ENVIRONMENTAL
Science & Technology

Emphasizing
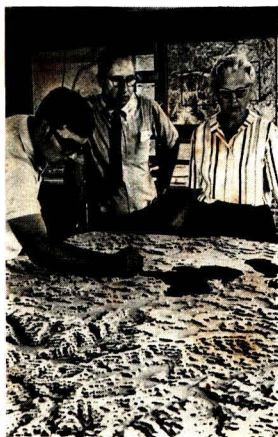
Water,

Air, &

Waste

Chemistry

JULY 1967

Pollution problems won't wait

Nalco can help you solve yours
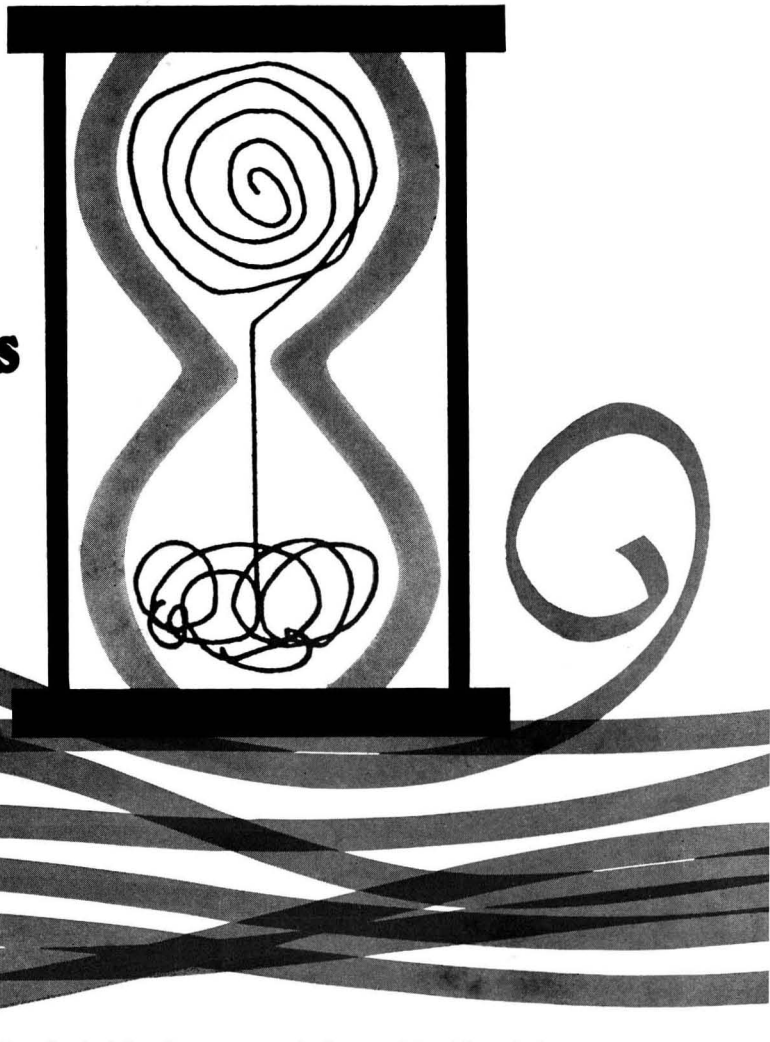
Pollution Control Services represents the combined knowledge and experience of all Nalco divisions—mobilized for action! This coordinated force can help you find a practical solution, regardless of what your industrial or municipal pollution problem may be. This includes control of the whole ball of waste, from raw water intake through manufacturing processes to the final effluent. It's simpler that way. And faster. For details, contact your local Nalco field representative, or write Nalco headquarters in Chicago for our "Management Guide to Pollution Control."

Nalco POLLUTION CONTROL SERVICES

Nalco Chemical Company, 180 North Michigan Avenue, Chicago, Illinois 60601
Circle No. 10 on Readers' Service Card
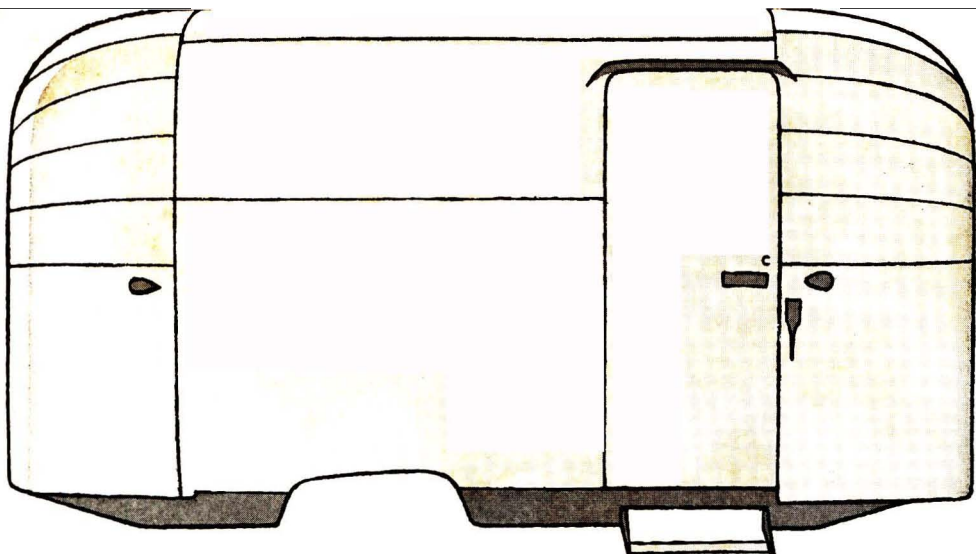
A successful air monitoring station is more than a trailer
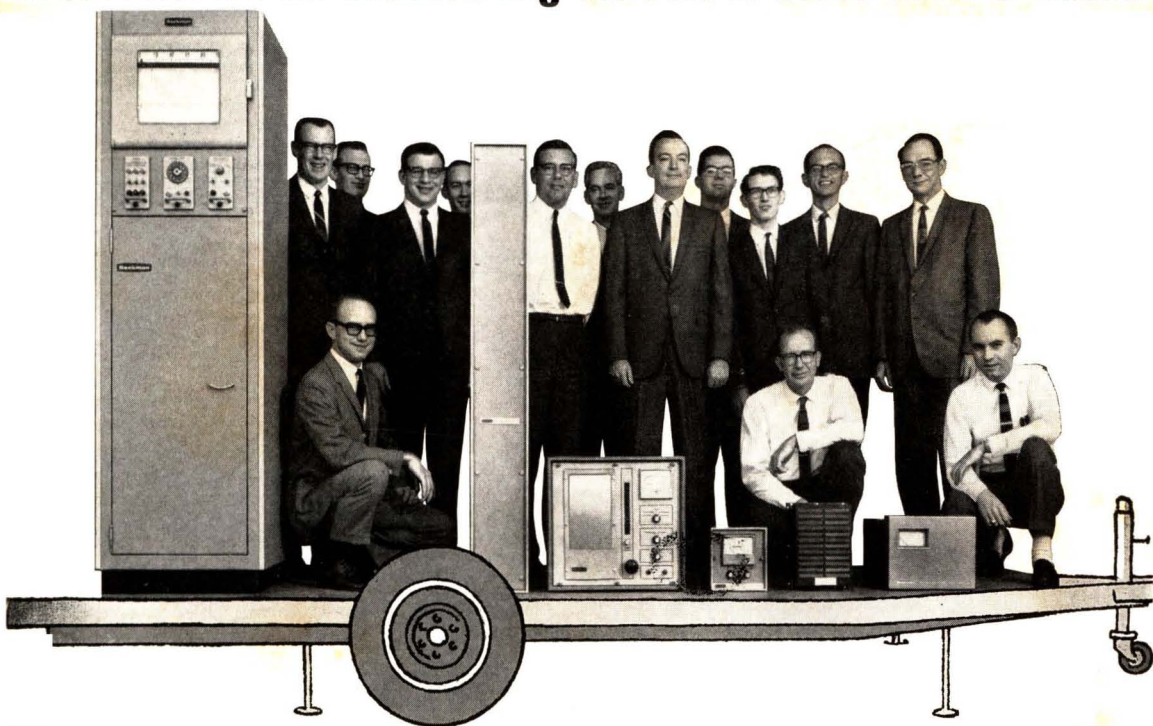
To begin with, it's instruments – analyzers to continuously monitor pollutants like sulfur dioxide, nitric oxide, nitrogen dioxide, oxidants, carbon monoxide, total hydrocarbons – all in a trailer especially designed for proper instrument installation.

But more than that—it's people. Your operator backed by Beckman specialists…sales engineers, service engineers, and application engineers. For Beckman not only furnishes quality instruments and sample handling systems that give dependable operation, desired accuracy, and repeatability – they also furnish assistance from experienced technical specialists, training courses for your operating personnel, and instrument maintenance by qualified field service engineers.

