theoretical titration error, %
Dalapon	0.02	1.25×10^{-2}	-1.15
	0.05	1.45×10^{-2}	
2,4-D	0.01	$1.7(1) \times 10^{-3}$	+0.34
	0.05	1.86×10^{-3}	
2,4,5-T	0.012	1.29×10^{-3}	+0.47
	0.03	1.31×10^{-3}	
2-CPA	0.02	1.04×10^{-3}	-0.36
	0.05	1.20×10^{-3}	
4-CPA	0.02	$1.0(2) \times 10^{-3}$	-1.18
	0.05	1.12×10^{-3}	
MCPA	0.012	8.07×10^{-4}	-0.57
	0.03	8.82×10^{-4}	
Fenac	0.02	1.69×10^{-4}	-1.10
	0.05	1.98×10^{-4}	
MCPB	0.02	$1.4(1) \times 10^{-5}$	+1.00
	0.05	$1.5(8) \times 10^{-5}$	

^a () in K value indicates a rounded number.

Table II. A Comparison of pK Values Reported for the Herbicides*

Investigator	Thermodynamic convention	pK							
		2,4-D	2,4,5-T	2-CPA	4-CPA	MCPA	MCPB	Fenac	Dalapon
Nelson (this work) ^b	See below ^{c,d}	2.73 ^c	2.88 ^d	2.92 ^c	2.95 ^c	3.05 ^d	4.80 ^c	3.70 ^c	1.84 ^c
van Overbeek <i>et al.</i> ^b	?	2.81	2.57
Wedding <i>et al.</i> ^b	Concentration	2.96
Behaghel ^e	Inf. Dil.	2.99	3.02
Ketelaar <i>et al.</i> ^e	?	2.64	3.28
Matell and Lindfors ^e	Inf. Dil.	2.90	2.83	...	3.01	3.11
Wershaw and Goldberg ^e	Inf. Dil.	2.92
Hayes and Branch ^f	Inf. Dil.	3.05	3.10
Audus	?	3.28
Freed ^g	...	3.31	3.14	...	2.36	3.87	1.53
Bailey & White ^d	...	2.63	3.14	...	3.56	2.90	4.86
							(60°)		
			2.80	3.46			3.40	6.21	
			(60°)						
		3.22							
		(60°)							
		3.31							

^a Temperature = 25° C. unless otherwise stated.

^b Potentiometric measurements.

^c $I = 0.05$.

^d $I = 0.03$.

^e Conductometric measurements.

^f E.M.F. measurements.

^g Literature review.

which wide variations have been reported in the literature, and to determine the constants of two herbicides for which single values have been reported. Some of the variations can be attributed to the variety of methods used in determining the dissociation constants (Table II). In addition, some of these literature reports did not cite the use of ionic strength control nor mention the thermodynamic context from which the dissociation constant was reported. Also, it is not surprising that such discrepancies exist, since the solubilities of the acids in water are so low.

The majority of the determinations by other investigators was accomplished by conductometric methods—for example, Behaghel (1926, 1929), Ketelaar *et al.* (1952), and Matell and Lindenfors (1957). Behaghel, Matell, and Lindenfors measured the conductivity of several compounds at several dilutions and extrapolated to infinite dilution, or zero ionic strength, to determine the thermodynamic constant. The determinations of Ketelaar *et al.*, done by "usual conductometric methods," were incidental to the main purpose of their work, and do not agree in two cases—2,4-D and MCPA—with the work performed by Matell and Lindenfors. The main problem with the conductometric method is that extrapolation is difficult to do accurately for weak electrolytes because of steep increases in equivalent conductance at high dilutions.

Wershaw and Goldberg (1967) also used the conductometric method to determine a "thermodynamic" dissociation constant of 2,4-D, but used an indirect method to overcome the problem of a weak electrolyte. They, instead, measured the conductivity of the sodium salt of 2,4-D, a strong electrolyte, for which graphic extrapolation to zero ionic strength is easily done, and then used the Kohlrausch method of independent ion mobilities, using the equivalent conductivity at infinite dilution of the strong electrolytes to calculate the equivalent conductivity of 2,4-D. The thermodynamic constant was then calculated from the Fuoss equation, and the values determined should be valid.

Hayes and Branch (1943) used an electromotive force method to measure the dissociation constants of several phenoxyacetic acids, of which only two were pertinent to this investigation—2-CPA and 4-CPA. Their dissociation constants were about 15% lower than those determined by classical conductivity measurements.

Potentiometric determinations were performed by van Overbeek *et al.* (1951) and by Wedding *et al.* (1954). van Overbeek *et al.* did the determinations of 2,4-D and 2,4,5-T, incidental to the main purpose of their work, by measuring the pH of a $10^{-3}M$ solution of each of the compounds containing 1% isopropyl alcohol. Since the work was done in a mixed solvent system, the values probably cannot be accepted as true thermodynamic constants for an aqueous system. In fact, their value

for 2,4-D is not in agreement with that determined by Wedding *et al.* by much the same method, but in a pure water solution. Perhaps the main argument against this method comes from an examination of the literature. Bailey and White (1965) report the solubility of 2,4,5-T at 25° C. as 280 p.p.m., which is equivalent to a $1.1 \times 10^{-4}M$ solution—the upper limit of 2,4,5-T solubility in water. Therefore, if 2,4,5-T was totally dissolved in van Overbeek's system, most of it must have been in the isopropyl alcohol, and the pK value would not be valid.

Nomenclature

f_{H^+}	= hydronium ion activity coefficient
$[H_3O^+]$	= hydronium ion concentration
(H_3O^+)	= hydronium ion activity
I	= ionic strength
K	= classical or concentration dissociation constant
L	= amount of acid in mmoles, equal to $M \times V_Q$
M	= normality of NaOH
v	= volume of titrant added— <i>i.e.</i> , the buret reading
V	= total volume
V_Q	= theoretical volume of titrant added at the equivalence point, calculated from the weight of acid herbicide used
V_e	= actual volume of titrant added at the equivalence point

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Received for review August 28, 1968. Accepted July 28, 1969. This research was sponsored by Research Grant ES-00016, Office of Resource Development, Bureau of State Services, U.S. Public Health Service, Washington, D.C. Paper of the Journal Series, N.J. Agricultural Experiment Station, Rutgers, the State University of New Jersey, Department of Environmental Science, New Brunswick, N.J.

Distribution of Mn, Fe, P, Mg, K, Na, and Ca in the Surface Sediments of Lake Mendota, Wisconsin

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■ Analysis of 32 surface sediment samples from different areas of Lake Mendota, Wis., indicated a high positive statistical correlation between Mn, Fe, and P concentration in the sample and the depth of water overlying the point of sample recovery. An inverse correlation was found for Mg and K. No statistical correlation between concentration and depth of sample recovery was found for Ca and Na.

Surface sediment samples were collected from Lake Mendota, Wis., during the summer and early fall of 1967. The purpose of the sampling was to assess the chemical composition of the sediments with respect to water depth and location in the lake. Studies conducted during the early 1950's reported by Rohlich (1963) indicate that N, P, and Fe concentrations become greater with increasing depth of water. Later work by Nriagu (1968) showed a correlation between the concentration of total- and sulfide-S and depth of overlying water for seven sediment samples collected from the central area of Lake Mendota, with depths ranging from approximately 11 to 25 meters. Gravity core sediment samples from different areas of Lake Mendota were collected by Murray (1956). The sediments in the deeper areas of the lake were typically black sludge or gyttja, resting on top of buff-colored marl deposits. The average CaCO₃ content of the black sludge is 32% (dry weight basis). The sludge in the deeper area of the lake generally showed a higher carbonate content than sludge in shallower areas.

Lee (1962) summarized previous studies that found shifting of the bottom muds in University Bay, located in the south-central part of the lake. This was determined by plotting concentration contours for the summer and winter seasons. The variations in the element distribution contours were attributed to the effects of bottom currents induced by strong winds which prevail during fall and winter. An extensive survey of the circulation of Lake Mendota was conducted by Bryson and Suomi (1952). They found that wind-driven epilimnetic waters resulted in a depression of the thermocline in the downwind portion of the lake. A resultant upward release of this depression created measurable hypolimnetic currents. These hypolimnetic currents would be sufficient to disturb the extremely flocculent surface sediments. Gardner and Lee (1965) reported that scuba divers operating in the waters above the surface sediments created sufficient water currents to agitate the sediments, resulting in highly turbid bottom water conditions. Thus, continuous wind-driven circulation of the epilimnion, followed by hypolimnetic circulation, would account for the displacement and partial alteration of sedimentary element distribution patterns.

The study reported here extends the available information

about the distribution of certain elements in the surface sediments of Lake Mendota. The results show the effect of depth and possibly bottom morphology on the concentration of elements in surface sediments, and thus can be used as a guideline for future sampling programs where such information is needed for nutrient or mineral budget computations.

Experimental Procedures

Surface sediment samples were collected with an Ekman dredge from 32 stations at various depths in Lake Mendota; maximum depth is approximately 24 meters. The wet sediments were homogenized in a blender and air-dried. Prior to acid digestion, sediment sample aliquots were ground, passed through a 100-mesh screen, and heated to constant weight at 105°C.

Acid digestion consisted of adding 5 ml. of 48% HF to a 0.50-gram sample in a 50-ml. polypropylene beaker. The sample was heated to about 100°C. for 8 to 12 hours, after which only a dry residue remained. The solid residue was removed from the beaker, transferred to a 100-ml. Kjeldahl flask, and further digested for two hours to decompose the organic matter in the presence of 5 ml. of concentrated HNO₃ and 60% HClO₄. After this digestion, the sample was heated in the presence of 5 ml. of concentrated HCl for approximately one hour, cooled, diluted to 30 ml., passed through a pre-rinsed Whatman No. 2 filter, and drained directly into a 100-ml. volumetric flask. This solution, or an appropriate aliquot thereof, was used for all analytical determinations. Iron was determined by the orthophenanthroline method (Olson, 1965) and P by the vanadomolybdophosphoric yellow colorimetric procedure (Jackson, 1958). Analyses for Mn, Mg, K, Na, and Ca were made by direct aspiration of the digestion solution, or diluted aliquots, into a Perkin-Elmer Model 303 atomic absorption spectrophotometer. Data for the precision of the analyses are given in Table I.

Figure 1 is a bottom contour map of Lake Mendota. The main tributary to the lake, the Yahara River, enters from the north. The only surface outlet from the lake is located on the eastern shoreline, and is indicated by an arrow pointing in a southeasterly direction. The outlet is actually a continuation of the Yahara River, which flows from Lake Mendota into

Table I. Precision of Analytical Methods

Element	Number of replicates, N	Average value of N replicates, mg./g.	Standard deviation, σ , mg./g.
Manganese	10	1.32	0.02
Iron	7	23.6	0.6
Phosphorus	5	1.37	0.02
Magnesium	5	13.1	0.4
Potassium	5	12.6	0.1
Calcium	5	110.0	2.0
Sodium	5	14.6	0.3

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Table II. Lake Mendota Surface Sediment Data

Sample number ^a	Depth of recovery, meters	Date of recovery, 1967	Mg./G. ^b						
			Manganese	Total iron	Total phosphorus	Total magnesium	Total potassium	Total sodium	Total calcium
1	22	June 12	1.34	22.4	1.35	12.5	12.5	14.2	108
1	22	June 19	1.33	22.8	1.35	13.2	12.5	14.6	111
1	22	June 21	1.32	22.8	1.38	13.5	12.7	14.9	111
1	22	June 22	1.32	23.6	1.38	13.4	12.5	14.7	111
2	19	June 12	1.19	21.2	1.29	17.0	13.0	15.5	112
3	15	June 12	0.90	19.1	0.85	17.8	12.5	15.6	114
4	12	June 14	1.22	23.0	1.30	14.9	15.0	16.5	114
5	9	June 14	0.76	20.8	0.92	15.3	14.3	16.7	100
6	18	June 14	1.19	24.2	1.45	13.2	13.0	15.1	105
7	9	June 15	0.64	21.2	0.89	15.7	14.7	16.4	80
8	17	June 15	1.22	21.4	1.29	14.0	12.0	14.8	114
9	22	June 19	1.26	24.4	1.45	11.6	12.3	15.0	112
10	15	June 19	1.11	22.3	1.01	15.9	10.5	16.4	108
11	9	June 19	0.76	20.8	0.89	16.4	12.3	16.6	125
12	10	June 19	0.90	16.0	0.84	26.0	26.0	13.6	80
13	23	June 21	1.40	25.6	1.35	13.0	12.5	14.6	103
14	10	June 21	1.04	19.5	1.17	15.2	11.5	14.6	117
15	12	June 21	1.11	20.8	1.02	12.7	12.2	14.4	90
16	21	June 21	1.12	24.8	1.42	12.3	12.2	14.3	97
17	21	June 22	1.34	25.2	1.38	11.8	12.2	...	90
18	19	June 22	1.17	24.4	1.42	12.8	13.5	...	89
19	23	June 26	1.30	23.4	1.47	13.0	12.2	15.1	99
20	23	June 28	1.34	23.4	1.53	16.0	12.0	14.7	100
21	22	June 28	1.20	23.2	1.37	12.1	12.0	18.4	98
22	21	July 5	1.18	25.0	1.62	11.1	13.1	14.2	78
23	20	July 5	1.34	25.0	1.52	12.6	13.8	15.0	88
24	21	July 5	1.04	24.8	1.22	10.9	12.3	15.2	97
25	18	July 6	1.14	21.2	1.20
26	18	July 6	1.15	21.4	1.25	13.7	11.8	15.1	113
27	18	July 6	1.15	22.3	1.26	12.9	12.5	16.4	120
28	23	July 12	1.32	24.0	1.50	11.4	12.3	16.8	109
29	18	July 12	1.00	21.2	1.09	14.6	12.3	15.5	109
30	19	July 12	1.00	23.0	1.15	11.8	12.0	15.8	106
31	23	Oct. 11	1.43	22.8	1.41	13.0	11.8	15.0	124
32	24	Nov. 6	1.50	26.7	1.82	12.2	12.2	15.0	112

^a Samples 1-30 were collected during summer thermal stratification. Samples 31 and 32 were collected during the fall circulation period.

^b Oven-dry weight (105° C.) basis.

Lake Monona and subsequently into two other lakes located toward the southeast.

The Ekman dredge sediment samples were collected at the 32 stations plotted in Figure 2. Sample numbers given in Table II relate the appropriate analytical data to the station numbers plotted in Figure 2, including the station depths and dates of recovery. Station 1, represented in the lake by a securely anchored buoy, was sampled four times during June, 1967. This was done to determine whether samples from the same location would give replicate analytical data from one sampling date to another during a short period of time.

Results and Discussion

The analytical data for Mn, Fe, P, Mg, K, Na, and Ca are listed in Table II. Close replicate analyses among the four samples from Station 1 taken on different dates were noted.

As an aid in the interpretation of the analytical data, statistical analyses were applied, comparing the elemental concentration (mg. per gram, dry weight basis) with the depth of sample recovery. The results of these calculations are given in Table III. Manganese, Fe, and P showed a positive statistical

correlation between concentration and sample depth. The Mg and K data also showed a correlation, although the *p* values were slightly less at the 0.025 level, compared with *p* = 0.001 for the three elements listed above. An inverse trend of decreasing Mg and K concentration with increasing sample depth was observed. On the other hand, Na and Ca showed no statistical correlation between concentration and sample depth. Statistical correlation does not necessarily imply causation, so that sample depth and morphology need not be the primary controlling factors bearing on element concentrations in the sediments. Other unmeasured or unidentified variables could be in operation, and these might just as easily be the factors responsible for the findings reported.

The difference between the significance levels of correlation for Mn, Fe, and P (*p* = 0.001) and Mg and K (*p* = 0.025) are not sufficient to warrant discussion. One possible reason for the slight dissimilarity is the fact that the standard deviations of the analytical procedures were not incorporated into the correlation computations. The slightly lower correlation coefficients for Mg and K—*r* = -0.59 and -0.40, respectively—still indicate a significant level of correlation between depth and concentration.

