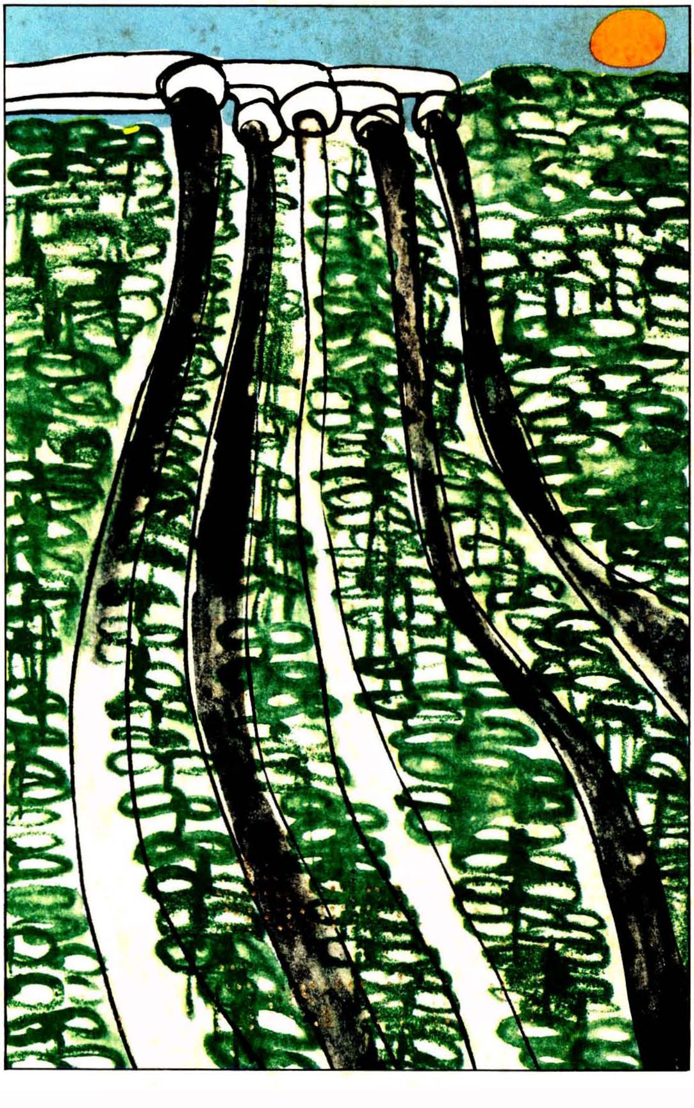
ENVIRONMENTAL Science & Technology

Emphasizing
Water,
Air, &
Waste
Chemistry

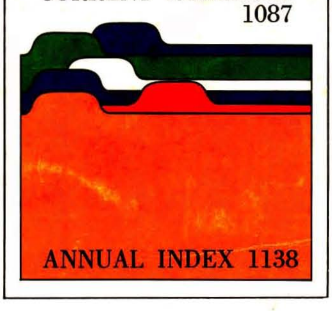
DECEMBER 1968



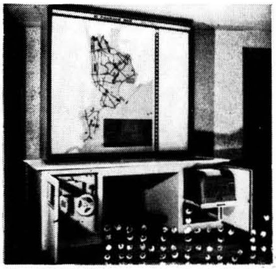
The Ultimate Problem

Disposal of Waste Water Concentrates to the Environment
1079

CURRENT RESEARCH
1087



ANNUAL INDEX 1138



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Currents

Outlook

Features

Bookshelf

New book restores and advances hydrology as unified science.

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CONTENTS

Current Research

Cation sorption on colloidal hydrous manganese dioxide 1087

H. S. Posselt, F. J. Anderson, and W. J. Weber, Jr.

Removal of the brownish yellow color in natural waters, which is imparted by the presence of colloidal manganese dioxide, is a major problem in water treatment operations. Sorption of seven metal ions—Ag^+, Ba^{++}, Ca^{++}, Mg^{++}, Mm^{++}, Sr^{++}, and Nd^{+++}—and one cationic organic solute on colloidal hydrous manganese dioxide are described by the Langmuir sorption equation. Exchange sorption is the principal mechanism, and equilibrium capacities range from 0.10–0.31 mole per mole of manganese dioxide. Neither the anionic nor the nonionic organic solute absorb appreciably.

Chemistry of manganese in Lake Mendota, Wis. 1094

J. J. Delfino and G. F. Lee

A proposed manganese system accounts for the presence of manganese in different forms in stratified lakes such as Lake Mendota, a hard-water, eutrophic lake of glacial origin. In field and laboratory studies, only Mn(II) was detected in anoxic waters, whereas both Mn(II) and manganese oxides are present in oxygenated waters. Throughout the year, manganese exists primarily in the Mn(II) form, and the small amounts of manganese oxides are not detected in the anoxic summer hypolimnion.

A theoretical model for the effect of an acute air pollution episode on a human population 1101

S. K. Friedlander

Appendix—An application of the model to the 1952 London "killer" fog 1104

A. L. Ravimohan

The increase in mortality rate accompanying a severe air pollution episode now can be predicted quantitatively using a recently proposed mathematical model. The model correlates well the data collected during the London "killer" fog of 1952, and can be used for setting standards and development of abatement strategies for urban areas.

Hydrocarbon reactivity and eye irritation 1109

J. M. Heuss and W. A. Glasson

Smog chamber irradiation studies reveal no correlation between eye irritation and chemical rates and products yields involving 25 hydrocarbons. But the studies employing a standard set of experimental conditions suggest a correlation between eye irritation and chemical structure of hydrocarbons. Benzylic hydrocarbons and aromatic olefins are the most potent precursors of eye irritants. Identified in the system was peroxybenzoyl nitrate, a lachrymator 200 times more potent than formaldehyde.

C_2–C_5 hydrocarbons in the Los Angeles atmosphere 1117

R. J. Gordon, H. Mayrsohn, and R. M. Ingels

No correlation has been found between the smog intensity in the Los Angeles area and the presence of atmospheric hydrocarbons having from two to five carbon atoms. Studies that included nearly 700 samples taken at two sites (downtown Los Angeles and Azusa) during the fall of 1967 reveal that concentrations of light alkanes, especially propane, were too high to be accounted for solely as automobile exhaust components. Also, the ratio of acetylene (an important constituent of automobile exhaust gases) and light olefins to oxides of nitrogen in these atmospheric samples was higher than typical automobile exhaust gases taken from a dynamometer testing.

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EDITORIAL

Take three giant steps forward

Let us begin a temple-building enterprise of our own, Udall says, to make all our cities fair and all our human relations amicable

The harsh reality of hindsight can serve to set the tone for present action and the scope for future plans. Or it can serve merely as a whipping boy, revealing present concern but no plans for progress. There is, in Stewart Udall's new book "1976: Agenda for Tomorrow," (1968. Harcourt, Brace & World, Inc., New York, N.Y. 10017. $3.75) some attempt to find a whipping boy, a tendency to judge society's past errors too harshly—in the light of current values and goals rather than in the context of the times and mores in which they evolved. Yet, there are in the retiring Interior Secretary's new book the beginnings of agenda for action, "agenda capable of restoring a vision, of reframing an American dream powerful enough to enlist our minds and persuasive enough to revive our ancient faith in the future of our country."

The book is a hodgepodge discussion of disparate elements that make up our total environment. It talks about waste—wasted lives, wasted human resources, wasted lands, wasted affluence, wasted time, wasted beauty and order, and wasted opportunity to build a truly grand civilization. But man must deal effectively with just this kind of hodgepodge if he is ever to work out a satisfactory accommodation with his environment (see ES&T interview with LaMont Cole, page 1069).

Secretary Udall has taken the occasion of the approaching bicentennial of the U.S. (1976) to suggest in his book that we, as a people, begin Project 76, "a temple-building enterprise of our own, a vast project to make all our cities fair, and all our human relations amicable." Udall proposes that Project 76 begin with the new President's appointment of a commission that would meet with the nation's leaders, including Congress, to prepare "The Agenda for the Third American Century." The commission would devise detailed goals, priorities, and budgets which, with the endorsement of cities, states, and Congress, would be implemented beginning at once, with completion set for the year 2000.

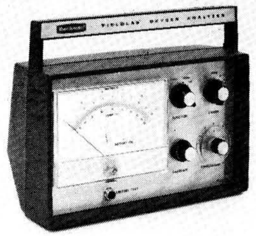
Project 76 would start with each community's drafting its own master plan of redesign and renovation to be accomplished before 2000. These plans would be coordinated into a comprehensive master plan to fulfill national goals and meet national guidelines. But, Udall notes, each community project would be guided by the community itself through its own community leadership and the interaction of local artists, designers, labor and business leaders, professionals, politicians, and anyone with a will to join in the effort.

While the planning is in progress (two or three years) the hard-core unemployed could be put to cleanup work. From the early work of reclamation and reconstruction, Project 76 would move to and through the middle phase of reshaping our cities, culminating at the end of the century with the construction of museums, health facilities, theaters, libraries, and centers of art and recreation.

Never known for timidity in facing national problems, Udall suggests that $5 billion in federal grants be set for the first year of the project—and that the level of support be advanced to $50 billion per year no later than 1985.

The plan is grand, to be sure. The details needed to flesh it out are multitudinous. The insight and concern of people and politicians to implement it demand an enlightened constituency and agreement on national goals and priorities. But if it causes man to move toward a brighter day, then its author will have succeeded. "We must," Udall says, "bring the human population of this planet into balance with its resources, and learn to avoid fouling our environment so that we make possible for men everywhere not mere animalistic survival but a life that permits the enjoyment of basic human values, the beauties of nature and of art, the flowering of individual creativity."

Melvin J. Josephs



President's Council Reports on the American Environment

Two and one half years in preparation, "From Sea to Shining Sea, A Report on the American Environment—Our Natural Heritage," states the U.S. long-range goals for improvement of our environment. Prepared by the President's Council on Recreation and Natural Beauty, the report does the following: • Outlines the progress in environmental improvement programs since the 1965 White House Conference on Natural Beauty. • Proposes and makes recommendations which will stimulate federal, state, local, and private action to further enhance the quality of our environment and the beauty of the nation. • Offers a guide for action by local officials, professionals, citizen groups, and individuals. The report concludes that the U.S. needs both renewal of cities and preservation of the wilderness, and that neither should be pursued at the expense of the other. President-elect Richard M. Nixon has indicated that the U.S. must find the time and energy to preserve and improve its natural heritage and prepare to hand it over to future generations in an improved condition.

MCA Pushes HEW on Air Quality Criteria

Manufacturing Chemists Association has filed a criticism of HEW's present procedure for the establishment of ambient air quality criteria with the Senate Subcommittee on Air and Water Pollution. MCA president, Gen. (ret.) George H. Decker says, "There is no mechanism, either prescribed [by the act] or provided in the procedures established by the Secretary, whereby anyone outside of the administrative agencies of the Federal Government or the Secretary's advisory committees can, prior to their release as a final document, review the criteria or introduce into the record any divergent views." Viewpoints at odds with those approved cannot be introduced into the record until either a governor petitions for a hearing or abatement proceedings are instituted, according to Decker. MCA would welcome placing the responsibility for drafting air quality criteria in the hands of an independent group such as a council similar to the recently established National Council on Radiation Protection and Measurement.

Midwest Air Abatement Recommendations

Five recommendations to curb air pollution in the seven-county area designated as the Kansas City, Kan.-Kansas City, Mo., metropolitan area recently became effective, according to Wilbur J. Cohen, Secretary of Health, Education, and Welfare. These recommendations, based on proposals made during phases I and II of the conference, cover the following items: • By the end of 1969, visible emissions from all sources will be limited to a density less than number one on the Ringelman Smoke Chart. • No new source of particulate emissions whose discharge exceeds a density of 20% opacity will be placed in operation in the area. The three remaining items specify pollution control from industrial processes, refuse disposal and salvage operations, and fuel burning installations. If adequate progress toward curbing air pollution is not made on these recommendations within six months, the Secretary of HEW can ask the Attorney General to initiate abatement action in U.S. courts.

Electric Utilities Invest Heavily in Air Pollution Control Equipment

The investor-owned, electric utility industry spent more than $127 million last year for air pollution control equipment, its operations, and maintenance, according to Robert H. Gerdes, president of the Edison Electric Institute (New York City), a trade association for investor-owned electric power companies. Based on Edison Electric's survey of 120 of its companies, which represent two thirds of the nation's fossil-fueled electric utility industry, $86 million was spent for new equipment and more than $41 million for operations and maintenance of the equipment.

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Ribicoff Proposes General Pollution Control Tax Relief

Senator Abraham A. Ribicoff (D.-Conn.), speaking at the dedication of the new international headquarters of UOP Air Correction (Darien, Conn.), proposed that "Congress amend the tax law to allow industry to depreciate the costs of pollution control equipment over a three-year period instead of a customary useful life period. This will provide further encouragement to industry to expand in antipollution activities." A prime mover in the passage of the Clean Air Act of 1963, Sen. Ribicoff (re-elected) noted that ". . . it is entirely appropriate that the public share with private industry some of the economic impact" of pollution control expenditures.

Oil Shale Development Must Also Protect Environment

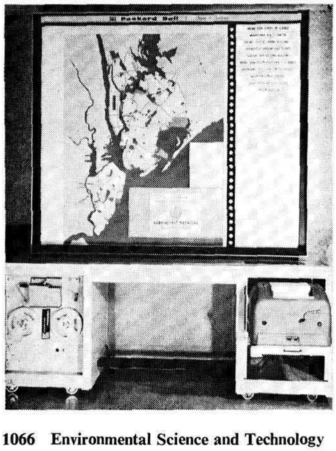
Mining, waste disposal, pollution control, and surface restoration practices are now required by Department of the Interior leases for its three oil shale lease sites, all of which are located in the Piceance Creek Basin in Rio Blanco County (Colo.). The new lease requirement calls for the protection and restoration of the area and preservation of environmental and recreational values.

Parties Agree in Government's First Air Pollution Suit

In a recent field consent judgment, HEW and the Bishop Processing Co. (Bishop, Md.) agreed that the discharge of malodorous air pollutants from the chicken and fish rendering plant on Maryland's Eastern Shore must be stopped, a step toward settling the Federal Government's first suit under the Clean Air Act of 1963 (ES&T, June 1967, page 463). According to the Department of Justice, the judgment does not specify how this stoppage is to be accomplished, but the Director of Air Pollution for Delaware now can obtain a court order directing the Bishop plant to close down upon his finding that the plant's odors are reaching into neighboring Delaware.

Multistation Air Monitoring Network Started

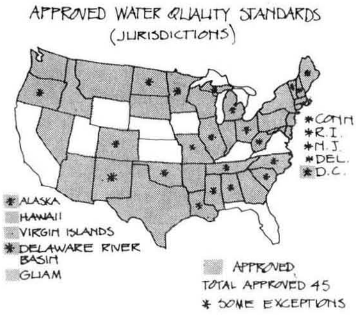
New York City's $500,000 air pollution monitoring network has been put into operation. The integrated system, which includes 250 major pieces of equipment, features a computerized central recording station which assimilates and compiles data from 38 remote sampling stations throughout the city. Each station monitors temperature, wind speed and direction, and the levels of three pollutants—sulfur oxides, carbon monoxide, and particulates. Analysis of atmospheric samples at 10 of the locations is continuous and completely automated, with results transmitted automatically to the central station. Samples from the 28 other stations are collected daily and returned to the laboratory for analysis and transmission of results. New York's Commissioner of Air Resources, Austin N. Heller, who pioneered with a similar system in Chicago (ES&T, December 1967, page 984), says with the system, ". . . the people in New York City can feel assured that we now have the most reliable and comprehensive system in the world for analyzing the dynamics of the urban atmosphere."



Display board

The telemetry system of New York City's aerometric monitoring network is displayed at the system's command station

ENVIRONMENTAL CURRENTS



Udall Emphasizes His Environmental Quality Commitment

At a recent news conference, exiting Secretary of the Interior, Stewart L. Udall, indicated that his tentative thinking on corrective action for the environment includes the formation of an international consulting firm on the environment which would involve industries, governments, and private foundations. Udall says, "We have failed, not only in this country but in the world at large, to do the kind of balanced work that we should be capable of doing with our technology, of constantly improving man's environment instead of diminishing it." Udall also noted that he expects to have approval for all water quality standards before leaving office. His personal plans include a return to an Arizona-based law practice.

Edwards Coordinates Water Resources Research Programs

Water resources research programs in the Department of the Interior (Geological Survey, Federal Water Pollution Control Administration, Saline Water, Water Resources Research, Reclamation, Sport Fisheries and Wildlife, Commercial Fisheries, and Mines) will be coordinated by Max N. Edwards who was recently redesignated Assistant Secretary for Water Quality and Research. Edward's new duties include the following: • Evaluation of proposed programs and projects. • Establishment of priorities. • Selection of projects and programs for Interior's water resources research effort. In 1968, these programs totaled $83 million, 70% of all federal water research expenditures.

Recently, Stewart L. Udall summarized the water pollution control programs in the U.S. by reporting that, during the past eight years, the Federal Government spent more than $1 billion for the construction of $4.4 billion worth of waste treatment facilities. He noted that this expenditure means cleaner water in more than 50,000 miles of our streams and rivers. Since 1962, more than 3000 pollution control R&D contracts and grants, costing the Federal Government $100 million, were aimed at directly translating research results into practice, Udall observed.

Sewage Treatment Costs Reduced by Homogenization

Homogenization of grease and oils in waste water may be one way of achieving some reduction in sewage treatment costs, according to Midwest Research Institute's Dr. William Garner. MRI has just received a $59,813 FWPCA grant to investigate processes for keeping such materials in solution throughout the treatment process so that they can be biologically degraded. Garner points out that lipids, greases, and oils which arise from such wastes as household soaps, garbage disposal effluent, and motor oils constitute about 25% of all organic material in municipal waste water. Normally, such materials separate and form scum layers at the top of the treatment tanks, and are either piped or scraped off for incineration or burial. "The materials should be biodegradable, but the bacteria can't get to them," Garner says. "If these materials can be forced back into solution, the microorganisms that cause biodegradation may work more effectively because of the increased surface area."

OUTLOOK

Porteous Process Unit Readied for Startup

This month will see the completion of construction of facilities for the steam treatment of sewage sludge at the Colorado Springs, Colo., municipal treatment plant. Start-up of the facility, now scheduled for late this month or early January, will mark the U.S. debut of the Porteous process, which is already used in Europe and elsewhere. About 25 units are either in operation or in various stages of construction abroad. BSP Corp., which has an exclusive U.S. license on the patented process from England's Hawker Siddeley Corp., is fairly optimistic about the U.S. market. P. J. Cardinal, Jr., manager of BSP's Sanitary Engineering Division, says the company expects to install as many as a half dozen more units in the U.S. in 1969—and hopes to do considerably more thereafter.

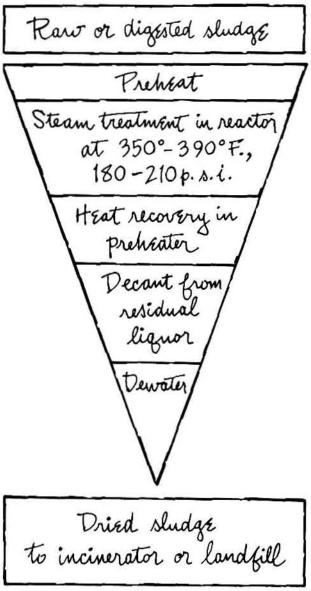
The process is a means for treating primary or secondary sewage sludge (including digested and waste activated sludge) with steam to stabilize it and facilitate dewatering. The main advantage of the process, according to BSP, is that it is a compact, continuous operation. Further, since it requires no sludge conditioning chemicals, the process has low operating costs. In addition, the process is adaptable to new or existing plants, and can be expanded easily to handle increases in capacity of the basic treatment plant.

The history of the Porteous process dates back to the mid-1930's, when William K. Porteous began his experimental work on heat treatment of sludge and founded a company to develop and promote the process. Several plants, which were built in England, were based on an early version of the process, but these had some disadvantages. They were essentially batch operations, requiring three or four separate treatment vessels, and were difficult to operate and control. The onset of World War II curtailed further development of the process, but work was resumed after the war. This post-war effort culminated five or six years ago in the development of a continuous process, which has been the basis for all the plants installed since then.

In the Porteous process, stored sludge from sedimentation tanks or digesters is heated prior to steam treatment in the reaction vessel. The main function of the preheat step is heat recovery, the heating medium in the preheat step being the treated sludge from the reaction vessel. Following preheating, the untreated sludge is fed to the reactor, where a steam jet circulator assures intimate mixing of steam and sludge. Typical reactor conditions range between 350–390° F., at pressures between 180–210 p.s.i.

Cycle time in the reactor is about 30 minutes. The main effect of the steam treatment is to coagulate the solids and break down their gel structure by reducing the hydration rate and hydrophilic nature of the solids. After heat recovery in the preheater, the sludge temperature is about 90° F.

From the heat exchanger, the treated sludge is fed to a decanting vessel which acts as a sedimentation tank. Because of the sludge solids' reduced affinity for water brought about by the steam treatment, settling of the solids in the sedimentation tank is fairly rapid. Dewatering rates of steam-treated sludge can reach many times that attained by chemical treatment.



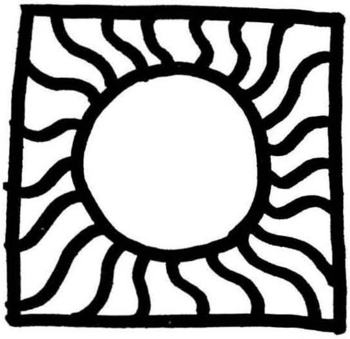
Increased settling rates and lower operating costs are the main advantages expected at the Colorado Springs plant. The treatment plant, which is capable of handling 25 m.g.d of waste, is equipped for dewatering by vacuum filtration.

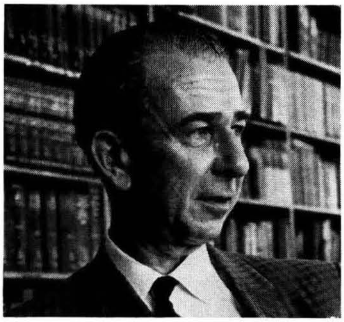
Prior to installation of the steam treatment process, chemical conditioning preceded the vacuum filtering step. Costs for the treatment chemicals, ferric chloride and lime, ranged between $18–25 per ton of dry solids treated. By contrast, operating costs for the steam treatment facility—which has a capacity for handling 4500 gallons per hour at 5.6% dry solids equivalent—are expected to be about $1.80 per ton of dry solids, an annual saving of $130,000–190,000. Total contract cost for the installation itself is $318,000, with another $28,000 going for general construction changes.

Aside from its low operating costs, the process has the additional advantage of versatility, according to BSP. The Colorado Springs facility, for example, will probably start up by treating digested sludge. However, it can switch to raw sludge—and it has the further capability of handling additional material from a proposed plant expansion which may incorporate an activated sludge process. The process can treat many other organic sludges such as wastes from food processing, pulp and paper mills, textile plants, and agricultural and industrial chemical plants, company spokesmen note.

In any of these applications, the final dewatering process can be chosen to accommodate a variety of treatment plant requirements. Based on past studies of the Porteous process, vacuum filter cakes with as little as 55% moisture can be obtained, and 35% moisture can be achieved with filter presses. The dewatered cakes, because of their relatively low moisture content, can be used for autogenous combustion in incinerators or steam boilers. Where local codes permit, the cake can be used for compost or landfill.

Ecological Soundings & Awareness





LaMont C. Cole

Ecology is a household word

Today, many of the urgent problems facing and threatening mankind are essentially ecological, since they concern man's interrelationship with the environment. Accordingly, scientists, as well as legislators and laymen, are beginning to recognize the promise that ecological research offers, both for the prediction of and solutions to, environmental problems. The Ecological Society of America (ESA) is stepping up its efforts to make the public aware of the ecologist's concern with environmental problems. In a recent interview with ES&T, ESA past president LaMont C. Cole, of Cornell University, described the status of this attempt to apprise man of his endangered situation and to suggest some routes toward improving his health and well-being. In January, Cole assumes the presidency of ESA's parent organization, the American Institute of Biological Sciences.

Despite the promise that ecological research appears to hold for solution of environmental problems, the science of ecology suffers—as do other environmental quality issues—from lack of adequate finances and manpower and the absence of national commitment. "I don't know of any area of ecology for which even minimally adequate financial support is available," Cole says.

The Ecological Society of America was founded in 1915. The society's prime objective is purely scientific: to consider all forms of life in relation to their environment. With a current membership of 3200, ESA holds meetings and publishes journals for the dissemination of research results. Although Dr. Cole feels that a poll of the ESA membership would reveal a conformity of views on approaches to environmental problems—for example, the International Biological Program (IBP)—he warns that no such poll is likely to be taken. Such a poll would threaten to inject ESA's view into policy decisions, he explains, which is not the objective of this society.

Public affairs committee

ESA was reluctant to enter the public area for many years. "As the fables have it, ecologists sat in their ivory towers and watched ecological problems surface to scientific awareness, and then be dealt with in an outrageous way," says ESA's past president. But ESA does not stand by idly. About five years ago, the society decided, by less than a vote of acclamation, to establish a public affairs committee. This committee was formed to furnish honest and objective advice on ecological matters to anyone in need of it.

Finally, in August 1967, after reconstitution, the public affairs committee emerged as a high-power group, and set out to inform legislators, other scientists, and the public that the committtee would serve as the forum for competent ecological advice.

Today, public awareness of ecological problems is on the horizon. "Ecology has entered the vocabulary of legislators. Even the speech writers of some presidential aspirants have been consulting ecologists," Cole adds.

Manpower

According to Cole, the National Register (ES&T, June, page 415) underestimates the number (1354) of biologists identified as ecologists. He explains that many ecologists, as well as biologists, describe their primary professional specialty as oceanography, limnology, forestry, game management, fisheries research, bioclimatology, biogeography, or the like. However, all these disciplines are represented in ESA's membership and accepted as having ecological interests.

From 600 to 700 persons each year receive doctorates in ecology, according to a recent ESA survey. For the purpose of the survey, the definition of an ecologist was very broad, Cole comments, and included, for example, a research collaborator on an ecological problem who might not necessarily be qualified to teach ecology per se. "On this basis, the response indicated that 2572 students of ecology are now training for the Ph.D.," Cole says.

Cole expresses concern over the number of ecologists in the U.S. In his opinion, not enough scientists are being trained to implement the ecological programs that will be recognized as necessary in the near future. "Now, we should be training the teachers," the Cornell ecologist stresses. "In turn, these teachers would be able to supply the demand for trained ecologists [which] will soon develop," he warns.

But Cole is not necessarily pessimistic about the training of ecologists.

For example, when Cornell University established its graduate curriculum for ecology and evolutionary biology, some 50 faculty members expressed their intentions of accepting graduate students in the program. The program is drawing people from diverse fields. By way of illustration, Cole tells of a plant ecologist on the Cornell staff who is a former engineer, of a chemical engineer who is working toward a Ph.D. in ecology, and of an electrical engineer who is doing graduate study in ecology. All are needed. And Cole feels that an increasing number of persons will be making such interdisciplinary shifts, as each becomes aware of ecological challenges.

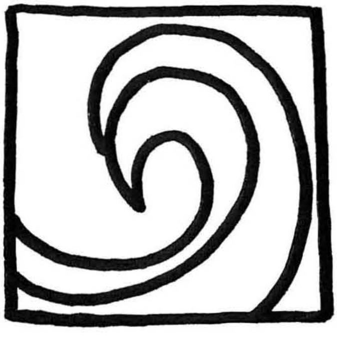
Ecologists' concerns

As an example of the type of problems ecologists are trained to attack, Cole cites his work on the **depletion of atmospheric oxygen.** A large portion of our atmospheric oxygen supply now is obtained from sources outside the U.S., according to Cole. Most of it probably comes from the Pacific Ocean. "For practical purposes, all of the oxygen in the atmosphere was put there by green plant photosynthesis," he explains. Oxygen is constantly being removed from this reservoir by such oxidative processes as support of life and burning of fossil fuels. At the same time, oxygen is constantly being replenished by photosynthesis.

By balancing the oxygen needed for the oxidative processes against that replenished by photosynthesis, Cole finds that, within the borders of the U.S., less than 60% of our oxygen need is being restored by photosynthesis.

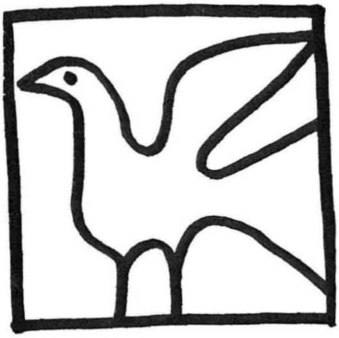
Ecologists now believe that they have found the factor that governs the maintenance of our oxygen reservoir —the activities of sulfate-reducing bacteria in anaerobic environments. So, if we destroy either enough of the photosynthetic organisms or the sulfate reducing bacteria, an oxygen crisis could ensue. This depletion could also occur by destroying the diatoms or bacteria in the Pacific Ocean, according to Cole.

Cole admits that he has no idea of the probability of such a disaster, but he asserts that the potential is both real and ecologically sound. He is not alone in his view on the subject. He was joined in sounding this warning by the late Lloyd V. Berkner, who, independently, also became aware of this potential, ecological disaster.



Ecologists also are concerned about those ocean areas known as **oxygen plankton upwellings,** which are exceptionally productive of marine life. Damage to these upwellings could result in ecological disaster, according to the consensus of ecologists. Each area is dependent in a complex manner on latitude, depth, topography of the bottom, and shoreline. These areas are located predominantly along the west coasts of continents, in middle to high latitudes. For example, some upwellings are found off California, Peru, Morocco, and Southwest Africa. Others are found in the North Sea and off the Newfoundland Grand Banks.

By way of example, Cole notes that the upwelling off the coast of Peru has occasionally failed in the past. As a result, the area is turned into literally a biological desert. Productivity fails. Fish and sea birds die in such large numbers that the hydrogen sulfide produced by their decay blackens the white paint on ships passing through the area. As a consequence of this failure, a financial crisis hits the indigenous guano and fishmeal industries. Cole adds that the same effect probably would result if a heavy dose of herbicidal chemicals found its way into an upwelling.



For a long time, it was suspected that the combustion of fossil fuel increased the **carbon dioxide content of the atmosphere.** Cole admits that he was skeptical of such talk. That is, until an Antarctic monitoring system was established as part of the International Geophysical Year. "Using sophisticated instruments, IGY scientists collected data which prove that not only is the increase real but the increase since IGY is appreciable," Cole says.

Cole explains that both carbon dioxide and water vapor are transparent to the wavelengths of radiation required for photosynthesis. But both are opaque to the longer wavelength of heat radiations from earth to space. So, an increasing carbon dioxide content in the atmosphere does not directly affect photosynthesis. It has, however, the potential to alter climate and thereby affect vegetation, so that agricultural productivity is the real issue at hand.

On the other hand, Cole explains further, clouds, smoke, dust, and oxides of nitrogen do absorb and reflect those wavelengths of light important for photosynthesis. The nation's increasing air pollution may be reducing our photosynthetic output, he notes.

Other problems

"Construction of the proposed **sea level canal** in the latitude of Panama to join the Pacific and Atlantic Oceans is not ecologically sound," says Cornell's ecologist. The full consequences of its construction are simply unknown. Many factors to be considered are apparent, however, including the following:

- The Pacific stands higher than the Atlantic at that latitude.
- The Pacific is colder than, and chemically different from, the Atlantic.
- What effect would a cold mass of Pacific water moving into the Caribbean have on climate, currents, and food industries?
- What effect would the exchange of species in the two oceans have on each of the species?

Added to these are the implications of the proposed nuclear detonations—equivalent to 170 megatons—to clear the area for the canal. Cole is frightened by the prospect. "The quantities of isotopes —^{3}H, ^{90}Sr, ^{131}I, ^{137}Cs —that behave as gases in cratering explosions would, in my opinion, lead to disastrous environmental contamination," Cole says confidently.

Population growth, biogeochemical

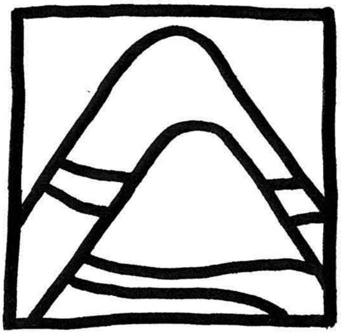
cycles, and ecosystems are some other ecological areas that urgently need more study at this time, according to Cole. Without a doubt, **population growth** underlies all of man's pressing environment problems. Unless population growth is checked, disaster is inevitable. Whether the disaster comes by way of famine, epidemics, wars, oxygen depletion, irreversible poisoning of our environment, or something else, is of little import. What matters is the fact that viability will slow down and eventually stop. Cole hastily points out that this problem is not independent of man's other problems; but it is number one.

Without the **biogeochemical cycles** of oxygen, sulfur, carbon, and nitrogen, man could not survive.. Each of these cycles involves several kinds of living organisms—for example, all organisms build their proteins from nitrogen. "If man inadvertently destroys any of at least a half dozen types of bacteria involved in the nitrogen cycle he could bring an end to life on earth," says Cole.

The elements potassium and phosphorus, although not cyclic in the usual sense, also are required by organisms. According to Cole, these elements simply are washing to the seas where they will stay for a geologically long period of time, unless, of course, man eventually begins to mine the ocean bottoms.

In many cases, the absence of phosphorus limits plant production, and the situation with this element is often ironic, according to Cole. On the one hand, man converts phosphate rock to fertilizers for increased plant production. In the process, severe damage is often incurred by our natural environment. Yet, on the other hand, phosphorus is thrown away in the form of spent detergents, sewage, garbage, leached fertilizers, or other waste products at such a rate that it is one of our most significant water pollutants.

An **ecosystem** is an area such as a lake, a forest, or an estuary, where plants, animals, and microorganisms are in a complex state of reciprocal interaction among themselves, with organisms elsewhere, and with the nonliving components of the environment. This interaction is affected by climate and chemical and other physical inputs to the system. In turn, the ecosystem can affect climate and other environmental characteristics.



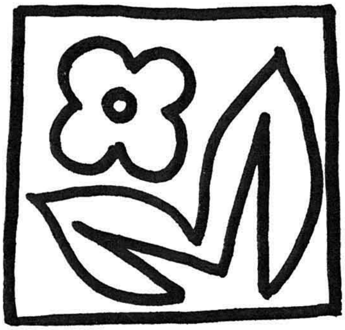
For the first time, Cole observes, ecosystems are being investigated by a multidisciplinary approach. Soon, computer simulation and modeling of such systems will be feasible.

By way of analogy, Cole notes that medicine didn't advance very far until studies of the anatomy and physiology of the normal healthy body were pursued. So, the cure of ecosystems damaged by man will not progress far until ecologists understand the anatomy and functioning of a normal, healthy, ecosystem.

From an ecological viewpoint, most of our agricultural and urban ecosystems are very sick indeed. Continuing the medical analogy, Cole says, "The slambang attempts at palliative measures with such medicines as fertilizers and pesticides are sheer folk medicine." Nevertheless, Cole concludes in a reassuring tone, he has no doubt whatsoever of improved agricultural production. Emerging ecological principles are slowly being put to the task of satisfying this understanding.

Ecological outlets

The **National Science Foundation** is also concerned with ecological affairs, and relations between ESA and NSF have always been cordial and mutually beneficial, according to Cole. In recent years, the NSF program director for environmental biology—who normally serves a one-year term—has always been an outstanding ecologist. Over these years, NSF has supported the Ecology Study Committee, a long-range planning group of ESA, and sent its observers to ESC meetings. But one deficiency in the relationship is that ESC lacks any formal input of ongoing R&D programs in NSF. This may be one area of improvement between the two groups, according to Cole.



Similarly, ecologists provide their ecological inputs to legislators by testifying before **congressional committees.** For example, Dr. W. Frank Blair, a former president of ESA and former chairman of its public affairs committee, testified in support of IBP earlier this year (ES&T, June, page 411). Other ecologists, notably those of the public affairs committee, maintain communication with members of Congress and other federal agencies.

Cole is optimistic about the prospects for support of the **International Biological Program**: "IBP has had an uphill struggle. But now, it is in good hands and adequate financial support should be forthcoming." On looking down the lists of subcommittees and panels for the U.S. National Committee for IBP, Cole notes that at least half of their members are highly competent ecologists. "It's quite a novel view," he says, "a major assault on ecological problems being guided by knowledgeable ecologists."

Plans for the proposed **National Institute of Ecology** have been approved by ESA's Ecology Study Committee. The institute will be controlled by a corporation. "A very preliminary sample instrument of incorporation has been drawn up," Cole says.

Nearly a dozen universities have unanimously supported the concept of the institute with minor differences of opinion on NIE's administrative structure. A more serious question, however, is whether the institute should have a research capability or be primarily a "think tank." For these reasons, Cole says, "I intend very soon to call a meeting of the study committee to consider these problems."

As its first function, the National Institute of Ecology would analyze the U.S. IBP data, if, of course, the institute comes into existence in time. In the absence of NIE, then individual subcommittees of IBP would have to evaluate and analyze the data and make it available for publication.