Only Beckman manufactures instruments to measure *all* major gaseous pollutants. Whether you want a single instrument or an entire air monitoring station in a trailer, in a van, or at a permanent location – contact your local Beckman Process Sales Engineer. Or write for Data File AP-16-167.

Beckman® INSTRUMENTS, INC.
PROCESS INSTRUMENTS DIVISION

FULLERTON, CALIFORNIA • 92634

INTERNATIONAL SUBSIDIARIES:
GENEVA; MUNICH; GLENROTHES, SCOTLAND; TOKYO; PARIS; CAPETOWN; LONDON; MEXICO CITY

Circle No. 23 on Readers' Service Card

ENVIRONMENTAL
Science & Technology

CONTENTS

ห้องสมุด กรมวิทยาศาสตร์

Detectability and system linearity identify the H-P Model 402 High-Efficiency Gas Chromatograph

A high-efficiency gas chromatograph is a complex instrument with a long list of specs that tend to obscure its real function, which is analytical performance. Reduced to this fundamental, the high-efficiency gc can be positively identified by two characteristics:

Detectability. Does it detect small quantities of hard-to-chromatograph substances? In other words, if you inject a nanogram, say, of an easily degradable material such as a steroid, will it analyze it without decomposition to produce a usable chromatogram? If it does, it has detectability, a system characteristic which is substantially more meaningful than the usual "detector sensitivity" found in a typical list of specs.

System Linearity. Does it respond proportionately to different amounts of hard-to-chromatograph substances? In other words, if you inject exactly twice the amount of that same material, will it produce a recorder peak size that's exactly twice as large? If it does, it has system linearity, a char-

acteristic that is incalculably more important than the usual "detector linearity" spec.

In the two series of chromatograms reproduced here, we offer convincing evidence that the H-P Model 402 High-Efficiency GC possesses system detectability and linearity to an almost perfect degree. In the first place, both trifluoperazine and testosterone chloroacetate are hard-to-chromatograph substances . . . and the 402 detected both in the nanogram range. Moreover, a quick glance at the linearity plot will show that the 402's response closely approaches the theoretical ideal.

You can get full information by writing for Bulletin 4020 (. . . it contains a "long list of specs") or by calling the nearest H-P sales office. Prices start at $3700.00.

Hewlett-Packard, Route 41, Avondale, Pa. 19311. In Europe: 54 Route des Acacias, Geneva, Switzerland. Elsewhere: 1501 Page Mill Road, Palo Alto, California 94304.

HEWLETT hp PACKARD

ANALYTICAL INSTRUMENTS

Superimposed on these two system linearity plots are the actual recorded peaks, accurately reproduced from the original chromatograms in the same scale.

43711

EDITORIAL
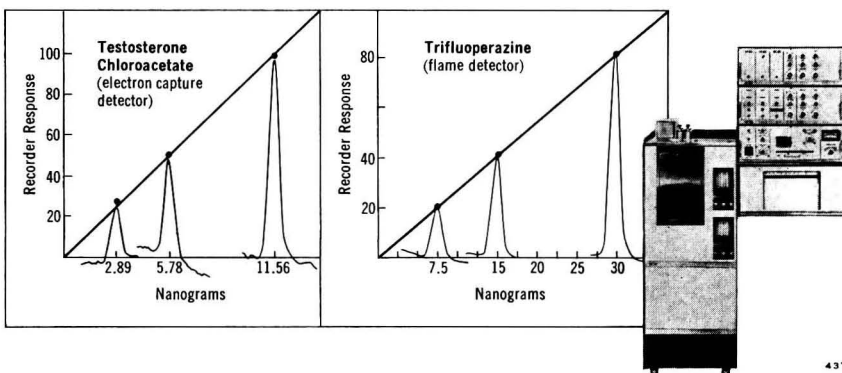
Pollution control should proceed from a sound base

There are sufficient data to make a strong case for pollution control programs without having to rely on scare tactics

When two youngsters in automobiles race toward each other down the highway median stripe, the name of the game is "chicken." When unions and managements parade in public their goals for upcoming talks, the name of the game is "bargaining." When responsible officials, well-intentioned citizen groups, or reader-seeking publications cry pollution at the drop of an unburned hydrocarbon, a rusty tin can, or a dead fish, the name of the game is "trouble."

The scare tactic can be as devastating to the cause of pollution control as the efforts of obstructionists who deny everything or the ostriches who do nothing and hope the problems will go away.

The scare tactic causes diversion of funds, effort, and priority perhaps all to no avail. The scare tactic misrepresents or exaggerates the truth and subverts it to devious uses.

Scare tactic incidents are many and certainly are not restricted to matters pertaining to pollution control. But with the sudden realization by the American public, industry, and government that pollution is a destructive and hostile force that has been loosed on the nation, there have emerged those opportunists who would subvert, either intentionally or by happenstance, the efforts of their neighbors. Thus, the cry of "pollution" can be related to the cry of "wolf," and soon perhaps no one will believe or be willing to do anything about it.

Recently in a newspaper in one of the nation's large cities there appeared a major article proclaiming that planes using the area's airport were spilling 35 tons of air-polluting, incompletely burned fuel on the area each day. The article went on to say that the rate was such that each year 8000 acres around the airport would be covered with a total of 12,775 tons of contaminants or about $1^{1}/_{2}$ tons per acre. And at that, the article continued, the amount being dropped today is half what was being dropped by half as many planes 10 years ago. Fine. A good, exciting, reader-catching article.

When ES&T called that day to check the details, we were told that detection equipment placed directly under the planes as they lifted off the runway at the airport was unable to detect any increase in unburned hydrocarbons above background levels. And the next day's paper carried a refutation by the Air Transport Association. All commercial planes in the area, according to ATA, together drop on the area each day only $2^{1}/_{2}$ tons of unburned hydrocarbons, an amount that is equivalent to 1 to 2% of the total air pollution in the area.

Because of this kind of article and other misleading presentations in the press, on the radio, in books, or on television, the public now is sated, confused, and, therefore, frequently not willing to listen to facts when they do appear.

The threats of pollution are real. Their economic consequences are real. Their health consequences are real. There are sufficient data to make strong cases based on facts. There is no need for the charlatan, for the rabble-rouser, or for the well-intentioned but misguided zealot.

Let the work toward cleaning our environment and restoring it to a desirable wholesomeness go forward. But let it proceed from an honest, efficient, and scientifically sound base.

Melvin J. Josephs

Afraid you'll goof on buying new air pollution control equipment?

Faced with the urgent need to clean up the smoke and gases billowing from your stack? Don't take a chance on making a costly mistake. Ask Research-Cottrell, the world's largest manufacturer of air pollution control equipment, for the most economical solution to *your* specific problem. We make all types of equipment. Much of it is not as expensive as you think! Simply fill out and mail the coupon...and you'll take the first step towards an objective analysis. You'll start breathing more easily.

Research-Cottrell

Research-Cottrell, Inc., P.O. Box 750, Bound Brook, N. J. 08805 / Electrostatic Precipitators • Mechanical Collectors • Wet Scrubber Systems • Fabric Filters

☐ Please send me literature that contains helpful hints on air pollution control.

NAME _____

TITLE _____

COMPANY _____

ADDRESS _____

CITY _____ STATE _____ ZIP _____
M
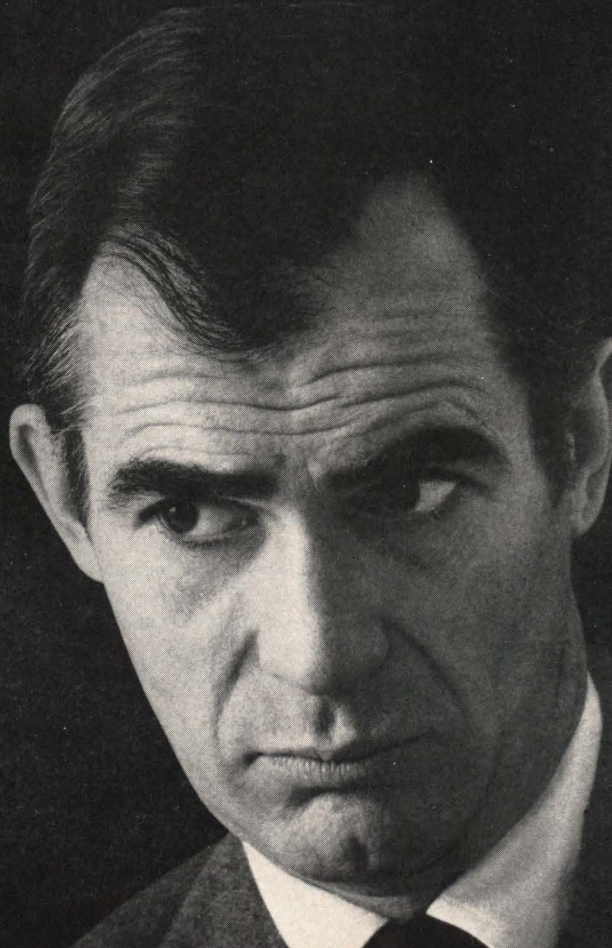
Air Quality Act of 1967 Triumphs in Senate

By a resounding 88-0 vote, the Senate passed the Air Quality Act of 1967. Behind the quick and easy trip through the Senate were the revisions the Senate Public Works Committee made to the Administration's proposal. Key revision: rejection of the Administration's bid for power to set national emission standards.