Table III. Statistical Correlation Data

Relationship Between Depth of Sample Recovery and Element Concentration

Element	r^a	p^b	s^c	n^d
Manganese	0.81	0.001	0.13	30
Iron	0.74	0.001	0.98	30
Phosphorus	0.82	0.001	0.22	30
Magnesium	-0.59	0.025	2.29	29
Potassium	-0.40	0.025	2.34	29
Sodium	-0.15	e	f	27
Calcium	0.04	e	f	29

^a Linear correlation coefficient from the equation $r = \frac{N\sum XY - \sum X \sum Y}{\sqrt{N\sum X^2 - (\sum X)^2} \sqrt{N\sum Y^2 - (\sum Y)^2}}$; X = element concentration, Y = depth of sample recovery.

^b Significance level of correlation based on "t" tables from the equation $t = \frac{r\sqrt{N-2}}{\sqrt{1-r^2}}$

^c Standard error of estimate of r from the equation $s = \frac{\sqrt{\sum Y^2 - (a\sum Y + b\sum XY)}}{N}$; i.e., the standard deviation of points from a least squares fitted line drawn on a plot of element concentration vs. depth of sample recovery.

^d Degrees of freedom, $n = N - 2$.

^e Not significant.

^f Not computed.

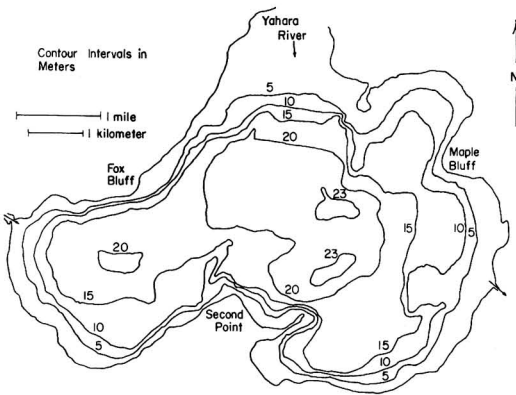


Figure 1. Bottom contour map of Lake Mendota, Wis.

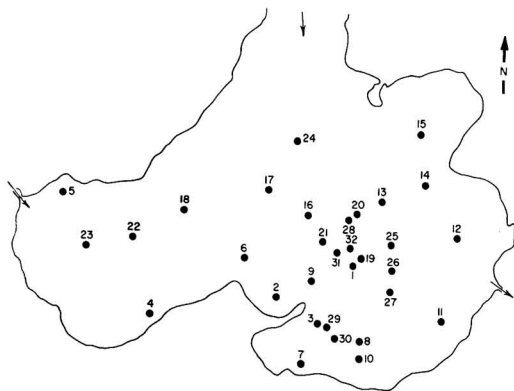


Figure 2. Location of surface sediment samples taken from Lake Mendota, Wis. Numbers indicate location of samples listed in Table II

Twenhofel (1961) discussed the nature of sedimentary environments. Since fresh waters generally permit slower settling of finely-grained sediments, in contrast to marine waters, he envisioned that portions of fine suspended sediments would be carried to the middle or central area of a lake and then deposited in some type of laminar formations. These laminations may or may not be readily apparent, due to the lake morphology, water circulation patterns, and bottom currents. The occurrence of fine-particle settling could explain the correlations found in this work. Since higher concentrations of Mn, Fe, and P were found at deeper depths in Lake Mendota, and since these deeper depths are essentially in the middle or central part of the lake, a relatively simple particle fractionation of tributary-borne suspended matter may have occurred. Particle size analyses of the sediment samples were not conducted, so that conclusive evidence is lacking.

Delfino and Lee (1968) reported that essentially all of the Mn in Lake Mendota waters was soluble and passed through either 0.45-, 0.22-, or 0.10-micron pore size membrane filters. Thus, any residual suspended particulate Mn would have to be on the order of less than 0.10-micron diameter. This would require the suspended material and its associated elements to be present in a very small colloidal form. Another possibility is that the elements carried in suspension primarily by the Yahara River tributary may be brought into the lake during the spring run-off period. After the particulate suspended matter had settled out, the element distributions in the water column would be independent of the transport mechanism, but the sedimentary distributions could be related to fractional settling of suspended particulate matter according to size and travel distance from the river mouth into the lake proper. Manganese, for example, as a soluble element in the water column, primarily comes out of the sediments during thermal stratification periods. Mn could be transported into the lake in a suspended form, originating as run-off, carried soil particles and erosion fragments, and then eventually settle out according to the particle sizes with which the element is associated. After deposition, Mn would be released from the sediments during stagnation periods and participate in the chemical sequences outlined previously (Delfino and Lee, 1968). The fates of Fe, P, Mg, and K similarly transported into Lake Mendota have not been extensively followed, but their initial distribution in the sediments may be related to the type and size of particulate matter to which the elements were found in soil, rocks, and other material in the tributary drainage area. If the particle size explanation is extended from Mn to the other elements, then Fe and P would be bound to small or finely-divided particles, while Mg and K would be associated with the more coarsely-grained larger particles. This interpretation is supported by studies of annual pollen deposition per unit area measured in sediment traps at Frains Lake in Michigan by Davis (1968). At Frains, the ratio of deposition, as measured in traps, to net accumulation, as measured in sediment cores, shows the pollen grains are deposited an average of two to four times before being buried deeply enough to escape further disturbance. Davis (1968) explains that the sediments in shallow water are apparently stirred up and resuspended more frequently or more extensively than sediment in deep water. The net result of repeated resuspension, mainly from shallow water sediment, followed by redeposition over the entire basin, is movement of material from shallow to deep water. Nichols *et al.* (1946) noted that copper sulfate applied to the bay areas of Lake Monona (1925-44) was recovered in highest concentrations in the deep portions of the lake. It seems that the natural grading process tended to carry the precipitated copper compounds to the deeper waters.

Frink (1967) collected bottom samples from Bantam Lake, Conn., and found that total P and N increased with water depth. The sediments in the deeper water of Bantam Lake contained more P, and an increasing proportion of this P was readily exchangeable (Frink, 1967). At a water depth of 6.4 meters, in the deep part of Bantam Lake, the total P concentration was 2.1 mg. per gram and the inorganic fraction 1.8 mg. per gram. The highest concentration of total P was 1.8 mg. per gram from the deepest part of Lake Mendota, and the concentration of P decreased by about one-half of the above amount in the shallower areas of Lake Mendota.

Magnesium and K concentrations showed a significant inverse correlation with depth of water, indicating that these elements are probably associated with coarsely-grained sediments. Presumably, this fraction may include clastic feldspars, clays, and aluminosilicate minerals. However, Ca and Na did not show any significant correlation with water depth. The Na content showed a fairly uniform distribution over the lake bottom. The total Ca concentration reported here represents Ca both as CaCO₃ and as other calcium-bearing minerals. The lack of analytical discrimination between the different forms of Ca limits the interpretation. However, Murray (1956) found that the sludge in the deeper area of the lake generally showed higher CaCO₃ content than sludge in shallow areas.

Conclusions

The results presented in this paper show a definite relationship between the concentration of certain elements in Lake Mendota sediments and the depth from which the sample is recovered. There is a significant positive correlation between water depth (sample depth recovery) and the concentration of Mn, Fe, and P. Presumably, these elements are carried to the center of the lake by a natural grading process bound to small and finely divided particles. A significant inverse correlation was found for Mg and K, but no significant trend was shown by the Ca and Na distributions.

The high correlation of P, Fe, and Mn concentration with

sample depth shows the need for preliminary surveys of lake sediment elemental compositions before extensive computations of nutrient balances in lake systems can be accurately completed.

Acknowledgment

Some of the results were obtained in the University of Wisconsin Laboratory of Limnology. The use of these facilities is greatly appreciated.

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Received for review July 15, 1968. Accepted July 23, 1969. This investigation was supported by Training Grant No. ST1-WP-22 and Research Fellowship No. 1-F1-WP-26,217-01, both from the Federal Water Pollution Control Administration. In addition, support was given this investigation by the University of Wisconsin Water Resources Center Project No. A-001-Wis., Annual Allotment Agreement No. 14-01-0001-1418, the College of Engineering Experiment Station, the Department of Civil Engineering, and the U.S. Office of Naval Research.

Rapid Direct-Reading Spectrographic Determination of Elements in Industrial Waste Water

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■ Monitoring of industrial waste waters frequently requires the analysis of a large number of samples and the rapid reporting of results. A direct-reading spectrochemical method is described, using a special push-up filter paper technique to minimize sample preparation. A computer program is used to calculate and report the results. Total analytical

time for reporting 14 element determinations is about 5 minutes per sample. The average standard deviation is 0.5 p.p.m. at the 3-p.p.m. level. The push-up filter spectrochemical technique is adaptable to many types of analysis where the sample can be absorbed, collected, or deposited on a filter paper support for introduction into the spark gap.

The need to reduce levels of pollution in natural waterways has made it necessary for industry and municipalities to monitor the metal content of industrial waste water. Two general classes of metallic elements are of interest. Heavy metal elements are harmful to aquatic life and toxic to bacteria—bacteria are an integral part of secondary sewage treatment processes and can be poisoned by heavy metals—and elements

that indicate the loss of valuable raw materials by spills, leaks, or improper disposal.

Continuous monitoring or frequent sampling of industrial waste water produces large numbers of samples which can be analyzed economically by a direct-reading spectrographic procedure, coupled with computer calculating and report writing. Previous methods of water analysis (Kopp and Kro-

ner, 1965) require sample preparation by evaporation, ion exchange, extraction, or precipitation to concentrate the impurities. The methods discussed by Kopp and Kroner require extensive sample preparation, and therefore are not adequate for rapid analysis of a large number of samples. They are also unsuited for the simultaneous determination of elements in the filtrable and nonfiltrable residue to provide an analysis for the total residue.

The method described requires a minimum of sample preparation for the combined analysis of filtrable and nonfiltrable residue. A direct-reading spectrochemical approach gives rapid analysis with adequate sensitivity and multielement coverage for monitoring industrial waste water. A computer program is used for calculating and report writing. Total analytical time for reporting 14 element determinations is about 5 minutes per sample.

Procedure

A representative 2-drop portion—approximately 0.1 ml—of the sample delivered with an eye dropper is absorbed into a filter paper (Schleicher and Schuell, Type 589-1H filter, 25-mm. diameter) and dried at 100° C. The dried filter paper is rolled into a cylinder for analysis.

Solutions for standards are prepared by dissolving metals or compounds of the elements of interest to give water solutions of each element in the 0.1- to 100-p.p.m. concentration range. Standard filters for establishing analytical working curves are prepared by absorbing and drying 2-drop aliquots of the element solutions into filters.

Spectra are produced and recorded using a Baird-Atomic Research direct-reading spectrograph, Model GX-1, and source unit, Model NB-1. The excitation conditions for the high-voltage a.c. spark are: capacitance, 0.0025 microfarad; inductance, 1200 microhenries; resistance residual; R.F. current, 6 amperes; and 6 breaks per half cycle.

The filter paper sample is introduced into the 2-mm. spark gap through a cylindrical sample electrode in a manner similar to the cellulose pellet method (Noar, 1957). The electrodes are high-purity graphite. The sample electrode is a 1/4-inch by 1 1/2-inch rod drilled with a 1/8-inch diameter axial hole. The counter electrode is a 1/8-inch by 1 1/2-inch rod.

The push-up electrode system is shown schematically in Figure 1. A motor-driven cardioid cam raises the push rod at a uniform rate to force the sample into the spark gap. In practice, the cardioid cam raises a lift arm which raises the push rod, as shown in Figure 2. The lift arm is fabricated from an insulating material, and the other components of the lift mechanism are fabricated from steel or aluminum. The lift distance is controlled by the position of the cardioid cam on its shaft. The rate of lift is controlled by the pulley-motor drive (1-r.p.m. synchronous electric motor). A lift rate of 2 inches per minute is used to push the sample into the spark gap. High-voltage spark excitation in an oxygen atmosphere consumes the filter paper as it is introduced into the spark gap during the 30-second excitation period. Oxygen flow rate is 30 SCFH to the atmosphere control jet (Figure 1).

Standard filter papers are burned in quadruplicate, and analytical curves are drawn relating the Baird readout system digital clock readings to the log of the concentration. A battery voltage, instead of an internal standard, is used to charge the reference capacitor during the exposure period. Standard filter papers are exposed prior to the analysis of samples to check instrument calibration. Minor corrections, if necessary, are made by adjusting the zero settings of the clocks.

The Baird readout system has been interfaced with an IBM 026 punch to punch the digital clock readings automatically

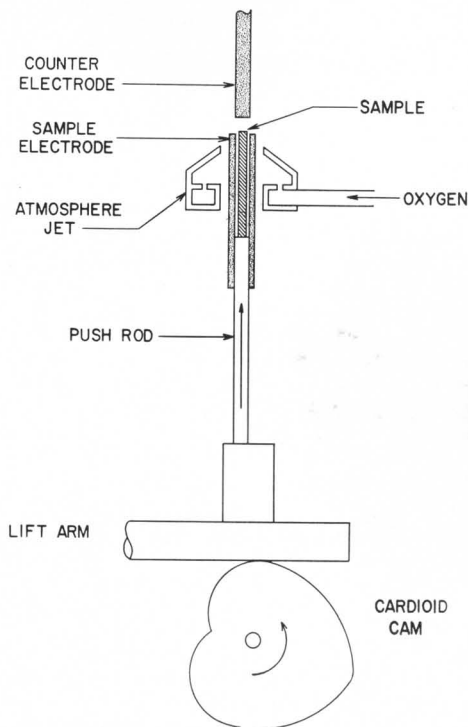


Figure 1. Schematic of push-up electrode system

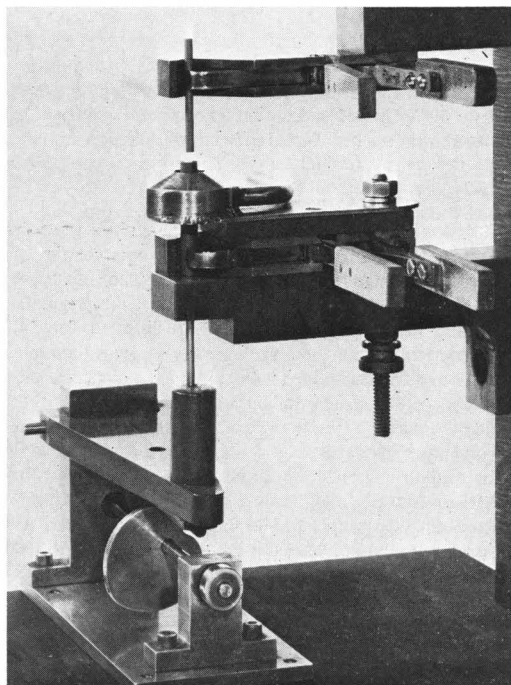


Figure 2. Push-up electrode system

Table I. Typical Report for Emission Spectrographic Analysis of Industrial Waste Water

Element	Cu	Cr	Ni	Pb	Cd	Zn	Sn	Ag	Mn	Al	Sub-total	Ba	Ca	Mg	Fe
Calibration limits, p.p.m.	0.1 to 100.0	1.0 to 100.0	0.3 to 100.0	1.0 to 100.0	0.1 to 100.0	0.3 to 100.0	1.0 to 100.0	0.1 to 100.0	0.1 to 100.0	0.3 to 100.0		1.0 to 100.0	1.0 to 100.0	0.1 to 100.0	0.3 to 100.0
Sample no.	Parts per million														
1	^a	^a	^a	^a	^a	1.0	^a	0.2	0.6	0.8	2.6	1.5	40.0	5.0	1.5
2	0.2	^a	^a	^a	^a	5.0	^a	0.2	0.8	0.5	6.7	^a	60.0	9.0	1.0
3	0.2	^a	^a	^a	^a	0.2	2.0	0.2	0.5	0.6	3.7	^a	50.0	7.0	0.8
4	0.2	^a	^a	^a	^a	2.0	^a	0.1	1.0	0.8	4.1	^a	80.0	10.0	2.0
5	0.7	^a	^a	^a	^a	2.5	^a	0.2	0.8	1.0	5.2	1.0	^b	6.0	1.5
6	^a	^a	^a	^a	^a	0.7	^a	0.1	0.5	0.8	2.1	^a	50.0	7.0	0.8

^a Less than lower calibration limit.
^b Greater than upper calibration limit.