Switching to Low Sulfur Oil: Con Ed's Story

Task force approach solved some knotty conversion problems within self-imposed six month time limit

At the beginning of New York City's observance of "Cleaner Air Week," Mayor John Lindsay pointed out that SO_2 emissions within the city have been reduced 25% below the 1966 levels. Almost all of this reduction has been attributed to Consolidated Edison's cutback in sulfur content of the fuels it uses for generating the city's power, a project which was substantially completed late last year. At a "Cleaner Air Week" symposium of the Metropolitan Engineer's Council on Air Resources, Con Ed's Malcolm C. Smith gave some insight into just how his company approached the task of converting to low sulfur fuel oil. Taking an interdepartment task force approach, the company was able to accomplish the changeover in the relatively short time of six months. Total price tag for the conversion, according to Smith: slightly more than $3 million for conversion of fuel oil handling facilities, and an increase of $7½ million per year in Con Ed's annual fuel oil bill of about $63 million.

According to Smith, Con Ed's position is that the best way to reduce air pollution, at least by power stations, is to build more nuclear plants. The company has one nuclear power station in operation at Indian Point, two more under construction, and two additional plants being contracted for. But for the short run, it just isn't practical and possible to replace fossil fuel boilers with nuclear plants en masse. In view of air pollution control regulations already enacted for the New York area, other arrangements had to be made for Con Edison's existing plants, most of which had been already converted to fuel oil, natural gas, or, in some cases, both.

New York City Local Law 14, passed in April 1966, limits the allowable sulfur concentration of fuel for power generation to 2% by May 1969, and to 1% by May 1971. However, in March 1967, Con Edison made the commitment to Mayor Lindsay that by October of that year all of Con Ed's fuel oil deliveries would contain 1% sulfur or less. This target date for the conversion was three years in advance of that which would have been required by the city code. However, New York State Public Health Law of October 1967 limits the amount of sulfur in fuel for electric power stations in Bronx, Kings, and New York counties to 1% after October 1, 1968, less than a year from the conversion date originally planned.

Smith pointed out that, for many years, Con Ed had been buying both coal and fuel oil with the lowest sulfur content available at reasonable rates. The company's major fuel oil supply came from Venezuela; oil from this source, however, usually exceeded the desired 1% sulfur limit. Thus, it was necessary for Con Ed's two main oil suppliers to conduct a worldwide search for natural sources of low sulfur oil, and obtain long-term purchase contracts for its supply. The search revealed African sources that met the required specification, but according to Smith, "it was necessary to overcome considerable obstacles to bring in these oils from Liberia and Nigeria. It was an especially difficult problem due to the unsettled political conditions in these countries."

Paraffin base

Obtaining a long-term supply of naturally occurring low sulfur oil was only part of the problem, however. The low sulfur oil, such as that from African oils fields, has a paraffinic or waxy base instead of the asphaltic base typical of the Venezuelan crude oil. This characteristic causes an elevation in the pour point of the oil. At temperatures above the pour point, the wax would tend to solidify and threaten to block the distribution lines.

Pour point of the oil in use in the past was in the range of 25–45° F.; the best guarantee on pour point which could be obtained with the low sulfur oil was 90° F. Present fuel oil handling and storage facilities had to be converted to handle the new oil in order to guarantee that the temperature at all times was maintained above the expected range in pour point.

The viscosity characteristics of the low sulfur oil were also of some concern. The low sulfur oil tended to be somewhat lower in viscosity, and would have caused excessive pump wear because of the lack of strength of the oil film. Therefore, it was necessary to specify a minimum viscosity of 80 SSF at 122° F. for the new oil, compared with a viscosity of 190 SSF for the oil which had been in use. Smith points out that "if it weren't possible for our suppliers to meet this criterion, it would have made a quick changeover to low sulfur fuel oil a very difficult problem."

The increase in viscosity near the pour point was the major problem, however, and the change in pour point characteristics was the only property for which special provision had to be made. In short, from the time the oil was received until the time it was actually used in the boilers, its temperature had to be held above the pour point. Applying a 12° safety factor to allow for the pour point test inaccuracy meant a minimum design temperature for the oil distribution system of 102° F. Thus, it was necessary to review Con Ed's complete fuel oil system, including its two major storage depots, and the lines that serve its twelve generating stations.

Facilities conversion

The scope of the conversion job which was required is evident from examination of Con Edison's fuel oil and storage facilities. The company maintains two major oil receiving and storage stations, one in Queens and one in Brooklyn. In addition, the company also supplies some of its generating stations from captive barges tied up at dockside. The twelve generating

stations themselves also represent a wide spectrum. The age of the boilers varies by more than sixty years; more importantly, they vary in size from small, 40,000 pound-per-hour package boilers to steam plants that supply 1000 megawatt generators.

In the modern stations, oil is normally stored in an unheated outdoor tank. Supply pumps which transfer the oil from the tanks to the generating station discharge through suction heaters, and the oil can be recirculated back to the storage tanks as necessary to hold the oil in the tank at the proper temperature. The bulk of the oil travels some distance to the station proper to main fuel oil discharge pumps which elevate the oil to the proper pressure for firing. Discharge heaters bring the oil up to about 200° F., and the oil then goes to the individual boilers, with a single header often serving two levels of burners. Almost all the boilers use steam atomization.

The older stations tend to be more complex in regard to piping, but are not too different in general concept from the newer stations. The older stations are generally of the header type, as contrasted with the unit approach in the newer stations. Oil is pumped from storage tanks to multiple pump rooms. At the pump rooms, oil is pumped through discharge heaters to a ring header. The ring header, which usually serves a row of three or four boilers, has take-offs for each boiler. A recirculating ring header also serves each boiler for at least startup, and sometimes continually, for control. This type of station has many more lines which run greater distances and has more instrumentation than does a typical modern station.

In order to hold the fuel oil above the pour point at all time in such systems, three methods were available: steam tracing of the supply lines, electrical tracing, or recirculation of the oil to a place where it was reheated. Electrical tracing was used in most cases for small and nonflowing lines such as instrumentation and control lines and burner supply piping. Steam tracing would have been difficult or almost impossible in many of these cases. Of the types of electrical heating available, contact heating tape or cable was preferable to induction or resistance heating. This method was the cheapest, required the least equipment, and offered the widest safety margin. Because of the importance of these circuits, they were backed up with emergency power sources.

The majority of the in-station lines were steam traced, with socket weld piping. Normally, the tracer line was placed directly under the oil line and held in place by stainless steel strapping. Most of the stations have a nominal two-hundred-pound saturated steam header which was used as a steam source for the tracing.

A new station, if originally designed to handle high pour point fuel oil, would have its storage tanks insulated and equipped with heating coils, Smith pointed out. The Con Edison tanks in use were designed for use with low pour point fuel, however, and most were neither insulated nor heated. In these tanks it is necessary to recirculate the oil through heaters in order to make up for heat losses from the tanks. Tests were run before deliveries of new oil to ensure that proper temperatures could be maintained.

Computer analysis

Interstation transfer lines required similar consideration. Most of these lines had been insulated previously, but few had been traced; if tracing had been required, it would have been very expensive to install. The size, length, and operating conditions of these lines were subjected to computer analysis, which showed that no additional tracing was required. The same computer output indicated the frequency of interstation pumping required to keep the oil fluid.

In view of the six-month time limit the company had committed itself to for the conversion, a number of short cuts had to be taken. First of these was establishment of a task force to cut across department lines and expedite engineering, equipment procurement, and construction. Smith, who headed up this task force, says "doing the job in the normal manner would have meant it couldn't possibly be finished in time. The task force met weekly and turned out to be an excellent example of the results possible with good cross-company cooperation."

Instead of the work being closely estimated at each station, Smith explains, two stations were used as measuring sticks. One was an example of a modern station, and the other, one of the older installations. The work at the remaining stations was scoped and compared with the detailed estimate made on the two stations used as a measure. In addition, instead of following the normal step-by-step design procedure, the design work was given to a small group of field engineers. These field engineers are stationed at the plant sites to give advice on projects engineered by the design group, and to act as liaison between engineering and operating personnel. By marking up existing drawings as necessary and working from field sketches, these engineers completed the engineering necessary for the conversion in a fraction of the time which normally would have been required, Smith pointed out.

The purchasing department had a very difficult problem during the project, Smith added, because of both the magnitude of the job and the equipment delivery times imposed. As an example, he cited the case of searching the entire East Coast for vendors to supply over 2200 valves, which were needed within weeks. Another minor problem arose during the construction phase of the project. Because of the high work load on Con Edison's own construction forces at the time, it was necessary to contract for almost all of the construction work. The contractors had trouble getting and keeping sufficient skilled personnel, especially during the summer months. But Smith feels that in spite of the rush nature of the job, good cost control was held and overtime kept to a minimum.

Indeed, Smith concludes that the transition to low sulfur fuel oil at Con Edison went essentially without incident. Since switching to the new fuel, Smith says the generating stations report there is almost no difference, other than pour point, in the operating characteristics of the oil. In fact there may be some improvement in boiler maintenance costs due to the lower vanadium and ash content of the fuel.

Professional Manpower for Environmental Protection

Ralph C. Graber

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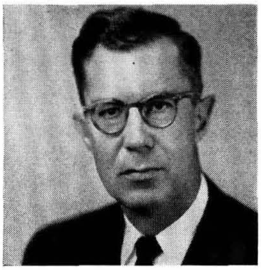

Ralph C. Graber *is Manpower Director, Consumer Protection and Environmental Health Service, U.S. Public Health Service, a position he has held since 1966. He previously held the post of Assistant Chief, Air Pollution Division, and has served with the U.S. Public Health Service since 1941. Graber received his B.S. from Pennsylvania State University (1940), and his M.S. from Harvard University (1947). A registered engineer in the State of Texas, he is a member of the Air Pollution Control Association, the National Society of Professional Engineers, and the InterAmerican Association for Sanitary Engineering; a fellow of the American Society of Civil Engineers, American Association for Advancement of Science, and American Public Health Association; and a diplomate of the American Academy of Environmental Engineers. Graber also is a member of Tau Beta Pi, Chi Epsilon, and Phi Eta Sigma.*

Environmental protection efforts require a wide range of scientific and engineering manpower, including botanists, chemists, ecologists, all types of engineers, epidemiologists, hydrologists, limnologists, meteorologists, microbiologists, pathologists, pharmacologists, physicists, physiologists, sanitarians, and toxicologists, as well as technicians and aides with a variety of backgrounds. Specialists such as administrators, analysts, attorneys, dentists, economists, information specialists, nurses, physicians, statisticians, and veterinarians are also needed.

These personnel are engaged in the application of knowledge to the prevention and control of environmental hazards, in research and development, and in teaching. Included are activities concerned with:

- Analysis and detection of environmental hazards.
- Biological and other effects.
- Development of standards and criteria.
- Planning and conduct of prevention and control programs.

The absence of a comprehensive roster of highly qualified engineers, scientists, and technologists primarily concerned with environmental protection in the U.S. was pointed out at a 1962 conference on educational needs in environmental health.

Presently, deterrents to the development of a meaningful roster include a lack of understanding of (1) the roles and functions of the various disciplines and (2) the interpretation of occupations in terms of basic discipline versus categorical program specialization. While neither of these factors is peculiar to the field of environmental protection little, if any, progress has been made in developing a better understanding in this rapidly developing and expanding field. The necessity for clearer definition of the roles and functions of these disciplines is urgent. The short- and long-term needs for the specific disciplines must then be quantified. In doing so, we must maximize the *interdisciplinary* approach to effective management of the complex problems of man's environment. To accomplish this objective, considerable innovation must be included in the educational, research, and prevention and control processes.

Historically, an effort has been made to delineate the manpower situation in two basic environmental categories: environmental engineering and sanitarian. Few or no meaningful data and information are available for the other basic disciplines. However, the total number of personnel employed in environmental protection activities exceeded 35,000 in 1967.

Environmental engineers

The environmental engineer applies engineering principles to the prevention, control, and management of environmental factors that influence man's physical, mental, and social health and well-being. During the last decade, the need for a comprehensive, systematic look at all environmental factors and their interrelationships has broadened the opportunities for engineers. Prior to that time, the engineer was primarily concerned with such factors as water supply and water pollution, and, thus, the use of the occupational title, sanitary engineer, was not inappropriate. The most comprehensive outlook required in recent years validates the caption of environmental engineer, and its use will become increasingly important.

An estimated 8000-9000 environmental engineers were employed in this country in 1965. The latest survey data are for 1962, at which time 5500 persons were identified as sanitary engineers. This listing was incomplete, the total supply at that time being estimated as 1000–2000 higher than the survey respondents.

A survey conducted in 1949–50 resulted in 4900 respondents, of whom 4200 were active in the profession. The American Public Health Association issued a "Roster of Public Health and Sanitary Engineers," and the Public Health Service analyzed the findings, concluding that there were "about 5000 practicing sanitary engineers in the United States" in 1950.

In 1956, the National Science Foundation and the Public Health Service cooperated in developing the sanitary engineer portion of the National Register of Scientific and Technical Personnel. The survey was repeated biennially until 1964, when the register was expanded to a more representative cross section of the engineering profession.

Characteristics of the survey respondents in 1962 indicate that equal numbers—about 1600—were employed by state and local governments, and by private industry and businesses, and the balance by the Federal Government and other organizations. Management or administration was the most important function, with nearly one third of the respondents engaged in that activity. About one third of those surveyed had a graduate degree, usually a master's.

There are a number of professional organizations concerned with the field of environmental engineering. Seven of these organizations—Air Pollution Control Association, American Institute of Chemical Engineers, American Public Health Association, American Society for Engineering Education, American Society of Civil Engineers, American Water Works Association, and Water Pollution Control Federation—have joined in sponsoring the Environmental Engineering Intersociety Board, Inc. (formerly the American Sanitary Engineering Intersociety Board, Inc.). The objectives of the board are to improve the practice, elevate the standards, and advance the cause of environmental engineering. Certification as a diplomate of the American Academy of Environmental Engineers (AAEE) is awarded by the board, based upon compliance with educational and experience standards, state licensure, and satisfactory completion of a written examination. Currently, the board certifies environmental engineers in four subspecialities: air pollution control, industrial hygiene, radiation and hazard control, and sanitary engineering. The roster is a well-qualified and experienced group of about 1100 persons, and environmental engineers are encouraged to seek certification as attestation of their competencies by professional peers.

Engineers should be licensed under the registration laws of the states where they are employed. All states have such requirements, although educational and experience requirements vary.

Sanitarian

The sanitarian should be prepared by education and experience to work in positions which require the professional application of the basic principles of a combination of the physical and biological sciences to the prevention, control, and management of man's environment. He should be able to apply his knowledge of environmental health concepts to one or more areas of environmental sanitation.

An estimated 15,000 sanitarians and sanitation technicians were employed in 1965. Prior estimates by the Public Health Service had indicated about 5000 in 1950 and 11,000 in 1960.

The first national survey of persons who regarded themselves as sanitarians was conducted in 1962. State and county governments were the major

Table I.

Academic institutions offering undergraduate programs in environmental health

Alabama	**Troy State College, Troy**
California	**California State College, Los Angeles** **California State College, Long Beach** **Fresno State College, Fresno** **Sacramento State College, Sacramento** **San Diego State College, San Diego** **San Fernando State College, San Fernando** **San Jose State College, San Jose**
District of Columbia	**George Washington University, Washington, D.C.**
Florida	**Florida State University, Tallahassee** **University of Florida, Gainesville**
Illinois	**Southern Illinois University, Carbondale**
Indiana	**University of Indiana, Indianapolis** **Indiana State University, Terre Haute**
Louisiana	**Louisiana State University, Baton Rouge** **McNeese State College, Lake Charles**
Massachusetts	**University of Massachusetts, Amherst**
Michigan	**Ferris State College, Big Rapids**
Montana	**Montana State College, Bozeman**
New Jersey	**Rutgers University, New Brunswick**
Oklahoma	**University of Oklahoma, Norman**
Oregon	**Oregon State University, Corvallis** **Portland State College, Portland**
South Dakota	**South Dakota State University, Brookings**
Tennessee	**East Tennessee State University, Johnson City**
Utah	**Brigham Young University, Provo** **Utah State University, Logan**
Washington	**University of Washington, Seattle** **Washington State University, Pullman**
Wisconsin	**Wisconsin State University, Eau Claire**

Source: National Association of Sanitarians employers of the 10,674 sanitarians identified at that time. Inspection, testing, and control were the major activities of half of those answering the survey questionnaire.

Thirty-one states—Alabama, Arkansas, California, Colorado, Connecticut, Florida, Georgia, Hawaii, Idaho, Illinois, Indiana, Kentucky, Louisiana, Massachusetts, Michigan, Montana, Nebraska, Nevada, New Jersey, New Mexico, North Carolina, Oklahoma, Oregon, South Carolina, South Dakota, Tennessee, Texas, Utah, Washington, West Virginia, and Wisconsin—require registration or licensing of sanitarians. An American Intersociety Board of Certification of Sanitarians, organized in October 1964 by the Sanitarians Joint Council, provides recognition of professional achievement.

Other occupational specialties

Environmental protection specialists are essential, whether these specialists practice their basic discipline per se or have acquired a categorical program specialization beyond their disciplinary specialization. There is a continuing need for a variety of chemists, for example, to work in environmental laboratories concerned with research and development, with studies and investigations, and in support of operational and control programs.

In 1961, the Surgeon General's Committee on Environmental Health Problems estimated that 7000 chemists, 3400 physicists, and 2000 biologists were working in the field of environmental health in the nation at large. It was estimated further that, by 1970, more than twice—perhaps triple—these numbers would be required.

Two examples of categorical program specialities are:

- *Industrial hygienists* conduct health programs in industrial plants or similar organizations to eliminate or control operational health hazards and diseases.

The industrial hygienist may make direct measurements of the industrial environment, evaluate the degree of exposure to the contaminant or stress, and recommend or design control measures. As a safety engineer, he may work with industrial physicians to institute nonengineering measures for control and correction of hazards. The

Table 2

Academic institutions offering graduate programs in environmental protection,

Location	School	Area of program emphasis[a]					
		Air pollution	Industrial hygiene	Radiation protection	Solid wastes	Water supply or water pollution	General[b]
	Total, 102 schools	**20**	**19**	**33**	**8**	**78**	**51**
Ala.	Auburn U.			X		X	
	U. of Alabama		X				
Alaska.	U. of Alaska					X	X
Ariz.	U. of Arizona					X	
Ark.	U. of Arkansas			X		X	
Calif.	Calif. Inst. of Tech.						X
	San Jose State					X	
	Stanford U.					X	X
	U. of Calif., Berkeley		X			X	X
	U. of Calif., Davis					X	X
	U. of Calif., Los Angeles		X	X			X
	U. of Calif., Riverside	X					
	U. of Southern Calif.	X					
Colo.	Colorado State U.			X		X	
	U. of Colorado					X	
Conn.	U. of Connecticut					X	
	Yale U.	X	X	X			X
Del.	U. of Delaware					X	
Fla.	U. of Florida	X		X	X	X	X
	U. of Miami			X			
Ga.	U. of Georgia						X
	Georgia Inst. of Tech.			X	X	X	X
	Emory U.			X			
Hawaii.	U. of Hawaii					X	X
Idaho.	U. of Idaho					X	
Ill.	U. of Illinois	X				X	X
	Ill. Inst. of Tech.						X
	Northwestern U.			X		X	X
Ind.	Purdue U.			X		X	X
	Rose Poly. Inst.						X
	U. of Notre Dame					X	X
Iowa	Iowa State U.			X		X	X
	U. of Iowa		X				X
Kan.	Kansas State U.					X	X
	U. of Kansas			X	X	X	
Ky.	U. of Kentucky					X	
La.	Louisiana State U.					X	
	Tulane U.	X					X
Me.	U. of Maine					X	
Md.	U. of Maryland					X	
	Johns Hopkins U.		X	X		X	X
Mass.	U. of Massachusetts					X	X
	Harvard	X	X	X		X	X
	Mass. Inst. of Tech.						X
	Northeastern U.					X	X
	Tufts U.					X	X
Mich.	U. of Michigan	X	X	X	X	X	X
	Michigan State U.					X	X
	Wayne State U.		X			X	X
Minn.	U. of Minnesota	X		X		X	X
Miss.	Mississippi State U.					X	

[a] Includes research training in each program.

[b] Includes one or more of following, as illustrations: public health, injury control, toxicology, food protection, systems planning, etc.

occupational health programs in large organizations also may be staffed with chemists, toxicologists, physicists, nurses, and laboratory personnel.

Nearly 2300 industrial hygienists were employed in the U.S. in 1965, a fourfold increase since 1950. Most of them worked in an industrial setting, but increasing numbers are being employed by transportation companies, public utilities, mining operations, insurance companies, universities, and health and labor departments.

- *Radiation protection personnel* at the professional level include health physicists, radiological physicists, radiochemists, radiobiologists, and others with special training in the health aspects of radiation. The radiation exposure problems with which they are concerned are associated with the use of x-ray machines, radioactive materials, nuclear reactors, and particle accelerators, and environmental radioactive contamination. Their work is conducted principally in industrial, medical, research, or educational institutions that use radiation sources, and in health agencies that have responsibility for protection of the public health. Approximately 4600 radiation protection personnel were employed in 1965. They are divided almost equally between professional and technical workers.

The Health Physics Society and the American Public Health Association serve as sponsors of the American Board of Health Physics, established in 1959 to improve the practice and elevate the standards of health physics. By 1967, through a system of written and oral examinations, the board had certified almost 500 people as professionally qualified to assume higher level positions in health physics. Requirements for certification include, first, graduation with a bachelor's degree in a physical science or a biological science, with a minor in physical sciences, and second, six years of responsible professional experience in health physics.

Education and training

The minimum educational requirement for most environmental protection personnel is the baccalaureate degree. However, the trend is towards a requirement of graduate education in

supported by selected federal grants programs: 1967

Location	School	Area of program emphasis[a]					
		Air pollution	Industrial hygiene	Radiation protection	Solid wastes	Water supply or water pollution	General[b]
Mo.....	U. of Missouri...........					X	
	Washington U.............						X
Mont...	Montana State U.........					X	
Neb....	U. of Nebraska..........					X	
Nev....	U. of Nevada............					X	
N.H....	U. of New Hampshire....					X	
N.J....	Rutgers, The State U.....			X		X	X
N.M....	New Mexico State U......					X	X
N.Y....	Columbia U..............			X			X
	Cornell U................					X	X
	City U. of N.Y...........		X				
	Manhattan College......					X	
	New York U..............	X		X		X	
	Rensselaer Poly Tech....			X	X		
	Syracuse U..............						X
	U. of Rochester..........		X				
N.C....	N.C. State U............					X	
	U. of North Carolina.....		X	X		X	X
N.D....	North Dakota State U....			X		X	X
Ohio...	Ohio State U............		X			X	X
	U. of Cincinnati..........	X	X	X		X	X
	U. of Akron.............					X	
	U. of Toledo............					X	
Okla...	Oklahoma State U.......					X	
	U. of Oklahoma..........		X	X		X	X
Ore....	Oregon State U..........	X		X		X	X
Pa.....	Pennsylvania State U....	X				X	X
	U. of Pennsylvania......			X			
	Drexel Inst. of Tech......	X	X		X		X
	Temple U................	X		X			
	U. of Pittsburgh.........		X	X		X	X
P.R....	U. of Puerto Rico........						X
R.I.....	U. of Rhode Island......					X	
S.C....	Clemson U...............					X	
S.D....	South Dakota State U....					X	
Tenn..	U. of Tennessee.........			X		X	
	Vanderbilt U.............	X				X	
Tex....	U. of Texas..............		X	X	X	X	X
	Texas A & M U...........	X				X	
	Rice U..................					X	
	North Texas State U.....					X	
Utah...	Utah State U.............					X	
	U. of Utah..............	X				X	
Vt......	U. of Vermont...........					X	
Va.....	Virginia Poly Tech........					X	X
Wash..	U. of Washington........	X	X	X		X	X
	Washington State U......			X		X	
W.Va...	West Virginia U..........	X			X	X	X
Wisc...	U. of Wisconsin..........					X	
	Marquette U.............					X	
Wyo....	U. of Wyoming...........					X	

Source: Department of Health, Education and Welfare, Public Health Service, Bureau of Disease Prevention and Environmental Control, and National Institutes of Health; Department of Interior, Federal Water Pollution Control Administration; Atomic Energy Commission; Department of Interior, Office of Water Resources Research one of the basic disciplines or in an area of categorical program specialization. In several basic disciplines the qualifying professional degree is at the doctoral level.

A number of graduate educational programs in the field of environmental protection are supported by several federal agencies. (See Table 2 for support of research training by category.) In 1967, stipend support, including research training, was provided for 664 engineers, 52 sanitarians, and 855 other environmental protection disciplines (Tables 3 and 4).

Now, 30 academic institutions offer undergraduate programs in environmental health (Table 1).

During 1968, the National Association of Sanitarians will initiate an accreditation program for undergraduate environmental health (or related) curricula, including those offered by junior colleges.

The Public Health Service offers a variety of technical, short-course training courses at the following locations:

- *The Environmental Control Administration* (ECA) offers courses in occupational health, solid wastes, food protection, computational analysis, and —beginning in February 1968—water supply and injury control, at Cincinnati, Ohio. ECA also offers courses in radiological health at Rockville, Md.; Las Vegas, Nev.; Montgomery, Ala.; and Winchester, Mass.
- *The National Air Pollution Control Administration,* at Durham, N.C.

In addition, short courses are conducted at other PHS field stations and selected locations in response to requested field presentations. During fiscal year 1967, over 4000 persons attended these courses. The number enrolled in each training activity was as follows: 1530 in air pollution; 1267 in radiological health; 693 in food protection; 454 in occupational health; 148 in solid wastes; and 113 in computational analysis. Courses in water pollution control, formerly given by the Public Health Service, now are being conducted by the Federal Water Pollution Control Administration, Department of the Interior.

There is urgent need for a wide variety of adequately prepared manpower to work in the environmental protection field. If we are to make any impact on the environmental problems, the number of people involved must be twice, perhaps three times, the number now employed in the public and private sectors.

Table 3

Stipends awarded under selected Federal Government training programs for graduate study in environmental protection: 1967

	All federal agencies			Public health service		
Type of program[a]	Environmental engineers	Sanitarians	Environmental specialists	Environmental engineers	Sanitarians	Environmental specialists
All programs	**664**	**52**	**855**	**350**	**52**	**698**
Air pollution	51	...	103	51	...	103
Radiation protection	49	...	327	49	...	327
Industrial hygiene	6	2	32	250	52	268
Solid wastes	31	...	27			
Water supply/water pollution	315	...	157			
General[b]	212	50	209			

[a] Includes research training in each program.

[b] Includes one or more persons from such areas as: occupational health, toxicology, food protection, injury control.

Source: Department of Health, Education, and Welfare, Public Health Service, Bureau of Disease Prevention and Environmental Control, and National Institutes of Health; Department of Interior, Federal Water Pollution Control Administration; Atomic Energy Commission

Table 4

Environmental health training for February 1967

	Total dollars (millions)	Total number grants	Total number trainees supported
Water Pollution Control (DI)			
Training grants	$2.98	72	466
Fellowships	0.63	105	105
Air Pollution Control (HEW)			
Graduate training grants	1.63	20	144
Specialist training	0.42	3	74
Fellowships	0.42	60	60
Radiological Health (HEW)			
Training grants	2.26	34	264
Technician training	0.24	7	149
Solid Wastes (HEW)			
Training grants	0.15	4	16
Atomic Energy Commission			
Fellowships (health physics)	0.40	67	67
National Center for Urban and Industrial Health (HEW)			
Training grants	1.24	24	193
Fellowships	.01	4	4
Bureau of Health Manpower (HEW)			
Curriculum	.57	19	...
Traineeships	1.05[a]	...	287[a]
Totals	$12.00	419	1829

[a] Environmental health.

Ultimate Disposal of Waste Water Concentrates to the Environment

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Advanced treatment of waste water is basically the separation of a valuable product—water—from its pollutants. The residue of substances which remains normally has no positive economic value, and must be degraded or disposed of (Weinberger, Stephan, and Middleton, 1966). In this respect, waste treatment is similar to other industrial processing: separating the wheat from the chaff, copper from its gangue, or wood pulp from lignin. These low value residues, like those from waste water treatment, are usually an economic liability and may become a pollutant. It is the assignment of the Ultimate Disposal Research Activity of the Federal Water Pollution Control Administration to devise methods for treating these residues so that they will not pollute the environment.

In this context, a pollutant is defined as a substance which interferes with the intended use of the water, air, or land surface. Since intended uses often conflict, society must decide on the best intended use. In the U.S., we are deciding that neither water nor air should be used for disposal of noxious substances. However, we still approve of controlled burial for unwanted organic matter and use of the atmosphere for carbon dioxide disposal. There is also no objection to putting clean water back into the river, and by corollary, there should be no objection to returning salt to the ocean.

A prime requisite of any disposal procedure is that a pollutant from one medium be prevented from causing pollution elsewhere. For example, incineration of sewage sludge requires control of particulate matter from the incinerator stacks. Wet scrubbers can effectively remove the fly ash from stack gases, but the water-ash slurry produced also requires further treatment before disposal. Although this seems to be an endless circle, each step of treatment does reduce considerably the quantity to be treated.

There are only three places where it is practical to dispose of polluting substances after they have been rendered innocuous: air, land, or the oceans. Surface fresh waters are not available for disposal. No substances except water itself can be disposed of in large quantities into fresh water without causing a pollution problem of some sort. The ocean has long been used for the ultimate disposal of human wastes, and the first man-made pollutant to attract attention in the ocean was fecal material. Removal of sewage solids by primary treatment deals with the obvious problems, and is often the only treatment given by seacoast towns today. However, warning signs are appearing. There is some evidence that the ocean's assimilative capacity is not infinitely large, and that the effluents from some ocean outfalls are not rapidly dispersed. To avoid pollution, these wastes must be treated to remove any material which will float to the surface. They must be placed far enough from shore and mixed with enough sea water to ensure adequate dilution. Disinfection may also be needed, especially if discharges are close to bathing beaches and beds of edible shellfish.

Brooks (1960) has discussed the design of ocean outfalls for dispersion of dilute wastes that are lighter than sea water. Many communities load heavy sludge on barges and dump it at sea where, hopefully, it sinks to the

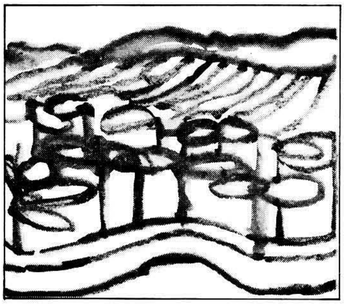
bottom. Fortunately, most toxic heavy metals present are converted to insoluble precipitates that settle to the bottom. Thus, they have a low rate of dispersion in the sea. Sea water also has a high buffer capacity and can neutralize large quantities of acids or bases.

Harmful or helpful

Disposal at or near the shoreline has the effect of increasing the fertility of offshore waters. The result may be beneficial, as in the case of an improved environment for shellfish breeding and survival, or harmful, as in the case of unwanted blooms of algae and microscopic organisms. In either case, not enough is known yet about the ecological effects of ocean waste disposal. One danger is that commerical fish catches may be the last link in a food chain that concentrates pesticides from waste waters to toxic levels. On the other hand, removal or neutralization of toxic substances could make possible the use of nutrient values of wastes to increase the productivity of the oceans.

Long distance transport of sludges and concentrates by pipeline was suggested by Wirtz in 1956. Relative costs of commercial carriers have been studied by Koenig (1968), who showed that pipelines are not the most economical method of transporting less than 10,000 gallons per day. Trucks are more economical than rail for hauls of less than 50 miles.

Solid materials may be disposed of on land, either as concentrated fill that is buried, or by dispersion on the surface. In either case, dissolved salts or toxic materials may pollute the ground water. Some states already prohibit the discharge of salt brines to unlined pits or dry watercourses. When solids are used for landfill, it is important that they be solid and capable of bearing a load. Organic sludges that decompose slowly cannot be used as fill under buildings, or even playgrounds, if the area is to remain level. Seepage from landfills pollutes surface and ground water (Weaver, 1961).



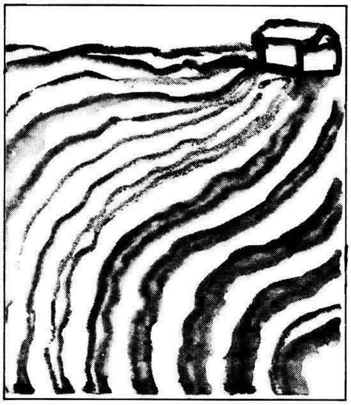
The cheapest, and oldest, method of sewage disposal is spreading of the liquid sludge on land (Kershaw and Wood, 1966). Odor problems and seepage to streams resulting from uncontrolled use of the technique have made spreading unpopular. Nevertheless, the method is still under study, since most soils have a considerable capacity for dewatering and oxidizing organic matter.

Land spreading of soluble organic salts or toxic material is, of course, undesirable. Farmers in some countries abroad use human wastes, without dilution, as a soil nutrient. However, the nitrogen, phosphorus, and potassium content of sludge is much lower than synthetic fertilizers, and the many U.S. attempts to market dried sludge as a fertilizer have been generally unsuccessful (MacLaren, 1961). The organic content of sludge is useful in improving the quality of sandy soils, although market value in this application hasn't been assessed realistically.

Market for sludge

Thus, the use of land surfaces as low cost dewatering and oxidizing systems has some promise. In many areas, farmers compete for available wet sludge to spread on their fields, indicating the possibility of developing some market value. In a typical operation, sludge is sprayed from a tank truck. If the soil is too wet to bear the weight of a truck, a high pressure hose and sprinkler may be used to bring sludge from the roadside. Soils can oxidize and destroy large quantities of sludge each year, provided they are kept well aerated. However, heavy metals in some sludges have caused loss of fertility after many years (Rohde, 1962).

Some form of digestion or stabilization is required before sludge can be applied to the land. For sale on the retail market, sludge is dried and heat-sterilized. Air-dried sludges are given away to farmers and greenskeepers all over the country. Anaerobically digested sludge is spread wet in many areas. A trend toward aerobically stabilized or digested sludge has been noted, particularly for smaller treatment plants. Aerobically stabilized sludge has fewer nutrients in the supernatant liquor and is more stable than conventional anaerobically digested sludge (Irgens and Halvorson, 1965). Some states prohibit the application of unsterilized sludges to root or leaf crops.



A pipeline has been proposed to transport sludge to low quality land in Cook County and ultimately to land some 67 miles distant(Dalton et al., 1968). Morgantown, W. Va., has a grant to pipe sludges five miles to a strip mine spoil area to reclaim the soil. In both cases, local opposition to dumping of sewage "in our backyard" has developed. Proper communication is obviously important. Two plants near Pittsburgh, only 70 miles from Morgantown, are distributing wet sludge to farm land and finding it highly acceptable to the farmers (Wolfel, 1967).

Soluble waste such as salt solutions can be pumped into deep disposal wells —if the subsurface geology is suitable. This method is used widely for the subsurface return of oilfield brines. One drawback to the technique is that the pores of the underground aquifers can be clogged by solids suspended in the liquid. If underground rock formations can be fractured to open up bedding planes, suspended solids are less of a problem (Warner, 1965). Disposal into underground rivers in limestone formations is also practiced. Pollution of ground water is a concern for both shallow and deep wells, and earthquakes have also been attributed to underground injection of wastes (Healy et al., 1968).

Mined cavities, such as those used for underground storage of fuel gas, are more expensive than other means of ultimate disposal. They are more suitable, however, for disposal of radioactive wastes which require continuous monitoring.

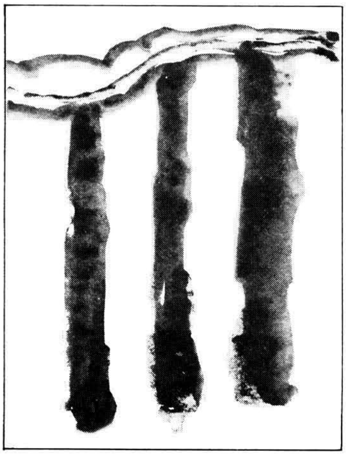
Any logical approach to the problems of ultimate disposal must really begin with the chemistry of the pollutants. Fortunately, fewer than half of the elements are common enough to be encountered in the search for solutions to disposal problems. In fact, only 29 of the elements constitute over 99% of the ultimate disposal problems. (Disposal of radioactive isotopes will not be included in this analysis. Their use and disposal are subject to strict Atomic Energy Commission control.)

The major problem facing municipal sewage treatment plants in the disposal of organic matter is not the carbon compounds themselves, but the associated water. A 5% primary sludge contains nearly 20 times as much water as all other matter. Obviously, it is not economical to use fuel to dry sludge beyond the point where it will support its own combustion. Sedimentation and filtration are two common methods of dewatering.

Oxidation by combustion is one method of ultimate disposal of organic matter which also provides heat that can be used to dewater sludge. Combustion of one pound of dry sludge may produce only enough heat to evaporate two pounds of water, whereas a greasy or oily sludge will be able to evaporate more than three pounds. In addition, the design of an incinerator has a large influence on the percent of water which can be evaporated without using supplementary fuel (Sebastian and Cardinal, 1968).

Fuel value

The fuel value of dry sludge is comparable to that of low grade coal (Owen, 1957), and can be measured accurately in a bomb calorimeter. With ordinary sludges, fuel value can be estimated from the percent volatile solids. However, because of the uncertain quantities of bound water in hydrous oxides, it is not safe to use this method to estimate the fuel value of sludges that are high in ash.