Following the pattern set by federal water pollution control legislation, S. 780 gives the Federal Government back-up powers to act when states or local governments fail to act. The Administration got a couple of things it hadn't asked for: sweeping powers to deal with pollution emergencies and a $700 million kitty to finance the federal air pollution effort during the next three years.

The bill now goes to the House, where—if it follows the pattern of water pollution legislation—it will have considerably rougher sledding, although there seems little doubt that the measure will go through essentially as written. The Senate bill is a carefully prepared compromise of the Administration's goals, industry's concerns, and the Senate Public Works Committee's desire to draft a bill that has a reasonable possibility of becoming law.

Obviously sensitive to possible complaints that the revisions in the original bill have led to a watered-down version, Sen. Muskie at a special press conference called just prior to the bill's passage said: "The Air Quality Act of 1967, therefore, serves notice that no one has the right to use the atmosphere as a garbage dump, and that there will be no haven for polluters anywhere in the country .... It should be emphasized that it is the intent of the committee to enhance air quality and to reduce harmful pollution emissions anywhere in the country; and to give the Secretary authority to implement that objective in the absence of effective state and local control."

Economics of Sulfur-Free Stack Gases

Many systems may eventually be used for removing sulfur dioxide from power plant flue gas. Economics will determine the choice of one over the other, according to Sidney Katell and K. D. Plants of the Bureau of Mines. Location, technical advances, the type of fuel used, and marketing environment for the sale of by-products—all affect the choice. The alkalized alumina and the catalytic oxidation systems, both of which use hot solids as the absorbent, are now undergoing intensive investigation in the U.S.

The BuMines scientists told the Cleveland meeting of the American Association of Cost Engineers that the operating costs for both systems are about equal when the by-product is sulfuric acid. However, the alkalized alumina system can also produce sulfur, which would be an advantage if market conditions were unfavorable for sulfuric acid. Other processes are also being studied. Pilot plants are operating using dolomite as the absorbent. Japanese scientists are working on three separate processes. And BuMines is in the preliminary stages of investigating a promising new approach: phosphate rock is used to adsorb SO_3 following catalytic oxidation of SO_2 in the flue gas.

Welcome Mat Spread for Low-Sulfur Oil

The Interior Department has modified the oil import program to encourage more imports of low-sulfur fuel oils. "The changes will accomplish no miracles in air pollution abatement," the department says. However, "they should make a substantial contribution toward alleviating a serious problem." The changes to the Presidential proclamation governing oil imports involve fitting No. 4 fuel oil and certain other low-sulfur oils, formerly subject to import quotas, into the definition of "residual fuel oil," which can be readily imported on the East Coast. The changes also authorize Interior to:

• Provide a system for allocating low-sulfur residual fuel oil imports to the West Coast, which now has none.

• Provide special allocations to refiners for the low-sulfur fuel they make from imported oil.

• The changes will not disturb domestic production, the overall levels of imports, or the traditional pattern of imports, Interior says. Some of that oil may end up in Philadelphia, where four major municipal installations are switching to low-sulfur oil. Philadelphia believes it is the first municipality in the country to contract for such fuel, even though it is not required by local, state, or federal law. The one-year contract is for $580,000 worth of oil having a maximum of 1% sulfur. The cost is approximately $102,000 more a year than for oil having 1.8% and up sulfur content the city had been using.

Industry Must Help Tackle the Solid Waste Problem

Industrial research and development can make a big contribution toward solving the solid waste disposal problem. Perhaps the most challenging and promising field for industry lies in waste recycling and reuse, according to Leo Weaver, chief of the Public Health Service's solid wastes program. He points out that wastes can be used to generate power. Although the typical mix of urban solid wastes has about half the thermal energy of coal, the wastes wouldn't have to be transported hundreds of miles, as coal frequently has to be.

At a Washington meeting of the U.S. Chamber of Commerce, he suggested another possibility for industry: "If systems could be perfected for the very long transport of urban solid wastes at costs well below those that now prevail. And if the huge amount of organic materials now being lost through the wasteful disposal of solid wastes could be salvaged, vast areas of this country could be transformed from arid, worthless lands into farms."

Weaver sees a new departure for American industry, one predicated on a new kind of conservation. "This new departure will take many forms.

• It will involve bold applications of the products of research and development.

• It will involve a new conception of design in which reuse and disposal of products is as essential a design determinant as its primary use.

• It will involve the development and installation of new systems both in industrial plants and in entire cities for the collection, processing, and reuse of what would otherwise be waste materials—gases, liquids, and solids."

Government Accepts First State Water Quality Standards

"This is the beginning of the end of gross abuse of this country's invaluable water resources," said Secretary of the Interior Stewart L. Udall at a recent press conference on water quality standards called by Udall to mark approval of water quality standards submitted by Georgia and Indiana. Under the Water Quality Act of 1965 as reinforced by the Clean Water Restoration Act of 1966, all states had to submit proposed water standards by June 30. All states met the deadline except Alaska, Oklahoma, and the territory of Guam. Almost fully accepted are the standards submitted by Oregon, New York, South Dakota, and Alabama. Secretary Udall said that he will set standards for the delinquent states if they remain delinquent, but that he would prefer to have some meaningful input from these states. Although he has the power to set standards, he is "reluctant to use that power" because he is "determined to develop the picture of a national program."
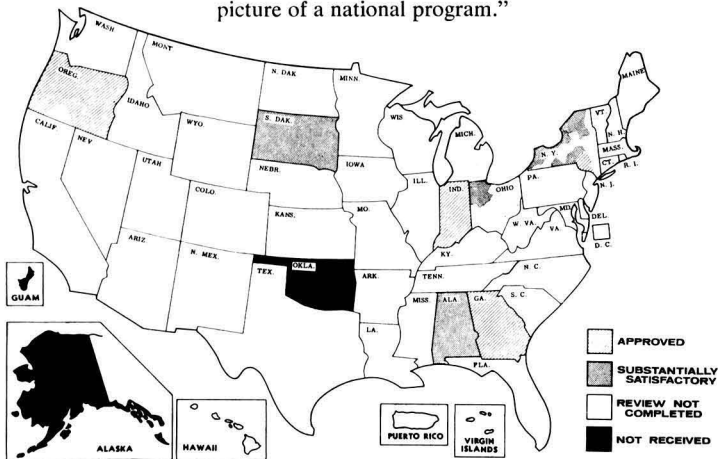
Picture of the start of a national program for water quality standards

APPROVED

SUBSTANTIALLY SATISFACTORY

REVIEW NOT COMPLETED

NOT RECEIVED

The most significant thing about the standards, according to Udall, "is that they all call for a minimum of secondary treatment for all municipal wastes and a comparable degree of treatment for industrial wastes." But the standards become goals, he continued, and the goals become action programs. The states now have the responsibility of getting on with the job of implementation. Communities and industry that have been laggards had best recognize that "action is the order of the day," that enforcement is the key, and that, therefore, it will be tough, he warned.

Udall commended the action of the five Technical Advisory Committees on water quality criteria set up in February. These committees collated vast quantities of scientific information and have prepared recommendations for water quality criteria for various major categories of water use, such as recreation and esthetics; public water supplies; fish and other aquatic life and wildlife; agriculture; and industrial water supplies. One recommendation that came from these committees, and one that Udall promised would be a major one considered in reviewing state standards, deals with temperature requirements of fish and aquatic life. Thermal pollution is "an emerging problem across the nation," he cautioned.

NSF Talks, Writes, and Does Something About Weather

Cautiously stating that "While the evidence is still somewhat ambiguous, there is support for the view that precipitation from some types of clouds can be increased by the order of 10% by seeding," the National Science Foundation this month discussed its weather modification progress in its eighth annual report titled *Weather Modification*. NSF then called for additional studies to confirm the positive results in treated regions and to determine what, if any, decreases in precipitation might occur outside the treated area. Although it claims to be able to increase precipitation under some conditions, NSF said that it has yet found no practical way to dissipate warm fog, that results on hail suppression are inconclusive, that lightning suppression shows some promise of success, that hurricane modification is inconclusive, and that no attempt has been made to modify larger storm systems such as tornadoes. NSF also pointed out that weather modification programs are under way in the Departments of Interior, Commerce, Defense, and Agriculture, and by the Federal Aviation Administration and the National Aeronautics and Space Administration.

Environmental Management Requires New Partnership

Substantial progress must be made in pollution abatement techniques simply to maintain the present quality of our environment, according to a recent U.S. Chamber of Commerce publication, *The Need: To Manage Our Environment*. The pamphlet recommends a government-industry-public partnership approach to pollution control, and states that the chambers of commerce are uniquely suited for bringing this partnership into being and making it a success. Specifically, the treatise says that businesses should become more heavily involved in managing our environment because they have special expertise and talent available; that the Federal Government should provide a large portion of the funds required for research because pollution is a public problem; and that the public should be educated in its positive responsibility to see that our environment is managed wisely.