Table II. Typical Precision Data for Industrial Waste Water

Element ^a	Average concentration and standard deviation, p.p.m.
Aluminum	1.9 ± 0.3
Barium	3.5 ± 0.4
Cadmium	4.8 ± 0.8
Calcium	3.7 ± 1.0
Chromium	2.1 ± 0.4
Copper	1.6 ± 0.3
Iron	2.4 ± 0.5
Magnesium	2.2 ± 0.4
Manganese	2.7 ± 0.4
Nickel	2.4 ± 0.4
Silver	2.8 ± 0.6
Zinc	5.4 ± 1.1

^a Precision was not determined for lead and tin.

into punch cards. A computer program containing the equations for the analytical working curves converts clock readings to concentration values. Table I shows a typical report.

Results and Discussion

The selection of elements to monitor in industrial waste water is predicated on potential heavy metal contamination or on elements which indicate excessive loss of valuable materials from the industrial complex. Such a group of elements and the measurable ranges (calibration limits) are listed in Table I. These lower calibration limits are generally adequate for monitoring untreated or undiluted industrial waste waters. Preconcentration methods, in addition to the method described, would be required for the analysis of samples expected to meet drinking water standards.

The method described for rapid elemental analysis of industrial waste water may be used with any spectrograph or direct-reading spectrometer. The Baird-Atomic Research direct-reading spectrograph used is limited to 14 channels. The

number of elements or the elements determined are restricted only by the instrumentation (wavelength range), detector system (photographic plate or number of multiplier phototube channels), and the sensitivity provided by the high-voltage excitation conditions.

Sensitivity may be improved by a background correction technique to enhance signal recognition. The addition of more than a 0.1-ml. aliquot of sample to the filter paper would increase sensitivity, but would require multiple additions and drying. This would defeat the purpose for a method with minimum sample preparation. Improved sensitivity for the determination of minor elements in the filtrable portion of the sample is obtained by preconcentration—evaporation or coprecipitation—and a single sample addition of the concentrate added to or collected on the filter paper.

Precision was determined on 16 replicate exposures of a synthetic sample. An average standard deviation of 0.5 p.p.m. at the 3-p.p.m. level (Table II) is obtained. Duplication of results on typical samples showed that uniform sampling is achieved using 2-drop portions (0.1 ml.), even when a nonfiltrable residue is present.

Industrial waste water may be analyzed rapidly using a push-up filter paper spectrochemical technique as a novel manner of introducing the sample into the analytical gap with a minimum of sample preparation. The sensitivity and precision of this method is generally adequate for monitoring industrial waste water to detect and measure the elements in the total residue, filtrable and nonfiltrable material. The direct-reading spectrochemical method with computer calculating and report writing provides a rapid analysis, 5 minutes per sample, for handling a large number of samples. The push-up filter paper spectrochemical technique is also suited to the analysis of liquids, particles, or precipitates which can be absorbed or collected on filter paper or on a suitable support for introduction into the spark gap for analysis.

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Received for review June 18, 1968. Accepted July 23, 1969.

Loss of Weight, ^{60}Co , and ^{137}Cs from Tree Litter in Three Subsystems of a Watershed

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■ Losses of weight, ^{60}Co , and ^{137}Cs from alder, sycamore, and oak leaves exposed for one year in a forest, a pond, and a brook, were exponential. Loss coefficients increased in the order: weight < ^{60}Co < ^{137}Cs at the ratio 1:1.9:4.1. For species loss, coefficients increased in the order: alder < sycamore < oak at the ratio 1:2.7:4.6. The effects of site, species, and substance were highly significant ($P = 0.1\%$), and without significant interaction ($P = 10\%$). Differences between weight and minerals appear to be controlled primarily by leachability, differences between species by microbial breakdown rates, and those between sites by rates of leaching and mechanical abrasion.

Release of minerals from dead plants and animals affects soil fertility and water quality, and thus controls biological productivity, both qualitatively and quantitatively, in terrestrial and aquatic environments. Leaf litter is the main medium for returning mineral elements from primary producers to soil and water. Loss of elements from decomposing leaf litter has been described for both environments (Attiwill, 1968; Slack and Feltz, 1968), but no direct comparisons of mineral release rates in terrestrial and aquatic situations are available. Current interest in landscape studies with the watershed as an ecological unit prompted our study comparing mineral release from litter in three main watershed subsystems *viz.* forest, pond, and brook. The two aquatic subsystems were chosen because they contrast two extremes of the recognized effect of leaching on mineral release. The terrestrial subsystem was the forested slope of the brook.

The mineral elements chosen for leachability contrast were ^{60}Co , representing divalent ions with relatively low solubility, and ^{137}Cs as a monovalent and readily soluble ion. Both isotopes are easily traced and knowledge of their kinetics is of health physics interest because of their strong γ -radiation and long physical half-life.

Loss of weight and minerals from leaf material is not only a result of direct leaching, but also of microbial and animal decay. Therefore, microbial densities and respiratory activity of all biota were measured as probable indices of biological decay. Loss of weight was used as the main index of decay.

Leaves used for the study were of tree species which naturally occurred in and around all three subsystems. Thus time, place, materials, and organisms of the experiment were chosen realistically to yield results which will be of interest to those concerned with water quality and the management of forests and waters.

Materials and Methods

One-year-old shoots of alder [*Alnus serratula* (Ait.) Willd.], sycamore (*Platanus occidentalis* L.), and white oak (*Quercus*

alba L.) were cut about two weeks before leaf fall. The shoots were put in beakers containing either tapwater or solutions of $^{60}\text{CoCl}_2$ or $^{137}\text{CsCl}$. After two weeks the alder leaves contained 30 nano (10^{-9}) curies (nCi) of ^{60}Co and 29 nCi of ^{137}Cs per gram of dry weight. Corresponding figures for oak were 304 and 3264 nCi, and for sycamore 263 and 2617 nCi, respectively. About 2.5 grams were put in each of 99 fiberglass net bags. The empty bags measured 10×10 cm., with net openings of about 3 mm. Nine bags of untagged leaves of each species, one bag with ^{60}Co , and one bag with ^{137}Cs , were strung onto a line at 15-cm. intervals. One such line of each species was secured between metal posts in a forest, brook, and pond habitat. All sites were located in the AEC Oak Ridge reservation.

The forest site was on the east bank of the brook, under a canopy of several tree species containing the three species used for the experiment.

The brook (north fork of Raccoon Creek) was from 20–60 cm. deep, with a flow rate of 3–60 cm. per second. The brook water is oligotrophic and similar to the brook feeding the pond (500 meters west of the laboratory) in which the third line was exposed. All lines rested on the bottom and were only raised at each of the nine sampling times.

The leaves were placed in the field Nov. 13. One bag with untagged leaves and the two bags with tagged leaves were collected from each string after 1, 2, 3, 4.5, 6.5, 7.75, 9, 10.5, and 12 months. The bags were allowed to drain; snails, other visible animals, and prominent algal growth were removed. All bags were placed in plastic envelopes and taken to the laboratory. The bags with tagged leaves were assayed for ^{60}Co and ^{137}Cs contents, using a Packard Armac 440 scintillation detector and Packard 410A auto-gamma spectrometer. These bags were then returned to the field. Contents of the bags with untagged leaves were weighed wet and divided among one to four 25-ml. Warburg vessels, depending on the amount of litter remaining in the bag. Uptake of O_2 by the leaves and associated organisms from the forest site was measured in air, those from the brook and pond in 15 ml. of distilled water. The O_2 determinations were made during three 30-minute periods at 26°C .

Leaves from each bag were then recombined and a 1-gram representative sample was stirred in 1 liter of distilled water for 15 minutes for microbial assay. The rest of the leaves were oven-dried to determine the water content.

The microbial assay consisted of fungal colony counts from 1 ml. of diluted (10X and 100X) stirred leaf suspensions in peptone-dextrose agar. Bacterial counts were made from 100X and 1000X diluted suspensions in Difco nutrient agar. All counts were made after one week of incubation at 26°C .

Results

Loss of weight, ^{60}Co , and ^{137}Cs appeared to be exponential (Fig. 1). Linearized logarithmic regressions $y = bx$ were fitted

Table I. Loss Coefficients and Half-Lives for Two Minerals and Weight in Litter of Three Tree Species at Three Sites

Site	Measurement	Loss coefficients (%/month) for			Effective half-lives (month) for		
		alder	sycamore	oak	alder	sycamore	oak
Forest	¹³⁷ Cs	11.2	28.0	29.4	6.2	2.5	2.4
	⁶⁰ Co	6.1	4.5	16.4	11.3	15.5	4.2
	Weight	5.2	6.6	9.4	13.2	10.5	7.4
Pond	¹³⁷ Cs	34.4	79.0	71.1	2.0	0.9	1.0
	⁶⁰ Co	25.4	37.4	35.6	2.7	1.9	1.9
	Weight	8.5	15.9	11.0	8.1	4.4	6.3
Brook	¹³⁷ Cs	51.8	135.8	136.9	1.3	0.5	0.5
	⁶⁰ Co	39.3	68.9	48.9	1.8	1.0	1.4
	Weight	12.5	23.3	36.7	5.5	3.0	1.9

Table II. Means of Oxygen Uptake and Microbial Densities for Litter of Three Tree Species Exposed for One Year at Three Sites

Site	Oxygen uptake at 26° C. (ml./g. hr.) by			Fungal colonies × 10 ⁻⁷ from 1 g. of			Bacterial colonies × 10 ⁻⁹ from 1 g. of		
	alder	sycamore	oak	alder	sycamore	oak	alder	sycamore	oak
Forest	79	127	135	164	328	381	130	427	262
Pond	37	45	35	75	70	59	58	661	128
Brook	42	50	71	13	17	12	33	240	40

⁶⁰Co in Table I. The half-life for losses other than physical decay, $T_m = TpTe/(Tp - Te)$. For ⁶⁰Co $Tp = 63$ months, and $T_m = 63Te/(63 - Te)$.

The loss coefficients and effective half-lives (Table I) show that, without exception, losses were slowest in the forest and fastest in the brook, with intermediate rates in the pond. With only one exception (⁶⁰Co in sycamore leaves in the forest) the loss coefficients decreased in the order Cs > Co > weight (Figure 1). The mean of all loss coefficients for ¹³⁷Cs and ⁶⁰Co were 4.1 and 1.9 times greater than that of weight (95% lower and upper confidence limits 3.2 and 5.3, and 1.5 and 2.5, respectively). Mean coefficients for ¹³⁷Cs were 2.1 times greater than for ⁶⁰Co.

Loss coefficients for minerals and weight were lowest in alder. The same exception was noted for ⁶⁰Co leaves in the forest for the order of losses of minerals and weight. The losses from sycamore leaves exposed in the forest were slower than those from oak leaves whereas the order was reversed in the pond. In the brook, ⁶⁰Co loss coefficients were greater, and ¹³⁷Cs and weight were lost slower from sycamore than from oak. In general, differences in loss coefficients among sycamore and oak were small. Analysis of variance of the coefficients over the residual showed that the effects of species, site, and the material lost (⁶⁰Co, ¹³⁷Cs, weight) were all significant at the 0.1% probability level, but that the interactions among these effects were not significant at the 10% level.

Loss coefficients may be as high as 136% per month or 4.5% per day for ¹³⁷Cs from sycamore and oak leaves in the brook. The corresponding effective half-lives are around 15 days. Losses of ¹³⁷Cs from sycamore and oak in the brook are 5.8 and 3.7 times faster than the respective losses of weight. The corresponding ratios in the forest are lower, viz. 4.2 and 3.1. This difference may reflect the greater leaching of Cs in the brook than in the forest. On the other hand, loss coefficients for ⁶⁰Co and weight of alder leaves in the forest were only around 5% per month with corresponding half-lives of about one year. Loss of ¹³⁷Cs is only 2.1 times faster than loss of weight in this case, and leaching appears to be slow, possibly as a result of microbial immobilization of ¹³⁷Cs.

Characteristics of the microflora, O₂ consumption, and weight loss of the leaves are summarized in Table II. The usual positive relationship between rates of weight loss and respiration of leaf litter in the forest floor (Witkamp, 1966) did not occur when comparing losses at the various sites. However, within sites, O₂ consumption did parallel loss of both weight and isotopes, that is, it increased in the order alder < sycamore < white oak, with the exception again that the white oak-sycamore order was reversed in the pond. Fungal colony counts were highly correlated with O₂ uptake ($r = 0.92, n = 8, P < 1\%$) whereas bacterial counts were not ($r = 0.25$). The colonies on our plates increased in

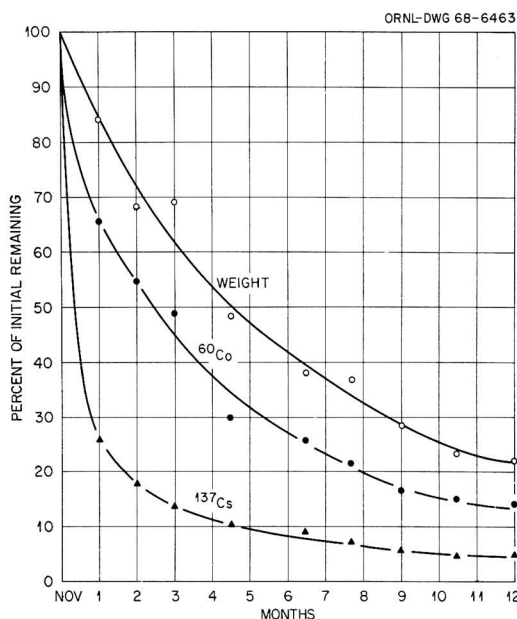


Figure 1. Mean percent loss of weight, ⁶⁰Co, and ¹³⁷Cs from three leaf species (alder, sycamore, oak) exposed for one year at three sites (forest-pond-brook)

where $y = \log_e$ (fraction remaining) at time x in months. The resulting loss coefficients (b) and corresponding half-lives (Te) in months ($Te = \log_e 2/b = 0.693/b$) are given in Table I. These effective half-lives reflect the combined loss of isotope decay, leaching, diffusion, mechanical nonbiological loss (from wind, pelting, current, cracking, etc.), mechanical biological losses (from insects, worms, snails, birds, etc.), microbial decomposition, and mineral uptake by algae, mosses, etc., at the leaf surface. Because of the long physical half-life (Tp) of ¹³⁷Cs (30 years) relative to the effective half-lives in litter (Table I), mineralization of stable Cs is adequately described by the effective half-lives. For stable Co a correction is required because the physical half-life for ⁶⁰Co of 5.25 years approaches the longer effective half-lives for

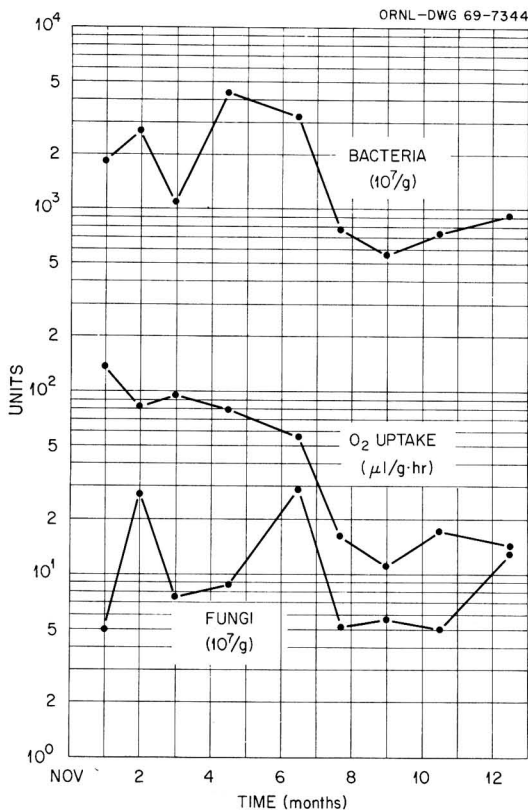


Figure 2. Mean rates of O₂ consumption at 26° C. and mean microbial densities for three leaf species (alder, sycamore, oak) exposed for one year at three sites (forest-pond-brook)

numbers in the order alder < oak < sycamore at all sites. The rates of O₂ consumption at 26° C. decreased throughout the year. Fungal and bacterial colony counts were highest in spring after 4.5 and 6.5 months, respectively, and declined thereafter.