Various pretreatments of sludge are used to reduce the cost of drying. Anaerobic digestion, for example, reduces the quantity of sludge which must be handled. Digestion may also make the sludge somewhat easier to filter. A properly operating anaerobic digester reduces the filterable solids by up to 50%, fermenting them to methane and carbon dioxide and producing a supernatant liquor rich in nutrients and BOD (Barth, Mulbarger, et al., 1966). The methane can be burned to heat the digester or, in large plants, to generate power. In either case, it is oxidized to CO_2 and water vapor. The supernatant liquor is ordinarily returned to the plant where it increases the oxygen requirements and raises the levels of nutrient salts. The supernatant liquor is by far the most polluted stream in ordinary municipal sewerage systems.

The filterability of sludge can be improved greatly by the Porteous system of pressure-cooking at 370° F. The method was developed in England where it has since been abandoned at some plants (Evans and Roberts, 1947). A new heat treatment plant has been built recently in Switzerland (Lancoud, 1965). Pressure-cooking the sludge hydrolyzes the slimy substances that make filtration difficult, and also destroys living cells and spores; however, it liberates soluble nutrients and BOD to the supernatant liquor. Ten to 20% of the BOD and 60–80% of nitrogen is returned in the soluble fraction. In this respect, the supernatant liquor from cooking puts a greater load on the biological plant than a digester which, at least, coverts some of the soluble BOD to methane.

The Zimmerman wet oxidation process involves cooking the sludge in the presence of dissolved air (Teletzke, 1964). A high temperature version of this process, which operates just below the critical temperature of water, produces a sterile inert sludge, aldehydes, acids, and CO_2 from oxidation of the organic substances, and solubilized nitrogenous compounds. Lime may be added to retain the phosphates in the solids. The low temperature process products a sterile sludge cake that is high in organic matter, but can be filtered easily. The supernatant liquor is rich in amino acids and plant nutrients (Teletzke, Gitchel, et al., 1967). Like anaerobic digestion, heat treatment produces a strongly polluted stream which is difficult to treat in a biological plant.

Sludge stabilization

Aerobic digestion stabilizes solids against subsequent putrefaction and retains most of the nutrients and BOD in the insoluble fraction. It may produce a high level of nitrates in the supernatant liquor. There are small reductions in total BOD and nitrogen and no useful increase in filterability. Aerobic digestion, therefore, has little value as a pretreatment to filtration and incineration. Its principal use is stabilizing sludges for land spreading.

Organic matter applied to the soil is oxidized by the soil microorganisms to produce CO_2 and humus. Phosphates and ammonia are adsorbed on soil minerals and utilized by the crops. There may be some denitrification of soluble nitrates. Pathogenic organisms in raw sludge must be controlled by some form of treatment. Digestion—either aerobic or anaerobic—commonly is considered sufficient because the sludge should be held long enough in an unfavorable environment for pathogens to be killed. Heat treatment is ideal, but expensive, and chlorination of sludges is not practical. Lime treatment might be effective; most pathogens are destroyed above pH 12.

Phosphorus, perhaps the major uncontrolled pollutant in waste water, (Sawyer, 1965) occurs in at least three forms in raw sewage: orthophosphate, condensed phosphate, and organic phosphorus. Of these, the orthophosphate form is the primary nutrient for algal growth in surface waters. Present treatment methods remove only a fraction of the phosphate load as organic sludges. Biological treatment hydrolyzes about 90% of the total phosphate to orthophosphate in secondary effluents (Hurwitz, 1965; Neale, 1964).

Under certain conditions which are still not understood, activated sludges accumulate a large fraction of the phosphate present in waste water (Vacker, Connell, et al., 1967). Studies are under way to maximize this process since it could become a low cost way to remove phosphates. The phosphate accumulated by active sludge can easily be lost by relatively short anaerobic periods, and a large fraction of the phosphates is redissolved in digester supernatants (Shapiro, Levin, et al., 1967). If returned to the head of the plant, this supernatant adds to the phosphate load to be handled. In-soil, making it unfit for agriculture. Organic-rich sludges cannot be converted to aluminate because humic acids will dissolve. One successful, though expensive, method is to freeze the sludge (Doe, Benn, et al., 1965), which removes the water and yields an alumina that filters as easily as sand. Aluminum hydroxide with adsorbed phosphates apparently is not dissolved in anaerobic digesters, according to recent studies by Barth and Ettinger (1967). Incineration of the sludge should produce insoluble aluminum phosphates in the ash.

Iron salts also hydrolyze to gelatinous hydroxides which adsorb phosphates. Ferric phosphate is reduced in anaerobic digesters to insoluble ferrous phosphate (Thomas, 1965). If sulfides are present, the less soluble ferrous sulfide precipitates, liberating the phosphate. Ferric hydroxide, or the oxide after incineration, can be redissolved in acid but this also dissolves any phosphates. The Guggenheim process for chemical treatment of sewage with ferric sulfate, followed by incineration and recovery of ferric oxide by solution in sulfuric acid (Gleason and Loonan, 1933), was unsuccessful because phosphates accumulated with the iron. Unlike aluminum, it is not possible to dissolve ferric hydroxide at high pH. Iron salts may be useful for removing phosphates where low cost waste streams containing iron are available, such as acid mine wastes or pickling liquors. Leaching by ground water would probably not liberate phosphates from incinerated sludge containing iron phosphates.

Many other polyvalent metals can precipitate phosphates and some may be recovered by redissolving the precipitate at high or low pH. None of these metals is as cheap as lime, alum, or iron, and high recoveries would be necessary to justify the use of any other metal to precipitate phosphate.

Nitrogen compounds, like phosphates, are a serious pollutant in municipal waste waters and can stimulate the growth of algae to nuisance conditions. Some algae are nitrogen fixing, also converting atmospheric nitrogen to organic nitrogen which then enters the nitrogen cycle.

Nitrifying bacteria

Organic nitrogen compounds can be hydrolyzed to ammonia by microorganisms under aerobic or anaerobic conditions. Extended aerobic treatment develops nitrifying bacteria which convert ammonia, first to nitrites, and then to nitrates. High-rate biological treatment usually leaves most of the nitrogen in the form of ammonia. Extended aeration converts nearly all of the ammonia to nitrates (Barth, Mulbarger, et al., 1966).

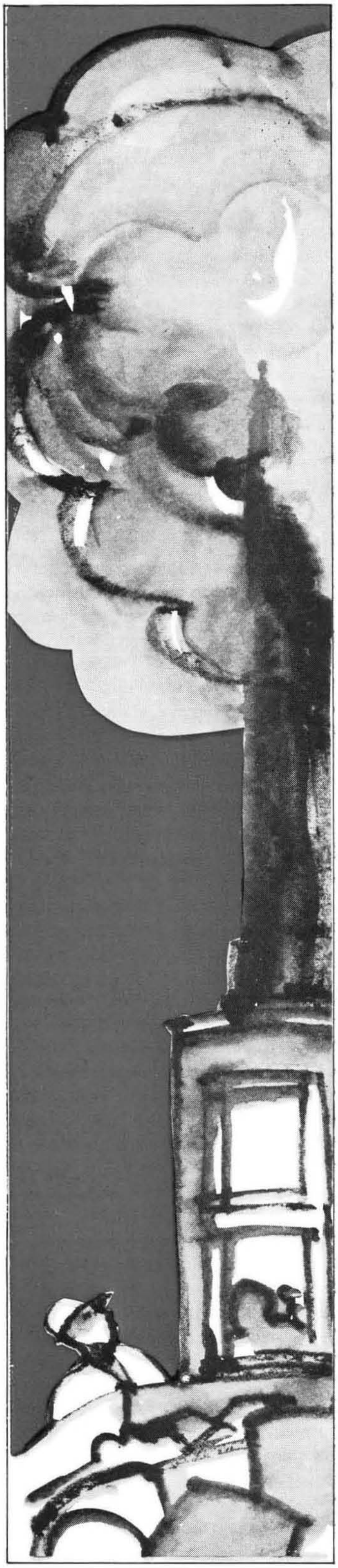
Most nitrogen in waste water is in the form of either ammonia or ammonium ion at a typical concentration of about 15 mg./l. as nitrogen (Neale, 1964). If the waste water is to be treated for reuse, its ammonia content must be brought below 1 mg./l. The ammonia can be converted to gaseous nitrogen by chlorination, but such treatment requires 10 mg. of chlorine per mg. of ammonia nitrogen (McKee and Brokaw, et al., 1960). Such heavy chlorination would cost between five and ten cents per thousand gallons of water treated.

Air stripping

Ammonia is present almost entirely as ammonium ions at the alkalinity of normal secondary effluents, but above pH 10 it is mostly present as a dissolved gas. If the pH is run high enough at some stage of the treatment process—for example, by lime addition to remove phosphates—large cooling towers can be used to air strip the gaseous nitrogen. During aeration, the equilibrium is strongly in favor of the water phase, and about 300 cubic feet of air are required per gallon of water treated. The cost of air stripping is usually under two cents per thousand gallons (Slechta and Culp, 1967).

The large volumes of air necessary to remove ammonia make a preconcentration step desirable. Some zeolite minerals selectively adsorb ammonium ions in preference to sodium, calcium, and magnesium ions (Mercer et al., 1968). Battelle-Northwest is currently investigating natural zeolite for adsorption of ammonium ions from waste waters. Regeneration by lime and aeration of a few percent of the total volume to remove ammonia appear feasible. Ammonia levels in air from stripping towers will be extremely low (micrograms per liter), about comparable to nitrate nitrogen from electrical discharges in the atmosphere. Ammonia in the air is eventually adsorbed by soils and surface waters.

Ammonium ions applied to soils are adsorbed by soil minerals such as natural zeolites and clay, and are available to growing plants. Excess ammonia is converted by soil bacteria to nitrates by the same route that exists



in extended aeration. Nitrate ions are also utilized by growing plants but are not adsorbed on soil minerals. Excess nitrates, when leached out of soils, produce nitrates in ground water or crystals of saltpeter in caves and cellars.

The Public Health Service limit for nitrates in drinking water was set at 10 mg./l. as nitrogen in 1967. Higher levels are toxic to infants, causing methemoglobinemia, or "blue babies," although children and adults can handle large quantities of nitrates without difficulty.

As algal nutrients, nitrates in surface waters are not significantly different from ammonia on a nitrogen basis (Flaigg and Reid, 1954). Nitrates, however, are denitrified by many species of microorganisms in the presence of food, if oxygen levels are low. The oxygen in nitrates is utilized by the organisms, and the nitrogen is liberated as nitrogen gas (Johnson and Shroepfer, 1964). Nitrates can be beneficial in heavily polluted surface waters, but are detrimental in clean waters.

Denitrification by microorganisms is a useful route for ultimate disposal of nitrogen. Several schemes involving activated sludge have been proposed for denitrification. One system being studied at Pomona, Calif., uses microorganisms growing on carbon columns to denitrify water using methanol as a food source (Parkhurst, Dryden, et al., 1967).

Sulfur in waste waters occurs primarily as sulfates derived from tap water. Sulfates are not considered pollutants, except when they contribute to total dissolved solids. Moreover, sulfates cannot be removed from waters by precipitation with calcium because a saturated solution of calcium sulfate contains nearly 1300 mg./l. of sulfate.

Sulfates are reduced to sulfides in anaerobic digesters and can be precipitated by metals especially iron which forms slightly soluble ferrous sulfide. When sludge containing ferrous sulfide is burned, the sulfur is released as oxides of sulfur and may be an air pollution problem. Soluble sulfides, including ferrous sulfide, will precipitate most heavy metals except chromium, and, thus, remove them from the system. For this reason, it has been suggested that sulfates be fed to digesters to prevent poisoning by heavy metals, especially copper and zinc (Masselli, et al., 1967). Sulfides are possible precipitants for mercury, silver, arsenic, and lead as well, but liberation of the metal under oxidizing conditions must be considered.

Any form of reduced sulfur, as well as sulfate salts of ammonia and organic cations, will liberate oxides of sulfur upon incineration. Sulfur concentrations up to 2% in digested sludge, on a dry solids basis, make this fuel as bad as many grades of coal, from an air pollution point of view. One way of controlling pollution from sulfur in fuels is to supply calcium and magnesium oxides to the combustion zone (Potter, Harrington, et al., 1968). It is quite possible that lime, waste lime sludges, or even ground limestone or dolomite added to the sludge would control sulfur oxide emissions from sludge incinerators. Much will depend on the design of the incinerator. Furnaces for burning the black liquor from paper pulp production successfully control sulfur losses when burning sodium sulfide and organic matter dissolved from wood (Malo, 1967).

Adequate disposal means for soluble salts in inland areas are presently unavailable, except in locations where deep-well injection is practical (Koenig, 1964). Cations of sodium, potassium, calcium, and magnesium, in combination with anions of chloride, bicarbonate, and sulfate, make up the principal components of total dissolved solids. The Public Health Service Drinking Water Standards of 1962 recommend not over 500 mg./l. total dissolved solids, although up to 1000 mg./l. is acceptable in some areas. Chlorides are further limited to 250 mg./l. In irrigation waters, monovalent ions, especially sodium and chloride, are more harmful than calcium, magnesium, sulfate, carbonate, and bicarbonate ions (McKee and Wolf, 1963). Only calcium and magnesium can be economically precipitated from water, and their removal ordinarily does not significantly improve the level of total dissolved solids. The extreme dilution of the soluble salts makes their recovery for use as raw materials uneconomical (Christensen, McIlhenney, et al., 1967). Because they are pollutants, the uncontrolled discharge of brines to unlined surface pits is prohibited in some states. In many arid areas, it is possible to evaporate brines to dryness in properly lined solar evaporation ponds. This, at least, reduces the cost of transporting brines to the ocean or of storing the solids in sealed cavities.

The only acceptable sites for disposal of salts in solution are the ocean or salt lakes. In some areas, salt brines collected in lagoons are discharged to the river during a spring flood. Properly controlled, salts in limited quantities might not pollute some rivers at high flow.

Residual flows from such advanced waste treatment processes as reverse osmosis, electrodialysis, ion exchange, or distillation ordinarily are not concentrated more than tenfold, and contain 5000 to 15,000 mg./l. TDS. This is still much more dilute than sea water, which contains 35,000 mg./l. TDS. Higher TDS concentration precipitates scale on the membranes or heat transfer surfaces (Neale, 1964). Calcium carbonate deposits first, followed by calcium phosphate. Scale from these salts can be controlled by the addition of sufficient acid to neutralize the alkalinity or by prior lime treatment of the water. The next scale to deposit is usually a form of calcium sulfate. These precipitates form slowly and may continue to form scale for days. Magnesium chloride hydrolyzes in hot water to form insoluble magnesium oxychloride, liberating HCl.

Scale formation and slow equilibrium of precipitates cause minimal trouble in solar evaporation ponds. Fortunately, many water-short inland areas, where desalting techniques will be required, also are arid areas with low cost land where solar evaporation ponds can be used. Submerged combustion evaporates water without involving any solid heat transfer surfaces, and may be useful where solar evaporation is impractical (Cronan, 1956). Scaling problems need not be insuperable, even for high-efficiency, multiple-effect, evaporators. Again, the experience in the pulping industry shows that salt solutions containing organic material can be concentrated to 50% solids on a continuous basis.

Ion exchange

The hardness-forming ions, calcium and magnesium, can be removed as calcium carbonate and magnesium hydroxide. There may be a market for magnesium oxide from magnesium hydroxide in some cases, but it will probably be more economical to recover magnesium from raw water before it enters the municipal distribution system. Ion exchange resins and zeolites used to remove hardness from water are regenerated with an excess of brine or with a combination of acidic and basic regenerants. The latter contains calcium and magnesium chlorides and excess sodium chloride. Some areas prohibit disposal of this waste salt solution to surface or ground waters.

Borates in sewage originate from cleaning compounds, especially the perborates used in solid bleaches. Borates are not very toxic to animals and microorganisms, and present no problem in drinking water. However, many agricultural crops, especially fruit trees, can be poisoned by less than 1 mg./l. of boron (McKee and Wolf, 1963). Currently, there is no satisfactory method for removing borates from irrigation water. Borates stay with the dissolved salts in desalting processes. Ion exchange resins with selectivity for borates have been claimed but their efficiency and useful life are unknown. The regenerant brine from such a resin would contain the borates in solution and would have to be disposed of as a salt brine.

Trace elements may occur in municipal waste waters as a result of spillage, corrosion, and additives to some cleaning and processing compounds. Many metals form insoluble hydroxides or carbonates. Calcium, magnesium, strontium, barium, aluminum, trivalent chromium, manganese, iron, cobalt, nickel, and copper can be removed by lime clarification. Lime precipitate may also remove zinc, cadmium, mercury, arsenic, tin, antimony, and lead by adsorption. Sulfides, as already noted, precipitate heavy metals, and septicity in sewers may reduce pollution by removing mercury, zinc, and copper ions from the sewage. Some metals—notably mercury, cadmium, and zinc—are strongly adsorbed on organic matter and are collected in primary or secondary sludges (McDermott, Barth, et al., 1963). Oxidation may liberate these metals, producing toxic flue gases or poisoning solids. Chromates in municipal waste waters may come from electroplating rinse waters, tanning wastes, or from cooling tower water. Removal of hexavalent chromates is difficult (Gurnham, 1965). Chromates can be reduced with sulfur dioxide or under anaerobic conditions to trivalent chromic salts which form insoluble carbonate and hydroxide precipitates.

Cyanides are also found in electroplating waters. Because they are highly toxic, strong controls on their disposal are required. The most common disposal method for cyanides is oxidation by chlorine to cyanates which hydrolyze to urea (Gurnham, 1965). Selenium occurs in some surface waters and may get into sewage from industrial spills. There is no satisfactory way to remove selenium from waste waters. Heavy metals, cyanides, selenium, and arsenic all are so toxic and difficult to deal with in dilute solution that they should be controlled at the source and not permitted to enter municipal sewers.

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Cation Sorption on Colloidal Hydrous Manganese Dioxide

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■ The sorption of several slightly hydrolyzing metal ions and of tensioactive organic substances on colloidal hydrous manganese dioxide has been studied. These metal ions and organic solutes have included: Ag^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Nd^{3+}, Sr^{2+}, dodecylbenzene sulfonate (anionic), nonylphenoxynonylethoxyethanol (nonionic), and *p*-dodecylbenzyltrimethylammonium chloride (cationic). Ionic strength and pH have been investigated as system variables. Rates of sorption of all metal ions studied are rapid, with equilibrium attained within a matter of several minutes. Adsorption of the cationic organic solute is also rapid, but neither the anionic nor nonionic organic solute adsorbs to any appreciable extent. Exchange sorption appears to be the principal mechanism involved in the sorptive uptake of the metal ions and the cationic organic solute. Equilibrium distributions of all sorbate ions between solution phase and sorbed state may be described rather well by the Langmuir sorption equation. Equilibrium capacities range from 0.10 to 0.31 mole per mole of manganese dioxide.

Manganese is a widely distributed element, existing commonly in the form of the minerals manganite, hausmannite, manganese spar, hauerite, and braunite, or associated with the silicates and carbonates of calcium, magnesium, and iron. This element is present in most natural waters (Davis and DeWiest, 1966) as a result of the dissolution of manganese-bearing minerals, frequently in appreciable concentration in oceanic and mineral waters. Manganese may also occur in natural waters as a result of the discharge of mine wastes or the wastes from ore and metal processing operations, and is introduced to many water supplies in the form of the oxidant permanganate.

Present knowledge concerning the significance of manganese in limnological transformations and in the ecology of aquatic environments has been adequately discussed by Lee (1964), Morgan and Stumm (1964a), and Wangersky (1963), among others. As indicated to some extent by each of these authors, many of the significant reactions of manganese involve surface or interfacial phenomena—this because the solubility of manganese is quite low in natural waters.

The principal focus of the present paper is on the behavior of the colloidal form of the most common natural oxide of manganese, MnO_2. Colloidal hydrous oxides of manganese occur in water as products of the oxidation of Mn(II), and are formed as well by reduction of Mn(VII) in waters which have been treated with permanganate for control of tastes and odor or for oxidative removal of ferrous iron. Even at low concentrations, the colloidal dioxide of manganese imparts an objectionable brownish yellow color to water, and is therefore of major concern in water treatment operations.

In the course of previous studies of the coagulation-flocculation characteristics of hydrous manganese dioxide, Posselt, Reidies, *et al.* (1968) noted a strong dependence of the stability of this hydrous colloid on the presence of slightly hydrolyzed metal ions. This observation has been made also by Morgan and Stumm (1964b) and by Kozawa (1959). The stability of hydrous manganese dioxide suspensions is markedly decreased in the presence of Ca^{2+}, for example (Posselt, Reidies, *et al.*, 1968). This effect, illustrated in Figure 1, has been explained in terms of a reduction of the potential of the colloidal oxide—and thus of its stability—as a result of exchange sorption of the Ca^{2+} ion. The objective of the present investigation has been to explore more fully the sorptive characteristics of hydrous manganese dioxide, in the hope of further defining its behavior in natural waters and providing information for establishing guidelines for its removal from water supplies.

Properties of Hydrous Manganese Dioxide

Manganese dioxide is the natural end product of the reduction of Mn(VII), as well as of the oxidation of Mn(II). The dioxide can also form as a result of the disproportionation of soluble complexes of Mn(III). In aqueous solution, manganese dioxide commonly forms a relatively stable hydrous colloid of needle-like shape. The occurrence of the needle form of the material has been evoked to support the contention that the principal mode of formation of the MnO_2 is by disproportionation of Mn_2O_3, a process in which

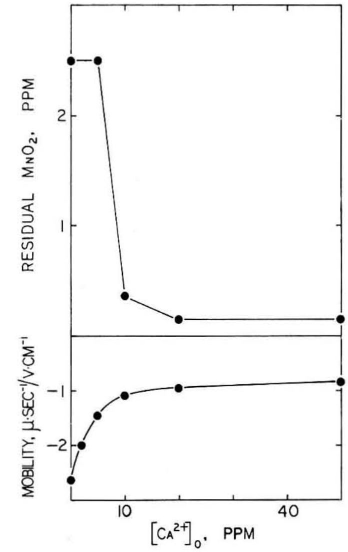

Figure 1. Destabilization and electrophoretic mobility of hydrous manganese dioxide as a function of calcium dosage at pH 5 (Posselt, Reidies, *et al.,* 1968)

polymerization of the tetrahydroxide, $Mn(OH)_4$, would play an important intermediate role (Chevillot, 1964). Indeed, $Mn(OH)_4$ and $Mn(OH)_3$ may be two of the principal forms of soluble and colloidal manganese in oxygen-bearing natural waters (Sillen, 1961). For purposes of the present discussion, it will be assumed that manganese dioxide can be represented by the formula MnO_2. However, the colloidal oxide which results in aqueous solution from the reactions described above is actually a hydrous product of indefinite stoichiometry. If we neglect varying degrees of hydration, the material may be represented as $MnO_{(1+x)}$, where the value of x ranges from about 0.1 to 0.95, depending upon particular conditions of formation. The oxide seems to have a poor degree of crystallinity in its δ-MnO_2 form, while the γ-MnO_2 form is more organized or more ordered (Gabano, Etienne, *et al.*, 1965; Morgan and Stumm, 1964b).

For MnO_2, as for most hydrous metal oxides, the extent and character of the surface in large measure determine the colloidal properties of this material. Gabano, Etienne, *et al.* (1965) reported values up to nearly 150 sq. meters per gram for γ-MnO_2, and Morgan and Stumm (1964b) noted that values of the order of 300 sq. meters per gram have been found for δ-MnO_2. Figure 2 is a schematic arrangement of surface atoms for MnO_2 similar to that proposed by Gabano, Etienne, *et al.* (1965). As suggested by the configuration given in Figure 2, which assumes a relatively well ordered crystal, surface-bound hydrogen and hydroxide ions may be exchanged at the surface of the MnO_2 in response to changes in the relative activities of these ions in solution phase. Thus—at least in the absence of other ionic species—H^+ and OH^- function as potential-determining ions, and the surface charge of the MnO_2 is largely determined by the pH of the solution, the charge becoming more negative as pH is increased as a result of the increased ratio of OH^--bound to H^+-bound. At very low pH, the H^+ ions bound at the surface predominate, and the colloidal MnO_2 bears a net positive surface charge.

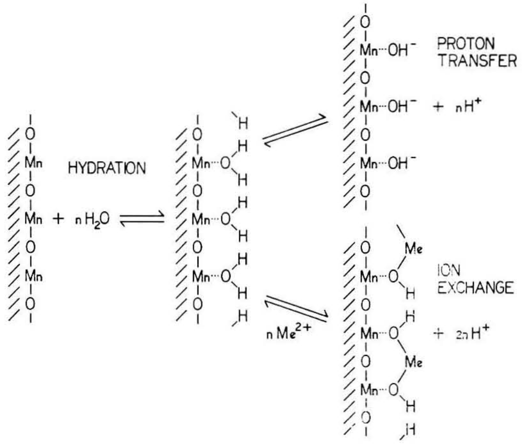

Figure 2. Schematic representation of the surface structure and surface reactions of manganese dioxide

That the hydrous manganese dioxide surface exhibits protonic acidity and is amphoteric in terms of net charge is reasonably certain. Less certain is the exact value at which equilibration of surface-bound hydrogen and hydroxide ions occurs—i.e., the zero point of charge (ZPC).

A comprehensive summary of ZPC values for various oxides, solid hydroxides, and aqueous hydroxo complex systems, including MnO_2, has been presented recently by Parks (1965). Covington, Cressey, *et al.* (1962), Healy, Herring, *et al.* (1966), Morgan and Stumm (1964b), and Posselt (1964), among others, have given values ranging from 2.8 to 4.5 for the ZPC for hydrous MnO_2. Although there are some differences among the values reported, largely owing to differences in measurement techniques and to differences in the actual forms of the oxides tested, it appears quite clear that colloidal hydrous manganese dioxide exhibits a net negative surface charge within the pH range (5 to 11) of principal interest for natural waters and for water treatment operations.

Experimental

The present investigation has involved study of the sorption of several slightly hydrolyzed metal ions and three tensioactive organic compounds on hydrous manganese dioxide. The metal ions include Ag^+, Mn^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+}, and Nd^{3+}. The organic compounds have been selected to include: an anion, dodecylbenzene sulfonate (DBS); a neutral molecule, nonylphenoxynonylethoxyethanol (NPNEE); and a cation, *p*-dodecylbenzyltrimethylammonium chloride (DBTMA). Ionic strength and pH have been investigated as system variables.

The experiments have been designed to represent as closely as possible the conditions normally encountered in water treatment operations with respect to the mode of formation of hydrous MnO_2 sols—that is, the colloidal oxide has been formed in the presence of the sorbing ion. All experiments have been conducted in 600-ml. reaction flasks with rapid mixing provided by a magnetic stirring unit. MnO_2 sols have been prepared at constant pH by simultaneous addition of sodium hydroxide and sodium permanganate to distilled water solutions of Mn^{2+}, Na^+, ClO_4^-, and the particular sorbate ion being studied, to yield suspensions equivalent to a

1-m*M* concentration of MnO_2. The reaction by which the MnO_2 forms under these conditions is:

$$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+ \quad (1)$$

The pH of each experimental solution was maintained constant at a predetermined value over the entire course of each run by continuous monitoring and appropriate additions of strong acid ($HClO_4$) or strong base (NaOH). Total initial ionic strength was controlled by addition of appropriate quantities of $NaClO_4$.

Filtration of the samples for analysis through membrane filters of 100-mμ pore size yielded complete separation of the MnO_2 suspension from the solution phase. Residual concentrations of the metal ion sorbates were determined by standard titrations with EDTA, except for the silver, which was analyzed by a modified Liebig method with *p*-dimethylaminobenzalrhodanine as indicator. Spectrophotometric techniques were employed for analysis of the organic sorbates.

Unless otherwise indicated, the following experimental conditions were maintained for each experiment: pH 5.0; ambient temperature; initial ionic strength, $\mu_0 = 1 \times 10^{-2}$; MnO_2 concentration of 1×10^{-3} mole per liter; and a reaction time of 30 minutes.

Rates of Reaction

To establish the reaction time required to ensure attainment of an equilibrium condition in each of the experimental systems studied, individual and independent measurements of sorption rates have been performed for each of the metal ions studied, as well as for the organic solutes. That equilibrium conditions prevail is an experimental condition required for meaningful definition of appropriate solid-solution phase distribution relationships for each system.

The rate measurements have established that the kinetics of the exchange reaction at the hydrous manganese dioxide surface are quite rapid. Figure 3 gives rate data for the uptake of Mg^{2+} from $5 \times 10^{-5}M$ solutions at pH 5.0 and pH 8.9. These curves are typical of those obtained for all of the other metal ions studied; each solute has demonstrated a similar pattern for sorption rate, with the reaction reaching an equilibrium condition in less than 5 to 10 minutes in all cases. As illustrated in Figure 4, initial sorption of the organic DBTMA is also reasonably fast, being nearly complete after 10 minutes. The purpose for studying the neutral, cationic, and anionic tensioactive organic species was to explore whether sorption of such surface active materials on the manganese dioxide hydrate might occur by some mechanism other than exchange sorption or direct ionic attraction. Both the anionic DBS and the neutral NPNEE have been found in these experiments not to adsorb to any measurable extent on the MnO_2, despite the relatively large surface area of this material. These results suggest that ionic forces of attraction are the principal forces involved in the sorption of such organic species on hydrous MnO_2.

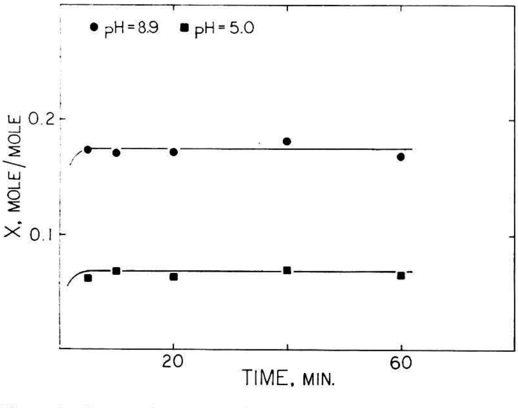

Figure 3. Rates of sorption of Mg^{2+} from $5 \times 10^{-4}M$ solutions

Plot of the mole-ratio capacity *X* (in moles Mg^{2+}/mole MnO_2) *vs.* time (in minutes)

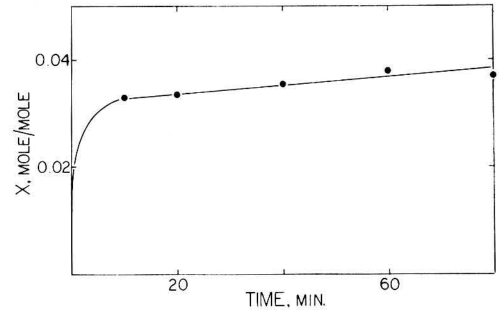

Figure 4. Rates of sorption of the *p*-dodecylbenzyltrimethylammonium cation from a $5 \times 10^{-5}M$ solution at pH 7.65

The findings of the present investigation regarding rates of sorption of the several metal ions studied are qualitatively in accord with the observations of Morgan and Stumm (1964b) on the rate of uptake of Mn^{2+} from dilute solution by hydrous MnO_2 at pH 7.5. Gabano, Etienne, *et al.* (1965), however, have reported that 15 hours of contact was required for equilibrium uptake of Zn^{2+} at pH 7.0. The differences in rate may be partially attributable to the fact that Gabano, Etienne, *et al.* utilized a γ-MnO_2 for their sorption studies, while a poorly ordered δ-MnO_2 was employed in the present studies, as well as in those of Morgan and Stumm. However, the greatest difference between the two latter investigations and that of Gabano, Etienne, *et al.* is the ionic strength of the medium from which adsorption occurred. The ionic medium employed by Gabano, Etienne, *et al.* in their studies—2*M* ammonium chloride—was four orders of magnitude greater than that of the present rate studies and of the highest value used in the rate studies of Morgan and Stumm. The latter investigators found that the rate of uptake of Mn^{2+} is decreased by addition of $NaClO_4$. They have attributed this decrease in rate to the fact that the increased concentration of Na^+ ion resulted in an increased degree of flocculation of the MnO_2, necessitating slow diffusion of the Mn^{2+} to less readily available sites in the flocculated suspension. As noted by Morgan and Stumm, Gafgen (1961) has reported similar rate behavior for sorption of Mn^{2+} by δ-MnO_2. Thus, it is not unexpected that Gabano, Etienne, *et al.* required longer times of contact to attain conditions of equilibrium in their experimental systems.

As noted previously, the primary purpose of the present rate studies has been simply to establish the contact time required for attainment of equilibrium. In subsequent equilibrium studies, a reaction time of 30 minutes was utilized to ensure this condition.

Sorption Equilibria

Equilibrium distributions of metal ion between solution phase and the sorbed state for all systems investigated in the present studies are described rather well by the Langmuir sorption equation. Gabano, Etienne, *et al.* (1965) and Morgan and Stumm (1964b) found the Langmuir equation to be adequate for description of sorption equilibria between various metal ions and hydrous MnO_2. The fact that experimental data for sorption of metal ions on hydrous MnO_2 can be described by an equation of the Langmuir type should not, of course, be construed as validation of the applicability of the Langmuir model for description of the process, because it is apparent that not all of the basic assumptions of the Langmuir model are satisfied. Nonetheless, the equation itself is useful for describing the data.

The Langmuir equation for sorption equilibria has the form

$$X = \frac{X_m bC}{1 + bC} \qquad (2)$$

where X is the quantity sorbed per unit quantity of sorbent, X_m is the limiting value for X ("monolayer" capacity), b is a constant relating to the energy of sorption, and C is the residual concentration of sorbate in solution phase at equilibrium. In the present discussion, X and X_m are given in units of moles of metal ion sorbed per mole of MnO_2.

To facilitate evaluation of the characteristic constants, X_m and b, from experimental measurements of X and C, Equation 2 may be written in the linear form

$$\frac{1}{X} = \frac{1}{X_m} + \frac{1}{X_m bC} \qquad (3)$$

For data which may be described by the Langmuir equation, a plot of $1/X$ *vs.* $1/C$ should yield a linear trace with an intercept of $1/X_m$ and a slope of $1/X_m b$. Figure 5 is a typical plot of experimental values for $1/X$ *vs.* $1/C$ for sorption of Sr^{2+} on colloidal hydrous MnO_2. Similar linearization of experimental data has been obtained by this means for all of the metal-ion systems studied. Figure 6 is a plot of X vs. C for the Sr^{2+}–MnO_2 system, the solid line in this figure being the calculated Langmuir isotherm. The linearized data for sorption of the organic cation DBTMA on the hydrous MnO_2 at pH = 6.6 is given in Figure 7; Figure 8 is a plot of X as a function of C for the experimental data for this system, along with the calculated Langmuir curve. Good description of the sorption equilibria for the organic DBTMA by the Langmuir model may also be observed from this figure.

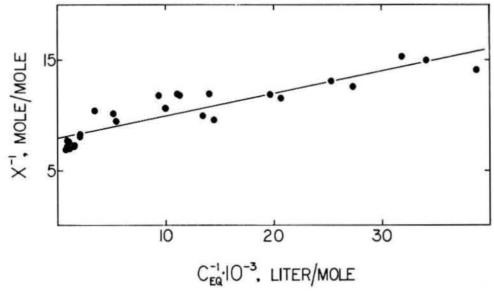

Figure 5. Langmuir plot of data for equilibrium sorption of Sr^{2+}

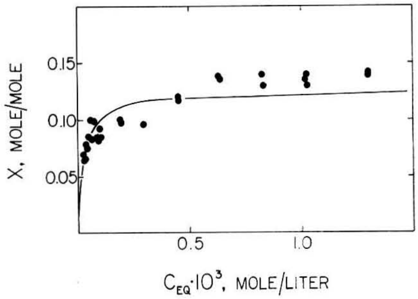

Figure 6. Adsorption isotherm for Sr^{2+} (solid line is calculated Langmuir isotherm)

Plot of the mole-ratio capacity X (in moles Sr^{2+}/mole MnO_2) *vs.* the residual sorbate concentration in solution phase at equilibrium C_{eq} (in mole Sr^{2+}/liter)

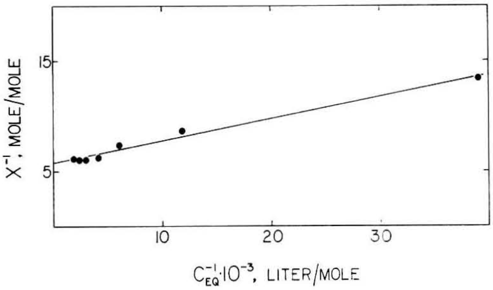

Figure 7. Langmuir plot of data for equilibrium sorption of the -dodecylbenzyltrimethylammonium cation at pH 6.6

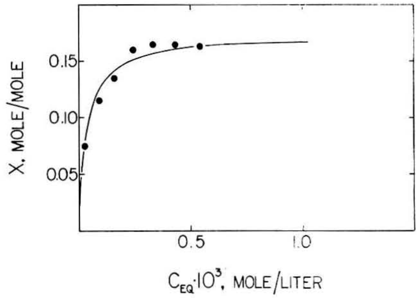

Figure 8. Adsorption isotherm for the *p*-dodecylbenzyltrimethylammonium cation at pH 6.6 (solid line is calculated Langmuir isotherm)

Langmuir parameters (X_m and b) have been determined for each of the metal ions and for the organic DBTMA cation. These values are tabulated in Table I, and Figure 9 is a summary plot of the respective Langmuir isotherms calculated from the experimental data for the metal-ion systems.