Begin at the Beginning

Waste control and reduction during manufacturing, not waste treatment at the end of the line—this is the way to control pollution and also the way to improve manufacturing efficiency. James J. Flannery, chief economist of the Federal Water Pollution Control Administration, maintains that "treatment of final wastes would be considered only after cost and other analyses showed that the wastes volume was reduced at each step in the production process as much as feasible." And government policy should promote this concept, he told the American Association of Cost Engineers meeting in Cleveland. The President's Council of Economic Advisers is now coordinating studies on possible incentives, including tax considerations, to encourage industry to control both air and water pollution. These studies are still several months away from even tentative conclusions.

Urban Problems Met in Environmental Centers

Center for the Biology of Natural Systems, Washington University

... was created to test the hypothesis that man can learn how to adapt science to the urgent need for understanding the natural biology of the environment, and so to help preserve the community of life from extinction by the hand of man. Faculty and students from diverse fields join in informal meetings to pursue their common interests in inherently complex systems— although they remain in their own fields of specialization. Research projects are designed to explore speculative approaches to those complex natural systems, at all levels of complexity from the cell to the ecosystem, on which human health depends

The inception of environmental management activities in this country occurred at different times in history in response to clearly discernible needs. It is this time differential that has played a significant role in the evolution of our segmented approach—water pollution, air pollution, land pollution, solid wastes, and urban planning—to the solution of urban problems.

While intensive efforts dedicated to these facets of man's environment are crucial to our health and well-being, a correlative need exists for an integration of environmental management activities into a total system.

A significant and novel effort has taken form through a new program initiated in 1965 by the Public Health Service. I refer to the Environmental Health Center program. Recently such centers have come into being—one at Washington University (St. Louis, Mo. See ES&T, May, p. 390), one at the University of Cincinnati (Ohio), one at the University of Wisconsin (Madison, Wis.) one at Cornell, and one at the University of Southern California. Other universities are in the planning and development stages of additional centers. Among these are Harvard University and Louisiana State University.

These centers are designed to advance understanding of the man-environment interactions that affect man's health and well-being. They call for a voluntary association of interested scholars, representing a variety of disciplines within a university, to create an innovative, coherent plan for producing knowledge, for training people, and for educating the public—all to the end of managing and improving the quality of man's environment.

New relationships

In the research and special training activities of a center, novel faculty-student relationships create new understanding of the complexity of environmental problems and clarify the diversity and importance of the contributions that must come from many professional fields. A center acquaints people who need to work together and who have been strangers to each other's work in the past. The urban designer and planner, architect, economist, political scientist, behavioral scientist, sociologist, anthropologist, and many others just join forces with the more traditional environmentalists who come from the fields of engineering, medicine, and the biological and physical sciences.

A center attempts to give structure and focus to the environmental effort without establishing a new college or a new department. It preserves the freedom and flexibility of the participants while encouraging venturesomeness and spontaneity. The partnership I describe regards the university as its chairman and its own urban area as its laboratory.

Most of the research and teaching personnel associated with a center will derive from the applicant university. Its members will retain their titles and academic prerogatives in their respective departments. Moreover, they will participate in departmental as well as center activities.

Centers are expected to differ widely in purpose, size, and composition. Since the nature of the group associated with center programs will vary from university to university, the particular approaches designed by each group will also vary. This diversity of scope and approach is indeed desirable, for the di-

Harry P. Kramer
Office of Program Planning and Evaluation,
Bureau of Disease Prevention and Environmental Control, Washington, D.C. 20201

versity will make for complementary efforts and understanding among the disciplines and professors. Similarity, where it exists, will make for reinforcement of the knowledge gained.

What is sought universally, however, is knowledge coupled with imaginative, creative approaches to complex environmental problems.

A salient responsibility of the center is the conceptual and functional integration of participants and programs that emanate from different departments, schools, and colleges within the university, without compromising the traditions of the university itself.

In such an arrangement the universities fulfill prime functions: the production of knowledge and trained personnel. Those emerging from center programs should have, in addition to their specialty, a breadth of comprehension of the complexity of man's environment, a keen appreciation of the importance of contributions from other disciplines, and a creative attitude toward solutions to problems. They should possess to a high degree the ability to communicate with many types of specialists. Indeed, they should be well equipped to fill roles of leadership in meeting urban problems.

As Secretary John W. Gardner of HEW said, "Very few of our most prominent people take a really large view of the leadership assignment. Most of them are simply tending the machinery of that part of society to which they belong.... These people may tend it very well indeed, but they are not pursuing a vision of what the total society needs. They have not developed a strategy as to how it can be achieved and they are not moving to

accomplish it.... The best students are carefully schooled to avoid leadership responsibilities."

Our present institutions are not capable of coping with the urban challenge of our modern society unless they are led by people who have a vision and who take a responsible view of the leadership assignment. So, it follows that the training of leaders is one function of environmental health centers that promises to have important and far-reaching salutary effects.

Sophisticated citizenry

That this training function must be filled more effectively than it is at present is recognized widely. "Education at Berkeley," a report of the Select Committee on Education, deals with a related problem. The report points out, for example, that "... members of the College of Engineering are considering a one-quarter course in Contemporary Technology, recognizing that many of today's most challenging social problems—e.g., poverty, population, pollution—... require an informed and technologically more sophisticated citizenry to initiate and support intelligent decision making.... It [the course] would call for faculty contributions from throughout the University."

"Education at Berkeley" also notes: "Many if not most observers would admit the need ... to offer greater varieties of educational experience, and above all to develop our capacity to adapt and innovate continuously in the light of changing conditions." And, at a later point in the report: "We must heed the recently renewed warning that our universities are still training experts rather than educating leaders, despite

Model systems. *Natural environmental systems and man's occupation of the local environment can be traced through the use of models such as the one shown here of the natural terrain around Madison, Wis. Staff members of the Environmental Sciences Pilot Project at the University of Wisconsin use this model to analyze patterns of urban sprawl*
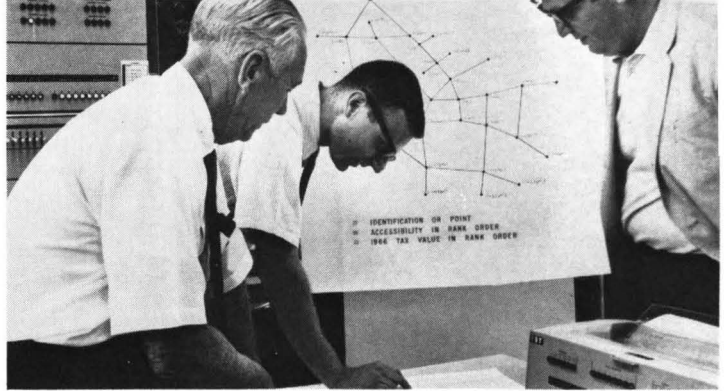
Environmental Sciences Pilot Project, University of Wisconsin

... deals with interrelationships in the environment and actions by man that bear upon the well-being of human populations. The program serves as a basis for intelligent action for the preservation and enhancement of the environment. Research projects at this center are concerned, in general, with pollution and perturbation of the environment, advertently or inadvertently, in water, soil, or space systems, particularly the transport of these pollutants and the means of perturbation. To investigate the impact of these forces on biota, especially man, and upon climate, health and disease etiology are studied. Projects also involve alternative systems of environmental management

Institute of Urban Ecology and Environmental Management, University of Southern California

... is a systems-oriented interdisciplinary center for research, graduate education, and community service in the field of urban environmental quality planning and management. Currently it is conducting research on urban environmental quality standards, the development of new communities, and the application of systems analysis methods to the solution of community air pollution problems

so many expressions of concern about this problem."

Public agencies

So far, I have been talking about the university contribution to the center. Other important contributors to such centers are the public agencies. Traditionally, the public agencies, the Federal Government in particular, have played the major role in environmental research, investigations, field studies, and related enterprises. Federal support for university research and training has exhibited considerable growth in recent years.

Now public agencies must, in addition, actively seek new policies and procedures that will enable us to manage our ever more complex environment. As an inherent part of this responsibility the public must be enabled to make informed choices about the quality of environment it wishes—choices based on specific benefits and on the bill the public must pay for such benefits.

Temporary exchanges of personnel among universities, public agencies, and industries could occur as part of the partnership operation of the environmental health centers. Public agencies could provide unique internship opportunities for both predoctoral and postdoctoral personnel—to enable students to deal experimentally with real problems in the laboratory of the urban community. A training experience of this nature provides for a continuous renewal of talent because the training deals with actual problems.