Discussion

The highly significant effects of leaf species, site, and material lost, and the absence of significant effects of the interactions of these factors, indicate that they affect transfer of matter independently. The effect of leaf species is presumably a result of microbial mineralization. This presumption is supported by the parallels between losses of weight and isotopes and the consumption of O₂ within sites, that is, increased losses and consumption in the order alder < sycamore < white oak, with the exception that the white oak-sycamore order was reversed in the pond.

The effect of site is not likely to be primarily a result of microbial mineralization because, among sites, there is no linear relationship between O₂ consumption and losses of weight and minerals. Possibly O₂ consumption does not reflect differences in metabolic activity of the biota at the various sites. There may be more anaerobic mineralization in the aquatic environment, which would not be reflected in rates of O₂ uptake than in the terrestrial environment. Also, the relatively rapid O₂ uptake in forest litter may be an artifact as a result of the introduction of soil CO₂ with the litter bags (Witkamp, 1966). The rapid average increase in loss rates in

the order forest < pond < brook at the ratio 1:2.7:4.6, however, would suggest that not metabolic mineralization but rather the large differences in the rates of leaching between the three sites primarily cause the site effect. Presumably rates of leaching not only affected loss of soluble and colloidal matter, but caused mechanical loss as well. This mechanical loss was most evident in the brook during winter when white oak leaves lost 90% of their weight in 4.5 months, and when biological activity in the oligotrophic water, mean temperature 9° C., was presumably low. The strong winter current was seen to transport sand and small pebbles which fragmented the leaves.

The significant differences in loss coefficients for the various materials appears to be a result of differences in solubility and mineralization. Average losses increased in the order weight < ⁶⁰Co < ¹³⁷Cs at the ratio 1:1.9:4.1. The water soluble substances of fresh litter usually do not exceed 20% of the dry weight (Nykqvist, 1963), whereas almost all of the ¹³⁷Cs in tree litter is in ionic form and readily soluble (Brown, 1964). Our loss rate of 50% of the initial ¹³⁷Cs from oak leaves in 2.5 months agrees well with similar loss rates for Na and K from Eucalyptus leaves in Australia (Attiwill, 1968). Loss rates of Ca and weight from the usually hard Eucalyptus leaves were, however, slower than from oak. Cobalt occurs in enzymes and vitamin B₁₂, which are not immediately leachable. After the initial losses of immediately soluble matter, microbial and faunal decay presumably reduce insoluble compounds to usually simpler soluble forms and open up tissues that heretofore were not accessible to leaching.

Thus it would appear that the main processes affecting differences in losses according to leaf species, site, and matter are primarily results of differences in rate of decay, rate of leaching, and solubility, respectively. As suggested before, the high O₂ consumption per unit weight lost in the forest, relative to that in the aquatic environments, may in part reflect some anaerobic decomposition in the aquatic environment. This suggestion is supported by the significant positive correlation between rates of O₂ consumption and fungal colony counts. Fungi are almost exclusively aerobic, in contrast to bacteria, the colony counts of which were unrelated to rates of O₂ consumption.

The decreasing rates of O₂ consumption at 26° C. apparently indicate a declining breakdown potential as the leaves lost their most readily decomposable components (Nykqvist, 1963; Witkamp, 1966). Because microbial breakdown is primarily a function of temperature, rates of O₂ consumption in the field during winter probably were much lower than the rates measured in the laboratory. A late spring maximum would coincide with fungal and bacterial population maxima.

Exponential loss of 99% of an element requires seven half-lives; thus, 99% of ¹³⁷Cs in sycamore and oak leaves in a brook may enter the stream water in 3.5 months (7 × 15 days). On the other hand, a similar loss of ⁶⁰Co from alder and sycamore leaves in the forest may take from 7–10 years. Isotope decay would account for less than 1% of the 99% loss of ¹³⁷Cs in the example above. However, for ⁶⁰Co, isotope decay would account for 60 to 70% of the loss of initial ⁶⁰Co influx. The health physicist interested in ⁶⁰Co in the environment will use the indicated T_e values, whereas those concerned with the movement of stable Co must use T_m values. For example, in the case of sycamore leaves on the forest floor, T_e for ⁶⁰Co equals 15.5 months and T_m for stable cobalt is 20.6 months. Corresponding T_e and T_m values in the brook differ by less than 2% (1.00 and 1.02, respectively). Therefore, rates of mineralization and the subsequent mineral enrichment of terrestrial and aquatic environments from

decaying leaf litter can be described successfully using radio-nuclides. The resulting rates within sites can be related to microbial activity, whereas rates of leaching primarily control differences in mineralization between sites.

Acknowledgment

Thanks are due to D. G. Gosslee, Statistics Department, Mathematics Division, Oak Ridge National Laboratory, for aid with the statistical analyses.

Rapid Estimation of 7H-Benz[de]anthracen-7-one and Phenalen-1-one in Organic Extracts of Airborne Particulates from 3-Hour Sequential Air Samples

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■ Thin-layer chromatography using glass-fiber paper impregnated with silica gel (ITLC^G), tradename used by Gelman Instrument Co., Inc., was used to separate 7H-benz[de]anthracen-7-one and phenalen-1-one found in acetone extracts of airborne particulates from 3-hour sequential air samples. Only 15 min. was required to separate 0.2–1.25 mg. of the crude extract with pentane-ether, 19 to 1 v./v. Compounds to be assayed were located on the chromatogram by use of relative *R_f* values and changes in fluorescence colors in an acidic environment under long-wavelength ultraviolet light. Direct fluorometric measurement and scanning at F 418/550 and F 409/490 indicated concentrations ranging from 2 to 48 μg. per 1000 m.³ of air for 7H-benz[de]anthracen-7-one and from 0.3 to 17 for phenalen-1-one. For 7H-benz[de]anthracen-7-one, the precision of the method calculated as relative standard deviation was ±3.2%, with a detection limit at 5 nanograms. For phenalen-1-one, the precision was ±1.0%, with a detection limit at 2 nanograms. The method was applied in analysis of 3-hour sequential air samples taken with Hi-Vol samplers over two 24-hour periods during January 1968.

In earlier air pollution studies, the infrared spectra of organic extracts of airborne particulates showed the presence of a strong carbonyl band (Sawicki and Hauser, 1959). Procedures have been described for column and thin-layer chromatographic separation of polynuclear ring-carbonyl compounds (Sawicki, Stanley, *et al.*, 1965a). Analyses of samples from urban atmospheres and effluents from air pollution sources have shown the presence of 7H-benz[de]anthracen-7-one and phenalen-1-one (Sawicki, Stanley, *et al.*, 1965b). Also, a comparison has been made of methods for fluorometric assay for 7H-benz[de]anthracen-7-one in the particulate fraction of air samples and in pollution source effluents (Sawicki, Johnson, *et al.*, 1967). Most of the existing procedures involve separations requiring 2 to 3½ hours and/or lengthy elutions and evaporations. Recently, a rapid method was developed for separation and analysis of phenalen-1-one and 7H-benz[de]anthracen-7-one by instant

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Received for review March 5, 1969. Accepted July 30, 1969. Research sponsored by U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

thin-layer chromatography (ITLC^G), tradename used by Gelman Instrument Co., Inc., (Engel and Sawicki, 1968). This method gives very good separation of these compounds from crude benzene extracts in less than 20 min. It does, however, involve elution and evaporation prior to fluorometric measurement of the salts in strong acid solutions.

Most air pollution data represent mean concentrations and give only a partial picture of a city's air quality. Some knowledge of diurnal concentrations is equally important. Our continuing efforts to assess the applicability of methods to analysis of sequential air samples have shown that direct spectrophotofluorometric examination of TLC chromatograms is the quickest way to characterize and estimate compounds present in complex organic mixtures. In this paper, we report an ITLC^G procedure for the rapid separation and direct spectrophotofluorometric estimation of 7H-benz[de]anthracen-7-one and phenalen-1-one in organic extracts of particulates from 3-hour sequential air samples.

Experimental

Apparatus. For all fluorescence measurements, an Aminco-Bowman spectrophotofluorometer was used with the following settings: slit arrangement, No. 2; sensitivity, 50; and RCA phototube, Type 1P21. The instrument was also equipped with an automatic strip scanner for paper and thin-layer chromatograms.

Hi-Vol samplers were obtained from General Metal Works, Cleves, Ohio, and calibrated before use.

Seven-day variable timers were purchased from International Register Co., Chicago, Ill.

Glass-fiber filters, Type A, (8- × 10-inch) and ITLC^G sheets, Type SG, were obtained from Gelman Instrument Co., Ann Arbor, Mich.

Fluorescence of the thin-layer chromatograms was observed with a Chromato-Vue (Ultra-Violet Products, Inc., San Gabriel, Calif.) with a 3600-A light source. Other thin-layer chromatographic apparatus was obtained from Brinkman Instruments, Inc., Westbury, N.Y.

Reagents. All solvents used for separation and analysis were obtained from commercial sources and purified when necessary. Purity of solvents was determined by investigation of background fluorescence.

Phenalen-1-one and 7H-benz[de]anthracen-7-one were obtained from Aldrich Chemical Co., Milwaukee, Wis., and crystallized to a constant melting point.

Cellulose dialyzing tubing was obtained from Harshaw Scientific, and 55 grams dissolved in 100 ml. of concentrated trifluoroacetic acid.

Samples. At an urban site, air was sampled at 3-hour intervals for 24-hour periods by use of a Hi-Vol sampler with preweighed glass-fiber filters. The particulate loading was determined by difference and the filter extracted for 6 hours with distilled acetone in a Soxhlet apparatus. The acetone was carefully removed by evaporation in a vacuum oven at temperatures just above ambient. Residues of the acetone extracts were covered and refrigerated prior to separation and analysis.

Separation. Residues of the acetone extracts and the standards were dissolved in redistilled methylene chloride. A 0.2- to 1.25-mg. aliquot of the sample and a 10-ng. aliquot of phenalen-1-one and 7H-benz[de]anthracen-7-one were added 1.5 cm. from the bottom of a silica gel ITLC^G sheet, 5 by 20 cm. The ITLC^G sheet was then placed in an equilibrated chromatographic chamber containing pentane-ether, 19 to 1 v./v. Development to 15 cm. was completed in 15 min.

Analysis. A metal strip, 1.5 × 15 × 0.5 cm., was covered on one side with black Mystic tape. The strip was placed in the scanner with black side forward and, by red visible light from the excitation monochromator, a witness mark was made near the top and bottom, indicating the center of the slit image. Standards and representative areas of the sample chromatograms were located by the similarity of fluorescence exhibited under a 3600-Å light source. The spots were easily removed by scoring firmly with a sharp stylus or 4H-lead pencil. Three to four drops of a viscous trifluoroacetic acid solution of the cellulose membrane were used to mount spots firmly with centers coincident with the slit image.

Fluorescence measurements and scans were made at F 409/490 and F 418/550, for phenalen-1-one and 7H-benz[de]anthracen-7-one, respectively. Concentrations were calculated according to the following formulas:

$$\mu\text{g. found per gram of organic extract} = \frac{W_s(A_x R_x)}{W_a(A_s R_s)}$$

and

$$\mu\text{g. found per 1000 m.}^3 \text{ of air} = \frac{10^3(W_s A_x R_x)}{V(W_a A_s R_s)}$$

where

W_s = weight of standard in nanograms

W_a = weight of sample in milligrams

$A_s R_s$ = area of standard spot (mm.²) times the product of the meter multiplier and transmittance readings

$A_x R_x$ = area of sample spot (mm.²) times the product of meter multiplier and transmittance readings

V = volume of air sampled in cubic meters

In the investigation and application of the method reported in this paper, all laboratory personnel exercised caution to avoid contact with and inhalation of trifluoroacetic acid vapors. The Aminco-Scanner is equipped with 0.25-inch tabulation, and this was attached to a vacuum line.

Results and Discussion

All samples were collected at an urban site with procedures and equipment prescribed by the National Air Sampling Net-

Table I. Milligrams Organics and Particulates Found in 3-Hour Sequential Air Samples

Time	1-4-68		1-25-68	
	Org. ^a	Part.	Org. ^a	Part.
12-3 a.m.	6.6	60	4.9	56
3-6	6.6	65	13	56
6-9	8.3	90	17	120
9-12	6.3	110	74	160
12-3 p.m.	4.5	62	14	80
3-6	4.3	74	13	120
6-9	3.9	68	21	110
9-12 p.m.	2.7	60	17	80

^a Methylene chloride soluble residue from 6-hour extraction of particulates with acetone.

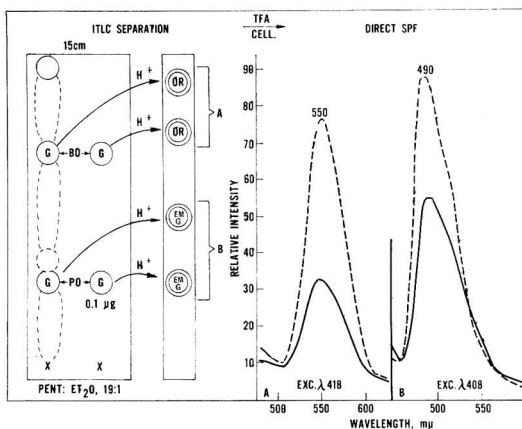


Figure 1. Instant thin-layer chromatographic (ITLC^G) separation and direct spectrophotometric analysis of 7H-benz[de]anthracen (BO) and phenalen-1-one (PO)

Standards (—)

Sample (---)

work of the National Air Pollution Control Administration. Three-hour sequential air samples were taken on Jan. 4, 1968, with temperatures ranging between 2° and 22° F., and winds predominantly from the north; and on Jan. 25, with temperatures ranging from 12° to 14° F. and winds from the south by southeast. Each sample was extracted 6 hours with acetone; after careful evaporation, the residues were transferred to smaller containers with methylene chloride. After each transfer, a very thin film of light-gray material remained in the original container, and most of this material was soluble in water. The weight of methylene chloride solubles and particulates was determined for each sample (Table I). The sample collected between 9 a.m. and 12 p.m. on Jan. 25 was extremely dark and yielded an unusually large weight of organic material. No malfunction of equipment or other evidence was found to explain this phenomenon.

From 0.2 to 1.25 mg. of the samples and 10 ng. of the standards were separated on ITLC^G sheets in 12 to 15 min., giving the characteristic chromatogram shown in Figure 1. Most of the polynuclear aromatic hydrocarbons present in the sample moved with the solvent front. After application of the samples and standards to the ITLC^G sheets, the areas of the spots observed at the origin were much smaller and more uniform than those that are possible with thin-layer chromatographic plates and adsorbents normally used for this purpose.

On exposure to trifluoroacetic acid fumes, the fluorescence color of the spot of phenalen-1-one changed from green to emerald green, and that of 7H-benz[de]anthracen-7-one from green to orange, with marked increases in intensity. This spot test technique was used to define the circumference of sample and standard spots before scoring and removing. The very viscous solution of trifluoroacetic acid and cellulose was used to firmly mount the spots on the scan-strip and form the fluorescent salts of these weakly basic compounds (Figure 1). The fluorescence of the salts of these compounds was stable for 20 min. and then gradually faded. Once most of the acid had evaporated, the hardened spots could be peeled away with the cellulose film and the metal strips used for many subsequent analyses without further preparation. The trifluoroacetic acid-cellulose solution was stable during the entire investigation.