Table I and Figure 9 show that both the limiting capacity, X_m, and the energy parameter, b, increase regularly with the crystalline ionic radius for the cations in the Group II series (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}). This behavior is not unexpected, for upon hydration of the ions, the order of effective size is exactly opposite of that suggested by the order of the ionic radii for this series of ions; the order of the hydrated radii is $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+}$. Thus the smaller ions can ac-

Table I. Langmuir Constants for Sorption on Hydrous Manganese Dioxide

Sorbate	Crystalline Ionic Radius, A.	Langmuir Constants	
		X_m, mole/mole	b, l./mole
Ag^+	1.26	0.314	17.5
Mn^{2+}	0.80	0.284	38.9
Nd^{3+}	1.08	0.256	31.9
Ba^{2+}	1.35	0.180	41.3
DBTMA	. . .	0.174	28.4
Sr^{2+}	1.13	0.135	29.6
Ca^{2+}	0.99	0.113	21.3
Mg^{2+}	0.65	0.100	5.9

complish "closer approach" to the active surface of the manganese oxide, resulting in higher capacities and an increased tightness of binding.

In accord with the findings of Morgan and Stumm (1964b) and Gabano, Etienne, *et al.* (1965), the sorptive capacity of the hydrous MnO_2 for the Mn^{2+} ion is considerably greater on a mole-ratio basis than for any of the other divalent ions studied. One plausible explanation for the greater affinity of the hydrous oxide for the manganous ion is that a specific equilibrium is established between the surface of the MnO_2 and the Mn^{2+} ions in solution, according to the reaction scheme

$$Mn^{2+} + MnO_2 + 2H_2O = 2MnOOH + 2H^+ \quad (4)$$

The value of 0.284 mole Mn^{2+} per mole of MnO_2 at pH 5 agrees rather well with the capacity measured by Morgan and Stumm (1964b) for this pH.

As might be anticipated on the basis of ionic charge effects, the molar ratio for adsorption of the Nd^{3+} ion is greater than for any of the divalent metal ions, except the Mn^{2+}. Because of the much higher atomic weight of the Nd^{3+} ion, the capacity of the MnO_2 for this material on a weight-per-mole basis is greater than for any of the other cations studied. Gabano, Etienne, *et al.* (1965) also found lower molar capacities for the trivalent ions Al^{3+} and In^{3+} than for the divalent Mn^{2+} ion for adsorption on hydrous manganese dioxide.

The data presented in Table I and Figure 9 show that the monovalent silver ion has the greatest limiting molar capacity for adsorption of all of the ions studied. On a weight-per-mole basis, silver is second in capacity only to the trivalent neodymium ion. As might be anticipated, the latter has a considerably higher value for the Langmuir constant, *b*, suggesting a higher energy of sorption, while that for silver is relatively low. The high capacity for silver adsorption relative to the other ions is somewhat unexpected; other investigators (Gabano, Etienne, *et al.*, 1965; Murray, Healy, *et al.*, 1968) have found that the capacity for sorption of monovalent cations on hydrous MnO_2 is much less than the capacity for sorption of multivalent cations.

Competitive Effects

At first it was considered possible that localized surface precipitation of the silver occurred under the experimental conditions, thus leading to high apparent values for sorption. To test this possibility, the sorption of silver ion was followed in several experimental systems in which varying amounts of Cs^+ ion had been added. The results are presented in Figure 10, in which the mole-ratio capacity, *X*, for sorption of silver ($C_0 = 1.065 \times 10^{-3}$ *M* for all systems) is plotted against the logarithm of the initial concentration of cesium ion (added as $CsClO_4$). The Cs^+ competes with the silver for sorption on the hydrous MnO_2, thus reducing the capacity of the oxide for the Ag^+ ion. This observation all but rules out the possibility that localized surface precipitation is responsible for the significant uptake of the silver. Although precise measurements of Cs^+ sorption were not performed, it was observed that this material was taken up from solution by the hydrous MnO_2. This suggests the possibility for some sorption of the Na^+ ion also, and thus a competitive effect between this ion and other ions in solution.

The competitive effect noted between Cs^+ and Ag^+ has been studied further in mixed systems containing Mn^{2+} and Ca^{2+} at pH 6.25; the results of these experiments are presented in Figure 11. For the experiments represented by the data in Figure 11, the MnO_2 was brought to sorptive equilibrium with a solution of Ca^{2+} to yield a sorption value of $X = 0.14$ mole Ca^{2+} per mole of MnO_2. Manganous ion was then added in increasing quantities, and the sorption of this ion was followed as a function of the amount added.

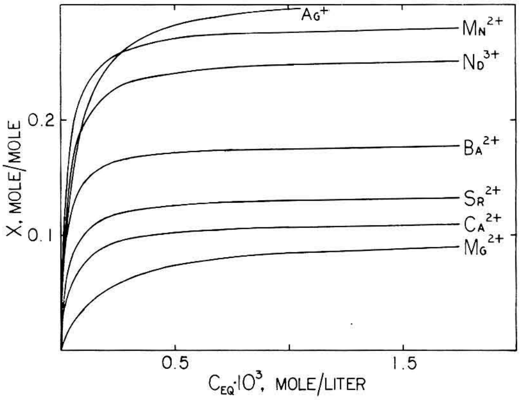

Figure 9. Summary plot of Langmuir isotherms at pH 5 calculated from experimental data

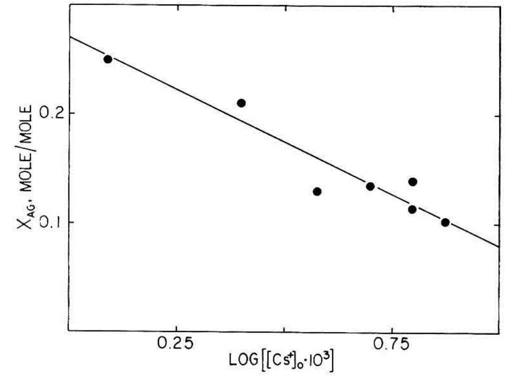

Figure 10. Adsorption of Ag^+ from $1.065 \times 10^{-3}M$ solution in the presence of different initial concentrations of Cs^+

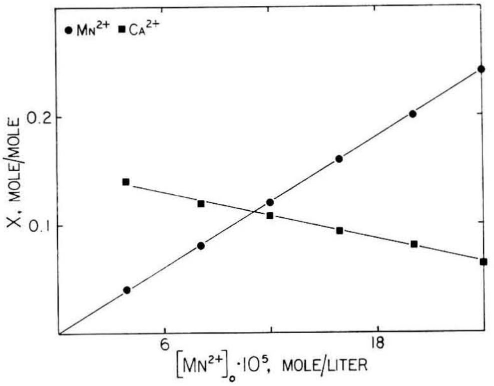

Figure 11. Adsorption of Mn^{2+} and Ca^{2+} as a function of the concentration of Mn^{2+} in bi-solute systems at pH 6.25

Plot of the mole-ratio capacity X (in moles Ca^{2+} or Mn^{2+}/mole MnO_2) *vs.* the initial concentration of Mn^{2+} (in mole Mn^{2+}/l. $\times 10^5$)

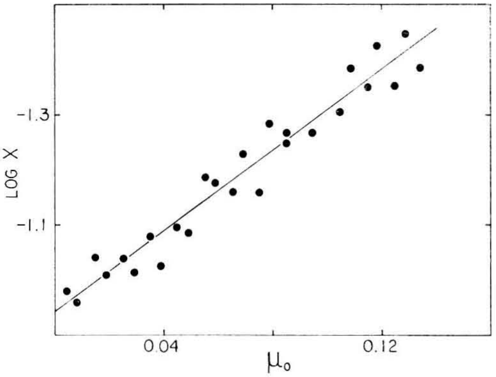

Figure 12. Adsorption of Ca^{2+} from a $1.098 \times 10^{-3}M$ solution as a function of initial ionic strength

Plot of the logarithm of the mole-ratio capacity X (in mole Ca^{2+}/mole MnO_2) *vs.* the initial ionic strength μ_0

The desorption of Ca^{2+} was followed simultaneously, with the results indicated in Figure 11. Increasing concentration of Mn^{2+} leads to increasing uptake of this ion with a concomitant and proportional displacement of presorbed Ca^{2+} ions.

Ionic Strength

As mentioned previously, observations of the significant sorption of the monovalent silver ion and the competitive displacement of this ion by cesium suggest the possibility that sodium ion may be sorbed to some extent by hydrous MnO_2. Although $NaClO_4$ has been used for adjustment and maintenance of ionic strength in the present experiments, the relative values of the adsorption parameters presented in Table I and Figure 9 are valid, regardless of possible Na^+ sorption, because ionic strength and pH have been maintained essentially constant. Nonetheless, it is of interest to explore the effects of ionic strength on the sorption of metal ions by hydrous MnO_2. A large number of experiments were run in which initial ionic strength was varied from $\mu_0 = 4 \times 10^{-3}$ to $\mu_0 = 13.4 \times 10^{-2}$. For these experiments, equilibrium measurements were made of the extent of sorption of Ca^{2+} ion from a solution of initial concentration of $1.098 \times 10^{-3}M$. The results, presented in Figure 12, show that sorption capacity is decreased with increasing ionic strength, or increasing concentration of Na^+ and ClO_4^-. The logarithm of the sorption capacity decreases proportionately with increasing ionic strength.

pH Effects

The effects of pH on sorption of metal ions by hydrous MnO_2 have been studied by a number of investigators (Gabano, Etienne, *et al.*, 1965; Morgan and Stumm, 1964b; Murray, Healy, *et al.*, 1968; Posselt, Reidies, *et al.*, 1968), and have been further investigated during the present experiments. In general, the results for all of the metal ions studied followed a pattern very much like that described by Morgan and Stumm (1964b) for Mn^{2+}.

After a procedure described by Kurbatov, Wood, *et al.* (1951), the pH dependence for sorption of a metal ion on a hydrous oxide can be characterized in terms of mass-law relationships. If sorption of the metal ion, M^{n+}, is assumed to follow a course similar to complexation with a weak acid, and if the activity of the solid phase is assumed unchanged by the sorption reaction, then it can be shown readily that

$$\log\left(\frac{[M^{n+}]_{\text{solution}}}{[M^{n+}]_{\text{sorbed}}}\right) = Z + n\log[H^+] \qquad (5)$$

The left-hand side of Equation 5 is the logarithm of the solution-solid phase distribution coefficient; the term Z is a constant which is dependent upon the total mass of sorbent and upon the mass-law equilibrium constant for the sorption-complexation reaction.

A plot of the left-hand side of Equation 5 *vs.* log $[H^+]$, or pH, should yield a linear trace with a slope of n. Figure 13 is such a plot for sorption of Mg^{2+} on hydrous MnO_2. In addition to the data presented in Figure 13, similar measurements were performed for several other metal ions and for the organic DBTMA. In all cases, the experimental data are linearized well when plotted according to Equation 5.

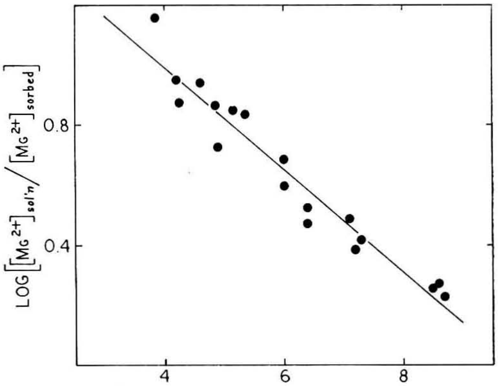

Figure 13. Logarithm of the distribution coefficient for Mg^{2+} as a function of pH

Figure 13 shows that the slope of the linear trace obtained by plotting the logarithm of the distribution coefficient for magnesium *vs.* pH is not $n = 2$, as one might expect for exchange sorption of this divalent metal ion. However, the relationship given in Equation 5 is based on the assumption that the activity of the sorbent is constant over the course of the exchange reaction. This is not the case for the present experiments, in which the sorbate/sorbent ratio is quite significant. Thus, while the linear relationship is obtained, the slopes of the traces should not be expected under these circumstances to indicate directly the hydrogen ion displacement per metal ion sorbed.

Discussion

Several investigators (Gabano, Etienne, *et al.*, 1965; Kozawa, 1959; Morgan and Stumm, 1964b; Murray, Healy, *et al.*, 1968) have demonstrated that hydrous manganese dioxide exhibits ion exchange characteristics and that these exchange properties are associated with acidic functional groups at the surface of the MnO_2. Indeed, the exchange reactions of several ionic species with hydrous manganese dioxide have been followed in detail by measurement of acid liberated during the course of the sorption reaction (Kozawa, 1959). The hydrated surface of the MnO_2 is believed to behave as a weak acid (Figure 1), and from this, one may logically develop an explanation for metal ion exchange phenomena. Gabano, Etienne, *et al.* (1965) have confirmed that when adsorption experiments are carried out under well-defined conditions of pH, the reaction of hydrous manganese dioxide with metal ions is one of specific surface exchange.

Murray, Healy, *et al.* (1968) have suggested that the results of their studies with Group I metal ions indicate that at lower concentrations of metal ion, sorption occurs primarily as a result of counterion uptake in the diffuse part of the double layer. This explanation is inconsistent with results at higher Group I metal ion concentrations, however. These same authors conclude that some small specific sorption potentials are operative in the cases of Ca^{2+} and Ba^{2+}, and much more so for the uptake of Ni^{2+}, Cu^{2+}, and Co^{2+}.

For the present systems, it would thus appear that surface exchange is the principal mechanism involved in the sorptive uptake of the slightly hydrolyzed metal ions studied.

To explain the observed behavior of the hydrous MnO_2 as an ion exchanger with respect to the metal ions investigated, reference may be made to the classification established by Hofmeister for the affinity of ions for exchange sorption by any cation exchange resin (Kunin, 1958). Hofmeister found, with few exceptions, that the order of affinity for exchange sorption of various ions is generally $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ < Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+} < Al^{3+}$, etc. As noted previously, in the cases of those ions studied in the present experiments, the same general order of exchange affinity or capacity has been found. The widely accepted explanation for the order of exchange affinity observed by Hofmeister is that the affinity is a function of ionic size. Within a given group of elements, the larger the crystalline ionic radius, the larger is the exchange affinity (note, for example, the Group II metal ions listed in Table I). This phenomenon is related to the solvation of the ions; again, within a given group of elements, the smaller the crystalline ionic radius, the greater is the actual ionic radius of the hydrated ion. The strongly hydrated ions are less likely to undergo exchange sorption because of their increased size, which necessarily introduces steric hindrances.

Numerous references to the significance of the oxides of manganese in natural waters, in limnological transformations, and in water treatment operations may be found in the scientific and technical literature, yet the surface chemistry of these oxides is not clearly understood. Hopefully, the present studies will provide an additional step toward the definition of the surface properties and colloidal behavior of these materials in aqueous systems.

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Chemistry of Manganese in Lake Mendota, Wisconsin

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■ The environmental water chemistry of manganese was studied under field and laboratory conditions. Mn(II) was the principal form of Mn measured in Lake Mendota, Wisconsin, throughout an entire seasonal cycle. Only Mn(II) was detected in anoxic waters, whereas both Mn(II) and Mn oxides were present in oxygenated waters. Rates of oxidation of Mn(II) appeared to be slow in the environment and the effect of pH seemed important. Sorption reactions of Mn(II) with Mn and Fe oxides occurred during oxygenation processes and were probably part of the mechanism involved in the removal of Mn from the water column. The presence of Mn(II) in reducing environments yielded rare computed supersaturated conditions with respect to $MnCO_3$ and MnS. These compounds may have limited Mn(II) solubility on those occasions.

Information has become available in recent years regarding the behavior of Mn in well-defined systems. Studies of Mn in aqueous laboratory solutions were conducted by Morgan and Stumm (1963, 1964, 1965a) and Hem (1963, 1964, 1965), in which various parameters were controlled to allow accurate descriptions of the chemical reactions which occurred.

Theoretical descriptions of aqueous Mn behavior, such as those given by Morgan and Stumm (1965a) and Morgan (1967a,b), have evolved from these studies. The descriptions are chemical models which utilize fundamental principles of thermodynamics, redox equilibria, kinetics, and solute interactions in the computation of stability and solubility fields of Mn species predominance.

This paper presents the results of a study of the chemistry of Mn in Lake Mendota and discusses the observed data in terms of previously published theoretical models. Lake Mendota is a hard-water, eutrophic lake of glacial origin in south central Wisconsin.

Theoretical Model

A theoretical model for aqueous Mn can be considered to contain separate sections based on thermodynamic redox equilibria, chemical kinetics, solubility relationships, and sorption and complexation phenomena. The model is abiotic in the sense that direct biological influences on Mn are not considered. The indirect effects of organisms on lake chemistry are inherent in the discussions—e.g., alteration of pH through photosynthesis and respiration.

The first section is a thermodynamic redox equilibrium model, based on free energy and standard potential data given by Latimer (1952) and Morgan (1967a). Redox stability field diagrams have been constructed and presented by Garrels and Christ (1965), Hem (1963), and Morgan (1967a). The Mn species predominance fields in the redox diagrams are based on computed equilibria under various oxidation-reduction conditions. The ordinate *Eh* values are computed from Nernst equation relationships and do not imply correspondence with environmental *Eh* measurements. The redox diagrams demonstrate that some form of oxidized Mn will be in equilibrium with Mn(II) under oxidizing conditions (high *Eh* and pH) and that some form of Mn(II) may be in equilibrium with $MnCO_3$ under reducing conditions (low *Eh* and pH). These assumptions are subject to modification, depending on the presence of other equilibria which might be influencing the Mn system. In most natural waters, oxidizing conditions are generally characterized by high dissolved oxygen and pH values, whereas reducing conditions typically involve oxygen-poor or anoxic waters and low pH.

Attainment of thermodynamic redox equilibrium states can be affected by reaction rates. The kinetics of oxygenation of Mn(II) have been studied in detail by Morgan (1967a). The oxygenation reaction followed an autocatalytic rate expression, wherein Mn oxides, initially formed in the reaction sequence, participate in subsequent Mn(II) oxygenation steps. Oxygenation rates are pH-dependent. At pH about 8.5 and above, an intermediate cation-oxide complex is reportedly formed which involves the sorption of Mn(II) onto Mn oxides (Morgan and Stumm, 1965a). The sorption reaction is relatively fast compared to the initial Mn(II) oxidation. Subsequent oxidation of Mn(II) in the sorbed complex, as outlined by Morgan and Stumm (1965a), may take place, but at a different rate than the initial oxidation. As a result, thermodynamically predicted redox equilibrium states are attained only after reaction times of hours or days have elapsed.

When thermodynamic redox and kinetic rate conditions allow a significant amount of Mn(II) to exist as a stable species in equilibrium with MnO_2 or other Mn oxides in the aqueous environment, precipitation reactions between Mn(II) and certain anions may occur. Solubility relationships based on laboratory studies include the equilibria between Mn(II) and $MnCO_3$, MnS, and $Mn(OH)_2$ (Morgan, 1967a). Compounds of the Mn(III) and Mn(IV) oxidation states are not considered in the solubility model. Mn(III) is thermodynamically unstable in aqueous solutions under normal conditions (Cotton and Wilkinson, 1962) and Mn(IV) compounds are generally insoluble at typical environmental pH values (Morgan and Stumm, 1965a).

A solubility diagram for Mn(II) under conditions similar to those present in Lake Mendota was given by Morgan (1967a). $MnCO_3$ might be the dominant precipitation product of Mn(II) in Lake Mendota under the conditions of approximately 10^{-3} *M* total dissolved carbonate and 10^{-4} *M* total dissolved sulfide. However, the MnS field closely parallels that of $MnCO_3$ at pH less than about 9.0, so that slightly higher sulfide-carbonate ratios in the hypolimnion might allow the MnS field to predominate. The $Mn(OH)_2$ field appears only at very high pH and should not be important in waters containing the carbonate and sulfide concentrations represented by the model.

Sorption and complexation reactions are not easily quantified in diagrammatic form. The reactions are related to the models presented above and are best described in conjunc-

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tion with them. Sorption of Mn(II) by MnO_2 and $Fe(OH)_3$ has been observed and measured in laboratory systems. The pH-dependent nature of the reactions was demonstrated by Morgan and Stumm (1965a), who found significant sorption of Mn(II) by hydrous Mn and Fe oxides above pH 8.5. The high sorptive capacity of the oxides could control Mn(II) reactions in natural waters when pH conditions are favorable. The occurrence of Mn(II) in the presence of hydrous Mn and Fe oxides above pH 8.5 would result in sorption and subsequent removal of Mn(II) from solution.

If the removal is complete, and the sorbed cation-oxide complex settles out of the water column, Mn(II) will remain in a metastable complexed state. It is possible for further oxidation to occur if the sorbed complex comes in contact with oxidizing conditions or, perhaps, combined reduction and desorption reactions will take place if reducing conditions are encountered, as in an anoxic hypolimnion.

Inorganic complexes stabilize Mn(II) and can retard the oxidation rate. Complexing ligands, such as HCO_3^-, have been found to reduce the oxidation rate of Mn(II) in synthetic bicarbonate solutions (Morgan, 1967a). Organic molecules could form stable complexes with Mn(II) if the organic concentrations are high. However, the existence of Mn(II)-organic complexes has not been clearly demonstrated in environmental waters, although Rona, Hood, *et al.* (1962) postulated that a small amount of Mn in sea water may be present as an organic complex.

Experimental Procedures

Water samples were collected from Lake Mendota with a Van Dorn sampler or a generator-powered pumping system described by Lee and Harlin (1965). Total Mn was determined by the persulfate method (American Public Health Association, 1965), with a standard deviation of ±0.01 mg. per liter. Mn forms were measured by passing selected aliquot volumes through prerinsed (100 ml. of distilled water) membrane filters of various pore sizes. The filtrates were analyzed by the persulfate method. The filtrates were also tested with *o*-tolidine reagent (Morgan and Stumm, 1965b) and crystal violet reagent (Presley, Brooks, *et al.*, 1967) for the existence of oxidized Mn. Negative color reactions were observed at all times. Thus, for purposes of differentiation, the total Mn which passed through 0.45-, 0.22-, or 0.10-micron membrane filters (Millipore Filter Co., Bedford, Mass.), was assumed to be some form of Mn(II)—i.e., the free ion or a complex compound. Oxidized Mn particles were qualitatively identified by the procedure of Ormerod (1966). All of the detectable particulate Mn oxides in Lake Mendota were held by 0.45-micron membrane filters. Approximate detection limits of the Mn oxide procedure were of the order of 1 to 5 μg. per liter.

Dissolved oxygen was measured by the Winkler-azide procedure, alkalinity was titrated with $0.02N$ H_2SO_4 to the methyl purple end point, and total sulfide was determined by the methylene blue method, all given by the American Public Health Association (1965). *In situ* temperatures were measured with a Whitney underwater thermometer and pH values were obtained by use of Beckman pH meters (Models GS and N). All chemical analyses were completed within 24 hours after sample collection.

Activity coefficients (γ_i) used for ion activity product (IAP) computations were calculated by the Debye-Hückel expression:

$$\log \gamma_i = -\frac{Az_i^2\sqrt{\mu}}{1 + Ba\sqrt{\mu}}$$

The ionic strength of Lake Mendota (μ) was computed to be 0.006. The values for constants A, B, and a were taken from Klotz (1950).

Results

The seasonal variation of total Mn in Lake Mendota for 1966 and 1967 is shown in Figures 1 and 2, respectively. The observed Mn data followed general discussions given by Hutchinson (1957). The increase in total Mn in the bottom waters closely paralleled the development of thermal stratification in early summer. The initial release of Mn from the lake sediments occurred prior to the depletion of dissolved oxygen. Analytically significant increases of Mn in bottom waters were found in the presence of 5 mg. per liter of dissolved oxygen at pH 8.0 or less. The details of the seasonal Mn isopleths were different for 1966 and 1967. The differences were most likely the result of climatological factors which included thermal structure variations and mixing patterns related to seasonal wind stress on the lake.

The typical forms of Mn measured during the sampling period are summarized in Table I. Mn which passed 0.45-micron or smaller membrane filters was taken to be Mn(II). Mn oxides (unidentified structure and composition) held on 0.45-micron filters are identified as detectable (+) or nondetectable (−) in Table I.

The data showed that a significant fraction of the total Mn in Lake Mendota throughout the study period passed specified membrane filters and gave negative color reactions with the reagents mentioned earlier. This means that most of the total Mn in Lake Mendota was soluble and present as some form of Mn(II). The analytical procedures did not detect colloidal Mn oxides in the membrane filtrate fractions, but such forms may have been present in very small concentrations.

Mn oxides were present in all oxygenated waters, independent of depth and season. No Mn oxides were detected in anoxic waters which contained dissolved sulfide. On occasion, small concentrations of Mn oxides were found in waters

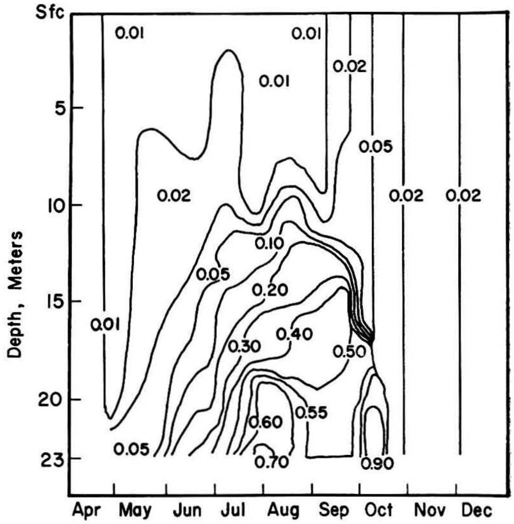

Figure 1. Lake Mendota Mn data, 1966

Seasonal variation of total Mn at the deep hole station, total depth 23 meters. Data in mg. per liter

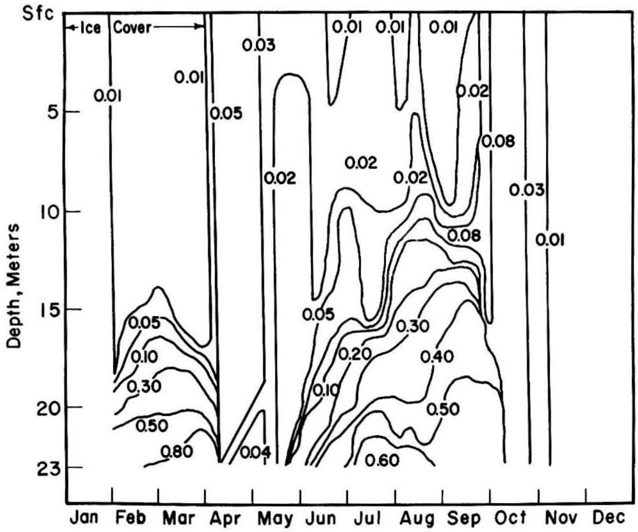

Figure 2. Lake Mendota Mn data, 1967

Seasonal variation of total Mn at the deep hole station, total depth 23 meters. Data in mg. per liter

which had just become anoxic but did not have any detectable sulfide concentration. These small amounts are denoted as (±) in Table I. There was a time lag of about one week between the beginning of anoxia in the bottom waters and the disappearance of detectable Mn oxides and approximately the same time interval elapsed before sulfide initially was detected. Attempts to determine the nature of the particulate Mn oxides failed because of the completely amorphous characteristics found by x-ray analytical techniques.

Total Mn which passed the 0.45-micron membrane filters was defined as Mn(II) and the concentrations were substituted into solubility computations. The activity coefficients used for the IAP expressions were, respectively, Mn^{2+}, 0.73; S^{2-}, 0.73; HCO_3^-, 0.92; and CO_3^{2-}, 0.72. Table II presents the results of such computations for oxygenated and anoxic waters. The data in Table II show that on two occasions $MnCO_3$ might have limited Mn(II) solubility in oxygenated Lake Mendota waters. The IAP/K_{sp} ratio exceeded 1.0 at those times with both samples from deep water beneath the winter ice cover. No sulfide was detected on those sampling dates. The ratios were not large enough, however, to indicate significant supersaturation, since small analytical differences would alter the exact values. Despite this uncertainty, the data pointed to the possibility that saturation equilibrium between Mn(II) and $MnCO_3$ might occur in bottom waters in contact with carbonate-rich sediments. Temperature corrections were not made for the calculations of the IAP/K_{sp} ratios. This may have affected the outcome of the winter data computations.

For purposes of interpretation, IAP/K_{sp} ratios which equal 1.0 indicate that the ion activity product of (Mn^{2+}) times (CO_3^{2-}) is equal to the solubility product of $MnCO_3$. If the ratio is significantly less than 1.0, the system is undersaturated with respect to $MnCO_3$, while ratios in excess of 1.0 indicate supersaturation. Small variations above and below 1.0 are not considered very significant, since variations in analytical procedures could account for the small differences. However, large variances of the IAP/K_{sp} ratio from 1.0 would be considered significant.

Under anoxic conditions in the summer hypolimnion, the solubility of MnS might limit Mn(II) concentrations, although only one IAP/K_{sp} ratio in Table II exceeded 1.0. That value did not necessarily indicate saturation equilibrium or supersaturation, because of possible analytical variations, but showed that equilibrium between Mn(II) and MnS might be important when high sulfide-carbonate ratios exist in the bottom waters.

A laboratory aeration experiment was conducted to estimate the relative rate of oxidation and removal of Mn(II) in Lake Mendota waters. Approximately 20 liters of anoxic Lake Mendota bottom water were collected and placed in a borosilicate glass vessel. The system was oxygenated with water-scrubbed laboratory compressed air. Dissolved oxygen reached near saturation levels at room temperature (22° ± 1 °C.) within 1 to 2 hours and remained at or near saturation for the duration of the experiment. The pH increased rapidly during the first few hours because of stripping of CO_2. A pH of about 8.5 was reached after 3 days of aeration and remained constant (±0.05 pH unit) thereafter. Results of the aeration experiment are depicted in Figure 3.

No Mn oxides were detected on 0.45-micron membrane filter pads until at least 30 hours had elapsed. This showed that oxidation of Mn(II) occurred relatively slowly under the conditions employed. The analytical differences between total Mn and Mn which passed 0.45-micron filters were not significant. The gradual decrease of total Mn in the system was due to the formation of a reddish brown flocculent material composed of Mn, Fe, and algal cell debris. This material gradually adhered to the sides of the reaction vessel and a rough film was observed on most of the interior surface in contact with the water column. Present in the flocculent material were amorphous Mn and Fe oxides and probably a cation-oxide complex composed of Mn(II) bound to Mn and Fe hydrous oxides.

Table I. Forms of Mn Measured in Lake Mendota in Deep Hole Area

Total depth = 23 to 24 meters

			Mg./L.				
					Mn Passing		
Depth, M.	Temp., °C.	pH	Dissolved oxygen	Total Mn	0.45 μ	0.22 μ	MnO_x
			April 25, 1966				
8	6.5	8.85	13.2	0.04	0.02	...	[a]
22	6.2	8.70	12.8	0.03	0.01	...	[a]
			June 22, 1966				
1	22.0	8.95	[a]	0.01	0.01	...	+
17	10.6	8.00	5.66	0.05	0.02	...	+
23	10.1	7.72	1.84	0.40	0.27	...	+
			August 17, 1966				
2	24.0	8.68	9.34	0.01	0.01	...	+
14	13.8	7.50	0.00	0.25	0.18	...	±[b]
21	11.5	7.38	0.00	0.60	0.57	...	−
			September 24, 1966				
2	18.2	8.30	8.70	0.02	0.01	...	+
17	12.0	6.95	0.00	0.52	0.47	...	−
22	11.3	6.80	0.00	0.55	0.53	...	−
			October 26, 1966				
1	11.7	7.90	9.25	0.02	0.01	...	+
22	11.3	7.80	8.80	0.02	0.01	...	+
			December 3, 1966				
Sfc.	2.5	8.20	13.90	0.02	0.01	...	+
22	3.1	8.20	12.40	0.02	0.01	...	+
			February 4, 1967				
10	1.0	8.05	12.40	0.01	0.01	0.01[c]	+
20	1.9	7.80	8.89	0.16	0.16	0.16[c]	+
23	2.6	7.45	1.63	0.66	0.66	0.65[c]	+
			March 29, 1967				
10	2.0	8.00	10.35	0.01	0.01	0.01[c]	+
18	2.2	7.80	7.30	0.12	0.11	0.10	+
22	3.3	7.50	0.50	0.79	0.79	0.79[c]	+
			May 6, 1967				
9	8.3	8.60	12.00	0.03	0.03	[a]	+
21	7.6	8.53	11.40	0.04	0.03	[a]	+
			June 12, 1967				
5	18.7	8.45	10.65	0.02	0.01	0.01	+
15	13.0	7.98	8.30	0.04	0.02	0.02	+
21	12.1	7.80	6.27	0.13	0.10	0.10	+
			August 24, 1967				
1	21.7	8.87	10.17	0.01	0.01	0.01	+
15	13.8	7.72	0.00	0.20	0.17	0.17	±[b]
22	12.3	7.38	0.00	0.45	0.44	0.43	−
			September 30, 1967				
5	16.4	8.40	9.62	0.08	0.05	[a]	+
15	16.4	8.28	9.42	0.07	0.05	[a]	+
22	12.6	6.98	0.00	0.57	0.56	[a]	−
			October 23, 1967				
5	12.4	8.10	9.09	0.03	0.01	[a]	+
15	12.3	8.10	9.08	0.03	0.01	[a]	+

[a] Not determined.
[b] Indicates slightly positive reaction.
[c] 0.10-micron pore size used instead of 0.22.

Table II. Lake Mendota Mn Solubilily Data, 1967

Date	Depth M.	(Mn^{2+})[a]	(CO_3^{2-})[a]	(S^{2-})[a]	(H^+)[a]	IAP/K_{sp} $MnCO_3$	IAP/K_{sp} MnS
			Oxygenated Waters				
Feb. 1[b]	1	1.35E-07[c]	1.52E-05	[d]	7.94E-09	0.05	[e]
	21	6.49E-06	1.38E-05	[d]	1.26E-08	1.6	[e]
March 29[b]	5	1.35E-07	1.26E-05	[d]	1.26E-08	0.3	[e]
	22	1.07E-05	4.00E-06	[d]	3.16E-08	1.1	[e]
April 5	1	5.41E-07	8.13E-06	[d]	1.35E-08	0.1	[e]
	23	6.75E-07	1.10E-06	[d]	9.76E-09	0.01	[e]
May 30	3	2.70E-07	4.12E-05	[d]	2.69E-09	0.3	[e]
	23	5.41E-07	3.52E-05	[d]	3.16E-09	0.5	[e]
June 19	1	1.35E-07	8.10E-05	[d]	1.32E-09	0.3	[e]
	21	2.57E-06	7.86E-06	[d]	1.41E-08	0.5	[e]
July 3	5	2.70E-07	7.48E-05	[d]	1.48E-09	0.5	[e]
	21	4.73E-06	4.23E-06	[d]	2.63E-08	0.5	[e]
Aug. 2	1	1.35E-07	1.06E-04	[d]	8.91E-10	0.4	[e]
Sept. 6	5	1.32E-07	5.45E-05	[d]	1.91E-09	0.2	[e]
Sept. 30	5	1.08E-06	2.76E-05	[d]	3.98E-09	0.7	[e]
Oct. 23	5	4.05E-07	1.41E-05	[d]	7.94E-09	0.1	[e]
	23	2.66E-07	1.32E-05	[d]	8.50E-09	0.1	[e]
Nov. 6	5	1.35E-07	1.13E-04	[d]	5.01E-09	0.4	[e]
			Anoxic Hypolimnetic Waters				
Aug. 2	22	7.19E-06	3.08E-06	1.72E-11	3.08E-08	0.5	0.2
Aug. 9	20	5.86E-06	3.04E-06	2.37E-11	3.70E-11	0.4	0.2
	22	7.96E-06	2.53E-06	3.02E-11	4.50E-08	0.6	0.5
Aug. 16	20	5.18E-06	1.43E-06	2.92E-11	7.60E-11	0.2	0.2
	21	5.99E-06	1.63E-06	4.46E-11	6.90E-08	0.2	0.4
Aug. 24	18	3.86E-06	2.92E-06	5.40E-11	3.80E-08	0.2	0.3
	20	4.78E-06	2.66E-06	9.80E-11	4.20E-08	0.4	0.7
	22	5.85E-06	2.69E-06	1.32E-10	4.20E-08	0.4	1.1
Sept. 6	20	6.92E-06	2.33E-06	7.96E-11	5.00E-08	0.4	0.8
	22	7.19E-06	2.48E-06	8.30E-11	5.00E-08	0.6	0.8
Sept. 11	22	7.45E-06	9.04E-07	[f]	1.20E-07	0.2	[f]
Sept. 19	21	7.45E-06	1.21E-06	4.00E-11	8.90E-08	0.2	0.4
Sept. 30	20	7.45E-06	1.68E-06	6.25E-11	6.80E-08	0.2	0.7
	22	7.45E-06	9.67E-07	4.45E-11	1.05E-07	0.2	0.5

[a] Activity, mole/liter.
[b] Winter ice cover was present.
[c] 1.35×10^7.
[d] Not present.
[e] Not calculated.
[f] Not determined.

Discussion

The published theoretical models for aqueous Mn can be evaluated by comparing the predicted equilibrium reactions with analytical data obtained from the environment.

The thermodynamic redox model predicted Mn(II) to be in equilibrium with MnO_2 (or, in general, hydrous Mn oxides) under oxidizing conditions. Mn oxides were observed in the presence of dissolved oxygen and high pH. Mn(II) was also present under oxidizing conditions, as well as in reducing environments, generally as the major fraction under both conditions.