Industry

Industry has a great stake and bears a heavy responsibility in such an as-

sociation. Industry depends upon the quality of research and manpower produced by the universities. Industry must, in its planning and its operations, comply with regulations affecting plant locations and plant operations. Industry is directly affected by the standards and criteria established by public agencies charged with the responsibility for protecting the quality of the environment.

Most important of all, it is industry that possesses the capability to develop the many new technologies that will provide us with the urban environments of the future.

Federal policy, of course, affects industrial research and development for pollution abatement. The report of the National Academy of Sciences–National Research Council, "Waste Management and Control," stresses the need for integrating the treatment of water, air, and solid waste pollution as a single system. It also emphasizes the need for contributions from many disciplines if effective environmental quality management is ever to be achieved. The report states: "Although the many scientific and technological problems are complex and challenging their solution may well be less difficult and time-consuming than those associated with public policy and institutional patterns."

Incentives

"The Adequacy of Technology for Pollution Abatement," a report prepared for the House Committee on Science and Astronautics, considers a variety of incentives to industry for pollution abatement. Fines have been considered, but they have been criticized as possibly being a license to pollute. Tax in-

Vehicle emissions. *A topological map of the Los Angeles Freeway is labeled for computer input at the Institute of Urban Ecology, University of Southern California*

centives have long been under discussion. What are needed are realistic incentives that will encourage industry to assume a major role in developing new antipollution technologies.

The relationship of industry to universities and public agencies in the Environmental Health Center program is one of narrowing the gap between the development of knowledge and the application of knowledge to new technologies. Contractural arrangements between the Federal Government and industry that are designed to meet the special conditions presented by waste-management technology must be created.

As environmental quality criteria become quantitatively defined and adopted as legal standards for control, the market for abatement products and processes can be expected to grow.

The costs of such products and processes will encourage continued development of industrial technology, with reduction of pollution assuming more and more importance.

The President's Science Advisory Committee concluded, in its report on "Restoring the Quality of Our Environment," "We need more basic research upon which to build both understanding and techniques of amelioration. We need more applied research to take advantage of basic knowledge in the discovery and shaping of such techniques in broad outline. We need exploratory development to bring new techniques to actual trial. And we need final development to produce techniques in a form suitable for general use.

"The Nation can look to industry for the accomplishment of some of this research and development."

Broadening. *Often the university student encounters only a few kinds of animals to observe and test. Classes, such as this one at the St. Louis Zoo, enable students in the Center for the Biology of Natural Systems, Washington University, to broaden their experience as well as the available base of laboratory animals used to study medical problems*
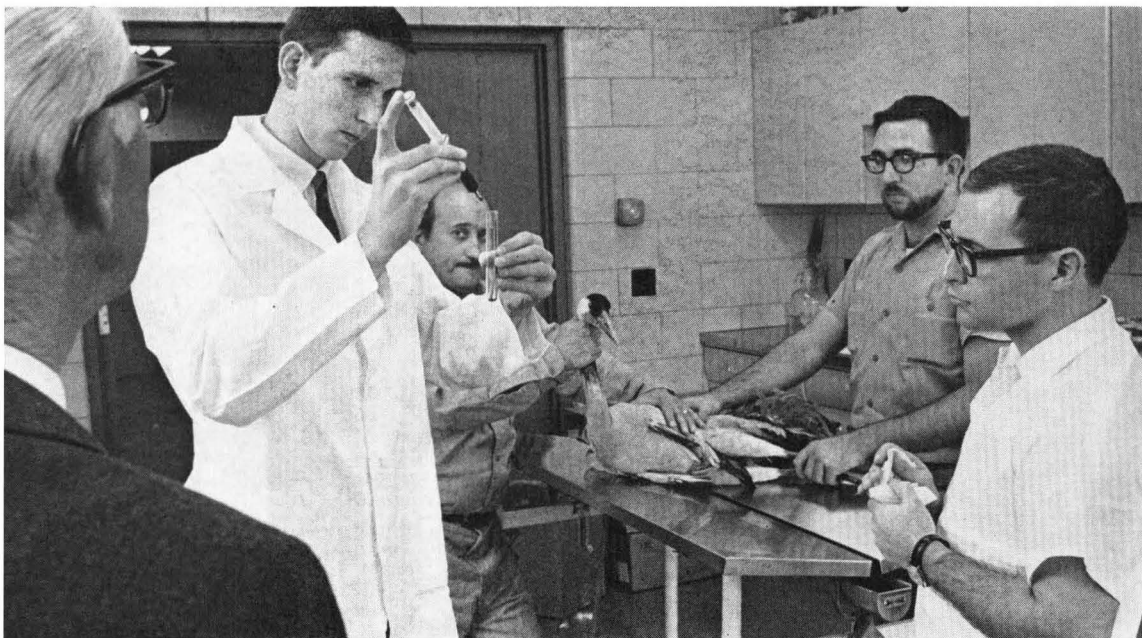
Center for Environmental Quality
Management, Cornell University

*...focuses on three vital elements
of environmental quality
management—the control of
ecological systems, planning and
control of physical systems, and
control of medical and social
systems. To encourage new
combinations of disciplines and
maintain communication between
them, a continuing interdisciplinary
academic forum has been established.
Research study groups, preliminary
research studies, and workshop
seminars are the mainstays of the
program at Cornell. Research
results from the center's
participants are integrated and
disseminated to the scientific
community*

Center for the Study of the Human
Environment, University of
Cincinnati

*... seeks to broaden the base of
participation in environmental
health studies and to promote
integrated activities with departments
which have not yet applied their
specialized skills to problems of
the human environment. The
biological effects of pesticides,
food additives, trace metals, and
varied industrial intermediates are
key areas of study. Related work is
directed to investigations of the
influence of urban design and land
usage upon environmental
contamination. The center encourages
the broad participation of visiting
scholars*

Systems analysis approach

The multivariant nature of environmental problems and the contributions of public agencies, industries, universities, and modern social institutions lends itself to a systems analysis approach. This approach adds considerably to our ability to weigh alternatives made up of many interrelated factors. The weighing of such alternatives is just what is involved in coping with the urban challenge of our modern society. Such techniques will be exploited in center programs.

Work of the centers will include both problem identifying and problem solution. While the centers seek to remedy and control existing environmental conditions, the larger task is to provide for the environment that we are about to build. The magnitude of this building effort for the next few years, in this country alone, is overwhelming.

We live in a time of unusually rapid social and economic change, and we must be prepared to face these changes. In The Netherlands last year in an address presented to the Royal Institute of Engineers, Gordon Fair, one of America's great engineering leaders and educators, stated: "John K. Galbraith, the economist, has popularized the new economic and social structure as the 'affluent society.' The British novelist, Aldous Huxley, who was strangely fascinated by the effluvia of great cities, has, in a play on words, dubbed it 'the effluent society.' Together the two slogans seem to fit future tasks of sanitary-environmental engineers, who will be more and more deeply concerned with the swelling effluents of an affluent society." Dr. Fair went on to say: "Remembered

in this connection must be that these effluents have acquired their objectionable properties in the service of important human wants and needs in dwellings and factories and on the land; remembered, too, must be that the encroachment of these effluents on the water, air, and land resources asks for solutions not only under present conditions but most probably in greater intensity under conditions yet to be engendered by future exploitation of our resources in more massive attack.

"This complementarity of resource development and resource pollution calls for an integral solution of the two problems. Indeed, it has been suggested in this 'systems-analysis-minded-age' that the inputs and outputs of the entire human environment be programmed and computerized for optimization."

Plan of action

"The technological problems to be solved in the management of man's changing environment," Dr. Fair continued, "are diverse and many—so diverse and so many, in fact, that one may well question whether the pace of impairment of the environment will allow enough time for the implementation of needed technologies. Not surprisingly, whenever the future is considered by scientists and engineers we come to the common consensus of our century: To solve our problems we shall have to make greater efforts in the field, in the laboratory, and in the classroom; we shall have to build better research facilities; we shall have to produce better trained investigators and more highly motivated and capable leaders, and support them more ade-

Interdisciplinary. *A regular program of seminars and tutorials is an integral part of the Center for the Biology of Natural Systems, Washington University (St. Louis). Here, at an interdisciplinary tutorial on biological information transfers are (left to right) Dr. Thomas Sandel (psychology), Dr. Barry Commoner (botany), Dr. Robert Yaris (chemistry), Robert Provine (psychology), Dr. Robert Rhodes (physics), Dr. James Burgess (physics), Kathleen Ochs (biology), Robert Ogden (mathematics), and Taghi Farvar (mathematics)*

ห้องสมุด กรมวิทยาศาสตร์
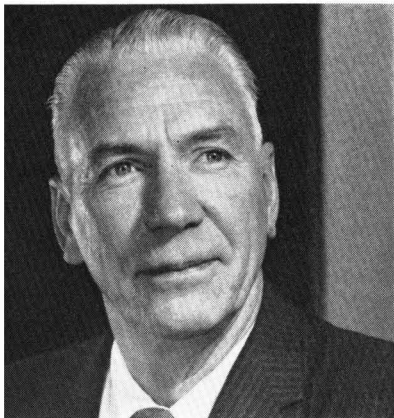
Harry P. Kramer *is Resource Development Officer, Office of Program Planning and Evaluation, Bureau of Disease Prevention and Environmental Control, U.S. Public Health Service. Previously (1949–65), he was with the Robert A. Taft Sanitary Engineering Center and (1934–49) the City of Chicago as a sanitary chemist. He received his B.S. (1930) from St. Mary's College (St. Mary's, Kan.), his M.S. (1932) from Creighton University (Omaha, Neb.), and an honorary Sc. D. from the University of Cincinnati (Ohio). Dr. Kramer has published numerous articles in the fields of sanitary engineering, chemistry, and microbiology. He is a member of many professional, educational, and honorary societies including ACS, AAAS, American Public Health Association, Conference of Federal Sanitary Engineers, Inter-American Association of Sanitary Engineering, National Society of Professional Engineers, National Society for Programmed Instruction, Water Pollution Control Federation, American Water Works Association, American Academy of Environmental Engineers, and Environmental Engineering Intersociety Board, Inc.*

quately than now; and, finally, we shall have to commission them not only to solve the environmental problems of our day, but also to foster fundamental research that will enable us to manage the emerging problems."