Areas of the spots of pure compounds on the ITLC^g sheets changed when we used high concentrations or low volumes. This factor was considered in derivation of equations for calculation of unknown concentrations. Whereas 10 to 100 ng. of pure compounds in 5- and 10- μ l. volumes of methylene chloride gave spot areas of 68 mm.² \pm 1%, areas of spots increased by a factor of 2 at concentrations between 100 and 1000 ng. and/or volumes below 5 μ l. Over the range of concentrations found during this study, the substitution of peak areas from the scan curves for spot areas gave results within the expressed precision of the method. The use of spot areas is recommended, however, and data reported in this paper were calculated from the equations shown.

Results of the analyses of 3-hour sequential samples taken over two 24-hour periods for 7H-benz[de]anthracen-7-one are shown in Table II. All values represent averages of at least three determinations. The highest concentrations were reached in the late afternoon and evening; mean values for Jan. 4 and 25, respectively, were 5.2 and 22 μ g. per 1000 m.³ of air, and 426 and 480 μ g. per gram of extract. The diurnal concentration levels did not coincide with the distribution pattern for total particulates and organics.

Based on 11 determinations, the relative standard deviation calculated for 7H-benz[de]anthracen-7-one was \pm 3.2%. The detection limit established with the pure compound was 5 ng.

Results of the analyses of 3-hour sequential samples over two 24-hour periods for phenalen-1-one are shown in Table III. All values represent averages of at least three determinations. Concentrations were very low in the mornings and relatively high in the afternoon for both 24-hour sampling periods. Average concentrations obtained for Jan. 4 and 25 were 7.7 and 6.7 μ g. per 1000 m.³ of air, and 85 and 133 μ g. per gram of extract, respectively.

Based on 11 determinations, the relative standard deviation calculated for phenalen-1-one was \pm 1.0%. The detection limit was 2 ng. of pure compound.

Conclusions

In this investigation ITLC^g and direct spectrophotofluorometry were applied to the rapid separation and analysis of 7H-benz[de]anthracen-7-one and phenalen-1-one in suspended particulates of polluted urban atmospheres. The methods are applicable to the assay of 3-hour sequential air samples and, therefore, to the study of pollutant levels during 3-hour segments that contribute to diurnal and longer pollution patterns.

In the absence of detailed meteorological and land-use data, no meaningful conclusions can be drawn to explain changes in concentrations of these compounds during the 24-hour

Table II. Direct Spectrophotofluorometric Analysis of 7H-Benz[de]anthracen-7-one. F 418/550

Time	1-4-68		1-25-68	
	μ g./1000 m. ³ air	μ g./g. organics ^a	μ g./1000 m. ³ air	μ g./g. organics ^a
12-3 a.m.	5	230	5	370
3-6	4	230	15	350
6-9	2	100	17	440
9-12	7	430	9	50
12-3 p.m.	3	180	24	360
3-6	5	510	23	760
6-9	8	770	38	700
9-12 p.m.	9	960	48	820

^a Methylene chloride solubles of residues from 6-hour extraction of particulates with acetone.

Table III. Direct Spectrophotofluorometric Analysis of Phenalen-1-one. F 409/490

Time	1-4-68		1-25-68	
	μ g./1000 m. ³ air	μ g./g. organics ^a	μ g./1000 m. ³ air	μ g./g. organics ^a
12-3 a.m.	0.8	40	0.3	20
3-6	0.5	30	0.6	15
6-9	0.7	40	0.7	18
9-12	0.5	30	2.0	10
12-3 p.m.	0.3	20	12	180
3-6	1.6	160	9	310
6-9	1.7	170	12	220
9-12 p.m.	1.6	190	17	290

^a Methylene chloride solubles of residues from 6-hour extraction of particulates with acetone.

periods investigated. Also, one can only speculate that other aromatic ring carbonyl compounds would be present and would show similar distribution. At the same site used for this investigation, a different diurnal distribution pattern was observed for four polynuclear aromatic hydrocarbons. However, the distribution patterns were consistent with peak concentrations occurring from 6-9 a.m. and from 3-6 p.m.

The direct spectrophotofluorometric procedure reported in this paper, and similar procedures, shows potential for application to more comprehensive air pollution studies.

Acknowledgment

The authors acknowledge the cooperation and technical assistance of persons in the Meteorological Program and the National Air Sampling Network of the National Air Pollution Control Administration.

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Received for review November 4, 1968. Accepted August 11, 1969. Presented at Division of Water, Air, and Waste Chemistry, 156th Annual Meeting, ACS, Atlantic City, N.J., September 1968. Mention of commercial products does not constitute endorsement by the Public Health Service.

Influence of Mineral Nutrition on the Sensitivity of Tomato Plants to Hydrogen Fluoride

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■ Tomato plants grown in sand culture and provided with a complete nutrient solution or solutions deficient in calcium, magnesium, or potassium were exposed to various concentrations of hydrogen fluoride (HF) for periods of three, five, or 64 days. In magnesium deficient plants, HF exposure resulted in a reduction in the dry weight of both tops and roots and an increase in the severity of magnesium deficiency symptoms on basal leaves. Foliar accumulation of fluoride was suppressed by magnesium deficiency. The effects of HF exposure on calcium deficient plants were characterized by reduced top growth, increased foliar chlorosis, and an enhancement of necrosis on apical leaves. Fluoride accumulation was unaffected by calcium nutrition. The responses of potassium deficient plants to HF were limited to increases in F accumulation and in necrosis on apical leaves. The differential responses of the elements to HF exposure were ascribed to differences in their mobility within plant tissues, the stability of fluoride salts formed, and/or their metabolic roles.

The nutritional status of plants is generally believed to be one of the factors that determine the susceptibility of plants to atmospheric fluorides. However, published experimental results on this subject are rare. Brennan, Leone, *et al.* (1950) demonstrated that deficient and superoptimal levels of nitrogen, phosphorus, or calcium retarded fluoride uptake and subsequent injury of tomato plants, whereas optimal concentrations of these elements favored fluoride-induced damage. Conversely, fluoride accumulation by bean seedlings exposed to hydrogen fluoride (HF) was enhanced under conditions of phosphorus, potassium, or iron deficiency (Applegate and Adams, 1960). Adams and Sulzbach (1961) reported that an acute exposure to HF resulted in obvious injury to leaves of nitrogen deficient bean plants. Although tissues of plants grown on phosphorus, potassium, iron, or calcium deficient media accumulated equivalent amounts of fluorine, they were not visibly affected. HF fumigation experiments by McCune, Hitchcock, *et al.* (1966) showed that increased tip burn of gladiolus leaf blades was associated with potassium, phosphorus, and magnesium deficiency, and decreased tip burn was observed in calcium and nitrogen deficient plants. The effects of calcium nutrition and HF fumigation on the fruiting of tomato plants were investigated by Pack (1966). Low calcium reduced the size of fruit, and, in combination with HF, fruit size was further reduced, resulting in partially or completely seedless fruit. Pack (1966) suggested that HF might interfere with calcium metabolism during fertilization.

The experiments described herein were performed to test the influence of three essential cations—calcium, magnesium, and potassium—on growth, fluoride accumulation, foliar injury, flowering, and fruiting of tomato plants exposed to gaseous HF.

Materials and Methods

Tomato (*Lycopersicon esculentum* var. Bonny Best) seeds were germinated in soil. When the seedlings were two weeks old, soil was washed from the roots and three uniform seedlings were transplanted to 5-inch plastic pots containing washed (Robbins, 1946) flint-shot quartz sand. Cultures were maintained in a greenhouse and irrigated with one-fourth strength Hoagland's solution for one week following transplanting. Two seedlings were then removed from each culture, leaving one uniform plant per pot, which was automatically subirrigated twice daily with one of seven nutrient solutions. The nutrient regimes included complete (Hoagland's) nutrient solution and solutions containing calcium, magnesium, or potassium at one-twentieth and one-fourth the concentration of the complete solution. Nutrient solutions were prepared as described by McCune, Hitchcock, *et al.* (1966). In deficient solutions, an equivalent amount of sodium was substituted for the element varied. When deficiency symptoms first became apparent on plants given the lowest nutrient levels (18–21 days after transplanting), all plants were transferred to Mylar-covered fumigation chambers (Hitchcock, Zimmerman, *et al.*, 1962) and exposed to HF or filtered ambient air. Four separate fumigation experiments were carried out. Exposure to average concentrations of: (a) 0, 4.7, or 12.0 $\mu\text{g. F/m.}^3$ for five days; (b) 0, 1.0, or 15.1 $\mu\text{g. F/m.}^3$ for five days; (c) 0 or 8.9 $\mu\text{g. F/m.}^3$ for three days; and (d) 0 or 3.1 $\mu\text{g. F/m.}^3$ for 64 days. (Control fumigations listed as 0 $\mu\text{g. F/m.}^3$ were known to be less than 0.2 $\mu\text{g. F/m.}^3$.) The two potassium deficient treatments were not included in the last experiment. Treatments were replicated four times, except in the 64-day fumigation, in which three replicates were used.

Before, during, and after fumigation, lateral shoots were removed as they developed to maintain plants with a single stem. Growth rates were estimated by periodic measurements of the distance between the cotyledonary node and the terminal bud. Foliar injury was subjectively assessed by rating the extent of chlorosis and necrosis on each leaf. An injury index of 1, 2, 3, and 4 was equivalent to no chlorosis, slight, moderate, and severe chlorosis, respectively; and 1, 3, 5, and 7 to no necrosis, slight, moderate, and severe necrosis. The number of nodes per plant (8–9) at the time foliar injury was assessed was relatively less variable than plant height. Therefore, the ratings for the uppermost four leaves of each plant were defined as apical injury and the ratings for the remaining leaves as basal injury.

Fluoride accumulation by vegetation was determined using the semi-automated method of analysis (Mandl, Weinstein, *et al.*, 1966; Weinstein, Mandl, *et al.*, 1963). Unless otherwise noted, surface fluoride was removed prior to analysis by washing for 30 sec. in Alconox-EDTA solution (*i.e.*, 0.05% Alconox plus 0.05% disodium ethylenediamine tetraacetic acid, w/v) followed by two successive 15-sec. rinses in deionized water.

Results

Visible symptoms of nutrient deficiencies. Foliar markings induced by nutrient deficiencies in the absence of HF are

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Table I. Effect of Nutrient Treatment on Stem Elongation of Bonny Best Tomato Plants During and After Fumigation with HF

Nutrient varied	Concentration relative to complete medium	Stem elongation (cm.) ^a	
		Elongation during fumigation	Post-fumigation elongation
None (complete)	...	11.18a	56.02a
Calcium	1/20	7.47c	9.72c
Calcium	1/4	11.72a	49.88b
Magnesium	1/20	7.48c	57.17a
Magnesium	1/4	10.71ab	55.12a
Potassium	1/20	9.68b	50.91b
Potassium	1/4	10.54ab	47.12b

^a Means within a column followed by different letters are significantly different at the 5% level (Duncan, 1955).

Table III. Effect of Nutrient Culture and HF Concentration on the Development of Chlorosis on Leaves of Bonny Best Tomato Plants

Nutrient varied	Concentration relative to complete medium	Chlorosis ratings after a 5-day exposure to HF concentrations ($\mu\text{g. F/m.}^3$) of		
		0	4.7	12.0
None (complete)	...	1.12	1.25	1.50
Calcium	1/20	3.88 ^a	4.75 ^a	6.75 ^{a,b}
Calcium	1/4	1.19	1.81	1.94
Magnesium	1/20	5.12 ^a	4.44 ^a	4.25 ^a
Magnesium	1/4	1.06	1.12	1.44
Potassium	1/20	1.19	1.31	1.38
Potassium	1/4	1.25	1.12	1.75

^a Significantly different from plants in complete medium (5% level).
^b Significantly different from nonfumigated plants (5% level).

Table II. Effect of Nutrient Treatment and HF Exposure (0 or 3 $\mu\text{g. F/m.}^3$ for 64 days) on the Dry Weight of Tops and Roots of Bonny Best Tomato Plants

Nutrient varied	Concentration relative to complete medium	Dry weight (grams) of tops exposed to HF concentrations of		Dry weight (grams) of roots exposed to HF concentrations of	
		0 $\mu\text{g. F/m.}^3$	3 $\mu\text{g. F/m.}^3$	0 $\mu\text{g. F/m.}^3$	3 $\mu\text{g. F/m.}^3$
		None (complete)	...	58.05	36.48 ^b
Calcium	1/20	8.61 ^a	6.22 ^a	2.73 ^a	1.44 ^a
Calcium	1/4	33.47 ^a	25.31 ^{a,b}	4.68	3.38
Magnesium	1/20	5.84 ^a	4.42 ^a	1.23 ^a	0.91 ^a
Magnesium	1/4	45.35	23.41 ^{a,b}	5.42	3.84 ^b

^a Significantly different from plants in complete medium (5% level).
^b Significantly different from nonfumigated plants (5% level).

summarized as follows. Symptoms of magnesium deficiency were first apparent on the oldest leaves and progressed acropetally. Magnesium at one-fourth the complete level induced intercostal chlorosis on leaves from the oldest 2 or 3 nodes. On plants supplied with magnesium at one-twentieth of that in the complete solution, symptoms progressed from mild chlorosis to severe intercostal chlorosis with intercostal necrotic lesions, and, finally, to desiccation and death. These progressive symptoms could be followed on a single leaf over a period of two weeks or by making comparisons of adjacent leaves along the stem. Symptoms of calcium deficiency were confined to apical leaves. One-fourth strength calcium resulted in a yellow-green color of expanding and young, fully expanded leaves. One-twentieth strength calcium resulted in marginal necrosis, intercostal chlorosis, and death of the terminal buds. Calcium shortage did not affect basal leaves. Potassium deficiency did not result in significant visible foliar markings. Occasionally, very mild marginal chlorosis of basal leaves was noted on plants cultured on the medium with the lowest potassium concentration.

Growth. Elongation of single-stem plants exposed to 0, 4.7, or 12.0 $\mu\text{g. F/m.}^3$ for five days was measured at three-day intervals throughout the experiment. No significant effect of HF exposure on growth within a nutrient treatment was observed during fumigation or the post-fumigation period. Therefore, the data for control and HF exposed plants were pooled in the analysis of the effects of nutrient treatment

(Table I). Elongation during fumigation was suppressed significantly in plants grown on media containing calcium, magnesium, or potassium at one-twentieth of that in the complete medium. Post-fumigation growth was inhibited more than 80% at the lowest calcium level. Calcium at one-fourth the complete level and both potassium treatments significantly reduced post-fumigation growth also. Magnesium deficiency did not affect post-fumigation elongation.

The dry weights of tops (above ground plant parts) and roots, measured after a 64-day exposure to 0 or 3 $\mu\text{g. F/m.}^3$, are given in Table II. In this experiment, lateral shoots were not removed periodically, and the plants were allowed to branch. Exposure to HF did not affect the already severe inhibition of dry weight induced by one-twentieth strength calcium or magnesium. In these plants the lack of calcium repeatedly killed terminal growth as new shoots developed, resulting in stunted plants having a witches'-broom appearance. Magnesium deficiency resulted in tall, spindly plants in which the reduction in dry weight may have been accentuated by desiccation and abscission of leaves from the lowest two or three nodes. HF significantly reduced the dry weight of tops of plants grown on complete nutrient and one-fourth strength calcium or magnesium. Although one-fourth strength calcium resulted in a significant reduction compared to the complete nutrient, in both fumigated and nonfumigated plants, a significant effect of one-fourth strength magnesium was present only in HF fumigated plants. Inhibition of the dry weight of roots was found only in plants provided the lowest calcium and magnesium levels (one-twentieth strength). Although root growth of plants exposed to HF was, in all treatments, less than that of those provided filtered air, the only statistically significant reduction due to HF exposure was in plants cultured on one-fourth magnesium. No visible symptoms of injury on roots were observed in treatments where root growth was inhibited.