The presence of Mn(II) as a dominant Mn form was apparently due to reaction kinetics. The rate of Mn(II) oxidation in environmental waters and subsequent equilibration with Mn oxides was slow compared with results from laboratory solution studies, such as those reported by Morgan (1967a). The high pH required in laboratory systems for rapid oxidation (pH 9.0 or above) was not often encountered in Lake Mendota except during midsummer algal blooms. At lower pH values, generally 8.0 to 8.5, oxidation proceeded slowly and longer reaction times were needed to attain equilibrium between Mn(II) and Mn oxides. Reaction kinetics seemed to influence the rate at which thermodynamic redox equilibrium between Mn(II) and Mn oxides was attained in Lake Mendota waters.

The solubility model suggested that $MnCO_3$ might be a stable precipitated form in equilibrium with Mn(II) in the presence of sufficient carbonate alkalinity. MnS was predicted to be the important form in equilibrium with Mn(II) only if the sulfide-carbonate ratio increased sufficiently. The model was only infrequently valid in Lake Mendota based on computed IAP/K_{sp} ratios. The ratios showed that either $MnCO_3$ or MnS could have limited Mn(II) solubility on rare occasions, if proper conditions prevailed. As noted earlier, temperature corrections were not taken into account. Attempts to identify the solid forms of Mn in the Lake Mendota sediments by x-ray methods were not successful. Thus, it appears that the forms of particulate Mn oxides in the water column, as well as the solid Mn forms in the sediments, are amorphous.

The roles of sorption and complexation were interrelated with the other reaction systems. The sorption of Mn(II) onto Mn and Fe oxides appeared to occur in Lake Mendota and was best demonstrated by the findings of the laboratory aeration experiment. The amorphous nature of the oxidation products of Mn(II) supported the incomplete oxidation theory and this implied sorptive uptake of Mn(II) by Mn and Fe oxides (cation sorption onto Mn oxides is favored by higher pH where negative oxide charges prevail). Complexation, particularly involving HCO_3^-, likely played a role in reducing the rate of Mn(II) oxidation, although this was not determined experimentally. Laboratory studies reported in the literature discussed the stabilizing effect of HCO_3^- solutions on Mn(II) oxidation compared to distilled water solutions with little or no HCO_3^- present. Lake Mendota generally has a HCO_3^- concentration of 2.5 to 3.5 mmoles per liter. This is equivalent to between 125 and 175 mg. per liter as $CaCO_3$.

Based on the field and laboratory observations, a Mn system can be postulated to account for the presence of Mn in different forms in stratified lakes, as represented by Lake Mendota. Figure 4 summarizes experimental results and certain necessary hypotheses based upon those results.

The thermal structure used as a framework in Figure 4 is a typical midsummer Lake Mendota profile. It could represent any moderately deep lake (maximum depth of Lake Mendota is about 24 meters) in the temperate zone. The chemical reactions shown in Figure 4 could take place if the required compounds and ions are present under the specified conditions in each of the strata.

The conditions in the epilimnion are considered to be oxidizing. Dissolved oxygen values are near saturation and pH is elevated to near pH 9 because of photosynthetic activity. The epilimnion is in constant circulation due to wind action and is generally in equilibrium with the atmosphere.

Manganese is present as Mn(II) and Mn oxides. Also present are uncharacterized Fe oxides. A number of reactions are possible under the oxidizing conditions. Mn(II) may be slowly oxidized to Mn oxides in the presence of dissolved oxygen. The rate is slow without sufficient or suitable catalytic surface sites. Mn(II) may sorb onto the Mn and Fe oxides, since the high pH favors sorption reactions. The Mn(II) sorbed onto the Mn and Fe oxides may be catalytically oxidized to form more Mn oxides. The oxides may initially be colloidal with small particle dimensions but in time may develop into particle sizes larger than 0.45 micron. Eventually, some of the oxide particles and sorbed cation-oxide complexes will sink and enter the thermocline region.

The thermocline zone has intermediate properties between the two surrounding zones. The upper part has dissolved oxygen but at lower levels than in the circulating epilimnion. Exchange of materials across the boundary with the epilimnion no doubt occurs but because of density differences, a time lapse probably exists. Essentially the same species in the epilimnion are present in the thermocline. These were present prior to the development of stratification or entered after the three stable zones were formed.

The thermocline is a transition zone and as such it is difficult to estimate the extent of the chemical reactions which occur within its limits. It is most likely that some of the epilimnetic reactions occur in the upper thermocline zone and similarly some hypolimnetic reactions occur at the lower levels of the zone. The waters nearest the two boundary edges of the thermocline would least be in equilibrium due to constant exchange with the other zones. A metastable state may exist within the thermocline, depending on the duration of its existence and the intensity of physical factors (currents, internal waves) which would tend to destabilize the zone.

The hypolimnion zone during thermal stratification is characterized by little or no dissolved oxygen, low pH values, and reduced temperatures. It is no longer in equilibrium with the atmosphere but rather is involved in exchange reactions with the sediments.

Mn is primarily Mn(II) in the hypolimnetic waters. Reactions may take place in the hypolimnetic water column whereby desorption of Mn(II) from Mn and Fe oxides occurs. The Mn and Fe oxides may be reduced, although these are generally not present in any significant amount. The presence of dissolved sulfide and carbonate may result in the precipitation of MnS and $MnCO_3$, respectively, although evidence for this is still circumstantial. These compounds could exist

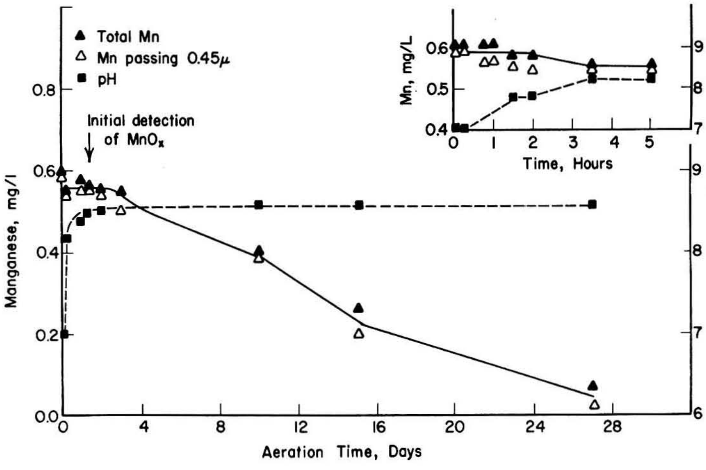

Figure 3. Laboratory aeration experiment.

Anoxic Lake Mendota bottom water taken from 22-meter depth in deep hole region Sept. 30, 1967

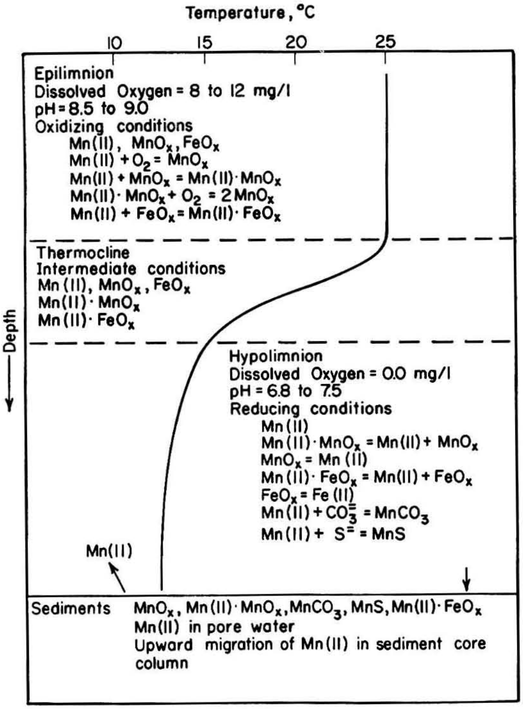

Figure 4. Mn system in Lake Mendota based on experimental results and hypotheses

in a stable colloidal suspension due to slow nucleation and precipitation rates and the absence of precipitation nuclei.

Mn(II) is released from the sediments under reducing conditions and pH was one of the most influential factors. The form of Mn in the sediments is probably complex. However, about 40% of the total Mn was easily exchangeable with 1*N* ammonium acetate, buffered at pH 7. This means that Mn(II) may be sorbed onto amorphous Mn and Fe oxides in the sediments. Mn may also be released by dissolution of compounds which are moderately soluble at pH about 7.0. Mn(II) released through the sedimentary pore waters may contribute a small amount to the total concentration. Mn can be supplied to the surface sediments from above and possibly from below. Mn may precipitate in upper waters and be deposited as the oxide, carbonate, or sulfide, or as a sorbed cation-oxide complex. There is evidence that Mn may migrate upward through the sedimentary column and become enriched in the upper sediment layers. Definite proof of this is lacking, but data of Lynn and Bonatti (1965) and Presley, Brooks, *et al.* (1967) from marine sediment cores showed that phenomenon might exist. However, data presented by Mackereth (1966) indicated that changes in the basin surrounding a lake, as well as variations in the redox conditions within a lake, could yield sedimentary Mn patterns suggesting migration. This particular process is still poorly understood and further work, possibly utilizing radioisotope tracers, is indicated.

If Mn(II) did in fact migrate upward in the core column, the enrichment of Mn in the upper sediment layers might occur during periods of circulation when oxidizing conditions prevail at the sediment-water interface. When Mn(II) ions were in the process of diffusing upward in the reduced sediment column, they would encounter oxidizing conditions in the uppermost sediment layers, become oxidized, and deposit as Mn oxides or sorbed cation-oxide complexes. The data indicate that a number of processes are occurring at the same time, and that the Mn forms in the sediments are no doubt complex, involving different compounds in different oxidation states.

Conclusions

The environmental chemistry of Mn in Lake Mendota is complex. A number of different chemical reactions may occur, independently or simultaneously, at different rates and involving different reaction intermediates. Chemical equilibrium may or may not be attained, depending on the nature of the reactions.

The principal form of Mn in Lake Mendota is Mn(II). Small amounts of Mn oxides are present under oxidizing conditions but absent in reducing environments. Mn oxygenation reactions are pH-dependent and sorption and complexation reactions could be interrelated with Mn(II) oxygenation processes. Precipitation reactions involving $MnCO_2$ and MnS might limit Mn(II) solubility under appropriate environmental conditions.

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A Theoretical Model for the Effect of an Acute Air Pollution Episode on a Human Population

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An Application of the Model to the 1952 London "Killer" Fog

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■ A quantitative theory for the increase in the mortality rate accompanying a severe air pollution episode has been developed, based on the following concepts: An individual dies when the activity of the gene-controlled, biochemical reaction steps in his respiratory system reaches a certain critically low value. The activity decays normally as a result of genetic changes in the somatic cells (the aging process); in the presence of severe air pollution, additional decay is produced by cytotoxic agents. The chemical effects depend on the time history of pollutant concentration in the tissue, determined by the rate at which material is transferred from the environment into the respiratory tissue.

A mathematical model based on these concepts was used to correlate the data for mortality rates and concentrations collected during the London "killer" fog of 1952. Three constants with well defined physical meanings appear in the theory. The model may be applicable to the setting of environmental standards and to the development of a strategy for coping with an acute air pollution episode in an urban area.

A major problem in environmental control is the development of rational methods for establishing permissible levels of atmospheric contamination (Breslow, 1967; Sargent, 1967). The criterion most often used in setting standards is human health and well being (Goldsmith, 1968), although esthetic considerations or industrial use may also be invoked. In the development of the California ambient air quality standards, three levels of pollutant concentration were defined in terms of their effects as follows (American Association for the Advancement of Science, 1965):

"**I. Adverse Level.** The first effects of air pollutants are those that will probably cause untoward symptoms or discomfort. Although they are not known to be associated with the development of disease, even in sensitive groups, such effects can disturb the population stability of residential or work communities. The 'adverse' level is one at which eye irritation occurs. . . .

"**II. Serious Level.** Concentrations of pollutants, or possible combinations of pollutants, that are likely to cause insidious or chronic disease or significant alteration of physiological functions in a sensitive group define the 'serious' level. . . .

"**III. Emergency Level.** Levels of pollutants, or combinations of pollutants, and meteorological factors likely to lead to acute sickness or death for a sensitive group of people define the 'emergency' level. . . ."

In setting standards, this set of definitions of contamination levels is used in evaluating data on the effect on human health of a specific pollutant. The data may come from a number of sources and one of the most useful has been the threshold limit values compiled by industrial toxicologists. A report based on the data and taking into account unusually sensitive groups of people is prepared by the staff of the State of California Air Pollution Medical Studies Unit. The report leads eventually to a statement of concentrations and exposure times corresponding to each of the three levels cited above. The report is submitted to a review procedure involving several committees of the State Department of Public Health as well as outside consultants. If it passes the committee review procedure, the proposed standard then goes to the State Board of Health, which, after public hearing, may incorporate it in the State Administrative Code.

An example of the third or "emergency" level of pollution attack often cited (Goldsmith, 1968) occurred in London in 1952; from December 5 to 9 the city was covered by fog, and a temperature inversion resulted in high concentrations of SO_2 and particulates. About 4000 deaths were counted in excess of the usual number for the 3-week period from December 5 to 27. The most severely affected were those with a history of respiratory illness. The excessive mortality was associated with irritation of the respiratory tract by the contaminants.

As shown in the Appendix (Figure A–5) the time history of the contaminant concentration in the 1952 fog episode is roughly of the form of a triangular pulse. The mortality rate for each age group increased rapidly with contaminant concentration until a maximum was reached at roughly the same time as the environmental contaminant concentration; thereafter the mortality rate decayed slowly while contaminant concentration returned to background level. A primary purpose of this paper is to devise a predictive theory which can be used to pass from the contaminant pulse to the pulse in the mortality rate. Viewed in this light, an analogy to the transfer function concept of systems theory becomes evident. The theory should be sufficiently general to permit incorporation of specific biochemical and toxicological data.

Biology of Aging and Death

Those most severely affected in an acute air pollution episode are the aged and the infirm. Hence, the present approach to the development of a theoretical model has been to modify the theory of aging and death to take into account environmental influences. According to the modern theory of the aging of higher organisms (Szilard, 1959), spontaneous mutations take place in large numbers in the genes of the somatic cells. Curtis (1966, 1967) has stressed the importance of chromosomal aberrations in cells which are seldom renewed, such as those in the brain, muscle, and kidney. Irreversible changes in the cell nucleus tend to be harmful; according to the one gene–one enzyme theory, gene damage would be expected to lead to production of faulty RNA and protein, with a concomitant damage to cell metabolic processes.

Eventually too many cells reach a state in which they are functioning poorly or not at all. At this point homeostasis breaks down, perhaps as a result of bacterial or viral infection, and the creature dies. Thus, according to this model, both aging and death are genetically determined, since the probability of chromosome aberration depends on the structure of the DNA molecules which are inherited by the creature from its parents. The experimental basis for this picture is not well established. Some of the most convincing evidence has been provided by Crowley and Curtis (1963) who studied the development of chromosome aberrations in the liver cells of two inbred strains of mice with markedly different life spans.

The liver cells of normal animals are seldom renewed unless destroyed. Hence, it is argued, the number of chromosome aberrations present at any age represent spontaneous mutations. Working with two strains of inbred mice, Crowley and Curtis destroyed parts of the liver by injection of carbon tetrachloride and sacrificed the animals 72 hours later. At the end of this period, a sufficient amount of regeneration had taken place to permit measurement of the frequency of chromosomal aberrations among the regenerated cells, assumed equal to the incidence present before destruction. The results of experiments with animals of different ages support the hypothesis that animals with higher chromosome aberration rates die at an earlier age.

Burnet (1959, 1965), while accepting Curtis' view of the importance of chromosomal aberrations in nonrenewable tissue, has emphasized the role of mutations among the renewable somatic cells in the aging process. Such cells line the respiratory and intestinal tracts and include the blood cells as well. The rapid turnover of cells exposed to the environment, such as those of the respiratory tract, probably serves to prevent loss of tissue function by replacement before environmental damage takes place. Chronic irritation of respiratory tissue by unfavorable environmental conditions—such as smoking or chronic air pollution—will presumably lead to increased rates of cell turnover. Burnet argues that mutations constantly occur during the replacement process, but probably at a rate so low that their presence would not ordinarily be manifest. The effect can be amplified, however, when a mutant is produced which has a selective proliferative advantage, perhaps as a result of producing antibody against one of the plasma proteins normally present in the internal environment of the individual. Clone descendants of the mutant cell may replace significant numbers of faithful replicas of the original cells composing the tissue, leading to a general loss of cell and tissue function with time—the aging process. An unfavorable environment leads to increased mutational rates and accelerates the aging process. In the extreme case when the clone descendants of mutant cells proliferate without effective control, the result is malignancy.

Rate of Loss of Gene Function

Respiratory illness is a major cause of death in acute air pollution episodes. In setting up our model, let us assume that we can consider the respiratory system and its breakdown apart. Let us further limit ourselves, for the moment, to a population of genetically identical individuals born at the same instant. At some reference time, each individual possesses n_o functioning genes among the cells of the respiratory system. These are the genes important to the functioning of the system and do not necessarily include all of the genes located on the chromosomes of the cells of that system. Let n be the number of those genes functioning without error at some time, t, after the reference time. Then for this class of genetically identical individuals we may write an expression for the decay of functioning genes as a result of spontaneous mutations:

$$\frac{dn}{dt} = F(n) \tag{1}$$

It is natural in constructing a theory of this type to assume that the decay rate is linear in the fraction of functioning genes:

$$\frac{dn}{dt} = -\lambda n \tag{2}$$

The first-order rate constant, λ, for respiratory tissue is a function of the rate of cell turnover which, in turn, is genetically determined but modified by the level of chronic air pollution (including smoking). For sufficiently short times (n not too far from n_o) this form is consistent with the approximately linear relationship between chromosome aberrations and time found experimentally for mouse liver by Crowley and Curtis (1963). There appear to be no equivalent data for renewable tissue such as the respiratory system.

According to the genetic theory of aging and death, when n reaches a sufficiently small value, the probability of homeostatic breakdown and death becomes very great. Three important variables determine the age at death: the fraction of inherited defective genes, $1 - x_o$, the first-order rate coefficient, λ, and the fraction of surviving genes at which death takes place, $x^* = n^*/n_o$. In his theory of aging, Szilard (1959) assumes that λ and x^* are the same for all humans and that "the main reason why some adults live shorter lives and others longer is the difference in the number of faults they have inherited." The data of Crowley and Curtis suggest that variations in λ are particularly important in determining age at death, while x^* differs for different inbred populations. The data indicate that values of x_o for the two populations studied did not vary greatly. For simplicity it is assumed that λ varies for groups of different genetic constitution but that x^* and x_o are the same for all groups. Variations in the coefficient λ seem plausible on physicochemical grounds and as a result of chronic environmental influences. The parameters x^* and x_o are kept fixed to preserve the simplicity of the model; methods of generalization will be apparent as the picture is developed.

Integrating Equation 2 from $t = 0$ to $t = t^*$, the age at which $x = x^*$, gives the following expression for the age at death:

$$t^* = \frac{1}{\lambda} \ln x_o/x^* \tag{3}$$

According to this model, all creatures of the same genetic group would be expected to die on the same day. In fact, as pointed out in this connection by Szilard, there is a difference in the ages at death even for identical twins. Kallmann (1957) reports that the mean age difference at death for female identical twins dying above the age of 60 is about 2.6 years. Clearly, the homeostatic state does not crumble at a particular value of x^*. To take this spread into account, we could introduce a probability distribution function for the likelihood that death occurs for various values of x near x^*. We would expect the probability to go from a value near zero for values of x a little less than x^* to unity for values of x a little greater than x^*.

It is possible to speculate concerning the value of x^*. Szilard suggests that the value corresponds to a fraction of functioning cells somewhere between $^1/_3$ and $^1/_{12}$. According to Brody (1955), there is a loss of more than 20% of the brain cells in the human body by the age of 70. This would correspond to a fraction of functioning cells of $^4/_5$, a considerably larger figure than the one suggested by Szilard. Of course, the figure may vary, depending on the organ system involved. According to Black (1958), for example, the nephron population of the kidney is reduced during the aging process to 60% of the original number.

Effects of Genetic Distribution

The model developed above holds for a cohort of genetically identical individuals. Since human populations are distributed genetically, we would expect a distribution in the gene mutation rate coefficient, λ, leading to a distribution of ages at death different in character from the sharp peak behavior discussed above. For this purpose, it is convenient to introduce a distribution function $f(\lambda)$ defined in such a way that the fraction of the individuals in the original cohort with gene mutation rates between λ and $\lambda + d\lambda$ is given by the expression

$$dw = f(\lambda)d\lambda \tag{4}$$

A possible type of distribution function is shown in Figure 1. The shaded area represents the fraction of the original population surviving at age t, corresponding to all classes with values of $\lambda < (\ln x_o/x^*)/t$. As t increases and the population ages, the shaded area moves to the left and decreases.

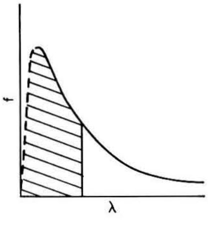

Figure 1. Schematic diagram of distribution function for gene mutation rates for group born at same time

Shaded area. **Fraction of population surviving at age *t***

The mortality rate in terms of the fraction of the original cohort dying at any instant is given by the expression

$$\frac{dy}{dt} = -f(\lambda)\frac{d\lambda}{dt} \tag{5}$$

When Equation 3 holds for the dependence of the age at death on λ, substitution in Equation 5 gives

$$\frac{dy}{dt} = \frac{\lambda f(\lambda)}{t} \tag{6}$$

This expression can be combined with observed results for the cohort mortality rate to obtain the distribution function, $f(\lambda)$. For example, if the cohort mortality rate can be approximated by a power law:

$$\frac{dy}{dt} = Kt^p \tag{7}$$

Then

$$f(\lambda) = K(\ln x_o/x^*)^{p+1}\lambda^{-(p+2)} \tag{8}$$

It is shown below that p is near 4, which means that Equation 8 can hold only for large values of λ.

Effect of Environmental Pollutants

When a chemical contaminant, a cytotoxic agent, is introduced from the environment, cells not damaged by gene mutation (aging) will begin to malfunction. We seek a rational way to weight loss of cell function by environmental damage and by gene mutation to arrive at a criterion for death:

If n is the number of functioning genes in the physiological system at any instant, there will be an equivalent number of biochemical reaction steps controlled by these genes (Tatum, 1959). When mutations occur, a certain number of genes cease to function properly, leading to the blocking of an equivalent number of reaction steps. In our previous model, adapted from Szilard, this is an on-off process: Either the gene (or reaction step) is functioning or it is not. The presence of a chemical contaminant, such as an enzyme inhibitor, may cause deviations of the rate of the reaction step from the range of rates corresponding to normal cell function. In this way a second concept is introduced in addition to the on-off mutation loss process—namely, the extent of the deviation of the rate of a functioning reaction step from the range for normal cell function (Figure 2).

Let γ_i be the activity coefficient for a single reaction step controlled by gene i. The activity coefficient is equal to unity when the organism has never been exposed to an environ-

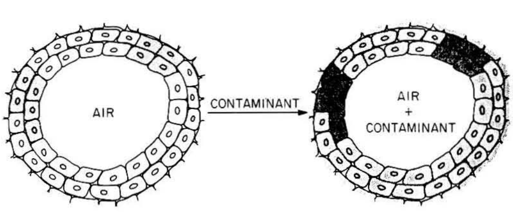

Figure 2. Schematic diagram of effect of contaminant on respiratory tissue

Left. **Clonal descendants of mutant cells shown stippled. These cells are presumably not functioning as effectively as unstippled ones, faithful replicas of original cells.**
Right. **Contaminant absorbed by tissue interferes with metabolic processes.**

mental contaminant and is less than unity when the rate of the particular step deviates from the normal range. (Obviously this is not the usual activity coefficient of chemical thermodynamics.) The activity of the gene-controlled metabolic system is defined as follows:

$$a = \sum_{1}^{n} \gamma_i = \bar{\gamma} n \tag{9}$$

where n is now the total number of gene-controlled reaction steps in the system and $\bar{\gamma}$ is the average activity coefficient. When $\bar{\gamma} = 1$, the activity is equal to n, the total number of functioning reaction steps in the system. We can now generalize our criterion for death to take into account environmental damage by assuming that death follows when the activity of the metabolic system falls to a critical value $a^* = n^*$, independent of contaminant concentration or nature.

The activity of the system when exposed to an acute air pollution episode is given by the relation

$$a = \bar{\gamma} n_o e^{-\lambda t} \tag{10}$$

Setting $a = a^*$ and differentiating

$$\frac{d\lambda}{dt} = -\frac{\lambda}{t} + \frac{1}{t}\frac{d \ln \bar{\gamma}}{dt} \tag{11}$$

By Equation 5, $\frac{d\lambda}{dt}$ determines the mortality rate. Hence the effect of the contaminant on mortality rate has been reduced to the determination of how $\ln \bar{\gamma}$ varies with time as a result of the contaminant. The dependence of $\bar{\gamma}$ on the type of contaminant is the molecular or toxicological information referred to in the introduction.

In the Appendix it is shown that mortality data can be correlated if the log of the activity coefficient depends linearly on the contaminant dose

$$\ln \bar{\gamma} = -\alpha \int_0^t c d\tau$$

or

$$\frac{d \ln \bar{\gamma}}{dt} = -\alpha c \tag{12}$$

where α is a proportionality constant and c is the concentration of the contaminant in the tissue. If we substitute Equations 11 and 12 in Equation 5, the mortality rate is given by

$$-f(\lambda)\frac{d\lambda}{dt} = f(\lambda)\left[\frac{\lambda}{t} + \frac{\alpha c}{t}\right] \tag{13}$$

During the time of the pollution episode, it can be assumed that λ and $f(\lambda)$ change relatively little. Introducing Equations 3 and 8 into Equation 13 gives

$$r \approx r_1 + \frac{f_1(\lambda)\alpha c}{t} = r_1 + K[\ln x_o/x^*]^{-1} t^{p+1} \alpha c \tag{14}$$

where r_1 is the mortality rate at t_1, the time when the episode began. The second term on the right represents the increase in the mortality rate resulting from the contaminant. The increase depends on the rate at which the contaminant accumulates in the respiratory tissue and is determined by an equation of mass transfer. Assuming that the respiratory tissue acts as a single compartment for the storage of contaminant, the mass transfer equation for an inert species can be written (Hatch and Swann, 1961):

$$V\frac{dc}{dt} = U(c_e - c) \tag{15}$$

where c = concentration of contaminant in the body compartment, and c_e = contaminant concentration in the inspired air. The volume of respiratory tissue is designated V and the over-all mass transfer coefficient, U, is discussed by Hatch and Swann (1961). It depends, among other variables, on the gas or particle diffusion coefficient, aerodynamic patterns, and gas solubility. This equation can be solved for c if the time history of the pollutant concentration in the environment is known. The situation becomes more complicated when the contaminant reacts chemically in the tissue. As shown in the Appendix, it is necessary to modify the rate equation for an inert species to correlate the experimental data.

Further Remarks on Model

A model was proposed for the response of a human population to an environmental pollutant. It was based on the genetic theory of aging and death and a mechanism was provided for the effect of an environmental pollutant, a cytotoxic agent which interferes with the gene-controlled metabolic processes. This general approach to the problem should be stressed, since the details are likely to require modification.

In our simple theory, it was assumed that death occurs as a result of the breakdown of homeostatic processes when the gene activity function, a, for the cardio-pulmonary system, reaches a critical value, $a^* = n^*$. The theory can be extended to the prediction of morbidity rates by choosing values of $a > n^*$ as a lower cutoff, below which all individuals are classified as ill.

From a theory of this type, it would be possible to predict in detail the effect of an acute air pollution episode on a human population. It might then be possible to decide which fraction of the population is most susceptible to a given type of contaminant and to take measures to shield or evacuate the population and control the contaminant level. In conjunction with benefit-cost analyses of the type proposed by Thomas (1964) and meteorological data, the theory may lead to improved methods for setting limits on atmospheric emissions. In particular, one might be able to answer the following question: "How much would it cost to reduce the probable number of deaths as a result of acute air pollution episodes to N per year in a given urban location?" As a step in this direction, the model is applied to the famous London fog of 1952 in the Appendix.

Appendix—An Application of the Model

On the morning of December 5, 1952, unusual meteorological conditions in the Thames Valley, including Greater London, led to the development of a temperature inversion and the accumulation of a fog containing smoke, SO_2, and other pollutants (Committee of Departmental Officers, 1954). Maximum concentrations of 4.46 mg. per cu. meter of smoke and 1.34 p.p.m. of SO_2, about ten times the pre-episode value, were recorded during December 6 to 8. On the morning of the 9th, a southwest wind gradually dispersed the fog.

A sharp increase in the mortality rate for Greater London occurred during the period of the episode. This was followed by a rapid fall to a level still significantly above that for the weeks preceding the episode. In all, it was estimated that some 4000 extra deaths could be attributed to the pollution episode. Postmortem examinations indicated that the components of the fog produced irritation of the bronchi and bronchioles and so accelerated death among those already suffering from diseases of the respiratory and circulatory systems (Committee of Departmental Officers, 1954). This conclusion is consistent with the model discussed above. A detailed breakdown of deaths by age group and cause is available only for the London Administrative County (LAC) (Glasgow Conference, 1953). Since pollution was most serious in the LAC, it was decided to use these figures to test the model.

Death rates in the model appear as dy/dt, the fraction of the original population of any age group which dies in a given time interval. It is therefore necessary to calculate the original population distribution–that is, the population at the time of birth of each age group. This was done in the following manner:

1. The nationwide statistics for the distribution of population in 1952 according to age group were obtained from the United Nations (1955). The number of people in the age groups 25 to 34, 35 to 44, 45 to 54, 55 to 64, 65 to 74, and 75+ in the LAC was calculated.
2. The nationwide statistics for specific death rate as a function of age (Figure A-1) were used to back-calculate by a numerical integration procedure the population of each group at the time of birth. This, of course, depends on the assumption that the specific death rate curve of Figure A-1 has remained constant over time.
3. The results of 2 were used to convert the death statistics of the Glasgow Conference to the form dy/dt.

The death rate in the form dy/dt has a mean value r_1 before the pollution episode. The log-log plot of r_1 *vs.* age yields a straight line with slope $p = 3.8$ (Figure A-2), which compares well with a value of 3.9 obtained from the corresponding national figures. Lines are shown in Figure A-2 for circulatory and respiratory causes, assuming that a certain constant fraction of the total death rate can be attributed to each of these causes. These fractions were obtained from the Glasgow Conference, and may change drastically during the pollution episode, but it can be assumed that at any given time they do not change appreciably from one age group to another. The lines of Figure A-2 also yield the values of K by Equation 7.

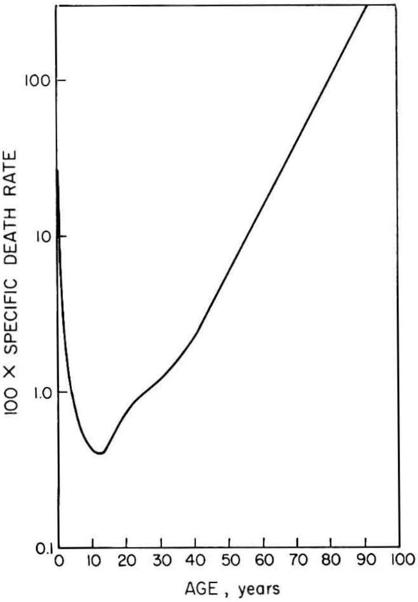

Figure A-1. Specific death rate as a function of age for England and Wales, 1953

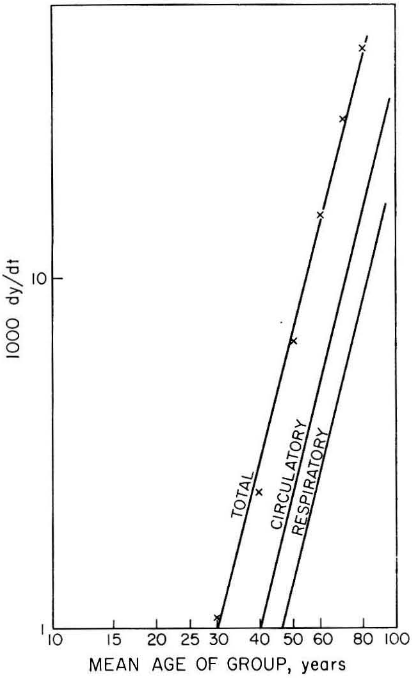

Figure A-2. Fractional death rate based on population of group at birth as a function of age group before air pollution episode

London Administrative County. Slope $p = 3.8$

At any time, according to Equation 14, a log-log plot of $(r - r_1)$ *vs.* age group should yield a straight line of slope $= (p + 1)$. Figures A-3 and A-4 present such straight lines for the 3 weeks ending December 13, 20, and 27. Reasonably good straight lines are obtained, and the slope is approximately 4.8 ($= 3.8 + 1$). This conclusion is true even for the death rate broken down into respiratory and circulatory causes (Figure A-4) by using the data of the Glasgow Conference (1953), as was done for obtaining Figure A-2. The intercepts yield the values of $G = K_1[\ln x_o/x^*]^{-1}\alpha c$ as a function of time. To test the model more completely, it is necessary to have values of G for each day between December 6 and 13. These were obtained by assuming that the daily breakdown of total death rates given by Logan (1953) is the same for all age groups.

Based on the experimental observations (Committee of Departmental Officers, 1954), the concentration of pollutant in the atmosphere behaves approximately as follows (Figure A-5):

$$c_e\ \beta(t - t_1) \qquad t_1 < t < t_2 \qquad \text{(A-1a)}$$

$$c_e = \beta(t_2 - t_1) \qquad t_2 < t < t_2' \qquad \text{(A-1b)}$$

$$c_e = -\beta[t - (t_2 + t_2' - t_1)] \qquad t_2' < t < (t_2 + t_2' - t_1) \qquad \text{(A-1c)}$$

Next it is assumed that the following laws apply to the concentration c of pollutant in the tissue,

$$V\frac{dc}{dt} = U(c_e - c) \qquad c < c_e \qquad (15)$$

$$\frac{dc}{dt} = -kc \qquad c \geq c_e \qquad \text{(A-2)}$$

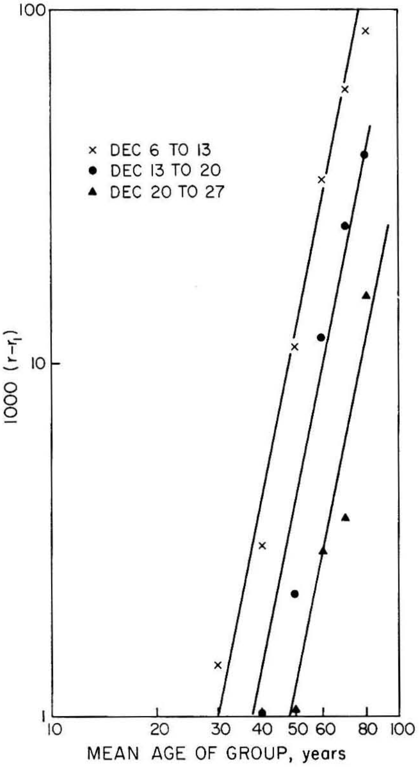

Figure A-3. Increase in death rate (all causes) over pre-episode value as a function of age group

Lines have slope of 4.8 = $(p + 1)$

Equation 15 is applicable to the transfer of an inert (nonreacting) material from the gas to the tissue; U should be considered an average value over the time of interest. During the clearance period, which corresponds roughly to $c \geq c_e$, Equation A-2 is introduced. This is equivalent to the assumption that an independent mechanism is responsible for the elimination of contaminant from the system. The exponential decay law derived from Equation A-2 is of the form usually encountered in the literature on the clearance of particles from the respiratory system (Morrow, Gibb, *et al.*, 1967). The primary justification for the use of these equations at present is in the success of the model in correlating experimental data.

The concentration c is given by

$$c = \beta \frac{V}{U}\left[\frac{U}{V}(t - t_1) - 1 + e^{-U(t-t_1)/V}\right] \qquad t_1 < t < t_2 \quad \text{(A-3a)}$$

$$c = c_{t_2}[t - t_2 e^{-U/V(t-t_2)} + e^{-U(t-t_2)/V}] \qquad t_2 < t < t_2' \quad \text{(A-3b)}$$

$$c = c_{\max} e^{-k(t-t_2')} \qquad t_2' < t < (t_2 + t_2' - t_1) \quad \text{(A-3c)}$$

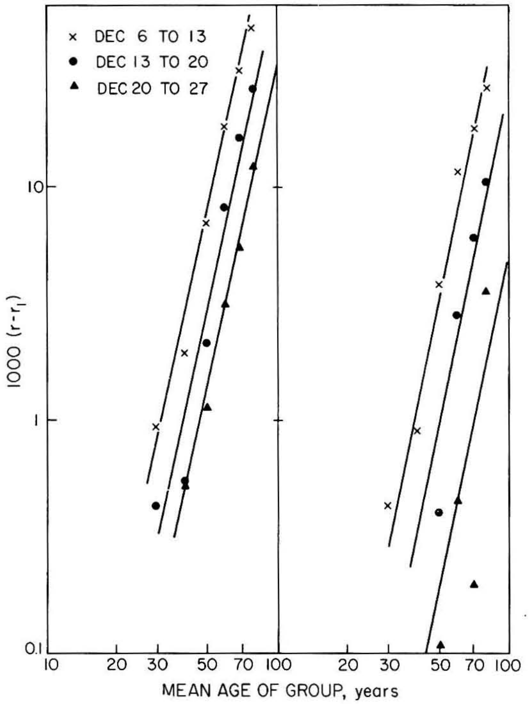

Figure A-4. Increase in death rate over pre-episode value as a function of age group

Left. **Respiratory death rate**
Right. **Death rate due to circulatory causes**
Lines have slope of 4.8 $(= p + 1)$

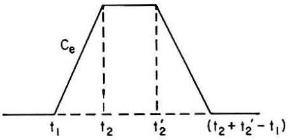

Figure A-5. Approximate form of SO_2 and particulate concentration–time history curves for 1952 London fog

where $c_{\max}$ is the maximum concentration of the pollutant in the tissue. This occurs soon after $t = t_2'$, and has been assumed to occur at $t = t_2'$.