Another way of saying all this is that there is a need to raise the priority of the whole pollution abatement effort within the structure of our national objectives.

The quality of life depends to a great extent on the quality of our environment.

Environmental Health Center program

This outline of the Environmental Health Center program is one method for dynamic institutions to meet certain important needs of our changing world. The method has been described in generalities because the program itself incorporates a minimum of formal structure.

The only fixed component is the program's mission: to attempt, through experimental combinations of people and institutions, to develop new patterns of educational, public, and industrial associations which promote the health and well-being of man in his chosen environment, the urban community.

Whether the problem is domestic in scope and involves the welfare of people in their communities, or international in scope and concerns peace, problem-solving requires similar innovative efforts in which the capacity for creative renewal is inherent. A center approach may be equally applicable to these and other areas of concern.

Selected additional reading

"The Adequacy of Technology for Pollution Abatement," Report of the Research Management Advisory Panel, Subcommittee on Science, Research, and Development, Committee on Science and Astronautics, U.S. Government Printing Office, 1966.

Caldwell, Lynton K., "Environment: A New Focus for Public Policy?" Public Administration Review, September 1963.

Doxiadis, C. A., "Anthropocosmos—The World of Man," Award Address, Delivered at the Aspen Institute for Humanistic Studies, July 29, 1966.

"Education at Berkeley," Report of the Select Committee on Education, Academic Senate, University of California, Berkeley, March 1966.

Fair, Gordon M., "Engineering Responsibility in the Management of Man's Changing Environment," Address, Delivered to the Royal Institute of Engineers, The Netherlands, Holland, June 1966.

Gardner, John W., "The Antileadership Vaccine," Annual Report, Carnegie Corporation of New York, 1965.

"Restoring the Quality of Our Environment," Report of the Environmental Panel, President's Science Advisory Committee, November 1965.

"Waste Management and Control," A Report to the Federal Council for Science and Technology, Publication 1400, National Academy of Sciences–National Research Council, March 1966.

New Data System Designed For Marine Chemical Data

Dorothy L. Whittington

John I. Thompson & Co., Washington, D. C.   20037

Computer programmers at the National Oceanographic Data Center (NODC) have recently designed an information processing system to fill a long-standing need—the effective storage and efficient retrieval of marine chemical data. Although individual scientists have, in the past, maintained personal data files, perused the literature on their own, and kept in contact with others in their field, there has been no centralized arrangement for storage and retrieval of data from the broad spectrum of marine chemical events. The new system will provide a centralized location, standardized terminology for storage and retrieval, common units of measurement wherever possible, and coverage of all related fields in order to include any pertinent data.

Some guidelines exist for handling limited aspects of chemical data (for example, oxygen and several minerals) in the computer oriented systems of such organizations as the National Oceanographic Data Center (NODC), Scripps Institution of Oceanography, University of Washington, and Woods Hole Oceanographic Institution. But the perspective and scope of these systems must be broadened to permit the effective exchange of information among those who are involved in generating data from the wide variety of marine problems being investigated.

Any functional comprehensive storage and retrieval system should be accessible to all interested scientists and engineers. To achieve such goals the system must be flexible, simple, yet complete. It should be able to handle any relevant data from a broad spectrum of sources and should be inexpensive to operate and maintain. In addition to these generalized basic criteria, the system must lend itself to the limitations of the data and the needs of requestors.

Data categories

Oceanographic chemical observations fall into two categories, routine and nonroutine. Routine data are generated from comparatively simple, accurate analytical procedures, and widely influence other disciplines. Nonroutine data require more rigorous or controversial analytical procedures or do not so heavily influence other disciplines.

The existing computer oriented data systems mentioned earlier successfully handle routine data, which are generated rapidly and voluminously. But these same systems cannot easily handle nonroutine data, which by their very nature present new problems in data handling.

For example, lengthy, often controversial, analytical procedures and the presentation of theoretical justifications are integral parts of nonroutine data. The existing bond between the data and all associated information should not be broken.

NODC system

The system proposed by NODC is designed to include routine as well as nonroutine chemical analyses. The system is designed to handle, with certain restrictions, heterogeneous types of data derived from marine chemical research, including analytical data derived from samples taken at a discrete point and time or data that have been collected by continuous sampling over a period of time and space. At the start the system will accept and store data from continuous recording devices until development of a more efficient method of storage is completed. The NODC system gives primary emphasis to analyses from the water column, although inclusion of certain analyses (such as the analysis of interstitial water) from sediment is also possible. Calculated data (such as A.O.U. or N_2/Ar) meeting the requirements for analytical data can be included, also.

The state of a measured constituent entered into the storage system will be described explicitly—organic, soluble, or particulate, for example. Because the rapid growth of the field prohibits any attempt to limit the variety of chemical parameters to be entered in the system, the system has been designed to accept data as general as total phosphorus or as specific as soluble As^{+5} or particulate tyrosine.

Such physical measurements as temperature and salinity will be stored in the system. All metric units will be accepted for input, with the computer converting to standard units for storage, computations, and output. Metric units other than standard units can be computed for output on request.

Data types

NODC's chemical system is computer oriented with variable parameter fields and field length to include the large variety of marine constituents now being measured and those that may be mea-

PROCESSING AND POSITIONAL DATA

(DATA TYPE—1)

VESSEL	ORIG. COUNTRY	SHIP CODE	BEGINNING LATITUDE	BEGINNING LONGITUDE	BEGINNING GMT DATE				ANAL. COUNTRY			DEPTH TO BOTTOM	NO. CONST. RPTD.	AIR TEMPERATURE		BAROMETRIC PRESSURE	NODC REFERENCE INFORMATION		CARD NO.	DATA TYPE	DECK NO.
					YEAR	MO.	DAY	HOUR						WET	DRY		IDENTITY NO.	CONSEC. NO.			
INSTITUTION	1 2 3 4	5 6 7 8 9 10 N S	11 12 13 14 15 16 17 E W	18 19 20 21 22 23 24 25 26	27 28	29 30 31	32 33 34 35 36	37 38 39	40 41	42 43 44	45 46 47 48	67 68 69 70 71	72 73 74 75	76 77	78 79 80	0 1 1

CONTINUED STATION NUMBER	ORIG. INST.	NAVIG. SYST.	ENDING LATITUDE	ENDING LONGITUDE	ENDING GMT DATE				ANAL. INST.	ORIGINATOR'S		CARD COUNT	CARD NO.	DATA TYPE	DECK NO.
					YEAR	MO.	DAY	HOUR		CRUISE NUMBER	STATION NUMBER				
PAGE NUMBER	1 2 3 4	5 6 7 8 9 10 N S	11 12 13 14 15 16 17 E W	18 19 20 21 22 23 24 25 26	27 28	29 30 31 32 33	34 35 36	37 38 39	40 41	76 77	78 79 80	0 2 1

CONSTITUENT	UNITS	SAMPLING DEVICE AND CAPACITY	PRELIMINARY TREATMENT	SEPARATIONS	METHOD OF ANALYSIS	INSTRUMENT	GMT DATE OF ANALYSIS				PRECISION		CONSTITUENT CODE	UNITS CODE	SAMPLING	TREATMENT CODE	SEPARATION CODE	METHOD CODE	INSTR CODE	CARD NO.	DATA TYPE	DECK NO.
							YEAR	MO.	DAY	TIME	VALUE	DEC										
							1 2	3 4	5 6	7 8 9	10 11	12 13	14 15 16 17 18	19 20	21	22 23 24 25 26	27 28 29 30 31	32	33 34	76 77	78	79 80

REMARKS:

| MESS. TIME | DEPTH | G L | Q | G + | VALUE | DEC. | Q | G L | G + | VALUE | DEC. | Q | G L | G + | VALUE | DEC. | Q | G L | G + | VALUE | DEC. | Q | G L | G + | VALUE | DEC. | Q | CARD NO. | DATA TYPE | DECK NO. |
| 1 2 3 | 4 5 6 7 8 9 | 10 | 11 12 13 14 15 | 16 17 | 18 | 19 | 20 21 22 23 24 | 25 26 | 27 | 28 | 29 30 31 32 33 34 35 | 36 37 | 38 | 39 40 | 41 42 43 44 45 | 46 47 | 48 49 | 50 51 52 53 54 55 | 56 57 | 58 | 76 77 | 78 | 79 80 |

sured in the future. Input into the system will be of three data types:

- Positional and reference data.
- Reference analytical information.
- Detail data.