Foliar injury. Foliar injury assessed three days after a five-day fumigation showed that HF exposure and the position of the affected leaves on the plant (apical vs. basal), significantly altered the amount and extent of chlorosis, necrosis, and foliar injury (the sum of chlorosis and necrosis ratings).

Chlorosis was significantly greater on plants grown on calcium or magnesium at one-twentieth of that in the complete medium (Table III). The only effect of HF on chlorosis was seen on plants provided the lowest calcium level. Chlorosis was significantly increased by exposure to 12.0 $\mu\text{g. F/m.}^3$.

Table IV. Effect of Nutrient Culture and HF Concentration on the Foliar Necrosis Ratings of Apical and Basal Leaves of Bonny Best Tomato Plants

Nutrient varied	Concentration relative to complete medium	Necrosis ratings of leaves after a 5-day exposure to HF concentrations ($\mu\text{g. F/m.}^3$) of					
		0		4.7		12.0	
		Apical	Basal	Apical	Basal	Apical	Basal
None (complete)	...	1.00a ^a	2.25abc	1.75ab	2.75abc	1.25ab	2.00ab
Calcium	1/20	13.00g	1.50ab	16.00h	2.00ab	19.75i	2.00ab
Calcium	1/4	1.25ab	1.50ab	3.75abcde	3.75abcde	5.00cde	3.25abcd
Magnesium	1/20	1.00a	5.75e	1.00a	10.00f	3.00abcd	11.50fg
Magnesium	1/4	1.00a	2.00ab	2.75abc	2.00ab	5.00cde	4.00bcde
Potassium	1/20	1.00a	1.00a	4.25bcde	1.25ab	4.75bcde	1.00a
Potassium	1/4	1.00a	1.00a	3.50abcde	2.50abc	5.25de	1.75ab

^a Any two means not followed by the same letter differ significantly at the 5% level (Duncan, 1955).

Table V. Mean Foliar Accumulation of Fluoride by Leaves of Bonny Best Tomato Plants as Affected by Mineral Nutrition and HF Exposure

Nutrient varied	Concentration relative to complete medium	Fluoride content (p.p.m. dry weight) after exposure for						
		3 days		5 days			64 days	
		0	8.9	HF concentration ($\mu\text{g. F/m.}^3$)			0	3.1
None (complete)	...	2.2	196.2	6.6	38.6	254.4	9.3	233.1
Calcium	1/20	1.8	131.3 ^a	6.9	37.6	263.2	9.6	273.9
Calcium	1/4	4.3	171.8	7.6	48.2	254.6	13.5	223.9
Magnesium	1/20	1.5	103.5 ^a	4.9	39.6	216.8 ^a	5.3	197.8
Magnesium	1/4	1.0	179.0	5.6	38.6	171.6 ^a	8.1	173.7 ^a
Potassium	1/20	1.0	245.0 ^a	5.4	40.3	301.4 ^a
Potassium	1/4	1.5	211.0	4.8	34.0	310.7 ^a

^a Significantly different from plants in complete medium (5% level).

Necrosis ratings revealed a relationship between nutrient treatment, HF exposure, and the position of necrotic leaves on the plant (Table IV). The lowest calcium and magnesium levels resulted in significant necrosis of apical and basal leaves, respectively, on plants that were not exposed to HF. Necrosis on apical leaves of plants cultured on one-twentieth strength calcium became more intense with each increase in HF concentration. Leaves of plants supplied one-fourth strength calcium did not exhibit increased necrosis when exposed to 4.7 $\mu\text{g. F/m.}^3$, whereas a moderate, but significant increase in terminal leaf necrosis was induced on plants exposed to 12.0 $\mu\text{g. F/m.}^3$. The appearance of necrosis was such that the contributions from each variable could not be separated to determine if HF enhanced the calcium deficiency symptoms or if calcium shortage favored HF-induced injury.

Necrosis induced by magnesium deficiency generally was confined to the lower leaves. Necrosis induced by one-twentieth strength magnesium on basal leaves was intensified by exposure to either 4.7 or 12.0 $\mu\text{g. F/m.}^3$. This necrosis clearly resembled magnesium deficiency symptoms and was not similar to HF-induced markings produced on younger leaves. Plants grown on magnesium at one-fourth the complete complement did not show significantly increased necrosis of basal leaves; however, exposure to 12.0 $\mu\text{g. F/m.}^3$ resulted in significant increases in necrosis on apical leaves.

The higher HF concentration induced apical necrosis on all potassium deficient plants. At the lower HF concentration, a significant amount of apical necrosis was found only on plants

grown with one-twentieth strength potassium. In general, the severity of necrosis on basal leaves was not affected by fumigation or by calcium or potassium shortage.

Fluoride accumulation. Post-fumigation analyses of tomato leaflets for fluoride showed that exposure to filtered ambient air for 3, 5, or 64 days did not result in significant fluoride accumulation. Deficiencies of the three cations elicited different responses with respect to fluoride accumulation (Table V). In plants exposed to 15.1 $\mu\text{g. F/m.}^3$ for five days, accumulation of fluoride was decreased by magnesium deficiency, increased by potassium deficiency, and unaffected by calcium deficiency. The accumulation of fluoride was similarly decreased by one-fourth strength magnesium in plants exposed to 3.1 $\mu\text{g. F/m.}^3$ for 64 days and by one-twentieth strength when exposed to 8.9 $\mu\text{g. F/m.}^3$ for three days. The only significant effect of calcium deficiency on fluoride accumulation was a reduction in plants grown at one-twentieth calcium and exposed to 8.9 $\mu\text{g. F/m.}^3$.

After one fumigation experiment (0, 1.0, and 15.1 $\mu\text{g. F/m.}^3$ for five days), tomato plants were fractionated into three groups: leaflets; stems; and the petiole fraction, which included the petioles, petiolules, and rachises. Analyses of the unwashed stem and petiole fractions showed that the amount of fluoride accumulated in these tissues was negligible and not affected by nutrient culture or HF exposure. Roots were not analyzed.

Flowering and fruiting. The indeterminate nature of flower production characteristic of the Bonny Best variety and within treatment variability made effects on flowering difficult to

asses. However, no flowers or fruit were produced on plants grown on media containing calcium or magnesium at one-twentieth the concentration of the complete medium. The time of flowering and the number of flowers produced on plants in all other nutrient treatments were not affected by exposure to HF at 4.7 or 12.0 $\mu\text{g. F/m.}^3$ for 5 days or to 0 or 3.1 $\mu\text{g. F/m.}^3$ for 64 days. Fruit production by plants cultured on complete nutrient media was not affected by HF during the 64-day period. External appearance and locule and seed development appeared normal in all fruits regardless of treatment.

Discussion

A discussion of the interacting effects of HF exposure and mineral nutrition must also take into consideration some of the pertinent factors of mineral nutrition in relation to plant growth and development. Plant nutrition is complex, and interactions between various nutrients essential for plant growth have been documented. When HF-induced responses in plants deficient in a given nutrient are considered, it should be understood that these responses may be due to a nutritional imbalance peculiar to that element, rather than to the deficiency of that element *per se*. Thus, it is possible that the observed interactions between nutrient deficiency and fluoride exposure may be indirect, rather than direct, effects.

The metabolic patterns of leaves differ with age. In young leaves synthetic reactions and growth predominate, whereas in older leaves, photosynthesis is the dominant function, and little growth occurs. Mineral nutrients are transported via the transpirational stream to all leaves; however, retransport from older leaves to actively growing tissues prevents the accumulation of toxic concentrations. The rate of retransport is a function of the mobility of a mineral. The location of mineral deficiency symptoms on the plant is also a function of mobility. Magnesium and potassium are relatively mobile elements, and, when the external supply is limited, retransport occurs and deficiency symptoms first appear on basal leaves. Calcium, on the other hand, is relatively immobile, and deficiency symptoms are first apparent on apical leaves. HF-induced foliar injury was limited to apical leaves, and was observed in calcium, magnesium, and potassium deficient plants. However, the increased injury to apical leaves in calcium deficient plants was more than additive, and, in magnesium deficient plants, injury to basal leaves was markedly increased by HF exposure. Thus, for both calcium and magnesium deficient plants, foliar injury resulting from the nutrient-HF treatments was related to the relative mobility of these cations and was most pronounced in tissues in which the nutrient shortage was most acute.

Although potassium shortage was the least effective mineral deficiency tested, fluoride uptake was enhanced in potassium deficient plants, whereas fluoride accumulation was generally suppressed by magnesium deficiency and unaffected by calcium deficiency. The observed enhancement of fluoride accumulation by potassium deficiency is in agreement with the data of Applegate and Adams (1960) for bean seedlings, and the absence of a relationship between calcium deficiency and

fluoride uptake is in accord with the findings of Pack (1966) and Applegate and Adams (1960). However, Brennan, Leone, *et al.* (1950) found that optimal levels of calcium increased fluoride uptake, and deficient and superoptimal levels suppressed its accumulation.

The response of plants to HF fumigation is not only a function of the concentration of the pollutant and the duration of exposure, but also of the rate and pattern of fluoride absorption, translocation, and accumulation. Therefore, any external or internal factors that affect one or more of these processes can also alter the sensitivity of plants to HF. In this investigation it was shown that potassium deficiency did not affect the sensitivity of tomato plants to HF, whereas calcium and magnesium deficiency rendered plants more susceptible to HF-induced growth inhibition and foliar injury.

These differential responses of the nutrients may be explained by considering their metabolic roles. Calcium and magnesium ions are required as cofactors in some essential enzymic reactions, and, when unavailable, these reactions cannot proceed. Potassium ions are also involved in essential enzymic reactions, but as activators rather than cofactors. When the amount of available potassium is low, the reactions are not completely inhibited, but usually proceed at reduced rates.

The relative stability of fluoride salts formed within plant tissues is another factor to account for the potassium effect. KF is relatively soluble and, when the external supply of potassium ions is limited, dissociation can occur readily, resulting in available potassium ions. CaF_2 and MgF_2 , on the other hand, are relatively stable salts and, when calcium or magnesium ions are in short supply, the effective concentration within the plant is further reduced due to the relative insolubility of these salts.

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Received for review February 24, 1969. Accepted August 21, 1969. This work was supported in part by Grant No. AP-00189 from the National Air Pollution Control Administration, U.S. Public Health Service. O. F. R. was in the NSF High School Teacher Research Participation Program (GW-1692), 1967.

COMMUNICATIONS

Instrument Response Time in an Analytical System for Continuous Glucose Measurement

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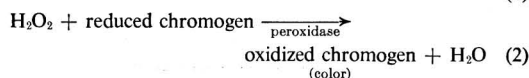
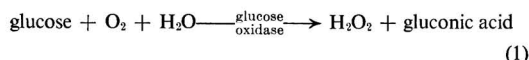
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■ To interpret a continuous record of glucose concentration plotted by the Technicon AutoAnalyzer, it is necessary to assess the effect of the instrumental lag on the recorded data. The effect of this lag is demonstrated by comparing the output record produced in response to a known input function with the input function itself. The known input function consisted of a 0 to 10 mg. per liter step function followed by an approximate zero order decrease in glucose concentration. Under these conditions, the concentration by which the output record lagged the input record approached an asymptotic value, which may be estimated according to the principle of superposition.

Continuous monitoring of glucose concentrations in microbiological culture medium by means of the Technicon AutoAnalyzer has been employed by Jeris and Cardenas (1966) and by Baillo (1968) to measure glucose uptake rates by biological systems. In the interpretation of these data, some consideration must be given to the response time limitations of the instrument. The effect of instrument lag time on the recorded glucose concentration profile is illustrated for the case where the uptake rate is approximately zero order.

Experimental

The method of glucose analysis employed in this study was specific for β -D-glucose, and was based on the oxidation of glucose to gluconic acid by glucose oxidase, and the subsequent reduction of H_2O_2 by a peroxidase, according to the following simplified reaction scheme.



The AutoAnalyzer flow diagram of Jeris and Cardenas (1966) was extensively modified in order to measure glucose concentrations of from 0 to 10 mg. per liter. The modified flow diagram is shown in Figure 1. The enzyme reagent was prepared by adding two vials of chromogen (Worthington Biochemicals, Freehold, N.J., cat. no. CHGX4) and two vials of Glucostat (Worthington, cat. no. X4G) to 400 ml. of distilled water.

The continuous-flow filter and dialyzer were necessary to eliminate bacterial cells from the sample stream during the actual glucose uptake experiments (Baillo, 1968).

To test the response speed of the instrument, the response to a known input signal was observed. The input signal supplied to the system can be stated as

$$\begin{aligned} H(\theta) &= 0, \text{ for } \theta < 0 && \text{(no glucose present)} \\ H(\theta) &= 1, \text{ for } \theta = 0 && \text{(glucose added at time zero, } C_0) \\ H(\theta) &= 1 - k, \text{ for } \theta > 0 && \text{(zero order glucose disappearance)} \end{aligned} \quad (3)$$

where

- $H(\theta)$ = C/C_0 , dimensionless input concentration
- C = glucose concentration in the sample stream, mg. per liter
- C_0 = glucose concentration in the same stream at time zero, mg. per liter
- $\theta = t/t_0$, dimensionless time (used to refer to input functions)
- t = time, minutes
- t_0 = the time constant of the instrument, minutes
- $K = at/C_0$, a dimensionless rate constant
- a = volumetric rate of glucose disappearance in the sample stream, mg. per liter minute

To simulate this signal, a baseline sample was drawn from a stirred beaker containing phosphate buffer (1.0 gram per liter of K_2HPO_4 , 0.5 gram per liter of KH_2PO_4 , pH = 7.1). At time zero, a quantity of glucose was added to the beaker in order to give a concentration, C_0 . Also, at time zero, addition of phosphate buffer to, and withdrawal of, solution from the stirred beaker was begun (Figure 2). A second AutoAnalyzer

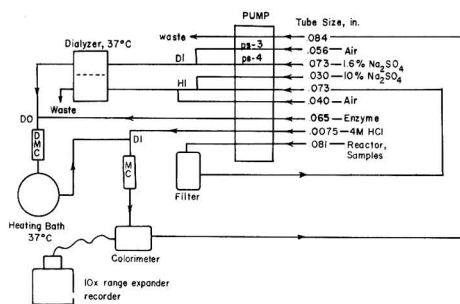


Figure 1. AutoAnalyzer flow diagram for continuous glucose analysis

DMC = double mixing coil
MC = mixing coil
ps = pulse suppressor

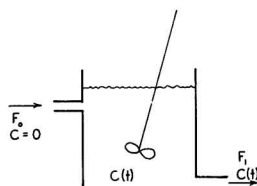


Figure 2. Continuous stirred reactor simulation

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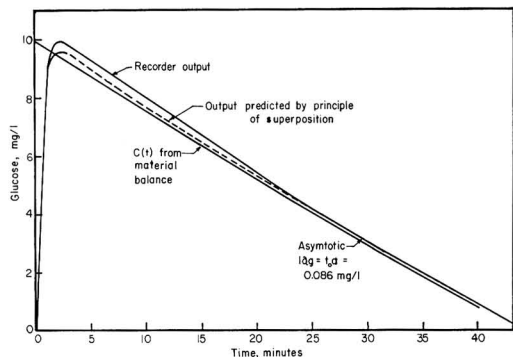


Figure 3. AutoAnalyzer response to linear input signal

pump was employed for this. For the arrangement depicted in Figure 2, an unsteady state material balance (Baillod, 1968) gives the concentration in the vessel as a function of time as

$$H(\theta) = C/C_0 = \left[1 - \left(\frac{F_1 - F_0}{V_0} \right) t \right] \frac{F_0}{F_1 - F_0} \quad (4)$$

where

V_0 = volume of fluid in the vessel at time zero, ml.

F_0 = rate of inflow, ml. per minute

F_1 = rate of outflow, ml. per minute.