Since $G = K[\ln x_o/x^*]^{-1}\alpha c = \text{const.} \times c$, the G values can be used to estimate the constants U/V, $\alpha[\ln x_o/x^*]^{-1}$, and k. The best values were found by trial and error (Table I) and were used to calculate "theoretical" values of the death rates. Figures A-6 and A-7 show the theoretical curves as well as the observed points. Figure A-8 is a plot of $(r - r_1)t^{-(p+1)}$ *vs.* time. The model predicts that the value of this parameter should be the same for all age groups at any given time. In spite of the considerable scatter among the points, the agree-

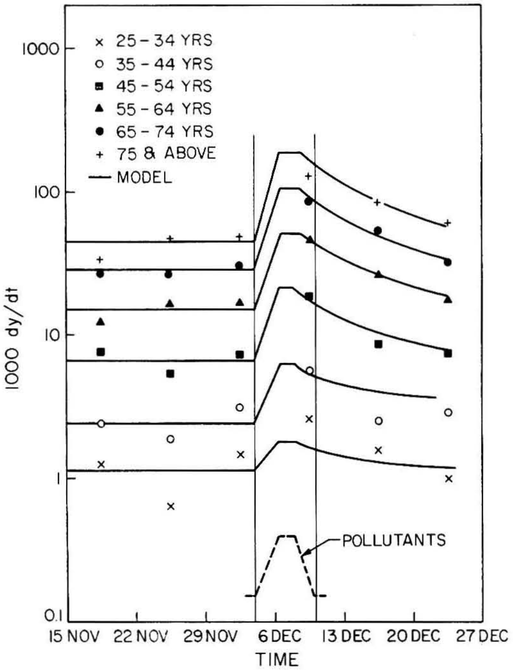

Figure A-6. Fractional death rates (all causes) as a function of time for different age groups, with lines calculated from theoretical model

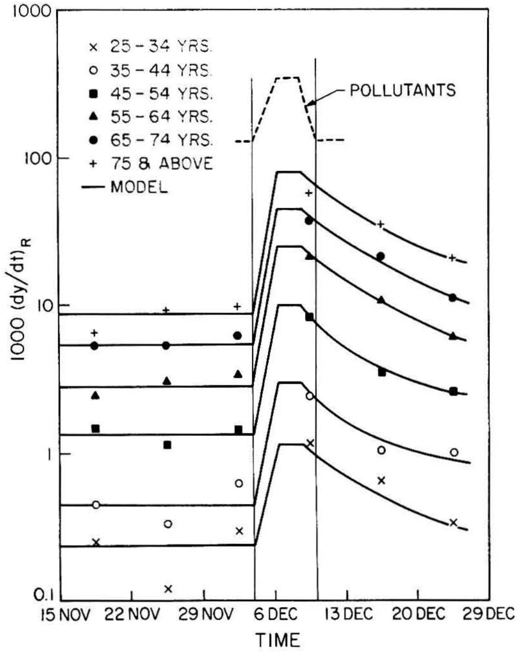

Figure A-7. Fractional death rates (respiratory causes) as a function of time for different age groups, with lines calculated from theoretical model

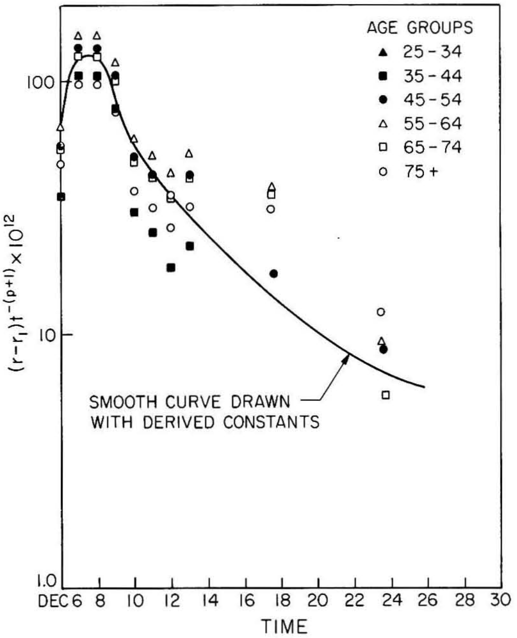

Figure A-8. Age-invariant death rate parameter as a function of time

According to theoretical model all data points should fall on single curve

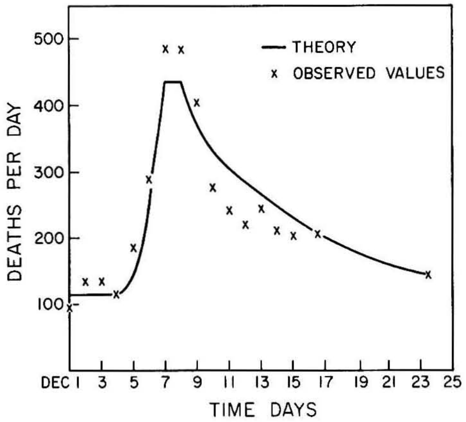

Figure A-9. Total number of deaths per day for all ages over 25 compared with calculated values

London Administrative County, December 1952 (total population 3,700,000)

Table I. Summary of Values of Constants for 1952 London Smog Episode

$$\begin{aligned}\frac{U}{V} &= 5 \text{ days}^{-1}\\ k &= 0.18 \text{ day}^{-1}\\ p &= 3.8\\ K &= 2.5 \times 10^{-9} \text{ (year)}^{-p-1} \text{ for all causes}\\ &= 8 \times 10^{-10} \text{ (year)}^{-p-1} \text{ for circulatory diseases}\\ &= 4.6 \times 10^{-10} \text{ (year)}^{-p-1} \text{ for respiratory diseases}\\ \beta &= 0.5 \text{ p.p.m./day for SO}_2\\ \alpha[\ln (x_o/x^*)]^{-1} &= 0.036 \text{ year}^{-1} \text{ (p.p.m. SO}_2)^{-1}\end{aligned}$$

ment with theory is not bad, considering the large number of uncertainties in the data and the calculations. Finally, Figure A-9 presents the death rates due to all causes and in all age groups above 25. Agreement with the curve predicted by the model is good.

Both SO_2 and particulate concentrations followed roughly the same course in their concentration-time history, and the two have been considered together as a single environmental contaminant in the calculations. Values of α and β are expressed in terms of SO_2 concentrations; these values would have to be modified for different particulate concentrations or properties, as would values of U/V and k. The values of the constants are summarized in Table I.

Nomenclature

c = tissue contaminant concentration expressed either as actual concentration or as equivalent equilibrium gas-phase concentration or tension
c_e = atmospheric contaminant concentration expressed in same units as c
F = functional dependence of gene decay rate on n
f = cohort distribution function of genetic decay rates
f_1 = value of f when air pollution episode begins
$G = K [\ln x_o/x^*]^{-1}\alpha c$
k = first-order decay rate for contaminant in tissue
K = proportionality constant in power law form of mortality rate
n = number of genes functioning without error at any time
n_o = number of genes functioning without error at some given reference time
n^* = number of genes functioning without error at which death occurs
p = age exponent in power law form of mortality rate
r = mortality rate, dy/dt
r_1 = mortality rate at time pollution episode begins
t = time or age of cohort
t_1 = time at which air pollution episode begins
t_2 = time at which pollutant concentration levels off
t_2' = time at which pollutant concentration begins to decrease
t^* = age at death
U = over-all mass transfer coefficient
V = volume of tissue in which contaminant is absorbed
w = fraction of individuals in a cohort (group born at the same time) with gene mutation rates $<\lambda$
x_o = fraction of defective genes present at some given reference time
x^* = fraction of surviving genes at which death takes place
y = fraction dead of individuals in a cohort

GREEK LETTERS

α = proportionality coefficient between $\ln \bar{\gamma}$ and the dose
β = slope of atmospheric concentration *vs.* time curve for environmental contaminant
$\bar{\gamma}$ = average activity coefficient for a cell or group of cells in the presence of a cytotoxic agent
λ = first-order rate constant of genetic decay
τ = dummy time variable

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Hydrocarbon Reactivity and Eye Irritation

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■ Twenty-five hydrocarbons have been irradiated in the General Motors smog chamber under a standard set of experimental conditions. Eye irritation and various chemical rates and product yields were used to measure hydrocarbon reactivity. Although the chemical measures of reactivity correlated with one another to a fair degree, there was no correlation between any of the chemical measures and eye irritation. A correlation was found, however, between hydrocarbon structure and eye irritation, and a hydrocarbon reactivity scale based on eye irritation is presented. The most potent precursors of eye irritation were benzylic hydrocarbons and aromatic olefins. A new and extremely potent eye irritant, peroxybenzoyl nitrate, a lachrymator 200 times as potent as formaldehyde, was identified as a product from the irradiation of benzylic hydrocarbons and aromatic olefins.

Photochemical smog results from the atmospheric photooxidation of hydrocarbons in the presence of oxides of nitrogen. Eye irritation is one of the prominent manifestations of these reactions. Over the years, atmospheric photooxidation reactions have been widely studied (Altshuller and Bufalini, 1965) and many products have been identified. Three in particular, formaldehyde, acrolein, and peroxyacetyl nitrate, have been found to be effective lachrymators in the parts-per-million range (Shuck and Doyle, 1959; Stephens, Darley, *et al.*, 1961). However, it has not been successfully shown that these compounds are present in the atmosphere in sufficient quantity to account for all the eye irritation observed (Renzetti and Bryan, 1961).

It has been known for many years that individual hydrocarbons react at widely differing rates in atmospheric photooxidations, and numerous chemical measurements have been proposed to characterize the reactivity of individual hydrocarbons. Altshuller (1966) has summarized the available data. Various techniques have been used at many different conditions so that with one exception (Glasson and Tuesday, 1965) the number of hydrocarbons investigated at any one set of conditions is small. Furthermore, the available chemical measurements could not be related to physiological smog symptoms (Altshuller, 1964, 1966).

A knowledge of the relative ability of hydrocarbon emissions to cause the effects associated with smog is necessary for effective control of emission sources. To increase this knowledge, eye irritation and various chemical measures of reactivity were determined in the General Motors (GM) smog chamber for 25 hydrocarbons at a standard set of experimental conditions.

Hydrocarbon Reactivity Measurements

Apparatus and Procedure. The 25 hydrocarbons included in this study were chosen to represent different structural types. Benzene, eight monoalkylbenzenes, three dialkylbenzenes, one trialkylbenzene, four terminal olefins, four internal olefins, one diolefin, and three paraffins were included. Research grade olefins and paraffins and research or pure grade aromatic hydrocarbons were used.

The hydrocarbons were irradiated in the GM smog chamber which is a stainless steel cylinder 9 feet in diameter and 5 feet high. Spaced symmetrically throughout the chamber are 19 vertical borosilicate glass tubes containing the irradiation lamps. The internal volume is 298 cu. ft. The facility has been described in detail previously (Tuesday, D'Alleva, *et al.*, 1965).

Two parts per million of each hydrocarbon were added to the preheated chamber. One part per million of nitric oxide was added and the mixture was irradiated for 6 hours at 95° F. The light intensity, as measured by the first order rate constant for the photolysis of nitrogen dioxide in nitrogen (Tuesday, 1961), was $K_d\ (NO_2) = 0.4\ \text{min.}^{-1}$. The dilution air used had a dew point of 55° F. which corresponds to 26% relative humidity at 95° F. Each hydrocarbon experiment was performed in duplicate or triplicate. Unless otherwise specified, all experiments were conducted at the standard conditions listed above. All concentrations are given in parts per million (p.p.m.) (v./v.), or parts per billion (p.p.b.) (v./v.).

Methods of Analysis. Ozone was measured with a Mast ozone meter which was calibrated against the neutral KI method as a standard using various concentrations of ozone added to the chamber. The nitrogen dioxide response of the ozone meter was determined using known concentrations of nitrogen dioxide in the chamber. Nitrogen dioxide responds on a molar basis only $^1/_{11}$ as much as ozone. All of the ozone measurements reported have been corrected for this nitrogen dioxide interference.

The oxides of nitrogen analyzers were originally Beckman Model K1003 and K1004 atmospheric analyzers. These analyzers, however, have been extensively modified to reduce the response time to $3^1/_3$ minutes for 50% response and $4^1/_2$ minutes for 90% response. One of the instruments measures the nitrogen dioxide content of the chamber while the other contains a dry dichromate oxidizer system (Ripley, Clingenpeel, *et al.*, 1964) and therefore measures the total nitrogen oxide content ($NO + NO_2$).

Formaldehyde was determined by the chromotropic acid method (Altshuller, Miller, *et al.*, 1961). Acrolein was determined with the 4-hexylresorcinol method (Cohen and Altshuller, 1961).

Peroxyacetyl nitrate (PAN) was measured with an F & M Model 402 gas chromatograph equipped for simultaneous flame ionization and electron-capture detection. A 6-cc. stainless steel sample loop together with a stainless steel sampling valve and stainless steel lines were used to sample the chamber contents. A 4-foot, $^1/_8$-inch glass column of 3.8% SE30 on 80- to 100-mesh Diatoport S was used. This column separated PAN at room temperature. The system was calibrated for PAN by sampling known concentrations from a long-path infrared cell (Tuesday, 1961). Concentrations in the cell were determined using the infrared absorptivities of Stephens (1964).

The disappearance of aromatic hydrocarbons was followed with the same chromatographic column described above. The disappearance of olefins and paraffins was followed with a Beckman Model 107 flame ionization analyzer. Since the flame ionization analyzer responds in varying degree to many products of the smog reaction as well as to hydrocarbons, measurements with this analyzer during or after irradiation are of limited significance. In an attempt to measure the unreacted hydrocarbons, a pretreatment of the sample stream was used. Since the bisulfite addition reaction is specific for aldehydes and ketones, the sample stream was passed through a midget impinger containing 15 ml. of a 1% sodium bisulfite solution maintained at 0°. The response of the flame ionization analyzer to the sample stream after this bisulfite treatment is considered a measure of the hydrocarbon concentration in the sample. This is, however, only an approximation since only those reaction products trapped by the bisulfite solution have been removed.

Eye irritation was determined after 6 hours of irradiation by a panel of employees not associated with any aspect of this work. Each panelist exposed his or her eyes for 4 minutes. The panelists pressed a button at the side of the port when they first felt irritation. This stopped a timer, which started at the beginning of the eye exposure when the shutter on the port was opened. The elapsed time was considered a threshold response and taken as one measure of eye irritation. The panelists also rated the eye irritation after the 4-minute exposure as: none, light, moderate, or severe. These ratings were assigned numerical values of 0, 1, 2, and 3, respectively. The eye irritation index was taken as the numerical average of the individual ratings.

Carbon monoxide was added as a tracer in all runs as a measure of dilution from both sampling and leaks. The average dilution was 17% in the 6-hour irradiation. The air sampled by the instruments is replaced by cylinder air which is automatically added to the chamber to maintain a constant pressure.

Results. The rate of nitrogen dioxide formation (the average rate to the half-time), the rate of ozone formation (defined as one-half the maximum ozone concentration divided by the time from the beginning of irradiation to one-half the maximum ozone concentration), the per cent of hydrocarbon reacted after 6 hours irradiation, the maximum ozone concentration, the formaldehyde yield at 6 hours, the PAN yield at 6 hours, and the eye irritation at 6 hours are reported in Table I. Table I gives the average of the results from one to three determinations per hydrocarbon together with the estimated reproducibility.

The rate of nitrogen dioxide formation has been suggested as a particularly significant measure of hydrocarbon reactivity because it is the first important reaction in smog formation and because several important products, ozone and PAN, are formed only after the nitric oxide is oxidized. The effect of structure on nitrogen dioxide formation rate is shown in Figure 1. For simplicity, the hydrocarbons are broken down into seven classes by structure. Owing to the variation of over 100 to 1 in the rate of nitrogen dioxide formation, a logarithmic scale is used. Benzene is the least reactive; paraffins and monoalkylbenzenes are also low in reactivity; terminal olefins and multialkylbenzenes are intermediate in reactivity; and 1,3-

Table I. Average Results of Irradiation of 2 P.P.M. of Hydrocarbon–1 P.P.M. of Nitric Oxide

Compound	No. of Experiments	NO_2 Rate, P.P.B./Min.	O_3 Rate, P.P.B./Min.	% Hydrocarbon Reacted[a]	Product Yields, P.P.M.				Eye Irritation Av. Threshold Time, Sec.	Eye Irritation Index (0 to 3 Scale)
					O_3 max.	Formaldehyde	PAN	Benzaldehyde		
n-Butane	2	4.6	0.33	5	0.16	0.15	0	0	240	0.0
n-Hexane	2	6.5	0.43	18	0.17	0.19	0	0	240	0.0
Isooctane	2	4.7	0.40	10	0.19	0.25	0	0	219	0.2
Benzene	2	1.6	0.10	13	0.05	0.08	0.01	0	216	0.2
Toluene	3	5.7	0.77	39	0.30	0.14	0.10	0.15	114	2.0
Ethylbenzene	3	7.2	0.47	29	0.21	0.11	0	0.10	138	1.6
n-Propylbenzene	3	5.7	0.43	30	0.21	0.10	0.01	0.20	111	2.5
Isopropylbenzene	3	6.6	0.47	33	0.19	0.28	0.01	0	202	0.6
n-Butylbenzene	3	6.0	0.53	33	0.24	0.11	0	0.44	86	2.3
Isobutylbenzene	3	5.0	0.35	28	0.17	0.10	0	0.50	104	2.5
sec-Butylbenzene	3	7.6	0.69	21	0.26	0.16	0	0.02	197	0.6
tert-Butylbenzene	3	3.8	0.23	28	0.13	0.15	0.01	0	219	0.3
o-Xylene	2	13.6	1.87	52	0.32	0.45	0.40	0	186	0.9
m-Xylene	2	15.5	3.30	54	0.39	0.39	0.50	0	171	1.3
p-Xylene	2	7.7	0.78	42	0.26	0.22	0.40	0	180	1.1
1,3,5-Trimethylbenzene	2	26.0	5.85	66	0.46	0.70	0.67	0	166	1.0
Ethylene	2	5.8	0.68	45	0.28	0.83	0.01	0	216	0.3
Propylene	2	12.1	2.60	73	0.54	1.17	0.35	0	148	1.2
1-Butene	2	13.1	2.45	85	0.47	0.90	0.05[b]	0	210	0.7
1-Hexene	2	9.6	1.75	80	0.41	0.78	0.02	0	157	1.2
trans-2-Butene	2	38.0	9.1	85	0.44	0.75	0.63	0	186	0.5
cis-2-Butene	2	28.0	6.3	90	0.44	0.69	0.36	0	201	0.6
2-Methyl-2-butene	2	50.0	9.5	95	0.49	0.68	0.85	0	195	0.5
Tetramethylethylene	2	170.0	11.5	95	0.60	0.63	0.65	0	207	0.7
1,3-Butadiene	2	25.0	4.05	92	0.48	0.80[c]	0.02	0	73	3.0
Estimated reproducibility[d] (%)		14	19	10	19	10	10[e]	15[e]	8	22

[a] Corrected for dilution. [b] PPN also formed. [c] 0.73 p.p.m. of acrolein also formed. [d] Calculated from the average of the average deviations from the mean for all hydrocarbons listed. [e] Only one determination for each hydrocarbon. Reproducibility estimated from calibration.

butadiene and internally double-bonded olefins are highest in reactivity.

Glasson and Tuesday (1965) have measured rates of nitrogen dioxide formation for 21 of the same hydrocarbons. Although the experimental conditions differ considerably between the two studies, the correlation coefficient between the rates Glasson and Tuesday measured and the rates measured in this study is quite high, 0.995.

Ozone formation is also an important reactivity measure since ozone formation is a common criteria for the existence of photochemical smog. As shown in Table I, the ranking of structural classes by their rate of ozone formation is similar to that for the rate of nitrogen dioxide formation shown in Figure 1. For the ozone rate, the overall variation is again greater than 100 to 1.

The over-all variation in the other reactivity measures listed in Table I is considerably less than 100 to 1. For instance, the per cent of hydrocarbon reacted at 6 hours ranges from about 10% for benzene and paraffins to over 90% for most of the olefins. The range in maximum ozone concentrations is only 12 to 1. In fact, it is only 4.6 to 1 if benzene is excluded.

The terminal olefins yield the largest amount of formaldehyde, a known eye irritant, as has been reported before (Shuck and Doyle, 1959), and as would be expected from the location of the double bond in these molecules. Multialkylbenzenes and internal olefins yield the largest amounts of PAN, another known eye irritant and a phytotoxicant, again in agreement with previous findings (Kopczynski, 1964; Stephens and Scott, 1962).

The aromatic aldehyde, benzaldehyde, was identified by gas chromatography as a product in some of the irradiation experiments. The benzaldehyde yields are listed in Table I. The formation of benzaldehyde indicates that side chain oxidation is taking place in some of the monoalkylbenzenes just as the formation of PAN from multialkylbenzenes is an indication of ring splitting (Kopczynski, 1964; Stephens and Scott, 1962).

The effect of hydrocarbon structure on eye irritation index is shown in Figure 2. The most potent precursor of eye irritation is 1,3-butadiene which forms both formaldehyde and acrolein (known eye irritants). However, the next highest structural class is the monoalkylbenzenes which range from very low to very high in eye irritation. As can be seen in Table I, none of the monoalkylbenzenes form very much formaldehyde or PAN so that high eye irritation from this hydrocarbon class was not expected.

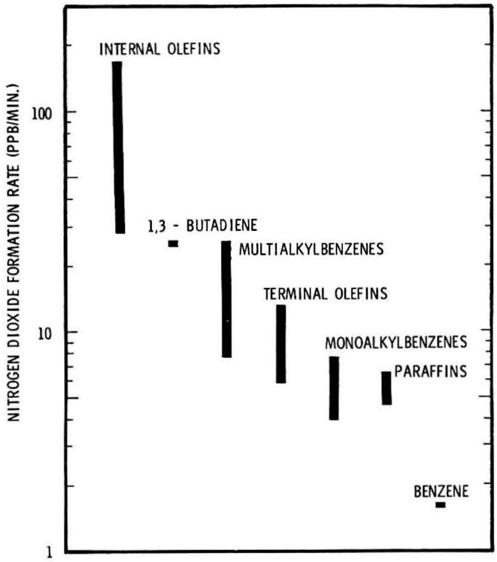

Figure 1. Effect of hydrocarbon structure on nitrogen dioxide formation rate

Hydrocarbon Reactivity Correlation. Correlation coefficients between the various reactivity measures were calculated and are listed in Table II. The correlation among the chemical measures is good. Seven of the 15 coefficients between chemical measures are 0.79 or higher. Nitrogen dioxide rate correlates best with ozone rate—the coefficient being 0.81. Ozone rate also correlates well with per cent of hydrocarbon reacted (0.80), maximum ozone concentration (0.79), and PAN (0.84) as well as with NO_2 rate. Per cent of hydrocarbon reacted correlates best with maximum ozone concentration (0.93) and also correlates well with formaldehyde (0.83). Maximum ozone concentration correlates best with formaldehyde (0.84).

However, none of the chemical measures correlate with either eye irritation index or eye irritation average threshold time. As would be expected, eye irritation index has a good inverse correlation with average threshold time (−0.97). It has been suggested that formaldehyde, acrolein, and PAN are responsible for the eye irritation in photochemical smog (Shuck, Doyle, *et al.*, 1960). A multiple regression between eye irritation and formaldehyde, acrolein, and PAN has a correlation coefficient of only 0.45, suggesting that other eye irritants were apparently also present.

Table I shows that the monoalkylbenzenes which produce heavy eye irritation all fall into a common structural subclass. They all contain the benzyl group ($C_6H_5CH_2$—). The nonbenzylic monoalkylbenzenes (nonbenzyls) all had low eye irritation. For instance, the benzylic hydrocarbon, *n*-propylbenzene, had an eye irritation index of 2.5 whereas the nonbenzylic hydrocarbon, isopropylbenzene, had an eye irritation index of only 0.6. The same dramatic effect of structure can also be seen in the four butylbenzene isomers. The benzylic hydrocarbons, *n*-butyl and isobutyl, had eye irritation indices of 2.3 and 2.5 while the nonbenzylic hydrocarbons, *sec*-butyl and *tert*-butyl, had eye irritation indices of 0.6 and 0.3.

As shown in Table I, the benzylic hydrocarbons were the

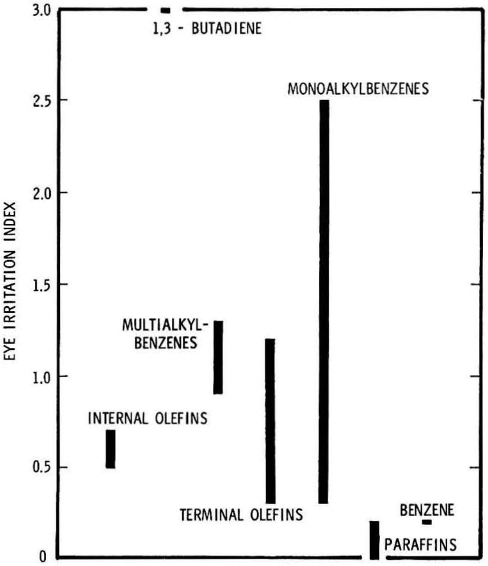

Figure 2. Effect of hydrocarbon structure on eye irritation index

Table II. Correlation Coefficients between Various Reactivity Measures

	O_3 Rate	HC Reacted, %	Max. O_3	CH_2O	PAN	Eye Irritation Index	Eye Irritation Av. threshold time
NO_2 rate	0.81	0.56	0.61	0.31	0.59	−0.10	0.12
O_3 rate		0.80	0.79	0.56	0.84	−0.12	0.08
% HC reacted			0.93	0.83	0.64	0.13	−0.16
Maximum O_3				0.84	0.68	0.11	−0.15
CH_2O					0.45	−0.09	0.03
PAN						−0.17	0.12
Eye irritation index							−0.97

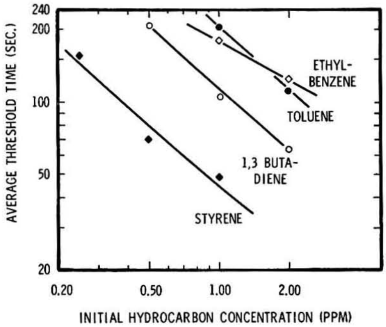

Figure 3. Relation of average threshold time and initial hydrocarbon concentration at constant HC/NO_x ratio (2)

only aromatic hydrocarbons that had a significant yield of benzaldehyde upon irradiation. A series of aromatic olefins which should produce benzaldehyde upon irradiation was, therefore, also investigated. Four aromatic olefins were irradiated at initial concentrations of 1 p.p.m. of hydrocarbon and 0.5 p.p.m. of nitric oxide. The results are shown in Table III. At one half the concentrations used in the other irradiations, two of the aromatic olefins produced an eye irritation index of 3—the maximum of the scale. Thus, the aromatic olefins are even more potent precursors of eye irritation than 1,3-butadiene which produced an eye irritation index of 3 with initial concentrations of 2.0 p.p.m. of 1,3-butadiene and 1.0 p.p.m. of nitric oxide.

The aromatic olefin irradiations were followed by gas chromatography, and a number of products were identified. The major and minor products identified in each case are listed in Table III. For each of the aromatic olefins, the major products identified indicate that aromatic olefins split at the double bond, but the finding of the minor products indicates that some oxidation of the α-carbon of the product resulting from double-bond scission also takes place.

Since 1 p.p.m. of the aromatic olefins produced severe eye irritation (the maximum of the subjective rating scale and higher than previously experienced by the GM panel), it was decided not to expose the panel members to the higher concentration of irritant necessary to measure the eye irritation from 2 p.p.m. of each of the aromatic olefins. Instead the average threshold time expected from the irradiation of 2 p.p.m. of each of the aromatic olefins and 1 p.p.m. of nitric oxide was estimated by extrapolation.

To form a basis for the extrapolation of the eye irritation results of aromatic olefins from 1.0 p.p.m. to 2.0 p.p.m., a number of hydrocarbons were irradiated at a set of different initial hydrocarbon concentrations. Styrene, 1,3-butadiene, toluene, and ethylbenzene were irradiated with a constant HC/NO_x ratio (2) at a series of initial hydrocarbon concentrations. The eye irritation results are shown in Figure 3 which is a log-log plot of average threshold time versus initial hydrocarbon concentration.

Since threshold response time should be inversely related to the concentration of irritant, or some power of the concentration (Wayne, 1967), a log-log plot of threshold time versus concentration of irritant should yield a straight line with equation ct^a = constant, where a is the slope of the line. The initial hydrocarbon concentration is certainly not equivalent to the concentration of the irritant, but it seems reasonable to assume as a first approximation that the two are proportional.

For three of the four compounds in Figure 3, straight lines of slope 1 fit the data. It seems reasonable, therefore, to extrapolate the eye irritation results for the aromatic olefins by assuming the relationship ct = constant applies. Thus, a

Table III. Results of Aromatic Olefin Photooxidations at 1 P.P.M. of Hydrocarbon–0.5 P.P.M. of Nitric Oxide[a]

	Styrene	α-Methylstyrene	β-Methylstyrene	Allylbenzene
NO_2 rate (p.p.b./minute)	7.4	4.0	7.8	7.0
O_3 rate (p.p.b./minute)	0.06	0.12	0.06	0.14
% Hydrocarbon reacted	90	75	78	76
Formaldehyde (p.p.m.)	0.49	0.51	0.50	0.33
EI index at 6 hours (0 to 3 scale)	3.0	1.5	3.0	2.9
EI Av. threshold time (seconds)	49	127	49	75
Major products	Benzaldehyde Formaldehyde	Acetophenone Formaldehyde	Benzaldehyde Acetaldehyde Formaldehyde	Phenylacetaldehyde Formaldehyde
Minor products	—	Benzaldehyde	—	Benzaldehyde
Estimated EI threshold time at 2 p.p.m. of hydrocarbon and 1 p.p.m. of NO (seconds)	25	63	25	38

[a] Temperature = 95° F.; light intensity = 0.4 $min.^{-1}$; dew point = 55° F.

doubling of the concentration will halve the threshold response time. The threshold response times for 2 p.p.m. of the several aromatic olefins were estimated by this method and are given in Table III.

Eye Irritation Reactivity

Eye irritation measurements can be used as the basis of a hydrocarbon reactivity scale. The use of the eye irritation index would fail to account for the potency of aromatic olefins since they reach a maximum on the index scale at lower concentrations than the 2-p.p.m. level used for most of the hydrocarbons. Therefore, the average threshold response time, t, was used as the basis for an eye irritation reactivity scale because it is simple, correlates well with eye irritation index, and should be related to the concentration of irritant (Wayne, 1967).

An eye irritation reactivity scale was developed from the average threshold time as follows:

$$\text{Eye irritation reactivity} = \frac{(240 - t) \times 10}{240}$$

This scale increases with increasing eye irritation from 0 to 10. The eye irritation reactivities for the hydrocarbons used in this study are shown in Table IV. The standard errors of estimate of the values in Table IV range from 0.1 to 1.1 and average 0.6.

The effect of hydrocarbon structure on eye irritation reactivity is shown in Figure 4. Since the precision of eye irritation measurements is limited, there is little or no statistically significant difference among compounds within a given structural class. However, there are differences statistically significant above the 95% confidence level between certain classes. Aromatic olefins are significantly more potent than benzylic hydrocarbons which in turn are significantly more potent than the other classes. The other aromatics and olefins are approximately equal in eye irritation reactivity and are significantly more potent than the paraffins and benzene.

Search for Eye Irritant

Benzaldehyde was identified as a product from the irradiation of benzylic hydrocarbons and aromatic olefins. However, the eye irritation index of 1 p.p.m. of benzaldehyde was found to be 0.0. The formaldehyde yields in these systems (less than 0.5 p.p.m.) are also not sufficient to account for the observed eye irritation. Hence, there must have been some as yet unidentified product present which caused eye irritation.

Table IV. Eye Irritation Reactivity

Hydrocarbon	Eye Irritation Reactivity	Hydrocarbon	Eye Irritation Reactivity
n-Butane	0	*m*-Xylene	2.9
n-Hexane	0	1,3,5-Trimethylbenzene	3.1
Isooctane	0.9	1-Hexene	3.5
tert-Butylbenzene	0.9	Propylene	3.9
Benzene	1.0	Ethylbenzene	4.3
Ethylene	1.0	Toluene	5.3
1-Butene	1.3	*n*-Propylbenzene	5.4
Tetramethylethylene	1.4	Isobutylbenzene	5.7
cis-2-Butene	1.6	*n*-Butylbenzene	6.4
Isopropylbenzene	1.6	1,3-Butadiene	6.9
sec-Butylbenzene	1.8	α-Methylstyrene	7.4
2-Methyl-2-butene	1.9	Allylbenzene	8.4
trans-2-Butene	2.3	β-Methylstyrene	8.9
o-Xylene	2.3	Styrene	8.9
p-Xylene	2.5		

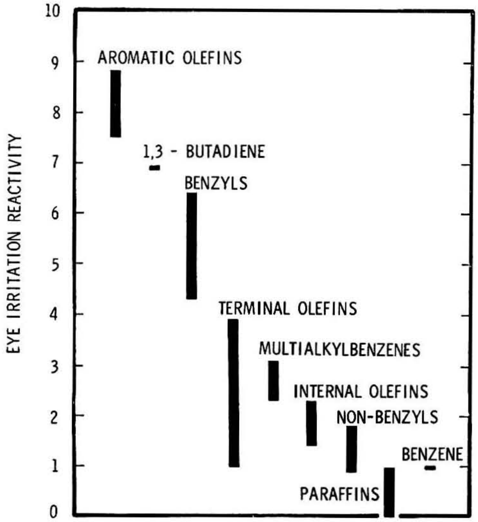

Figure 4. Effect of hydrocarbon structure on eye irritation

To determine the conditions necessary for the formation of this irritant, a number of screening experiments were carried out. Eye irritation in the reaction of 0.5 p.p.m. of styrene and 0.25 p.p.m. of nitric oxide was followed as a function of time. The results are shown in Figure 5. The irritation appears immediately after the nitrogen dioxide peak and builds up quickly suggesting that ozone is involved in the formation of the irritation. Reactions of various combinations of benzaldehyde, ozone, nitric oxide, and nitrogen dioxide in the light and dark were conducted in the smog chamber. Significant eye irritation was found whenever benzaldehyde, ozone, and nitrogen dioxide were present together. The formation of irritation took place both in the dark and with irradiation. Although these reactions were followed by gas chromatography, no product peaks were found.

The reaction, at 26°, of 2.0 p.p.m. of benzaldehyde with 1.0 p.p.m. of nitrogen dioxide and 1.0 p.p.m. of ozone was investigated in the long-path infrared cell at an oxygen pressure of 155 mm. of Hg and sufficient nitrogen to achieve a total pressure of 760 mm. of Hg. On addition of ozone to the benzaldehyde–nitrogen dioxide system, a rapid conversion of benzaldehyde took place. Major infrared absorptions were found at 5.54, 5.75, 7.65, 8.17, 10.13, and 12.67 microns. Hydrogen nitrate was also formed. Since the aldehyde–nitrogen dioxide–ozone system is formally analogous to the nitrogen pentoxide–aldehyde system demonstrated (Tuesday, 1961) as a method for the synthesis of peroxyacyl nitrates, the presence of the

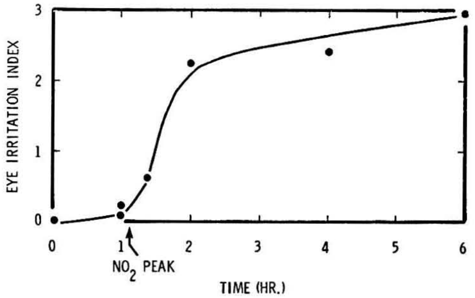

Figure 5. Eye irritation as a function of time in 0.5 p.p.m. styrene–0.25 p.p.m. nitric oxide system

hitherto unreported peroxybenzoyl nitrate (PBzN) ($C_6H_5C(O)OONO_2$) was suspected. This suspicion was strengthened by comparison with the infrared spectrum of peroxyacetyl nitrate (PAN) (Stephens, Darley, *et al.*, 1961).

Further evidence pointing to PBzN was obtained by studying the photooxidation of benzyl nitrite in air, in the long-path cell. Benzyl nitrite was prepared by treating, at 0°, a solution of benzyl alcohol in sulfuric acid with an aqueous solution of sodium nitrite. The nitrite was distilled in vacuo before use and was stored in the dark at −5°. The same infrared absorption peaks were found after irradiation of the benzyl nitrite system as were found in the benzaldehyde–nitrogen dioxide–ozone system. Extended photolysis experiments indicated that all of these infrared peaks disappeared to the same proportionate degree, indicating that these peaks could be attributed to a single product. Since the photooxidation of alkyl nitrites is a known (Stephens, Burleson, *et al.*, 1965) method for synthesizing peroxyacyl nitrates, the presence of PBzN was again indicated.