The first data type is necessary to identify the marine station or cast to which the data pertain. NODC's and the originator's reference numbers, position, time of collection, and certain meteorological data are included.

The second data type, reference analytical information, identifies the requisite related information on sample development—from collection through analysis—and includes such things as units, sampling device and capacity, preliminary treatment, date of analysis, separation technique, analytical procedure, and precision. Changing any of these items for a particular con-

stituent at a particular station causes no problem because provision is made in this data type to note any such changes and to record the depth at which the change occurred. For example, if in a particular cast, arsenic was analyzed first spectrophotometrically and then by neutron activation, both procedures would be recorded and the depths where each is first applicable noted. The scientist need only write in all available information. NODC will supply the appropriate codes for computer use.

The third data type, detail or parameter data, uses a floating point technique (scientific notation) which allows the storage of measurements widely different in value, time, and space. The field is limited to five significant digits. If a decimal point lies within the field, as in a salinity of 34.96 parts per

thousand, the number is recorded as it stands—34.96. If the decimal falls outside the field, as for a very large or small number, the significant figures are recorded followed by the appropriate power of ten and the correct sign. Thus, a thorium value of 2.7×10^{-12}, would be recorded as $2.7, -12$.

All samples that are filtered, decanted, or centrifuged before analysis are flagged by the presence of an f in the appropriate column. Semiquantitative maximum data are indicated by L (less than) and minimum data are indicated by G (greater than). A constituent code identifies each entry which means, therefore, that any number of data inputs may be included for each station or cast.

Punch card input

Each punch card will be identified by a common core which includes NODC reference and consecutive numbers, deck number (to identify the system), data type, and card number. Thus, the two cards necessary to data type I will have common identifiers in all cases except card number.

This system is not yet operational at NODC and there will undoubtedly be operating changes while it is becoming functional. The basic goals, capabilities, and format designs will remain largely unchanged. The author and NODC earnestly solicit suggestions for improvement of the system.

MASTER CARD INFORMATION —

MES. TIME	DEPTH	CONST ABBR UNITS PRELIM TREAT DATE SEPARATION METHOD INSTRUMENT PRECIS/ACCURACY G+ L−		QF DEC	CONST ABBR UNITS PRELIM TREAT DATE SEPARATION METHOD INSTRUMENT PRECIS/ACCURACY G+ L−		QF DEC	CONST ABBR UNITS PRELIM TREAT DATE SEPARATION METHOD INSTRUMENT PRECIS/ACCURACY G+ L−	QF DEC
025	0.	12.64	F		L 500	−06		− 1.23	
	10.	18.93			400			− 1.27	
	20.	20.57			100			− 1.39	
	30.	L 22.46	Q		900	−07		− 1.48	
	49.	19.61			600			− 1.62	
	74.	19.00			200			− 2.01Q	
	105.	18.39			800	−08		− 1.75Q	
		DATE CHANGE							
	125.	18.35	F		900			− 1.99	
	200.	17.99			700			− 2.16	
					METHOD CHANGE				
	300.	17.83			800			− 2.18	
	450.	17.64	Q		900			− 2.23	
	550.	16.95			100	−07		− 2.29	
								INSTR CHANGE	
	675.	16.41			200			− 2.36	
	790.	16.15			300			− 2.48	
	1000.	16.00			400			− 2.64	

NODC system. *The IBM 7074 computer system is used to process data for the National Oceanographic Data Center. Console and tape drives (in background) are shown here*

For data type III, two cards are necessary for each depth. Card numbers are assigned horizontally, then vertically (that is, the two cards for the first depth have card numbers of one and two). Certain repetitious data such as common core and repetitious constituent codes and processing numbers necessary for punch card handling will be deleted as the cards go into the computer for permanent filing.

Storage

All information contained in the input format will be stored on magnetic tape. Two tape sorts will be maintained, a geographic sort and a parameter sort. The geographic sort will arrange stations geographically according to the Marsden square notation system. The parameter sort will arrange information alphabetically by measured or observed species, phenomenon, or characteristic. Initially, the size of the system does not warrant two such files. However, the files will serve as practical retrieval tools as the volume of data grows.

Some information will be stored in manual files rather than on magnetic tape. Generally, data stored in this manual fashion will be information such as chief analyst, published reference for analytical procedure, published reference to all papers based on the data as well as the source document, and the equation for calculating pre-

cision. Such information could be incorporated into the computer system if ever warranted.

Output

The format of the printout is arranged for convenience in data analysis. Reference analytical data are abbreviated rather than coded for readability and are placed columnarly over the specific data column. Data calculated by NODC will appear to the right of related data (for example K/Cl ratio will print out beside K concentration).

If no appropriate observed data are being printed, calculated data will appear after all observed data are printed. Obviously, space limitations will occasionally prohibit the printing of all observed and calculated data for a station on one line. Under such conditions a second block of data will be printed below the first with a repetition of depths and the remaining data associated with a cast.

Retrieval

Several types of data retrieval will be available to users. Requests can be made for the computer to supply data on the basis of cruise and station number or on the basis of location and measured item. The user then has the option of receiving:

• All observed information associated with the station.

• Only the observed information that fills his special needs.

• Certain information calculated by NODC.

• A combination of the three.

Requests will be answered using a logical combination retrieval routine. The addresses for any combination of items may be fed into the computer. If the user requests only the data on arsenic or copper determined spectrophotometrically in Marsden squares 126 and 127 at depths between 100–200 meters, only these data will be retrieved.

NODC calculations

Certain information will be calculated by NODC upon request. Ratios of constituent concentrations can be calculated either as X/Cl or X/Y (where X and Y are constituent concentrations). Interpolated values can be calculated from observed data using a four-point Lagrangian interpolation. Both observed and calculated parameters can be plotted at NODC. The user designates the coordinate axis. No attempt will be made by NODC to interpret the plotted points.

Certain statistical parameters such as mean, variance, standard deviation, maximum, and minimum can be calculated from the data, for the periods of total record, or for a year, season, month, or some other specified intervals such as a diurnal or nocturnal cycle.

Calculations can be made horizontally for the water column from interpolated values, or from observed values over a range of depths, such as between 1500 to 2000 meters. Vertically, the entire water column in a limited area is considered.

System capabilities

The scope, function, capabilities, and potentials of the NODC chemical system are broad. Briefly, the system will:
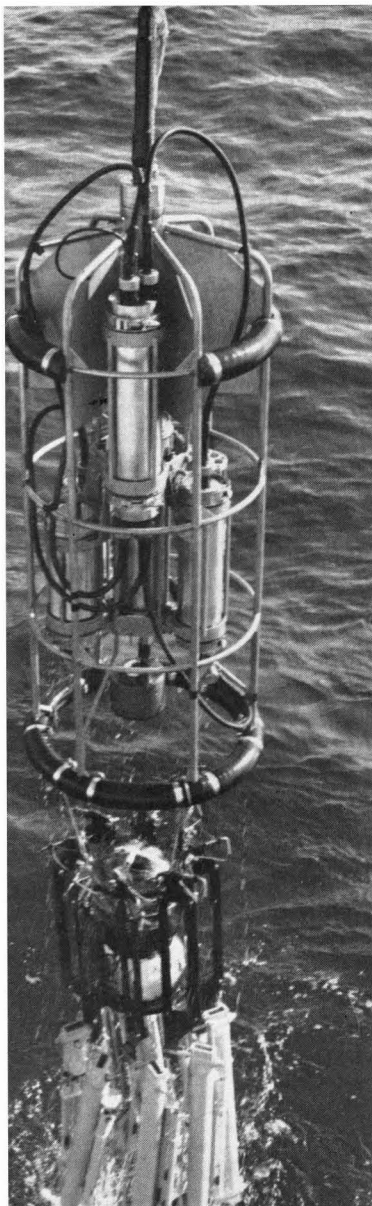
New instrument. *The electronic instrument for sensing salinity, temperature, and depth, shown here, will replace the Nansen bottle, the classical mechanical instrument for obtaining water samples for salinity and other chemical analyses. An array of the old-type Nansen bottles is shown hanging from instrument*

• Accept in any metric units physical and chemical data concerning the water column. Units will be converted to standard units, where possible, or alternate acceptable units.

• Accept calculated physical and chemical information that is time and space dependent.

• Calculate certain physical and chemical relationships (for example, N_2/Ar ratios).