Equation 4 indicates that, if $F_1 = 2F_0$, then C/C_0 will be a linear function of time. Slight variations between different pieces of pump tubing, however, resulted in values of F_1 slightly less than $2F_0$, so that the rate of change of concentration in the test vessel decreased slightly with time. The actual input function therefore, calculated with $F_0 = 2.45$ ml. per minute, $F_1 = 4.73$ ml. per minute, $C_0 = 10$ mg. per liter, and $V_0 = 100$ ml., was

$$C/C_0 = (1 - 0.0228t)^{1.075} \quad (5)$$

Results

The solid lines of Figure 3 show the input function given by Equations 3 and 5, along with the output record plotted by the recorder. To compare the input and output functions directly with the same time scale, the transport lag through the AutoAnalyzer was subtracted from the output time scale. The data indicate that the measured output function consistently lags the input function. However, the concentration by which the output lags the input appears to approach an asymptotic value of approximately 0.1 mg. per liter. In experiments with a pure culture of *Zoogloea ramigera* (Baillod, 1968), the glucose uptake rate usually decreased as the glucose concentration fell below 2 to 5 mg. per liter. For these cases, the concentration profile plotted by the recorder will tend to converge with the actual input concentration profile, and the concentration by which the output function lags the input function will decrease even further. Therefore, under appropriate conditions, the effect of instrument lag may be neglected when interpreting the final portion of the glucose concentration profile plotted by the AutoAnalyzer recorder.

Discussion

It is possible to describe mathematically the instrument output function produced in response to a known continuous input function if the instrument response to a step input func-

tion is known. This mathematical analysis, based on the principle of superposition, has been used by Mueller *et al.* (1967) to assess the effect of instrument lag on oxygen uptake rates measured by a galvanic cell oxygen probe. Applied to a linear instrumental system, this analysis predicts the instrument output record produced in response to a known input function as

$$G(\tau) = H(0)B(\tau) + \int_0^\tau B(\tau - \theta) \frac{dH(\theta)}{d\theta} d\theta \quad (6)$$

where

$G(\tau)$ = dimensionless output concentration plotted by the recorder, C/C_0

$B(\tau)$ = dimensionless output concentration produced in response to a step input function

$H(\theta)$ = general dimensionless input concentration

θ = dimensionless time-integrating variable, used for input functions

τ = dimensionless time, t/t_0 , used for output functions

$H(0) = H(\theta)$ evaluated at $\theta = 0$.

When the instrument was subjected to a step input function of 0 to 10 mg. per liter, it was observed that the instrument output function could be described by

$$B(\tau) = 1 - e^{-\tau} \quad (7)$$

The instrument time constant, t_0 , was determined by fitting Equation 7 to the recorder output produced in response to a step input function. The value of t_0 was approximately 0.35 minute. Combining Equations 3, 6, and 7 predicts the transient output function as

$$G(\tau) = (1 + K)(1 - e^{-\tau}) - K\tau \quad (8)$$

which, in the case of $\tau \gg 0$, reduces to

$$G(\tau) = 1 + K - K\tau \quad (9)$$

The concentration by which the output lags the input is obtained by subtracting the input signal from the output signal at $\tau \gg 0$.

$$G(\tau) - H(\tau) = C_{\text{lag}}/C_0 = K \quad (10)$$

Thus, the asymptotic lag concentration is given by

$$C_{\text{lag}} = at_0 \quad (11)$$

The dashed line in Figure 3 shows the output function predicted by the principle of superposition, as given by Equation 8. By comparing the predicted output function with the measured output function, it can be seen that the recorder "overshoot" is somewhat greater than that predicted by the principle of superposition. However, the asymptotic concentration of 0.086 mg. per liter predicted by the principle of superposition appears to agree quite well with that given by the recorder output. Therefore, it is reasonable to conclude that, under these conditions, Equation 11 gives a valid estimate of the concentration by which the AutoAnalyzer output function lags the input function.

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Received for review April 1, 1969. Accepted July 22, 1969.

Vanadium, Copper, and Aluminum in the Lower Atmosphere between California and Hawaii

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■ Atmospheric particulate samples were collected from a 20-meter-high tower on the windward coast of the island of Hawaii and from a ship between California and Hawaii. The samples were analyzed for Na by flame photometry, and for V, Cu, and Al by thermal neutron activation. The Na/Cu, Na/V, and Na/Al ratios for seawater were considerably greater than those for the particulate matter, indicating a nonmarine source for Cu, V, and Al. Elemental ratios suggest that Al and V probably come from the weathering of continental crustal material. The source of the high Cu concentrations is unknown, although contributions from man-made pollution on the west coast of North America is a possibility.

Although chemical studies of air pollution have attracted an increasing amount of scientific effort over the past several years, there have been very few investigations of the global transport of air pollution particulate matter. Analyses of Greenland ice cores showed that a sharp increase in the Pb content of Greenland snows occurred shortly after the use of tetraethyl lead in automobile fuels became common (Murozumi, Chow, and Patterson, 1965). Recent studies in Barbados (Delany *et al.*, 1967; Prospero, 1968; Risebrough *et al.*, 1968) have shown that dust and chlorinated hydrocarbon pesticides are carried across the Atlantic Ocean from Africa to the Caribbean by the northeast trade winds. Rex *et al.* (1969) have also shown evidence that quartz in Hawaiian soils has an eolian origin.

The atmosphere between California and Hawaii is an ideal location for examining the possible transport of particulate matter from the North American continent over long distances. The mean surface pressure patterns in this region, both in summer and winter, indicate a general wind flow from California to Hawaii (the northeast trades). This general pattern of circulation often persists to heights of 6000 meters in the summer and about 3000 meters in the winter, and suggests that continental-source particulate matter may often be transported toward Hawaii on these prevailing northeast trade winds.

Experimental

In this investigation particulate samples were collected from a tower 20 meters high located on a lava headland on the windward coast of the island of Hawaii, 9 km. east of Hilo and approximately 320 km. southeast of Honolulu. Samples were also collected on board a U.S. Coast and Geodetic Survey ship between San Diego, Calif., and Honolulu. The particulate matter was collected on glass fiber filters, using a Gelman

Hurricane high-volume pump. The filters have a collection efficiency of >95% for particulate matter with $r \geq 0.15 \mu$. From 1000 to 2500 m.³ of air were filtered per sample, at a rate of approximately 150 m.³/hr. The collecting instrument on board ship was located on the bow, and every effort was made to avoid contamination by stack effluents from the ship. A third set of samples was collected from the flying bridge of a ship between Kodiak, Alaska, and Hawaii. However, for some metals, these samples were apparently contaminated by products of the combustion of heavy fuel oil on the ship—indicating the great care which must be taken when sampling particulate matter from a ship.

The particulate matter collected between California and Hawaii was removed by agitation of the filters in 100 ml. of distilled demineralized water. Particulate matter from the Hawaii-tower filters was removed by agitation in 100 ml. of a strongly acid solution of 8-hydroxyquinoline. The aqueous solutions were analyzed for Na by flame photometry and for Cu, V, and Al by thermal neutron activation analysis using the nuclear reactor at the Massachusetts Institute of Technology, Cambridge, Mass. The California-Hawaii samples were not analyzed for Al. The samples were irradiated for 5 min., then inactive Cu, V, and Al carriers were added, and the three metals removed from other radioactive species by chloroform extraction from the aqueous phase using a 3% cupferron solution at a pH of 1. After washing with dilute sulfuric acid, the chloroform phase was counted, using a Packard 4096 pulse height analysis system. A 3-inch \times 3-inch NaI scintillation detector was used for the California-Hawaii samples, and a 35 cc. Ge(Li) detector with a FWHM of 5.0 keV for the 661 keV line of ¹³⁷Cs was used for all other samples. The gamma peaks used in the analyses were as follows: 1.7 MeV γ for 2.3 min. ²⁸Al; 1.04 MeV γ for 5.1 min. ⁶⁶Cu; and 1.43 MeV γ for ⁵²V. V chemical yields in the separation procedure were measured by adding a known amount of 16-day ⁴⁸V to the sample before chemical separation and measuring the 0.99 MeV γ of ⁴⁸V several days later. Cu and Al chemical yields were measured colorimetrically using dithizone and 8-hydroxyquinoline, respectively. A mixed Cu, V, and Al standard solution was irradiated simultaneously with each sample and the standard was counted directly with no chemical separation.

Results and Discussion

The results of the chemical analyses are given in Table 1. The ship positions indicated are those at the mid-point of each sampling period. Elemental mass ratios for all samples are given in Table 2, along with ratios for possible source material for the particulate matter. The uncertainties given in Tables 1 and 2 refer to the analytical precision of the analyses. Several blank filters were processed through both procedures. For the California-Hawaii samples, blank corrections were

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Table 1. Metal Concentrations of Particulate Filter Samples

Sample number	Date	Latitude, <i>N</i>	Longitude, <i>W</i>	Na $\mu\text{g}/\text{m}^3$	Cu ng/m^3	V ng/m^3	Al ng/m^3
California-Hawaii samples ^a							
1	6/29/67	31°10'	118°15'	2.0 ± 0.2	51. ± 15	0.82 ± 0.4	—
2	6/30/67	30°10'	122°15'	0.51 ± 0.05	21. ± 7	≤ 0.04	—
3	6/30/67	29°20'	124°00'	0.74 ± 0.07	8.5 ± 3	0.12 ± 0.08	—
4	7/1/67	28°00'	129°30'	0.39 ± 0.04	4.4 ± 2	≤ 0.02	—
5	7/2/67	26°30'	135°00'	2.0 ± 0.2	12. ± 4	0.060 ± 0.04	—
6	7/3/67	25°30'	140°20'	2.7 ± 0.3	7.4 ± 3	0.37 ± 0.23	—
7	7/4/67	24°00'	145°50'	3.2 ± 0.3	7.0 ± 3	0.044 ± 0.03	—
8	7/5/67	22°15'	151°30'	11. ± 1.	5.3 ± 2	0.016 ± 0.01	—
9	7/6/67	21°10'	155°40'	24. ± 2.	6.5 ± 2	≤ 0.02	—
Windward Hawaii tower samples							
10	11/15– 11/16/67	19°43'	155°00'	3.9 ± 0.4	15. ± 10	0.12 ± 0.07	5.0 ± 3.0
11	11/17– 11/18/67	19°43'	155°00'	2.8 ± 0.3	41. ± 15	0.18 ± 0.09	17.0 ± 6.0
12	11/28– 11/29/67	19°43'	155°00'	7.5 ± 0.7	120. ± 40	0.29 ± 0.15	32.0 ± 8.0

^a See Figure 1 for locations where samples were collected.

Table 2. Elemental Mass Ratios

Sample number	Na/Cu	Na/V ($\times 10^{-3}$)	Na/Al	Al/Cu	Al/V	Cu/V
California-Hawaii samples ^a						
1	39 ± 13	2.4 ± 1.3	62. ± 37
2	24 ± 10	≥ 12.	≥ 500.
3	87 ± 35	6.2 ± 4.2	71. ± 50
4	89 ± 40	≥ 20.	≥ 220.
5	170 ± 60	33. ± 23	200. ± 140
6	320 ± 120	7.3 4.5	20. ± 14
7	460 ± 200	80. ± 60	160. ± 120
8	2100 ± 800	690. ± 420	330. ± 230
9	3700 ± 1400	≥ 1200.	≥ 320.
Windward Hawaii tower samples						
10	260 ± 170	32 ± 20	780 ± 480	0.33 ± 0.29	42. ± 35.	130 ± 115
11	68 ± 27	16 ± 9	160 ± 60	0.41 ± 0.20	95. ± 58.	230 ± 140
12	54 ± 18	26 ± 14	230 ± 60	0.23 ± 0.09	110. ± 60.	470 ± 280
Possible source material						
Crust, avg. ^b	400	0.19	0.35	1200	540	0.47
Meteorite, avg. ^c	35	0.15	0.43	81	350	4.4
Seawater, avg. ^d	3.5 × 10 ⁶	5.3 × 10 ³	1.1 × 10 ⁶	3.3	5	1.5
Polluted air, west coast cities, avg. ^e	~20	~0.2	~0.5	~40	~400	~10

^a See Figure 1 for locations where samples were collected.

^b Goldschmidt (1954).

^c *Ibid.*

^d Goldberg (1965).

^e U.S. Public Health Service (1962).

less than 10% for Na and Cu, and up to 100% for V, with an average of about 50%. For the Hawaii-tower samples, blank corrections were less than 10% for Na and Cu, 5–60% for V, and 20–60% for Al. Unfortunately, since the method for removing the particulate matter from the filters was different for the two sets of samples, comparisons between the mea-

sured concentrations in the two sets are not valid. For example, it is apparent from Table 1 that the Cu concentrations for the shipboard samples collected near Hawaii are somewhat lower than for the Hawaii-tower samples. This is probably due to incomplete removal of the particulate matter from the filters during the water wash of the shipboard samples.

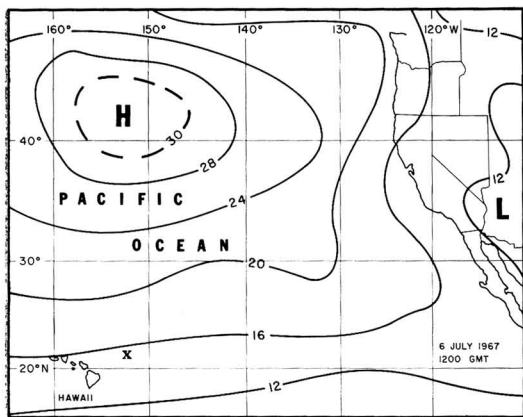
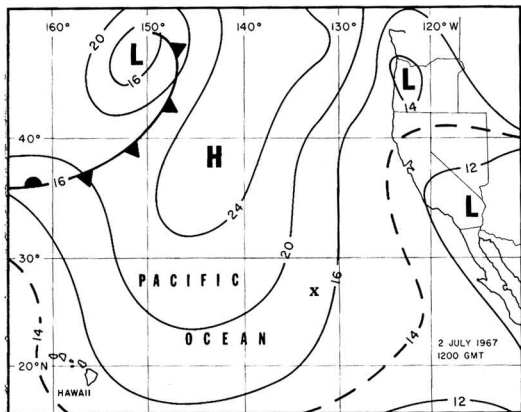
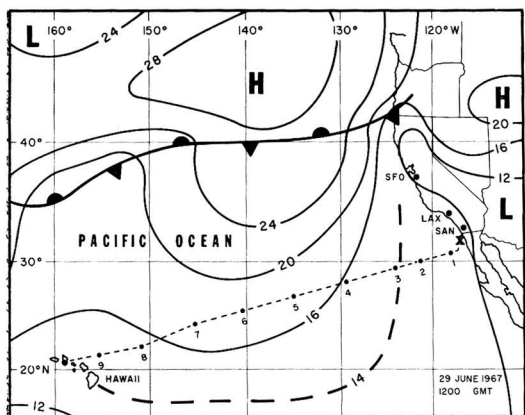


Figure 1. Surface synoptic charts covering the collection period for the California-Hawaii samples and showing collection points along ship route. Pressure in millibars (20 = 1020 mb). See text for details

However, comparisons between samples in a given set should be valid.

Some interesting trends are apparent within the California-Hawaii set. Figure 1 shows the surface synoptic weather charts for the northeastern Pacific at 1200 GMT, on June 29, July 2, and July 6, 1967, covering the sample collection period. All sample collection sites are shown on the June 29 chart. The x's give the ship's position at the valid time for each map.