The photooxidation of 0.20 p.p.m. of benzyl nitrite, which is not an eye irritant at this concentration level, in the smog chamber resulted in an eye irritation index of 2.9 after a 1.0-hour irradiation. This observation is consistent with the results from the benzaldehyde-NO_2-O_3 system noted earlier and taken with the results of the long-path study indicate that the unknown product is a very effective lachrymator.

Identification of Eye Irritant

To obtain sufficient quantities of the unknown product for identification studies, large scale benzaldehyde-NO_2-O_3 reactions were carried out in the long-path cell. Typically, 200 p.p.m. of benzaldehyde and 100 p.p.m. of NO_2 were added to the cell and tank nitrogen and oxygen added to achieve a total synthetic air pressure of 760 mm. of Hg. Ozone was then added in excess of the amount necessary to convert the NO_2 to N_2O_5. When the N_2O_5 had reacted, additional NO_2 was added. Alternate additions of O_3 and NO_2 were then carried out until the benzaldehyde reacted completely, as indicated by the disappearance of the aldehydic C—H absorption at 3.7 microns. The product was removed from the cell by circulating the cell contents through a U-trap filled with glass beads and immersed in a dry-ice bath. After sufficient product had been trapped (5 to 6 hours), the U-trap was removed from the system and the product washed from the trap with *n*-hexane. The hexane solution was washed with water (to remove any trapped hydrogen nitrate) and dried over anhydrous sodium sulfate. The product solutions from five runs were pooled, the hexane was removed under vacuum, and the crude product (about 1.5 grams) vacuum-distilled. The middle fraction was used for all subsequent measurements and was stored in the dark under vacuum at −78° to minimize decomposition.

Properties. The product was a pale yellow liquid (ρ^{23} = 1.31 grams per cc.) which boiled at 37° at a pressure of 0.2 mm. of Hg.

The stability of the product in the vapor phase was studied at low concentrations in the long-path infrared cell. The product, 1.4 p.p.m., was allowed to decompose at 26° in 760 mm. of Hg of air made up from tank nitrogen and oxygen both in the dark and in the presence of light, $K_d(NO_2) = 0.40$ min.$^{-1}$. The half-life of the product was 6.4 hours in the dark and 0.95 hours with the lights on. NO_2, CO_2, CO, and benzoic acid were the only decomposition products identified.

This product was subjected to elemental analysis with the following results: Found: C, 46.8%; H, 3.5%; N, 7.0%; O (diff.), 42.7%. Calcd, (PBzN): C, 45.9%; H, 2.7%; N, 7.6%; O, 43.8%. These results are subject to some uncertainty since three of the four attempted analyses resulted in loss of the sample, during combustion, due to explosion. Within the experimental error, however, the results are consistent with the calculated composition of peroxybenzoyl nitrate (PBzN).

Infrared Spectrum. The vapor and liquid phase (hexane solution) infrared spectra of the unknown product were identical except for small wavelength shifts probably associated with a solvent effect. The liquid phase spectrum also showed absorptions at 15.8 and 19.9 microns in the far infrared, a spectral region not available with the long-path cell.

The vapor phase spectrum is given in Table V along with the spectrum of benzoyl nitrate, a possible choice for the structure of the product. The sample of benzoyl nitrate was prepared by the method of Burton (Burton and Praill, 1955). Table V indicates that, although the two spectra are superficially similar, small shifts in the positions of a number of the major peaks and large differences in the intensities of the peaks in the 7.7- and 14-micron regions are clearly evident. This comparison demonstrates that the structure of the product is similar to, but not the same as, benzoyl nitrate. A comparison of the infrared spectra of peroxyacetyl nitrate (PAN) and acetyl nitrate (Stephens, Darley, *et al.*, 1961) showed general wavelength shifts and also intensity differences in the 7.7- and 14-micron regions similar to those noted in Table V. These observations lend support to the assignment of the product structure as that of PBzN.

The absorptivities of the major peaks in the vapor phase spectrum of the product are given in Table VI. The absorptivities of comparable peaks in the spectrum of PAN (Stephens, 1964) are given for comparison. The absorptivities of the two materials appear quite comparable, suggesting further that the unknown product is PBzN.

Ultraviolet Spectrum. The ultraviolet spectrum of the product (hexane solution) showed major absorptions at 233 millimicrons (ϵ_{max}, 1.7×10^4) and 276 millimicrons (ϵ_{max}, 1.2×10^3) and 284 millimicrons (ϵ_{max}, 9.2×10^2) where the absorption coefficients are given in the units 1 mole^{-1}cm^{-1}. This spectrum is similar to the spectrum of benzoyl peroxide (isooctane solution) (Selected Ultraviolet Spectral Data, 1960): 232 millimicrons (ϵ_{max}, 2.8×10^4); 275 millimicrons (ϵ_{max}, 2.1×10^3); and 282 millimicrons (ϵ_{max}, 1.6×10^3). The intensity difference between the two spectra is possibly due to the difference in the number of rings involved.

Table V. Infrared Spectrum of Product of Benzaldehyde-O_3-NO_2 Reaction and That of Benzoyl Nitrate[a]

Product λ (Microns)[b]	Benzoyl Nitrate λ (Microns)	Product λ (Microns)[b]	Benzoyl Nitrate λ (Microns)
3.27 (w)	3.28 (w)	8.17 (vs)	8.20 (vs)
3.89 (vw)		8.47 (m)	8.49 (m)
5.10 (vw)		8.55 (sh,m)	
5.23 (vw)		9.65 (w)	9.70 (m)
5.54 (s)	5.62 (s)	10.13 (vs)	9.96 (vs)
5.75 (vs)	5.78 (vs)	12.0 (w)	11.3 (br,w)
6.23 (w)	6.22 (w)	12.67 (vs)	12.72 (vs)
6.77 (w)		13.4 (w)	
6.90 (m)	6.86 (w)	13.5 (w)	
7.65 (vs)	7.61 (w)	14.4 (br,m)	14.18 (s)
8.07 (sh,m)	8.07 (sh,m)		

[a] Spectra were taken at a concentration of 2.0 p.p.m. in 760 mm. of Hg N_2 at path length of 120 meters.

[b] Intensity estimations are: vs-very strong; s-strong; m-medium; w-weak; and vw-very weak; sh indicates that the band is a shoulder on another peak and br indicates a broad peak.

Table VI. Infrared Absorptivities of Product from Benzaldehyde-NO_2-O_3 Reaction[a] and Peroxyacetyl Nitrate[b]

Product		PAN	
λ (Microns)	a × 10^4 (p.p.m.$^{-1}$ meter^{-1})[c]	λ (Microns)	a × 10^4 (p.p.m.$^{-1}$ meter^{-1})
5.54	6.9	5.44	10.0
5.75	22.8	5.76	23.6
7.65	8.8	7.68	11.2
8.17	15.6	8.60	14.3
10.13	17.8	—	—
12.67	9.5	12.6	10.1

[a] Spectra were taken in 760 mm. of Hg N_2 at 26° over concentration range 0.3 to 2.0 p.p.m. at path length of 120 meters.
[b] Stephens (1964).
[c] Absorptivities were calculated assuming the molecular weight as 183 grams per mole (mol. wt. of PBzN).

The major ultraviolet absorptions are therefore consistent with the peroxybenzoyl group of PBzN.

Three broad absorptions were noted at 329 millimicrons (ϵ_{max}, 8.6), 340 millimicrons (ϵ_{max}, 7.9), and 352 millimicrons (ϵ_{max}, 7.2). These absorptions increased with increased decomposition of the unknown product and are, therefore, attributed to decomposition products. Nitroaromatics, unsaturated carbonyl compounds, and nitrites are possible decomposition products consistent with these near ultraviolet absorptions.

Mass Spectrum. The mass spectrum of the unknown product was determined with a Bendix Model 12 Time-of-Flight mass spectrometer at an ionizing voltage of 70 volts. Major peaks were observed at mass/charge ratios of 28, 30, 44, 46, 77, and 105 corresponding to CO^+, NO^+, CO_2^+, NO_2^+, $C_6H_5^+$, and $C_6H_5CO^+$, respectively. These peaks are consistent with the expected pattern for PBzN by analogy with the mass spectrum of PAN (Stephens, Darley, *et al.*, 1961). Reduction of the ionizing voltage to 20 volts revealed a peak at a mass/charge ratio of 183. This value would correspond to the parent ion peak of PBzN.

NMR Spectrum. The NMR spectrum of the unknown product was determined in carbon tetrachloride solution with a Varian A-60 spectrometer using tetramethylsilane (TMS) as an internal reference. The spectrum indicated only aromatic protons were present except for those of TMS. The spectrum showed two complex sets of resonance lines, centered at δ-values of 8.05 and 7.63 p.p.m. downfield from the TMS peak. For comparison, the NMR spectrum of ethyl benzoate in carbon tetrachloride was determined. This spectrum also displayed two complex sets of resonance lines, which were centered at δ-values of 8.05 and 7.45 p.p.m. downfield from the TMS peak. The spectra indicate that the benzoyl group is present in the product molecule since the chemical shift of the ortho protons (the more downfield multiplet) is identical in both spectra. The differences in the chemical shift of the meta and para protons of the product relative to ethyl benzoate could be attributed to partial deshielding of the meta protons in the product by the nitro-group of PBzN.

Titration. Nicksic, Harkins, *et al.* (1967) showed that peroxyacetyl nitrate (PAN) reacts quantitatively with NaOH in methanol-water mixtures according to the equation:

$$\text{PAN} \xrightarrow[\text{CH}_3\text{OH—H}_2\text{O}]{\text{NaOH}} \text{methyl acetate}$$

where 1 mole of NaOH reacts per mole of PAN. By analogy, PBzN should react to form an equimolar amount of methyl benzoate. The reaction of the unknown product, in methanol-water solution, with NaOH was studied in two experiments. In the first, titration of 65.5 mg. of the product (0.358 mmole as PBzN) in 10 cc. of methanol required 0.370 mmole of NaOH. In the second experiment, 6.53 mg. (0.0357 mmole as PBzN) of the product, in 10 cc. of methanol, was treated with a slight excess of NaOH and the resulting solution diluted to 100 cc. with methanol. The ultraviolet spectrum of the solution indicated the presence of methyl benzoate at a concentration of $3.65 \times 10^{-4}M$, by comparison with an authentic methyl benzoate sample at a similar concentration in methanol. Therefore, 0.0368 mmole of methyl benzoate was formed from 0.0358 mmole (as PBzN) of the product. The results of the two experiments indicate that 1 mole (as PBzN) of the product reacts with 1 mole of NaOH in the presence of methanol to form 1 mole of methyl benzoate. These results indicate the chemical similarity between PAN and the unknown product and clearly establish the presence of a benzoyl group in the product structure.

From the various observations, the unknown product is identified as peroxybenzoyl nitrate.

Peroxybenzoyl Nitrate

Chromatographic Analysis of PBzN. To determine the eye irritation potential of PBzN and to demonstrate its presence or absence in the smog chamber photooxidations of benzylic hydrocarbons and aromatic olefins, a chromatographic method was developed to measure low concentrations of PBzN.

The electron-capture detector was a logical choice for the detection system since PBzN should, like PAN, have a high electron affinity. Because PBzN is unstable and will decompose or adsorb on surfaces, quantitative sampling was a major problem. High temperature chromatography was impossible because PBzN decomposed extensively about 80°. At room temperature, the high molecular weight and high polarity of PBzN led to long retention times on even very short nonpolar columns. However, a 10-inch × $^1/_8$-inch I.D. glass column packed with 3.8% SE30 on 80- to 100-mesh Diatoport S was found to separate PBzN at 50° with a retention time of 8 minutes and a minimum of decomposition (estimated not to exceed 10%). A large gas sample size and the maximum pulse interval of the electron capture detector were used to increase the sensitivity of the method. The chamber was sampled with a 20-cc. glass syringe to minimize adsorption losses. Controlled experiments indicated that at most a few per cent was lost in the syringe during sampling.

The resolution of a short column using a large sample is not good, but this was the best compromise available at the time. Efforts to further refine the method are continuing.

A quantitative calibration of PBzN was accomplished by liquid injection of measured volumes of known dilutions of purified PBzN in hexane. The minimum detectable concentration of PBzN with this system is 2 p.p.b.

PBzN Formation in Smog Chamber Reactions. The chromatographic method for PBzN was used to follow irradiations of 2.0 p.p.m. of several monoalkylbenzenes and an aromatic olefin with 1.0 p.p.m. of nitric oxide. In these irradiations, a number of unidentified peaks appeared which in some cases interfered with the determination of PBzN.

In the irradiation of β-methylstyrene, PBzN was formed after the nitrogen dioxide peak and built up to a concentration of 0.4 p.p.m. in 6 hours. In the irradiation of *n*-propylbenzene, PBzN was formed after the nitrogen dioxide peak and built up to a final concentration of 0.023 p.p.m. No measurable PBzN was formed from the irradiation of isopropylbenzene. The four butylbenzenes were irradiated with the following results: *n*-butylbenzene yielded 0.015 p.p.m. of PBzN, isobutylbenzene yielded 0.018 p.p.m., *sec*-butylbenzene yielded no measurable PBzN but nearby peaks interfered with the determination, and *tert*-butylbenzene yielded no measurable PBzN. Thus the benzylic hydrocarbons of high eye irritation reactivity (*n*-propylbenzene, *n*-butylbenzene, and isobutylbenzene) yielded 0.015 to 0.023 p.p.m. of PBzN and the nonbenzylic monoalkylbenzenes of low eye irritation reactivity (isopropylbenzene, *sec*-butylbenzene, and *tert*-butylbenzene) yielded no measurable PBzN. The severely irritating β-methylstyrene produced 0.40 p.p.m. of PBzN. In the irradiations of the benzylic hydrocarbons toluene and ethylbenzene, a number of large unresolved peaks are present which interfere with the determination of PBzN. It is estimated that at least 0.015 p.p.m. of PBzN is present in the toluene and ethylbenzene systems. Work is continuing to improve the resolution and sensitivity of the method so that a more quantitative determination of PBzN in toluene and ethylbenzene photooxidations can be made.

Eye Irritation Potential of PBzN. The eye irritation potential of PBzN was measured in a series of experiments in which PBzN was prepared in the smog chamber in various concentrations by the benzaldehyde-ozone-nitrogen dioxide reaction. The PBzN concentration was measured with the gas chromatographic method while simultaneously conducting an eye test. The results are shown in Figure 6 along with a calibration for the eye irritation potential of formaldehyde. PBzN is 200 times more potent as a lachrymator than formaldehyde. Only 0.01 or 0.02 p.p.m. of PBzN are required to produce light to severe eye irritation.

Stability of PBzN. The photolytic stability of PBzN in the smog chamber was determined by adding measured volumes of purified PBzN in hexane and irradiating at a light intensity of 0.4 min.$^{-1}$. PBzN vaporized slowly in the smog chamber because of its low volatility. Hence, it is possible that vaporization, adsorption, and heterogeneous decomposition, as well as photolytic decomposition were occurring simultaneously. In this system, the average half-life of a number of samples of PBzN was 3 hours. As PBzN disappeared, a number of unidentified decomposition products appeared which respond in the electron capture detector. As the PBzN concentration decreased, eye irritation also decreased indicating that the decomposition products are not significant eye irritants.

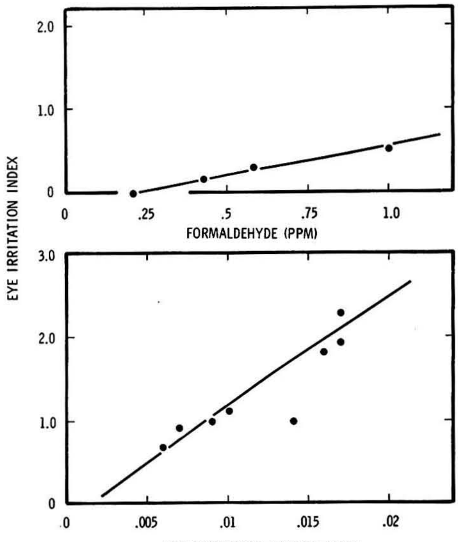

Figure 6. Eye irritation of peroxybenzoyl nitrate and formaldehyde

Importance of PBzN. The finding of a very minor product having such high lachrymatory powers raises the question of its contribution to eye irritation in smog and the possibility of other highly potent minor products.

Benzylic hydrocarbons are the most common aromatics in gasoline, and as a result also in auto exhaust, and are common solvents. Hence it is probable that PBzN is formed in the atmosphere under smoggy conditions. Only the development of very sensitive analytical techniques and careful research will answer the question of the relative contribution of PBzN to the eye irritation observed in photochemical smog.

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C_2–C_5 Hydrocarbons in the Los Angeles Atmosphere

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■ A joint study of the relationships among different pollutants on days of differing smog intensity was carried out in Los Angeles in the fall of 1967. Part of the study involved gas chromatographic analysis for light hydrocarbons (ethane to isopentane) at two sites. Almost 700 samples were run during 46 days. Averages are presented for the hourly samples subdivided into groups of high or low oxidant development. The concentrations of the light alkanes, especially propane, were too high to be ascribed to auto exhaust. The development of oxidant at various locations during the morning occurs at about the same rate, although concentrations of primary pollutants differ several-fold. The ratios of acetylene and light olefins to oxides of nitrogen are higher than the average in exhaust generated in a test cycle on a dynamometer.

Since the early application of gas chromatography to measurement of atmospheric hydrocarbons by Eggertsen and Nelson (1958), there have been several studies of Los Angeles air by this means. Altshuller and coworkers surveyed Los Angeles air at intervals from 1961 on, the latest report being that of Lonneman, Bellar, *et al.* (1967). Neligan (1962) reported analyses for morning air in Central Los Angeles. After preliminary work in 1966, a joint study was made in the fall of 1967. Participants were from the National Center for Air Pollution Control, the California Air Resources Board Laboratory, and the Los Angeles County Air Pollution Control District (APCD). The object was to define more closely the actual concentrations of oxides of nitrogen and various hydrocarbons in the Los Angeles atmosphere on a number of days of differing smog intensity. This report concerns part of the contribution of the California Air Resources Board Laboratory to this study.

Experimental

An automatic timed sequential air sampler was designed to fill three Tedlar bags of roughly 50-liter capacity during successive 1-hour sampling periods. A neoprene diaphragm pump supplied excess sample. The correct fill rate was achieved by a fixed throttling orifice on a dump line. Solenoid valves were actuated by timing circuitry to fill bags from 0500 to 1700 in the proper order for exactly 1 hour each, then to recycle. Two such samplers were constructed. They were located at the Los Angeles APCD air monitoring sites in downtown Los Angeles (DOLA) and at Azusa in the San Gabriel Valley 20 miles further east, as shown in Figure 1. (During the fall the prevailing mid-day winds are from the central Los Angeles basin approximately toward the San Gabriel Valley.) Couriers exchanged the Tedlar bags as needed and returned the samples to the analysts. Normally only the last daily sample was held overnight, during which a loss of less than 5% was experienced in the components of interest (as shown by repeat analyses on the same sample). Samples were collected on 46 weekdays. About a third of the time all 12 hourly samples were analyzed at one or the other site. The average number of samples per day per site was seven.

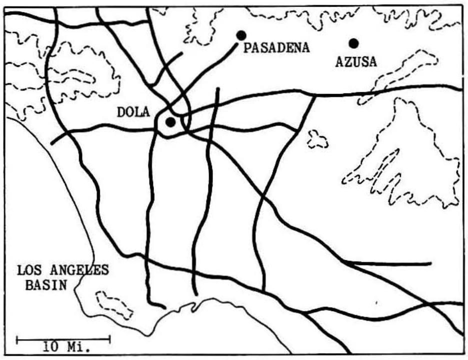

Figure 1. Map of Los Angeles basin showing hills to north and east, ocean to west, and freeway network

Atmospheric samples were chromatographed using a 12-foot, $^1/_4$-inch o.d. column packed with 12% didecylphthalate on 42- to 60-mesh firebrick. The column effluent was split and directed into two flame ionization detectors (Varian Model 600). The effluent to one of the detectors was first passed through a mercuric perchlorate subtractive column which removed olefinic and aromatic hydrocarbons (Ferrin, Chase *et al.*, 1961). Resulting peak areas were displayed on a dual channel Westronics 1-mv. recorder equipped with Disc Integrators. In consequence of this split and treatment, one recorder channel displayed total hydrocarbons, while the other channel showed paraffins only.

To obtain peak areas of measurable magnitude with atmospheric hydrocarbons, 300-ml. samples were analyzed, utilizing a freeze-out concentration technique (Feldstein and Balestrieri, 1965). Compounds C_1 through C_5 were individually separated, while heavier compounds were recorded without further separation, using a backflush valving apparatus and procedure (Mayrsohn and O'Neal, 1964). Calibration mixtures in helium were repeatable to approximately 2 p.p.b.

Atmospheric samples were repeatable generally to better than 10 p.p.b. and are reported here to 1 p.p.b.

Results and Discussion

Nearly 700 samples were analyzed for hydrocarbons from ethane through isopentane. All the data have been averaged hourly for each site and are given in Table I. Subaverages were also taken for sampled days on which the maximum oxidant levels were above 0.30 p.p.m. at either station (HiOx), and for days when neither station reached an oxidant maximum as high as 0.20 p.p.m. (LoOx). Each of these groups constituted roughly one-third of all days sampled. Some of the other contaminant concentrations monitored routinely were segregated into subgroups and averaged in the same way. The figures are derived from these subaverages so that all the hourly points in a given curve correspond to the same set of days.

Figures 2 and 3 show patterns during the day for carbon monoxide and oxides of nitrogen, respectively, averaged for the two stations on days of high oxidant (HiOx) or low oxidant (LoOx) maxima. Both contaminants show pronounced morning maxima followed by declines as dilution and ventilation occur, then increases in the late afternoon. During the morning hours the prevailing winds are weak (about 3 miles per hour) and are shifting from easterly to southwesterly. The shoulders on some curves may reflect a return of polluted air over the same area it traversed earlier. By noon the wind is from the southwest about 6 miles per hour and increasing.

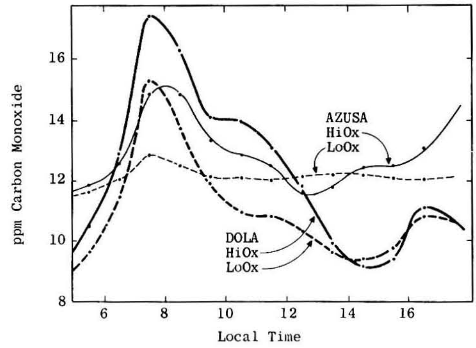

Figure 2. Diurnal patterns for carbon monoxide averaged for days of high oxidant or low oxidant maxima at two sites, fall 1967

The patterns for acetylene are shown in Figure 4. Acetylene is an important constituent of automobile exhaust and is not emitted to a significant degree from any other known large source. It is also unreactive in photochemical oxidation (except for oxidant production at low oxides of nitrogen concentrations) (Altshuller, Kopczynski, *et al.*, 1968) and serves as a tracer for auto exhaust. The patterns for acetylene are similar to those for carbon monoxide and nitrogen oxides. The secondary maxima on the Azusa curves around 1400 are at about the right time to represent the arrival of air from the

Table I. Average Atmospheric Light Hydrocarbon Concentrations, Fall 1967

Local Time	Days	Ethane	Ethylene	Acetylene	Propane	Propylene	Isobutane	*n*-Butane	Butylenes	Isopentane
		Component, P.P.B. Carbon[a]								
				Downtown Los Angeles (DOLA)						
0500	27	140	31	77	113	25	53	176	32	177
0600	28	140	49	112	113	36	61	200	34	224
0700	28	151	122	234	125	64	74	300	56	335
0800	31	145	102	212	126	54	75	304	49	346
0900	15	107	63	141	98	32	63	209	28	249
1000	33	126	67	152	118	38	64	260	34	303
1100	12	94	39	106	80	25	48	180	21	200
1200	32	106	39	101	108	20	63	200	15	199
1300	16	76	20	68	78	13	44	149	14	162
1400	38	94	26	74	97	17	57	156	19	155
1500	16	90	26	79	101	16	50	132	20	144
1600	34	75	36	95	81	24	46	139	21	141
				East San Gabriel Valley (Azusa)						
0500	32	143	29	60	87	13	36	101	14	104
0600	33	128	17	65	76	15	31	98	12	103
0700	30	180	30	103	102	24	41	136	18	144
0800	32	118	37	101	84	20	44	149	18	160
0900	18	93	31	79	65	15	36	114	15	114
1000	32	86	24	69	66	19	40	132	15	136
1100	18	90	21	57	62	11	37	107	10	101
1200	30	89	15	50	58	10	40	98	9	93
1300	16	111	16	66	67	18	46	121	17	111
1400	42	97	18	64	75	17	50	121	18	117
1500	16	92	20	65	75	15	81	175	15	125
1600	37	79	21	58	76	14	41	122	14	123

[a] Parts per billion parts air, as carbon.

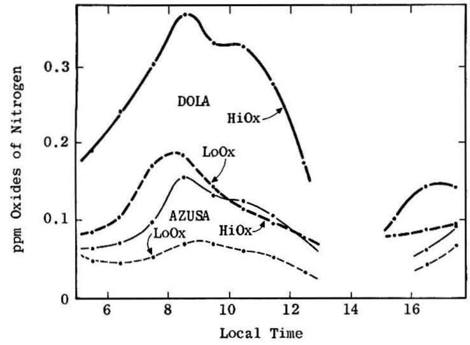

Figure 3. Diurnal patterns for oxides of nitrogen averaged for days of high oxidant or low oxidant maxima at two sites, fall 1967

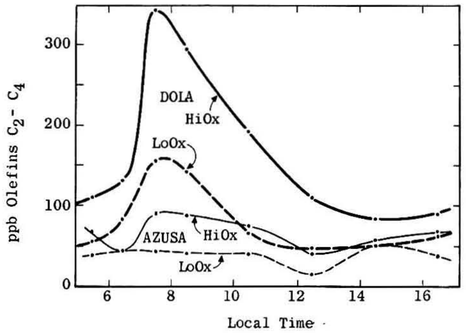

Figure 5. Diurnal patterns for C_2–C_4 olefins averaged for days of high oxidant or low oxidant maxima at two sites, fall 1967

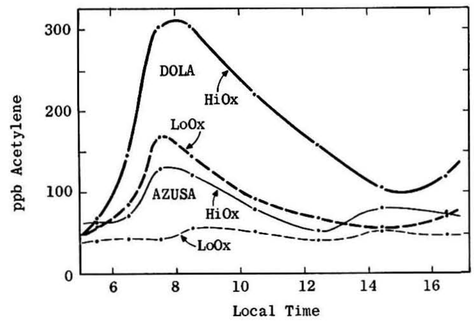

Figure 4. Diurnal patterns for acetylene averaged for days of high oxidant or low oxidant maxima at two sites, fall 1967

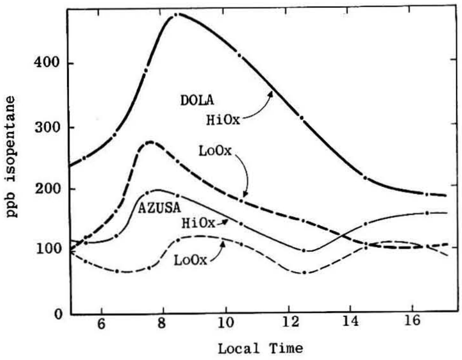

Figure 6. Diurnal patterns for isopentane averaged for days of high oxidant or low oxidant maxima at two sites, fall 1967

central basin near DOLA. For display, the olefins from ethylene through the butylenes have been combined in Figure 5. The patterns again are very similar to those for acetylene. This indicates either that their decrease through chemical reaction is small compared to dilution effects, or that they are replenished continuously through the day by further emission.

The alkanes are present in concentrations too high relative to acetylene to be accounted for solely as exhaust components. In Figure 6 isopentane patterns are not unlike those for acetylene, but the decline is slower and in some cases the maximum occurs later. This behavior is clearer in Figure 7, where the patterns for DOLA on high oxidant days show that ethane, propane, and isobutane not only reach the morning maximum later than acetylene, but also decline more slowly and reach a second maximum or shoulder early in the afternoon. These alkanes could arise from natural gas, gasoline evaporation, or crude-oil vapor losses (Stephens and Burleson, 1967). The curves in Figure 7 are consistent in timing with gasoline evaporation as a source if the first maxima are associated with the losses occurring during and just after the automobile warm-up during the morning commuting peak, and the second maxima with the peak daily ambient temperature. The ethane and propane concentrations, however, are relatively higher than expected for typical gasoline composition (for example, Sanders and Maynard, 1968).

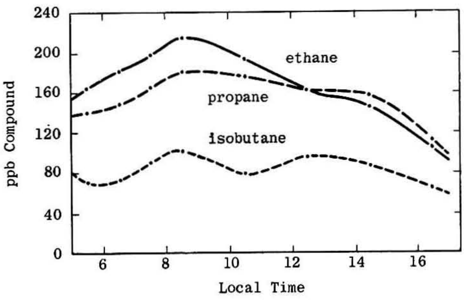

Figure 7. Diurnal patterns for three alkanes averaged for days of high oxidant maxima at DOLA, fall 1967

The oxidant patterns are shown in Figure 8. Although the levels of primary pollutants shown in Figures 2 through 6 are generally much lower at Azusa than at DOLA until afternoon, the oxidant values are very nearly equal hour by hour, during the same period. The declines from the oxidant maxima for the two locations can be related to dilution by cleaner air blowing onshore; the inland Azusa site receives this benefit on the average about 2 hours later. The average oxidant

Table II. Ratios of Acetylene and Light Olefins to Oxides of Nitrogen in the Los Angeles Atmosphere[a]

Local Time	C_2H_2/NO_x				$(C_2—C_4 \text{ Olefins})/NO_x$			
	DOLA		Azusa		DOLA		Azusa	
	HiOx	LoOx	HiOx	LoOx	HiOx	LoOx	HiOx	LoOx
0500	0.28	0.56	0.92	0.93	0.45	0.51	0.94	0.87
0600	0.48	0.49	0.72	0.83	0.43	0.49	0.46	0.83
0700	0.82	0.91	0.84	0.62	0.93	0.84	0.57	0.64
0800	0.91	1.02	0.93	0.83	0.89	1.00	0.66	0.58
. . .								
1000	0.80	0.92	0.76	0.98	0.69	0.67	0.73	0.77
. . .								
1400	1.01	0.69			0.81	0.62		
. . .								
1600	0.85	0.73	1.14	0.72	0.64	0.64	1.05	0.55

[a] Averaged for sampled days of high oxidant or low oxidant, fall 1967.

patterns for other stations not shown in Figure 8 likewise reach maxima at times depending on their location, but are also closely similar during the late morning hours. From this it appears that oxidant develops at least partly by way of a process which is not related simply to the quantities of primary pollutants present.

In a recent survey of 216 Los Angeles automobiles (Bonamassa, Gordon, *et al.*, 1968) for each test the exhaust was collected in a large plastic bag during the California test driving cycle. The average composition for all cars gave a ratio for acetylene/nitric oxide of 0.19 and for olefins (C_2-C_4)/nitric oxide of 0.31. The atmospheric ratios averaged either for days of high or of low oxidant were never as low as these. The minimum acetylene-to-NO ratio was 0.28, but most values ranged from 0.5 to 1.0; likewise the minimum olefin-to-NO ratio was 0.43, others ranging up to 1.0. These ratios are given in Table II. After 11:00 a.m., coincident analyses are too sparse to be very useful. The discrepancy with the automobile survey suggests that the California cycle exhaust may be higher in nitric oxide than the average exhaust produced in the streets. Work described by Hass, Sweeney, *et al.* (1966) indicated the cycle to result in about one-third higher nitrogen oxide concentrations than a representative Los Angeles road traffic route. The improvement of the test cycle has been under study (Hass, Bonamassa, *et al.*, 1967).

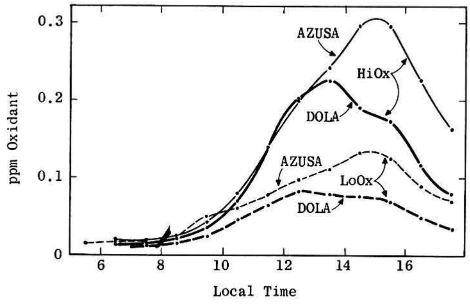

Figure 8. Diurnal patterns for oxidant averaged for days of high oxidant or low oxidant maxima at two sites, fall 1967

Conclusions

There are three findings of interest from this fall 1967 atmospheric survey. Light paraffins, especially propane, are found in anomalously high concentrations. Their source (possibly one of those suggested by Stephens and Burleson, 1967) has not been pinpointed. The average morning concentrations of oxidant at various locations are closely similar, hour by hour, in spite of large differences in levels of primary pollutants. The ratios of some exhaust hydrocarbons to oxides of nitrogen observed in the atmosphere are not in good agreement with those found in a large Los Angeles automobile exhaust survey using the California test cycle.

Acknowledgment

Frank Bonamassa and T. J. Elias participated in the planning and supervision of the air sampling project.

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BOOKSHELF

New book restores and advances hydrology as a unified science

Principles of Hydrology. By R. C. Ward. 403 pages. McGraw-Hill Publishing Co., Ltd., New York, N.Y. 1967. $11.00, hard cover. *Raymond L. Nace is Research Hydrologist, Water Resources Division, U.S. Geological Survey, Washington, D.C. 20242.*

By Raymond L. Nace

Advancement of the science of hydrology and application of its principles to practical problems have long been retarded by lack of a coherent portrayal of hydrological concepts as a unified science. Hydraulics, a branch of physics, is one of the means for testing and applying hydrological concepts. Hydraulic engineering includes the technology of water management. Most textbooks on hydrology deal extensively with fluid mechanics and are aimed largely at an engineering audience. In effect, these books treat hydrology as a branch of civil engineering, and, thus, hydrology as a science disappears in the forest of water technology.

Ward's book is a refreshing departure from the traditional parade of differential and integral equations. He starts with the basic fact, clearly expounded a generation ago by O. E. Meinzer, that the hydrological cycle is the central concept of hydrology. He builds his statement of principles on this concept, describing each of the principal processes in the cycle and summarizing the occurrence of water in each phase of the environment. For each phenomenon, the book includes information about some of the basic instruments for measurements and standard methods for analysis of data.

Modern works on hydrology generally have dual or multiple authorship. Ward is unique as a sole author, and his book is unique in its straightforward, systematic presentation of hydrological concepts. As might be expected in a first edition, the publication has some imbalances and not all sections are completely up to date. Nevertheless, as a treatise on the basic concepts of hydrology, this book has only three significant shortcomings. The first concerns the world ocean and solar energy; the second, the amounts of water that participate in the several phases of the hydrological cycle; and the third, chemical hydrology.

Ward recognizes the large role of the ocean in the hydrological cycle, but he makes the surprising statement: "For all that, the role of the oceans is peripheral to a study of the hydrological cycle which has been shown to be largely concerned with the disposition of water falling on the land surface . . . ."

His diagrammatic portrayal of the cycle (fig. 1.1) erroneously relegates the ocean to a negligible function. The value of the book would be greatly increased by a chapter on the energy balance of the oceans and the interaction between oceans and the atmosphere.

The hydrological cycle cannot be well understood without recognition that its operation depends on a huge amount of energy derived almost entirely from the sun. The world ocean is an enormous heat reservoir whose release of heat and vapor is the central phenomenon of the water cycle. The system earth-ocean-atmosphere is a giant heat engine, two of whose products are weather and fresh water in the land areas. Ward's approach obscures the essential fact that the water cycle is a global phenomenon, despite human preoccupation with the continental occurrence and behavior of water.

The volume's second important deficiency is the author's failure to deal, except in passing, with the amounts of water that take part in various phases of the water cycle. Natural groundwater reservoirs, for example, probably contain two to three thousand times the amount of water in river channels at any given time. Data of that nature alone can give perspective in a portrayal of the cycle. In view of the proliferation of water quality problems, chemical hydrology deserves more thorough treatment.

Concerning lesser phenomena, Ward occasionally lapses into inaccuracy. For example, he seems to assume (p. 286–287) that the Ghyben-Herzberg theory of a static lens of fresh groundwater floating on heavier salty groundwater accurately explains the relation between salt water and fresh in coastal areas. Actually, the relations are dynamic and the floating-lens theory is only an elementary starting point for explanation. Considering the many thousands of miles of the world's coastlines, these relations have prime practical importance.

Finally, Ward's treatment of artesian groundwater systems is barely adequate and he does not emphasize sufficiently that simple pipe hydraulics alone does not explain the discharge of water from artesian aquifers through wells. O. E. Meinzer's recognition a generation ago of the principle of compressibility and elasticity of artesian aquifers is one of the few fundamental discoveries in groundwater hydrology during the present century.

Aside from a few such deficiencies, the book is admirable. The chapters on precipitation, evaporation, and soil moisture are outstanding. Ward's style of writing is clear and reasonably concise. The book is well illustrated with many excellent graphs and line drawings. A principal contribution is the extensive reference lists for each chapter, which give an entrée to much of the recent important world literature.

This book should be excellent as a refresher for practicing hydrologists, as a college textbook, and as a source book. It also will have considerable value for the educated reader who wishes to understand water.

Eutrophication reference source made available

Eutrophication—A Review. A report to the California State Water Quality Control Board. By Kenton M. Stewart and Gerard A. Rohlich. Publication No. 34. iii + 188 pages. State of California, The Resources Agency, State Water Quality Control Board, 2115 J. St., Sacramento, Calif. 95816. 1967. $2.95, paper. *Ray T. Oglesby is Associate Professor of Aquatic Sciences, Department of Conservation, Cornell University, Ithaca, N.Y. 14850.*

By Ray T. Oglesby

Scientists and technologists concerned with the problem of eutrophication will find this publication a convenient and much needed reference source. However, those expecting a lucid analysis of the literature, a review of the basic principles, or a comprehensive discussion of research needs will be disappointed.

"Eutrophication—A Review" is essentially an annotated bibliography divided into subject matter categories. The authors provide some commentaries on specific publications. But, with few exceptions, these observations add little to either the readability or understanding of the subject. Generally, conclusions presented by the writers of the papers under review are accepted without critical comment.

Where differences of opinion or conflicting data occur in the various articles, no attempt is made to resolve or explain them even though each section has an introductory statement where this could appropriately be done. Furthermore, the quality of the abstracting itself is somewhat spotty. In one case familiar to me, the main purpose and conclusions of an interesting research project were ignored and the entire abstract devoted to describing a minor part of the study.

Drs. Stewart and Rohlich appropriately commence their review by considering definitions of the term *eutrophication*. Their subsequent organization of material is adequate but, unfortunately, overlaps substantially in some cases. For example, a review of the eutrophication problem and associated research on the Madison Lakes extends over several sections. A reader not previously familiar with this subject would be hard put to obtain a cohesive picture.

One of the virtues of "Eutrophication—A Review" is its broad geographical coverage. This broad view not only provides the reader with a variety of climatological, cultural, and geological situations in which the enrichment of natural waters occurs, but also gives him an indication of the quality, quantity, and temporal distribution of research on eutrophication. In striving to provide such coverage, trivial articles are sometimes included. However, perhaps even these are worthwhile in opening the eyes of the reader to research needs.

In the case of references concerned with studies on specific lakes, the location, mean depth, and maximum depth are given, providing useful reference points for the reader's orientation. The value of this approach would have been greatly enhanced by the addition of bathymetric maps and of precise geographical positioning of the lakes.

Very few data are presented in the form of figures and tables. This deficiency exemplifies the limited quantitative approach, not only of the present authors, but of the majority of reviewers dealing with this subject.

Probably any publication with as broad a title would have been disappointing to a scientific and engineering community thirsting for new ideas and information on this subject. "Eutrophication—A Review" is no panacea, but it is a useful beginning. I hope that both the current usefulness of this publication and its deficiencies will inspire more scholarly attempts not only to review but to summarize, interpret, and derive hypotheses from information now in this literature. ■

Recommended Guide for the Prediction of the Dispersion of Airborne Effluents. Edited by Maynard Smith. ix + 85 pages. American Society of Mechanical Engineers, 345 E. 47th St., New York, N. Y. 10017. 1968. Members, $3.60; nonmembers, $4.50, paper.

Sponsored by the ASME Committee on Air Pollution Controls, the book aims to provide a review of the important aspects of atmospheric dispersion, with emphasis on ordinary stack emission. Topics covered include meteorological fundamentals; behavior of airborne effluents; calculation of dispersion and deposition; sources of data and experimental methods. ■

Mineral Waste Utilization. Proceedings of the symposium. iv + 154 pages. Special Affairs, IIT Research Institute, P.O. Box 4963, Chicago, Ill. 60680. 1968. $12.50, paper.

Murray A. Schwartz was chairman of this 1st Symposium on Mineral Waste Utilization, cosponsored by the U. S. Bureau of Mines and IIT Research Institute. Papers by industrial, research, and government representatives are included in the report. Topics discussed from both technical and economic viewpoints include mining, processing, and scrap waste problems; solid wastes in the ceramics industry; some effects of metals on aquatic life; special Bureau of Mines projects. ■

Proceedings of the 1st Mid-Atlantic Industrial Waste Conference. 304 pages. University of Delaware, Newark, Del. 19711. 1968. $7.50, paper.

Proceedings of the conference held at the University of Delaware, Nov. 13–15, 1967. The publication presents current thought regarding industrial water and air pollution control. Contents include economics of waste treatment; process management and profitable air pollution control; dispersion as a tool for air pollution control; dispersion control; and other related topics. ■

Glossary of Environmental Sanitation. i + 30 pages. Institute of Sanitation Management, 1710 Drew St., Clearwater, Fla. 33515. 1968. Members $5.00; nonmembers, $10.00, paper.

The book lists and defines more than 800 terms and words basic to the general areas of industrial and institutional sanitation and maintenance and the management and work functions involved, particularly stressing cleaning agents, structural coating, pesticides, and floor coverings. ■

Marine Science Activities of Canada and the Nations of Europe. Survey by the National Council on Marine Resources and Engineering Development. iv + 160 pages. U. S. Government Printing Office, Washington, D. C. 20204. 1968. $.55, paper.

Marine Science Activities of the Nations of Africa. iv + 76 pages. $.35, paper.

Marine Science Activities of the Nations of East Asia. iv + 80 pages. $.35, paper.

Marine Science Activities of the Nations of the Near East and South Asia. iv + 55 pages. $.30, paper.

Marine Science Activities of the Nations of Latin America. iv + 55 pages. $.35, paper.

The 5-volume survey was prepared for policy officials and specialists concerned with developing domestic programs and planning further cooperation with other nations. A brief description of the economic importance of these activities to each country; the scope of marine research; facilities for coordination of ocean activities; and a listing of organizations and officials concerned with marine science programs are included. ■

In-Plant Treatment of Cannery Wastes —A Guide for Cannery Waste Treatment, Utilization, and Disposal. Prepared by Water Resources Engineers, Inc. State Water Resources Control Board. Publication No. 38. 78 pages. State of California—The Resources Agency, Document Section, P.O. Box 20191, Sacramento, Calif. 95820. 1968. $2.25, paper.

The book is broken down into 6 major sections, each dealing with a different aspect of the problem, from an introduction to the canning industry, through waste characterization, waste treatment potential, economics of alternatives, and preliminary design system, to a final summary and conclusion. The report is the result of a cooperative 3-year research project of the State Water Resources Control Board, the National Canners Association, municipal government, and the canning industry. ■

Roughness Characteristics of Natural Channels. By Harry H. Barnes, Jr. U.S. Geological Survey Water Supply Paper 1849. U.S. Government Printing Office, Washington, D.C. 20402. 1968. $2.25, paper.

This technical report contains roughness values and other interpretive information on 50 selected streams in the U.S. Prepared for civil and hydraulic engineers and others concerned with flood control and related problems, the book also contains part of the USGS fingerprint file. This file is a reference slide file showing segments of streams along which the roughness coefficients have been measured, and is used to identify similar roughness in other streams. The Water Resources Division is concerned with channel roughness because of the direct relationship between stream bed channel roughness and channel capacity.

More than 100 photographs are included in the report. The Geological Survey expects the report to be helpful in designing channel improvements and in the prediction of stream heights of future floods of a given discharge.

Microfauna of Biological Filters. By D. Martin. Bulletin 39, University of Newcastle-upon-Tyne, Department of Civil Engineering. 88 pages. Oriel Press, Ltd., 27 Ridley Pl., Newcastle-upon-Tyne, England. 1968. $2.40, paper.

The book was compiled in an attempt to fill the existing gap in literature on the microfauna of waste treatment units. Planned to be used in conjunction with a proposed Water Pollution Research Technical Paper on microfauna, the book is a guide to the majority of animals found in biological filters. Lists of the animals found in filters were compiled from literature and from species identified in the Newcastle University experimental filters. Although the work deals in particular with three types of protozoa, it also discusses rotatoria and nematoda. Illustrations of each species and a bibliography follow the text. ■

Proceedings of the 8th Industrial Water and Wastewater Conference. vi + 146 pages. Lubbock, Tex. 1968. $5.00 ($2.50 to FWPCA members), paper.

Sponsored by the Texas Water Pollution Control Association, Texas State Department of Health, and the City of Lubbock, the conference was held June 6 and 7, 1968. Papers presented at the technical sessions dealt with waste water renovation in agriculture and industry, and included: "Water—Our Most Priceless Resource"; "Economics of Water Pollution Control for Cattle Feedlot Operations"; and "State Agencies' Programs for Industry." ■

Basement Rock Map of the United States, Exclusive of Alaska and Hawaii. 80″ x 52″, 2 sheets. Distribution Section, U.S. Geological Survey, 1200 E. Eads St., Arlington, Va. 22202. $3.00.

Prepared by scientists of the U.S. Geological Survey and the University of Texas, the map summarizes present knowledge of the crystalline crust underlying the 48 states. The map is printed in 9 colors, at a scale of 1″:40 mi., with tones and patterns

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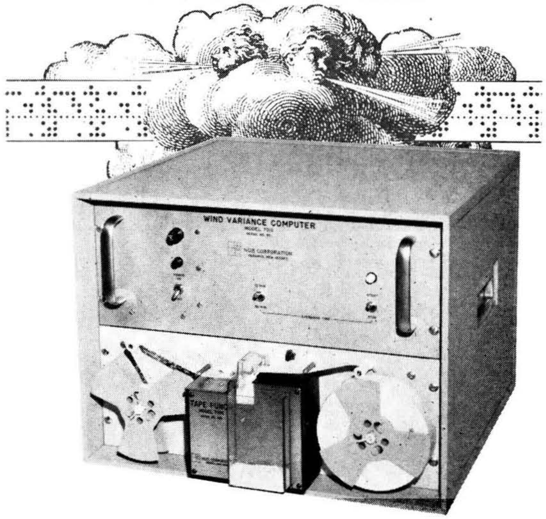

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to distinguish between exposed and concealed basement rocks, and contour lines at 1000-ft. intervals which show the configuration of the surface of concealed basement rocks.

The map should be helpful in the study of the origin and nature of the earth's crust, as well as in the study of earthquakes. ■

Correspondence Course Manual for Water Plant Operators. Class D. 2nd edition. Edited by John H. Austin. 2 volumes. South Carolina Water and Pollution Control Association, Columbia, S.C. 29201. 1968. $8.00, paper.

Designed to prepare water treatment plant operators for the Class D certificate examination, the manual was prepared under supervision of staff at Clemson University. The first of the two volumes contains the course work proper, beginning with an introduction to water supply and waste water disposal. The next chapters cover mathematical, chemical, biological, and physical aspects of the water plant operator's position; the book concludes with basic lab procedures and discussion of water plant installations and water plant operations and maintenance. The second volume contains problems and tests on the course content. ■

Air Pollution Manual. Part II—Control Equipment. x + 150 pages. American Industrial Hygiene Association, 14125 Prevost, Detroit, Mich. 48227. $15.00, hard cover.

The second of a two-volume set on air pollution, this book concerns equipment for control of air pollution sources, and is designed for use by the practicing plant or process engineer. Types of equipment are described; their characteristics, performance, advantages and disadvantages, and applications are described. The final chapter is devoted to disposal of collected material. A brief glossary completes the work. ■

Man and the Quality of His Environment. Western Resources Papers, 1967. Edited by J. Ernest Flack and Margaret C. Shipley. x + 251 pages. University of Colorado Press, Boulder, Colo. 1968. $5.00, paper. ■

NEW PRODUCTS DIGEST

Keeping America beautiful and clean

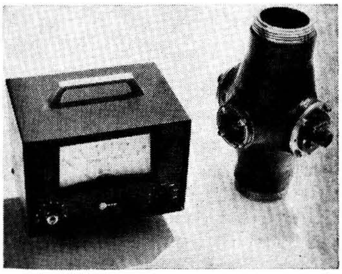
This past summer, Boyd L. Rasmussen, director of the U.S. Department of the Interior's Bureau of Land Management, announced a nationwide cleanup campaign. The symbol for the antilitter movement is Johnny Horizon, described as "a lean, square-jawed outdoorsman . . . the spirit and conscience of every American who loves and respects the land and wants to protect it."

To date, the campaign has been well accepted, especially in the Western states. Cooperation has been offered from outdoors clubs, the Outdoor Writers Assoc., boyscout troops, forestry associations, and private citizens. One group of 750 families cleaned up California's 8-mile-long Imperial Sand Dunes. Industry, too, is cooperating in the Johnny Horizon venture. The Pacific Light and Power Co. purchased quantities of Johnny Horizon litterbags, imprinted the PL&P logo on the back, and distributed them as a public service.

Plans are to expand the campaign even more, through the use of two traveling displays, one for the East and one for the West. Johnny Horizon appeals to classroom groups, industry, civic leaders, and individuals to rally to the theme, "This land is your land, keep it clean." For information and literature, contact George R. Gurr, Coordinator, Johnny Horizon Program, U.S. Dept. of the Interior, Washington, D.C. 20240

Auto Exhaust

Pollution from auto exhaust can be reduced by 15%, according to the manufacturers of the HeadLand Piston Compression Ring. The ring is placed $^1/_{16}$ inch below the piston head to reduce the space into which fuel can escape ignition, and to cut down on unburned fuel emitted with exhaust. Sealed Power Corp. **61**



Turbidity Measurement

The Model 861-B Turbidimeter features stainless steel sensing heads, solid-state electronics, and sealed sensing elements. The manufacturer claims the unit can handle flows to 600 g.p.m. at pressures to 150 p.s.i., and is capable of indicating from 0.01–500 j.t.u. on six reading ranges, with remote control calibrator. Bowser, Inc. **62**

Color Tamer

A machine designed for the elimination and destruction of color from waste water effluent is available. The ESI-FLX color destruction units are sized to treat the waste from one or any number of printing machines, are fully or semiautomatic, and are said

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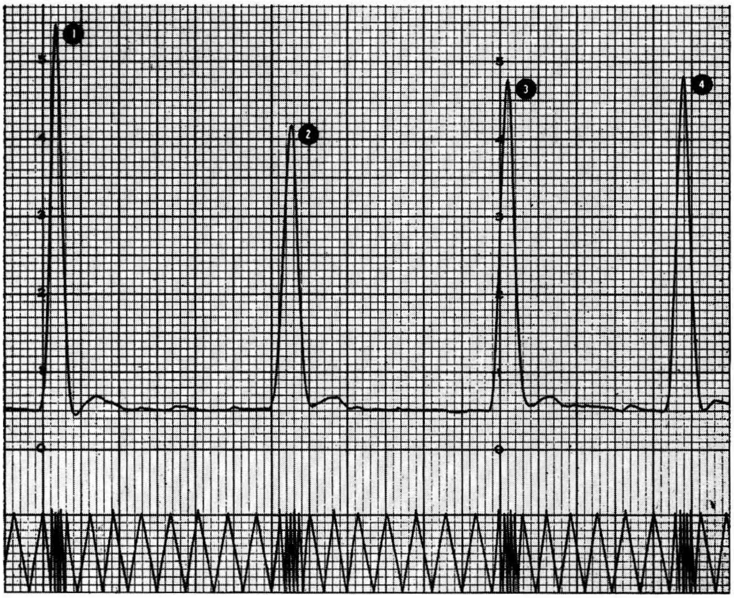
NITROGEN in WATER

or Oxygenated Hydrocarbons



5.6 μl injected

① $Mn(NO_3)_2$ soln. [10 ng N/μl] 56 ng N total — 102% of theoretical
② $Mn(NO_3)_2$ soln. [10 ng N/μl] 56 ng N total — 98% of theoretical
③ $Ni(NO_3)_2$ soln. [10.7 ng N/μl] 59.9 ng N total — 99% of theoretical
④ $Ni(NO_3)_2$ soln. [10.7 ng N/μl] 59.9 ng N total — 97% of theoretical

■ Long established as an ideal specific GLC detector and total constituent analyzer, the Dohrmann Microcoulometric Titrating System now becomes more useful than ever in trace elemental analysis. New methodology now permits determination of total organic or inorganic nitrogen in water or oxygenated hydrocarbons . . . in minutes . . . with a minimum of sample preparation.

This technique consists of pyrolysis of the nitrogen-containing sample to ammonia over a nickel catalyst, specific scrubbing and automatic titration.

The Dohrmann System is modular in concept to provide the flexibility needed for this and a variety of other specific analyses. Sensitivity of one nanogram allows analysis of nitrogen, sulfur and halogen containing compounds down to the 0.1 ppm level. Absolute specificity is achieved by use of interchangeable selective titration cells.

The Dohrmann Nitrogen Analyzer for total nitrogen in water is particularly suited for water quality control, industrial effluent monitoring, and as a replacement for most Kjeldahl determinations. For a detailed description of the technique and instrument specifications, please write for Applications Data File P-2.

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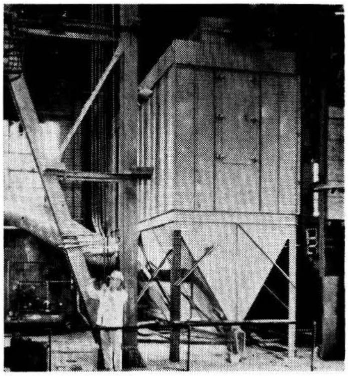
to remove color in a matter of minutes, utilizing the principles of adsorption, absorption, flocculation, and settling. Environmental Services, Inc. **63**



Large Capacity Air Filter

A large capacity fabric-type filter is designed to remove pollutants from the air and eliminate the need for several smaller filter units. By use of a bag cleaning method, the filters are adjustable to individual applications and dust loads, feature modular construction for easy assembly, and are equipped with a solid-state timer for automatic operation. Aerodyne Machinery Corp. **64**

Chromium Waste Treatment

A process for the treatment of chromium waste is available. In this process, waste liquid is pumped from the source into a reaction chamber where proprietary treatment chemicals are added. After mixing, the wastes flow into an integral sedimentation unit where the toxic ion is removed as dense chromate sludge; the clear water is collected in the unit's suspended weir, and returned to the rinses for reuse. The company claims that the system is capable of treating 1000–2000 gallons per hour, without the use of ponds, lagoons, settling tanks, or odorous and corrosive chemicals, and that treated water is suitable for discharge into sewer or streams.
American Can Co. **65**

Alarm Unit

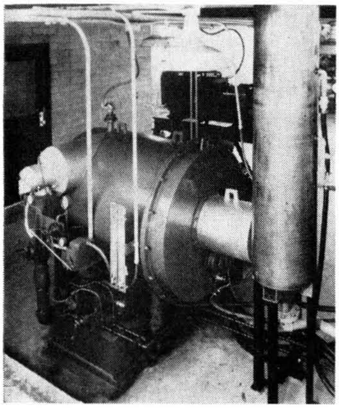
A wind direction alarm unit—which receives its input from a wind direction synchro transmitter—is available for use in air pollution control activities. The company says that the unit is designed for manufacturers who are interested in controlling boiler-blow to a time when the wind would carry particulates and excess smoke from populated areas. Bendix Corp. **66**

Small-Scale Chlorination

The 91-100 Chlorinator, effective for water and waste systems, pools, and industrial applications requiring up to 100 lb. of chlorine per day, is available. The device consists of three separate components—cylinder unit, control unit, and injector—packaged with installation hardware. Wallace & Tiernan, Inc. 67

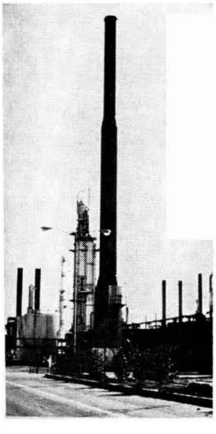
Feed Rate Regulation

The Dearborn Model 750C water treatment controller, which automatically regulates feed rate of chemical treatment, and controls bleed-off of cooling water in recirculating systems, is available. The unit—using solid-state circuitry to maintain the proper balance—continuously monitors the conductivity of water, cycles the feed pump, and operates the bleed-off solenoid valve to maintain the proper ratio of feed versus bleed and makeup. Weighing about 8 lb., the unit measures 8″ x 6″ x 4″, and is designed to be wall mounted or mounted on the cooling tower. W. R. Grace & Co. 68



Industrial Waste Incinerator

A compact furnace, called a cyclonic reactor, is available for the incineration of certain industrial wastes and of primary and secondary sludges generated by smaller sewage plants. Using the waste to be burned as the principal fuel, the furnace features an external burner which heats the combustion chamber wall, producing a cyclonic gas flow. The company claims that the reactor produces complete combustion of sludges and other wet organic waste solids, ensures complete deodorization, and permits only clean combustion gases and fine inert ash to discharge from the reaction zone. Dorr-Oliver, Inc. 69



NEW LITERATURE DIGEST

Corrosion prevention. Three booklets describing methods of corrosion control are available. "Corrosion, Cathodic Protection, and Common Sense" is a 4-page paper outlining categories of industrial corrosion problems and protection available. An 8-page booklet, "Fundamentals of Catholic Protection," discusses electrical methods of preventing corrosion, particularly the galvanic and rectifier type of cathodic protection, and their applications. "Cathodic Protection Systems for Corrosion Control" presents the company's services in this area, illustrated with diagrams, charts, and drawings. Harco Corp. **91**

Water clarification. A mixture of polyelectrolyte and specially processed bentonite, Coagulant Aid 18 is said to be effective in low pH ranges for industrial water clarification; at high alkalinities and temperatures; in cold, low turbidity water clarification; and in waters subject to sudden changes in pH and turbidity. Bulletin 12-29 lists product specifications, storage, packaging, feed, and patent data about the mixture. Calgon Corp. **92**

Fluid measurement. Bulletin DS-5930 describes a nonpenetration liquid level system designed to measure fluid by sonic echo. The Brooks-Leveldata Series 5930 mounts on the external wall of the vessel, requiring no tank penetration or internal probing. The company maintains that the system is suitable for measuring high viscous materials, as well as explosive or toxic fluids. A noncontact ultrasonic system that measures surface level of liquids, slurries, powders, and ores in storage containers such as vessels, bins, tanks, and silos, Brooks Leveldata System 5900 is described in Bulletin DS-5900. The 6-page book presents information on principle of operation, design features, system specifications, application, optional equipment, and ordering procedures. Emerson Electric Co. **93**

Water quality monitoring. Bulletin I110 describes an integrated water quality data aquisition system designed for the Metropolitan Sanitary District of Greater Chicago. The system includes 71 miles of inland waterways, with 11 monitoring stations, three secondary receiving stations—located at major sewage treatment plants—and a central receiving station. The 6-page folder also includes diagrams illustrating the operation of the two separate telemetering systems. American Chain & Cable Co., Inc. **94**

Nitrate determination. The Ionalyzer Nitrate Ion Electrode facilitates direct determination of water soluble nitrate in soil, according to Applications Bulletin #6. The bulletin describes the preparation of soil samples and standardizing solutions, explaining the calibration of the company's Specific Ion Meter, which gives readings in parts per million nitrate as nitrogen. The company claims that field measurements accurate to ±2% can be made with the electrode, over a pH range 2–12. Orion Research, Inc. **95**

Purification equipment. Catalog G-3 describes a line of filter systems, pumps, filter chambers, and systems for the removal of organic and base metal impurities. The 6-page folder identifies and discusses each piece of equipment, listing specifications, and the proper literature which describes the item in detail. Thermersion heaters, skimmers, dispersion units, and accessories are included in the catalog. Sethco Manufacturing Corp. **96**

Heaters. A 24-page publication describes a full line of packaged water heaters and heat exchange equipment for industrial, institutional, and commercial purposes. Included in Bulletin 1234-G are types of equipment ranging from a minimum storage heater to packaged units using any energy or fuel source, as well as the company's more recent developments—packaged waste water heat reclaimers and removable blade immersion elements. The book also contains selection and sizing charts for each type of heater and diagrams dipicting operating principles. Patterson-Kelley Co., Inc. **97**

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76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
106	107	108	109	110	111	112	113	114	115	116	117	118	119	120

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76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
106	107	108	109	110	111	112	113	114	115	116	117	118	119	120

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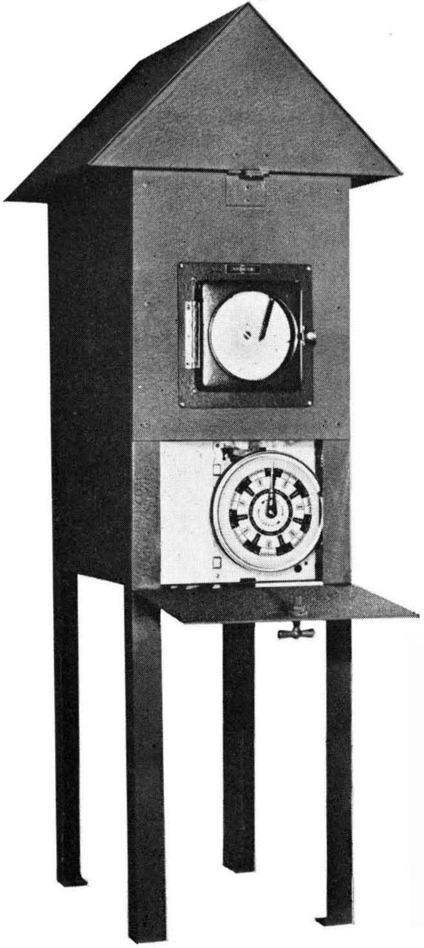
Oxygen analyzer. The Model 735 Dissolved Oxygen Analyzer and its polarographic oxygen sensor are described in a 4-page brochure. Bulletin 4092 discusses the advantages of the device, and highlights new features of the sensor, as well as information on the solid-state amplifier. The unit is said to provide direct readout in parts per million by weight of dissolved oxygen, regardless of temperature change, in water, waste water effluents of industrial complexes, or waste treatment activated sludge aeration tanks. Beckman Instruments, Inc. **98**

Handling polluted air. A line of building block air washer and fume scrubber systems, manufactured of unplasticized rigid polyvinyl chloride, is effective in controlling or eliminating corrosive and polluted air, according to the manufacturer. The units are listed in a 16-page catalog. Two main types of air washers are described, and their specifications and applications included in Bulletin M2-WEN-6-68. The brochure also discusses standard and alternate ducts, parts, fittings, and other equipment used with the washers. S&C Manufacturing Co. **99**

Catalog on instrumentation. A 336-page publication lists and describes the company's line of electronic test instruments and customer services. The *Honeywell Instrumentation Handbook* includes sections covering the product line, a guide to instrumentation selection, technical information, application of systems and instruments. In addition, a glossary of technical terms is included in several of the sections. For information on availability, contact: Honeywell, Test Instruments Div., P.O. Box 5227, Mail Station 218, Denver, Colo. 80212. (Write direct)

Underground water sources. Report 79, prepared by M. E. Broom of the U.S. Geological Survey, in cooperation with the Texas Water Development Board, discloses that most of the water used in an area in northeast Texas comes from underground supplies which are virtually untapped. "Ground-Water Resources of Wood County, Texas" also discusses the problems—high acidity and high iron content of the water—encountered in developing this source on a large scale. Texas Water Development Board, P.O. Box 12386, Austin, Tex. 78711. (Write direct)



Solid wastes. A supplement to PHS Publication 1821, "Solid Wastes Demonstration Grant Abstracts—Grants Awarded Jan. 1–June 30, 1968," is available on request. The 57-page report lists 26 projects, identified by type, title, and grant number, as well as descriptions of objectives and procedures followed. Names of grantees and project directors and duration of each project are also included. U.S. Public Health Service, Solid Waste Program, SWIRS, 222 E. Central Pkwy., Cincinnati, Ohio 45202. (Write direct)

Waste treatment. "Summary Report, Advanced Waste Treatment, July 1964–July 1967" is available. The 96-page booklet is publication WP-20-AWTR-19 in the Water Pollution Control Research Series. Included in the publication are discussions of conventional sewage treatment, organic, inorganic, and nutrient removal, ultimate disposal, and the practical status of advanced waste treatment. Publications Office, Ohio Basin Region, FWPCA, Cincinnati, Ohio 45226. (Write direct)

Sludge treatment. Publication WP 20-4, "A Study of Sludge Handling and Disposal," examines the subject in detail, reviewing and evaluating procedures, and discussing methods, materials, and equipment in use today and in the past. The report—which presents material in the same sequence as solids processing steps used at treatment plants—concludes that additional support should be given to research and development of better ways to treat the solid portion of waste waters after separation from liquid. Office of Information, FWPCA, 4676 Columbia Pkwy., Cincinnati, Ohio 45226. (Write direct)

Films

Coal fires. "Mine Fire Control" is a 16-mm. sound and color motion picture, dealing with the hazards involved from fires in abandoned coal mines, and the techniques developed for the control of such fires. The 26-minute film aims to be both technological report and forceful conservation story, and was prepared primarily for showing at educational institutions, to citizens groups, and on television. Prints of the film can be obtained on short-term loan. Motion Pictures, U.S. Bureau of Mines, 4800 Forbes Ave., Pittsburgh, Pa. 15213. (Write direct)

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MEETING GUIDE

December 2–6
NUS Corporation
Water Seminars
Statler-Hilton Hotel, Washington, D.C.

The 5-day sessions will feature two days devoted to effluent thermal effects, highlighting the regulatory and economic considerations related to the thermal aspect of power plant liquid discharges. The remaining three days of seminars will cover nuclear plant liquids; topics discussed will range from system cleanliness standards during construction to system decontamination following long-term operation.

December 9–11
National Society of Professional Engineers, and the Science and Technology Center of Sterling Institute of Washington, Inc.
Seminar on the Economics of Air Pollution
Watergate, Washington, D.C.

The 3-day program will feature engineers in the pollution control field, and will cover topics relating to the identification and effects of air pollutants, the present course of air pollution control, recent innovations in pollution control technology, and the need for technical advancement. The program has a limited enrollment. For information: Sterling Institute, Watergate, 2600 Virginia Ave., N.W., Washington, D.C. 20037

December 10–13
American Society of Agricultural Engineers
Winter Meeting
Sherman House, Chicago, Ill.

In addition to general agricultural topics, technical sessions will feature papers and discussions dealing with impact of air pollution on agriculture; pollution in groundwater hydrology; poultry and livestock environment; aspects of water treatment and use; and plant environment. An agricultural engineering and farm builder show is scheduled with the conference.

January 13–15, 1969
N.Y. State College of Agriculture
Cornell Agricultural Waste Conference
Hotel Syracuse, Syracuse, N.Y.

Theme of the 3-day meeting is Animal Waste Management. Technical sessions and symposia will cover the general areas: treatment of liquid wastes; utilization of wastes; land application; wastes from beef cattle feedlots; management aspects; odors; waste characteristics; and economics.

Courses

February 3–7, 1969
George Washington University School of Engineering and Applied Science
Short Course in Water Pollution Control

Designed for engineers, scientists, and researchers in the field of water pollution control, the course was developed in cooperation with the Federal Water Pollution Control Administration. The course includes discussion of topics such as principles of hydrology, threats to water resources and sources of pollution; workshop on abatement technology; and a panel discussion.

February 10–14, 1969
George Washington University School of Engineering and Applied Science
Short Course on Ocean Engineering—Instrumentation

The course aims to provide a background on the ocean environment, and will present study of types of instrumentation, problems, and methods of transmitting and processing data.

February 15, 1969 Deadline
National Research Council
Research Associateships

Applications are being accepted for postdoctoral research associateships for the 1969 academic year. Advanced training will be received at government research centers and laboratories, including the Environmental Science Services Administration, Bureau of Mines, Agricultural Research Center, U.S. Geological Survey, and Naval Research Laboratory. Stipends range from $11,500–12,500. For details: Associateship Office (JH604), National Research Council, 2101 Constitution Ave., N.W., Washington, D.C. 20418.

February 24–28, 1969
George Washington University School of Engineering and Applied Science

Short Course in Ocean Engineering—Minerals and Petroleum

Prepared in coordination with the U.S. Department of the Interior, this course is intended for engineers, scientists, and managers who are, or expect to be, engaged in extracting minerals, petroleum, or natural gas from the ocean floor.

1969–1970 Academic Year
Harvard School of Public Health

The Kresge Center invites candidates to submit applications for enrollment and fellowships for study leading to the M.S. and D.Sc. in occupational medicine, environmental physiology, toxicology, aerospace health and safety, radiological health, air pollution control, industrial hygiene, and general environmental health. Fellowship stipends range from $200–300 per month, with $500 per year for each dependent, plus full tuition and fees. For details: Dr. Dade W. Moeller, Assoc. Dir., Kresge Center for Environmental Health, Harvard School of Public Health, 665 Huntington Ave., Boston, Mass. 02115.

1969–1970 Academic Year
University of North Carolina, Institute for Environmental Health Studies

Environmental Health Fellowships applications may be filed for fellowships which provide tuition, fees, and a stipend, including a dependency allowance. Fellowships are available for masters or doctoral candidates, as well as for postdoctoral studies. Recipients participate in multidepartmental programs designed to prepare students for careers in research, teaching, and practice in the various specialized fields in environmental health. For details: Institute of Environmental Health Studies, Box 630, Chapel Hill, N.C. 27514.

Call for Papers

June 22–26, 1969
Air Pollution Control Association

62nd Annual Meeting

Americana Hotel, New York

The sponsors are soliciting papers for sessions in the following subjects: agriculture; air pollution control administration and management; air pollution measurement; atmospheric reactions; control equipment; fuels and power; legislation and air pollution standards; medical and biological effects; metallurgical industry; meteorological; motor vehicles; process industries; public relations, education and training; socio-economic; and waste disposal. Three copies of title and 200-word abstract should be submitted by Dec. 31, 1968, to: Elmer R. Kaiser, Senior Research Scientist, New York University, W. 177 St. and Cedar Ave., Bronx, N.Y. 10453

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January	1–78	July	481–570
February	79–156	August	571–644
March	157–234	September	645–718
April	235–312	October	719–984
May	313–386	November	985–1054
June	387–480	December	1055–1148

All authors' names and all names appearing in articles are indexed, except for those names appearing in meeting programs, feature articles, research papers, bibliographies, book reviews, and the Pollution Control Directory portion of the October issue.

SUBJECT INDEX VOLUME 2—1968

January	1–78	July	481–570
February	79–156	August	571–644
March	157–234	September	645–718
April	235–312	October	719–984
May	313–386	November	985–1054
June	387–480	December	1055–1148

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Publications reviewed, listed, or discussed at length are listed alphabetically by title under the heading **Books.** Books, films, charts, items appearing in the New Literature Digest, and similar sources of information are also indexed by subject. New literature is also listed by company name.

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^{l} Page reference to literature and other sources of information

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PDQ* *computer controlled data acquisition system*

for monitoring AIR and WATER POLLUTION

parameters from remote sites

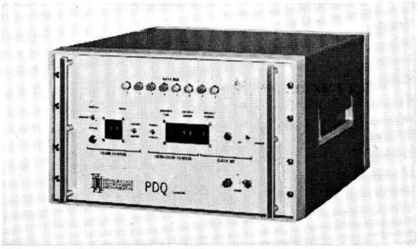
This system being manufactured for Michigan Department of Public Health Division of Occupational Health

collects data instantaneously / more accurately / at lower cost

Now you can collect environmental data at remote sites without sending a boy with a notebook or a high-priced technician. A PDQ mobile or fixed site unit, will take up to 1000 separate inputs from sensors, and transmit them over telephone lines to a central PDQ for data acquisition or reduction. The CPU can call up remote sites independently and ask for read outs. You can measure temperature, wind speed, wind direction, SO_2 concentration, oxides of nitrogen, hydrocarbons, and carbon monoxide in air and like measurements in water.

Why buy PDQ? It's flexible permitting the addition or deletion of sensors/It's capable of assembly of data without a CPU/It puts data in computer format/It may handle Multi Byte Instructions/Each sensor is directly addressable/It can be remotely calibrated/In addition to remote calibration it may handle other digital inputs from these remote sites.

Buy one.



Shown above is a PDQ* main frame

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*Programmed Data Quantizer

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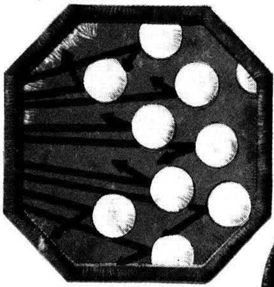

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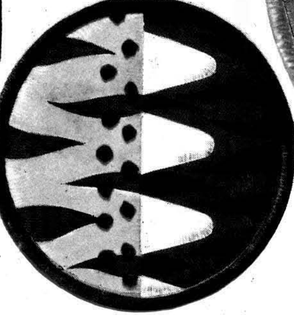
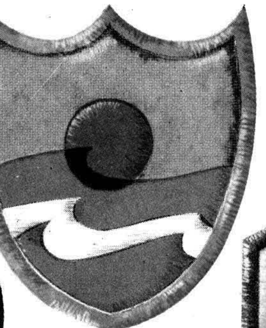
DIVISION



UOP JOHNSON DIVISION



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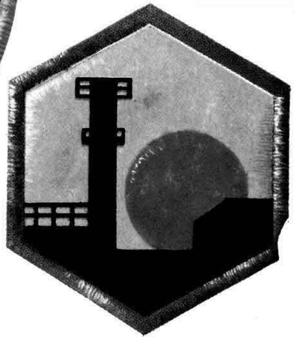

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In air correction, this is the one company offering the broadest selection of systems and equipment, in world-wide use. **UOP Air Correction Division** relieves you of the technical burdens of air pollution control, and provides you with the best equipment at the most economical cost. It offers eight basic types of control equipment, plus a complete range of services, from stack gas analysis to field start-up.

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