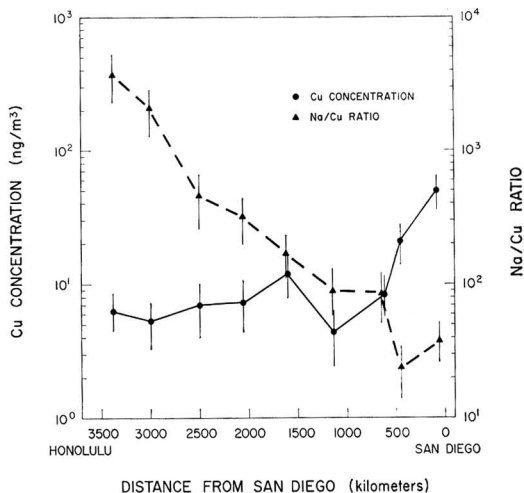


Figure 2. Variation in Cu concentration and the Na/Cu ratio for particulate matter with distance from San Diego to Honolulu

These synoptic charts show that, in general, the surface air through which the ship was passing had recently passed over parts of the North American continent, and that the direction of the general surface wind was from the west coast of North America toward Hawaii during this period. Figure 2 shows the variation of the Cu concentration and the Na/Cu ratio with distance from San Diego. As seen, there was a decrease in the Cu concentration for the first 600–1200 km., after which the concentration remained relatively constant to Hawaii, whereas the Na/Cu ratio increased consistently from California to Hawaii. It is suggested that this consistent increase in the Na/Cu ratio was initially due to the drop in the Cu concentration, as noted for the first 600–1200 km., and thereafter, when the Cu concentration had become stabilized, to an increase in the Na content of the surface air owing to increasing average surface wind velocities over the sea which were observed from the ship as it moved south-westward. It would appear from our data that the Na and Cu concentrations are not interdependent, *i.e.*, the primary source of Cu is not the sea, since the Na/Cu ratio in seawater was at least 10^3 to 10^4 times that in the particulate matter, indicating considerably more copper was present in the atmosphere than one would expect from sea spray alone. This was also true for the Hawaii-tower samples.

There may have been a slight decrease in the V concentration between California and Hawaii, but the large uncertainty in the analyses obscures any real trend. However, the Na/V ratio in seawater was approximately 10^2 times the particulate values for the California-Hawaii and Hawaii-tower samples, indicating a nonmarine source for the major part of the V. The Na/Al ratio in seawater was 10^3 to 10^4 times the Hawaii-tower particulate values, again showing very clearly that the primary source of Al is also nonmarine.

It is likely that the source of the Al in the particulate samples is dust from the weathering of aluminosilicate crustal material. The Al/V ratio for crustal rocks is only a factor of 5–10 different from that observed in the Hawaii-tower samples, and may indicate that weathering is the primary source of V as well. The Al/Cu ratios for the tower samples are lower than the same ratios in crustal rocks by a factor of about 4000, indicating that the major source of Cu is most likely not

crustal weathering. The source of the high Cu concentrations is not known, but it is possible that man-made pollution is a contributing factor. Extra-terrestrial material is an unlikely source for all these elements. Shedlovsky and Paisley (1966) have shown that even the particulate matter in the stratosphere is largely from the weathering of crustal rocks and the sea, rather than from meteoritic material.

Several factors complicate any attempt to assign source areas to these metals. The processes of physical and chemical weathering of crustal material probably work selectively in producing dust particles; thus, the chemical composition of the particles may differ from the rock or soil they came from. The initial particle-size distributions will vary for each metal, due to differences in the production mechanisms for the particles containing the different elements. The varying particle-size distributions will result in different residence times for the particles, which in turn will give different elemental ratios at various distances from the source area. It is also possible that the sea is contributing somewhat to the high Cu and V concentrations. It is known that sea salt particles contain significant amounts of surface active material whose source is the sea (Blanchard, 1964). V, Cu, and other transition elements are concentrated in certain marine organisms and it may be possible that the organic films on the sea salt particles are partially composed of organically bound V and Cu. This would cause the Na/V and Na/Cu ratios on particles from the sea to be less than that expected on the basis of the elemental composition of seawater. It would appear unlikely, however, that this mechanism could cause a V enrichment of 100 and a Cu enrichment of over 1000 on the sea salt particles.

Future samples will be collected on Delbag polystyrene filters, which have considerably lower blank concentrations for most metals than the glass fiber filters. Additional samples are being collected from the bows of ships in the northeast Pacific. Samples are only collected when there is no danger of local shipboard contamination. A new sampling tower, fully instrumented with recording meteorological equipment, is

now in operation in Hawaii for continuous sampling of particulate matter. In addition to the metals reported here, analyses for Pb, Mn, Co, Ca, Zn, Fe, Sr, K, and Mg will be performed on all samples.

Acknowledgment

We are grateful to the staff who operate the MIT Reactor for assistance in these analyses, and to Dr. A. H. Woodcock, Mr. Larry Wolfe, and Mr. Jarvis Moyers, University of Hawaii, for help in collecting samples. We also wish to acknowledge the U.S. Coast and Geodetic Survey, which granted us facilities and assistance on their ships for the collection of samples. This work was supported in major part by the National Air Pollution Control Administration, Consumer Protection and Environmental Health Service, Public Health Service, under grant ROI AP 00617-1. Hawaii Institute of Geophysics Contribution No. 288.

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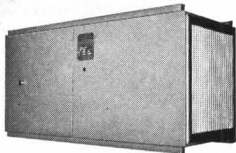
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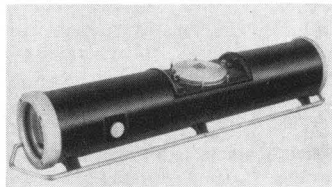
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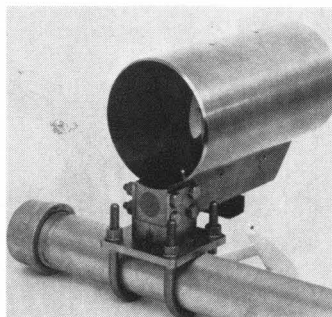
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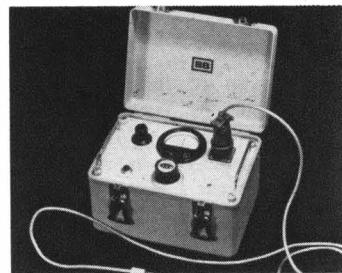
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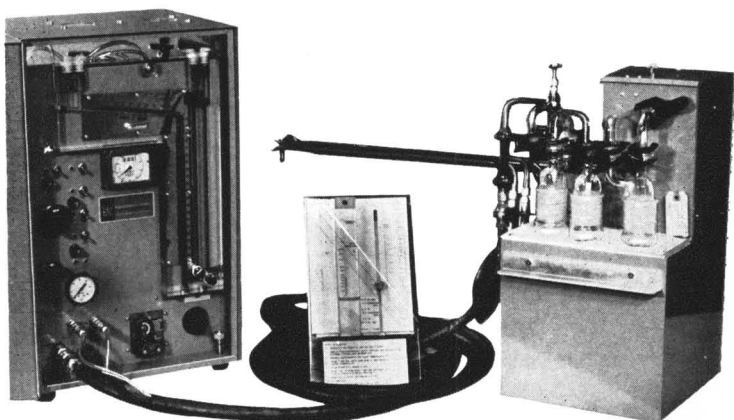
SO₂ control. A process for SO₂ and fly ash removal and recovery by a central process concept is described in a 4 page brochure. Economics and advantages of the concept are discussed, as well as removal efficiency, add-on capability, and space requirements. The company claims that the system offers a central service for various types of utility power plants and industrial facilities that fire sulfur laden fossil fuels in a geographic or air pollution region. Chemo/Basic **92**

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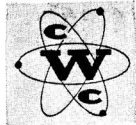
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meeting guide

November 12-14 University of Maryland, Johns Hopkins University, and others

3rd Mid-Atlantic Industrial Waste Conference

Center of Adult Education, College Park, Md.

This year's conference is designed to allow interchange of ideas on solid, liquid, and gaseous industrial waste management. Symposia will feature discussion of such topics as industry's role in environmental management, acid mine drainage treatment, and research activity toward SO₂ control.

November 16-20 American Institute of Chemical Engineers

62nd Annual Meeting

Statler Hilton, Washington, D.C.

Seven sessions of this year's meeting will be devoted to aspects of pollution control. Representatives of government, education, and industry will participate in discussion of such topics as assessment of the Air Quality Act of 1967; recent developments in design of waste water treatment; and chemical pollutants in industrial applications.

November 18 University of Missouri

2nd Annual Air Pollution Conference

University of Missouri, Columbia

The 1 day conference will emphasize the place of the automobile in air pollution. Among topics to be discussed are what has been done in California to reduce pollution; modifications made in the automobile engine; catalytic pollution control devices; the steam car, electric car, and turbine car. For information: Extension Division, Whitten Hall, University of Missouri, Columbia, Mo. 65201

December 4 Institute of Gas Technology

Seminar on Natural Gas Fueled Vehicles

Illinois Institute of Technology,
Chicago

The 1 day session will feature discussion of current activities, state of the art, problems, and future research and development needs on the subject of natural gas fueled vehicles. Pollution reduction potential for these new vehicular fuels will be covered.

**December 15-17
American Petroleum Institute and
Federal Water Pollution Control
Administration**

Joint Conference on the Prevention and Control of Oil Spillage

Americana Hotel, New York City
Included in the 3 day session are a review of recent major oil spill incidents; discussion of the federal government's plan for dealing with such incidents; and industry's plan to deal with oil spills. In addition, such topics as harvesting techniques and fate and behavior of oil in water will be covered. For information: W. A. Burhouse, American Petroleum Institute, 1271 Avenue of the Americas, New York, N. Y. 10020

**December 26-31
American Association for the
Advancement of Science**

136th Annual Meeting

Boston, Mass.

Featured at this year's meeting will be a 1 day symposium, Power Generation and Environmental Change: Reconciling man's desire for power with the needs of his environment. Another 1 day session will be devoted to a symposium on undergraduate education in environmental science. Information available through AAAS, 1515 Massachusetts Ave. NW, Washington, D.C. 20005

**January 19-21
Cornell University**

Agricultural Waste Management Conference

Sheraton Hotel and Motor Inn, Rochester, N.Y.

Major focus of this year's conference will be on the possible contamination involved in the application of agricultural wastes and chemicals to the soil, as well as possible solution to these problems. Animal wastes, food processing wastes, management to maintain environmental quality, and ground water contamination are among the topics to be covered.

Courses

**November 15-16
American Institute of
Chemical Engineers**

Short Course on Introduction to Air Pollution Control

Washington, D.C.

Designed to present the fundamentals of the air pollution control problem to chemical engineers who are entering into work in this area, the 2 day course will cover such topics as: causes and effects, instrumentation and sampling, meteorological aspects, atmospheric chemistry, technological control measures, and legislation for control. For information: H. I. Abramson, 345 E. 47th St., New York 10016

**November 17-18
Gulf General Atomic**

Short Course on Reverse Osmosis

Hilton Inn, San Diego, Calif.

The 2 day session will feature a seminar and workshop on applications of the reverse osmosis process to water treatment problems. Lectures, demonstrations, and discussions also will be included in the program, which is designed to bring water equipment designers and engineers face to face with engineers, scientists, and economists who have been working with reverse osmosis equipment.

**January 28-30
University of California**

Short Course on Pollution of Coastal and Estuarine Waters

University of California Extension Center, San Francisco

The 7th program of the Water Resources Engineering Educational Series, this 4 day session is planned to meet the continuing educational needs of the professional engineer working on water resources. The program will examine, through lectures, case histories, and discussion, the many facets of the pollution problem in coastal waters.

Call for papers

**December 1 deadline
Institute of Environmental Sciences**

16th Annual Meeting

The sponsors are accepting abstracts of papers for inclusion in technical sessions of the meeting, to be held April 12-16, Boston, Mass. Under the theme, Environmental Challenge of the 70's, papers may cover such topics in the general categories hostile environments, environmental stimulation, and laboratory management. For information: Technical Program Committee, Institute of Environmental Sciences, 940 E. Northwest Hwy., Mt. Prospect, Ill. 60056

**December 31 deadline
American Society of Civil Engineers,
and Department of Civil Engineering
and the Water Resources Research
Center, University of Massachusetts**

3rd National Symposium on Sanitary Engineering Research

Abstracts may be submitted for a Specialty Conference on Disinfection, to be held July 13-15, 1970, at the University of Massachusetts, Amherst. Topics to be covered in the symposium are mode of biocidal action by disinfectants and other agents; kinetics of disinfection; water disinfection; effect of waste water disinfection on natural streams. Further details available from: Tsuan H. Feng or Lawrence N. Kuzminski, Department of Civil Engineering, University of Massachusetts, Amherst 01002

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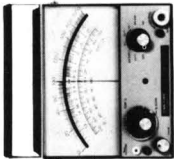
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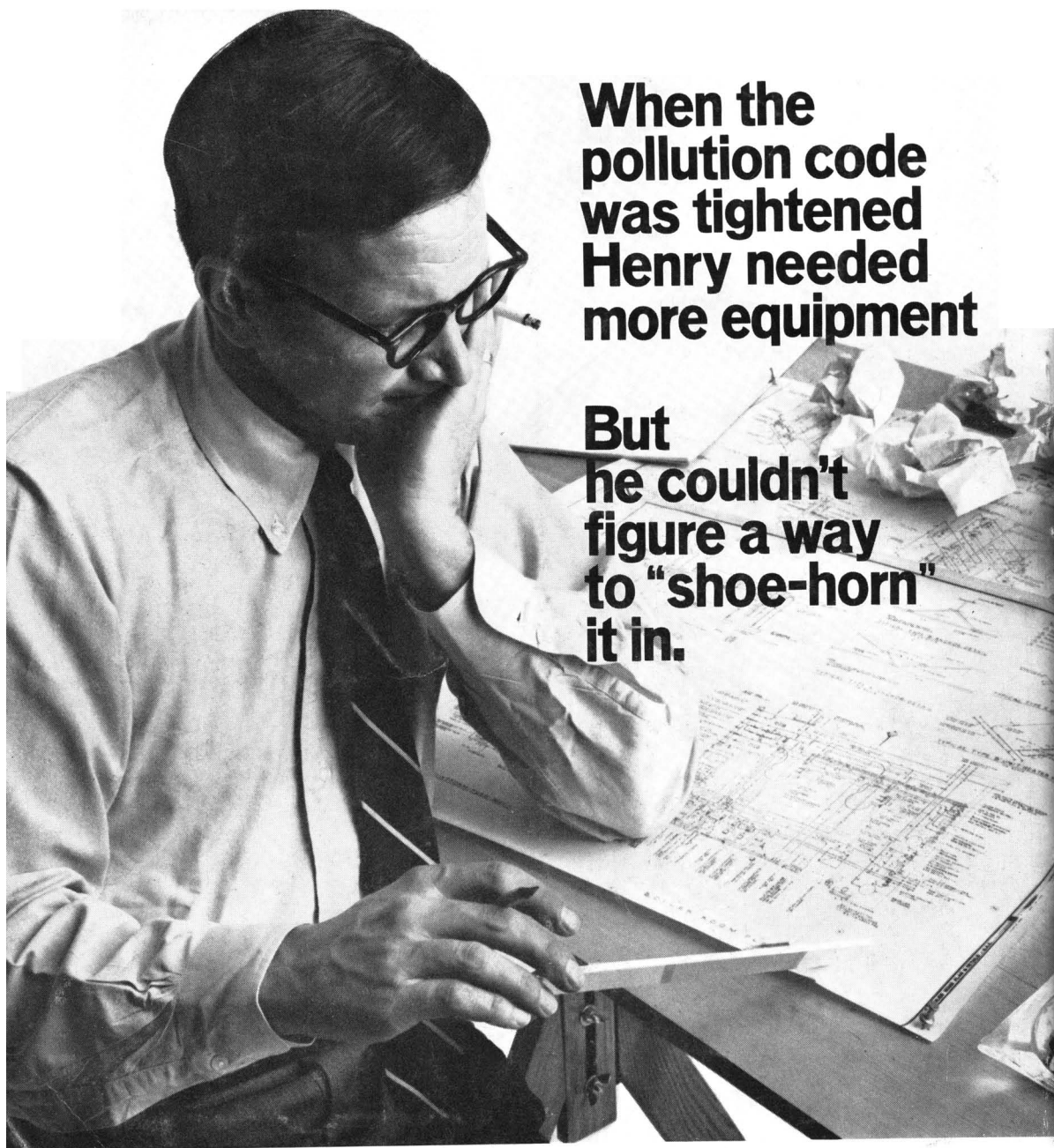
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