• Accept any size of constituent concentration or any range of values.

• Accept semiquantitative maximums or minimums.

• Indicate changes (and where they occurred) of sample development for each constituent (for example, kind of sampling device, separation technique, or method of analysis).

• Provide a bibliography of published material for all information related to the data but not categorized on the input format or directly derived from the system. Reference will be to the source document, to other articles pertaining to these data, and to the analytical technique used.

• Indicate the chief analyst and his institution.

• Indicate further analyses expected from the cruise.

• Indicate whether other data were collected at sampling station. If other data are present in the appropriate NODC systems, they can be forwarded with the chemical data.

• Retrieve any combination of information entries from the system, including such things as time, position, constituent, method of analysis, constituent within a desired concentration range or depth interval, and the like.

• Transmit only the data requested or all physical and chemical data associated with the cast, as specified.

• Calculate certain statistical information—such as mean, variance, standard deviation, maximum, and minimum—for specified time periods such as total record, year, season, month, diurnal, nocturnal, or other period. In the water column itself, the grouping can be either horizontal or vertical.

• Interpolate values for any physical or chemical information input.

• Plot data without drawing a curve (for example, G_t vs. As, depth vs. Cd, Cu vs. time, N_2/Ar vs. N_2, PO_4 vs. O_2, and the like).

Dorothy L. Whittington *is a systems analyst with John I. Thompson & Co., Washington, D.C. Previously (1964–66), she worked at the National Oceanographic Data Center as an oceanographer. While at NODC, Miss Whittington worked on a marine chemistry information system and developed the marine chemistry data system described in this article. Miss Whittington obtained her B.S. in chemistry from the University of South Carolina (1964). She has written articles on techniques for determining chemical constituents of sea water and on the physical and chemical changes that affect the intrinsic viscosity of irradiation-induced polyvinylacetate. Miss Whittington is a member of ACS, American Association for the Advancement of Science, and American Meteorological Society.*

California's Auto Smog Cauldron Continues to Bubble

The state's Motor Vehicle Pollution Control Board's pioneering efforts, now in their seventh year, have been described as nothing short of miraculous. They've also been described as ineffective and shortsighted

California leads the nation in the number of autos, the amount of auto pollution, and the scope of its efforts to control that pollution. These efforts, spearheaded by the Motor Vehicle Pollution Control Board, are directed at making California's air as pure as it was before World War II. MVPCB's executive officer Eric P. Grant recently gave this assessment: "Our achievements can be described as nothing short of miraculous since being created by the Legislature in 1960. We entered an unknown field, and at every step were faced with major decisions as to test procedures, criteria, and principles of control. There was no experience by others from which we could benefit."

The Los Angeles County Air Pollution Control District doesn't see it that way. Its outspoken chief, Louis J. Fuller, contends that auto pollution sources have scarcely been touched and that stricter controls are needed if Los Angeles, "the smog capital of world," is to have clean air within a decade.

Initial problems

MVPCB's first problem in coping with auto pollution was the auto industry itself, which was even reluctant to admit that autos caused pollution. In Grant's words: "The State of California forced the automobile industry to control their vehicles." Controlling the vehicles concentrated on the three sources of auto pollution: crankcase vapors, exhaust emissions, and fuel tank evaporation. The first is now completely controlled in California. The second, the major source, is only partially controlled. Complete control is in the offing for the third.

The crankcase devices carry blowby gases from crankcase to intake manifold or carburetor, where they are returned to the engine. Crankcase vapors account for about 25% of the hydrocarbons emitted to the air by autos.

MVPCB has approved more than 70 control devices for new and used cars. The devices have been factory installed (at a cost of about $5) on most '61 and '62 models and on all '63 and later models sold in California. Originally, MVPCB planned to require the devices on all used cars of a certain age. But disagreement arose over how good a job the devices did and whether they were worth the $12 to $25 cost of installation on used cars.

The legislature, responding to public opinion, blunted MVPCB's proposal and required that the devices be installed only when a car was sold and only in 10 counties having pollution problems. (These counties contain 80% of the state's autos.) Today, close to 7 million cars in California are equipped with crankcase control devices.

As yet, California has not required controls for that 10% of the auto hydrocarbon emissions that comes from fuel tank evaporation or from carburetor "hot soak" loss. However, federal standards will require such controls in all '69 models.

There are at least six principles for controlling evaporation losses: crankcase storage, charcoal trapping, sealing, catalytic conversion, carburetor drain, and condensation return. They are usually combined to make up a total control system.

Exhaust problems

The major source of auto pollution—and the last controlled—is the exhaust. It is responsible for all the carbon monoxide, as well as 65% of the hydrocarbons attributed to autos. Exhaust control devices must be factory installed on new cars sold in California–it started with '66 models. Costs for the devices must be less than $50. About 1.4 million California cars are now equipped with exhaust control devices.

Domestic manufacturers have been using two variations in the exhaust control systems. Chrysler uses a Cleaner Air Package, which depends on modifications to the carburetor and distributor. General Motors, Ford, and American Motors worked out an air pump system to induce secondary combustion to the exhaust manifold. But Chrysler's system seems to have won out. According to Fuller, 85% of the '68 models will use that concept.

To receive certification from MVPCB, a system must meet these standards of exhaust emissions:

Hydrocarbons	**275 p.p.m.**
Carbon monoxide	**1.5%**

MVPCB has been gathering surveillance data on '66 and '67 models. A controversy has arisen over interpretation of these data. "Our approach to the total vehicle problem," says Grant, "is on the basis of averaging all types of control approaches and all types of vehicles." Grant is for the absolute standard, but believes the averaging approach is the necessary first step.

Surveillance tests to date show:

'66 models, 669 tested	62% passed hydrocarbon standard 64% passed carbon monoxide standard
'67 models, 270 tested	75% passed hydrocarbon standard 69% passed carbon monoxide standard

Grant *Miraculous achievement*

The average emissions are now 290 p.p.m. hydrocarbons and 1.66% carbon monoxide for '66 models. But, Grant points out, the devices have reduced hydrocarbons by about 70% and carbon monoxide by about 50%. "This represents a significant accomplishment by the vehicle manufacturers in the first two years of regulation," he believes. "This does not mean to say that the exhaust controls are perfect. Emission controls may be compared to the early years of automatic transmission, for example. They work, but improvement is needed." Grant also points out that since 1960, when crankcase devices were introduced, hydrocarbon emissions in Los Angeles have been reduced, despite the increase in motor vehicles. In San Francisco, the smog level has decreased by 25% since 1965.

Another view

Fuller, on the other hand, believes the entire concept of averaging is wrong. Of the '67 cars tested, Fuller says that about 60% failed to pass both standards. The percentage of cars failing increases as total mileages increase; extrapolation of the figures to 50,000 miles indicate that essentially all the cars will fail to meet the standards. The high rate of failures at low mileages, according to Fuller, refutes the contention that poor maintenance is the reason exhaust control systems are not working properly. What is needed, Fuller says, is a system "so designed and so built as to deliver the required performance throughout its lifetime with the same minimum attention required for transmissions, differentials, carburetors, and electrical systems."

Fuller also believes that "it is possible to clean up pollution from motor vehicles with existing internal combustion engines and with existing technology, and without some radical breakthrough or innovation—if all emission controls now known to be feasible are installed by the automobile industry on new cars at the earliest possible time."

Fuller quarrels too with the standards and the way they were set. Pre-1940 air is the target, but no measurements were being made then. When the State Board of Health was setting the standards in 1960, it based them on six field surveys made in 1956. More accurate surveys were made in 1962 and 1963, Fuller maintains; they indicate the standard for Los Angeles should be 150 p.p.m. But even that may be too high. To get Los Angeles air back to pre-1940 quality may require that the standard be set at 50 to 100 p.p.m.

One result of this controversy over exhaust controls, some observers fear, is that the regulations may be blunted, just as they were in the early days of crankcase control devices.

Nitrogen oxides

In 1965, the Board of Health adopted an exhaust standard of 350 p.p.m. nitrogen oxides, the first time any agency has adopted a standard for this pollutant. The high temperatures in an internal combustion engine cause the oxygen and nitrogen in air to combine. The oxides then combine with hydrocarbons in the presence of sunlight to produce the photochemical smog characteristic of parts of California.

So far, MVPCB has not certified any nitrogen oxides control system. The problem in designing the system is this: Complete combustion favors formation of oxides, while incomplete combustion favors formation of hydrocarbons and carbon monoxide. And, just as in design of the other auto pollution control systems, fuel economy and engine performance must also be considered.

MVPCB requires that exhaust control devices meeting the hydrocarbon and carbon monoxide standards must not increase nitrogen oxides more than 15%.

Grant says the devices are meeting this regulation. Fuller, however, fears that the approach the manufacturers are taking—that of adding more air to the engine—makes it difficult to control oxides.

Federal pre-emption

Another problem California will soon have to face up to is the role federal regulations will play when they come into force on '68 models. There are two schools of thought:

• National standards should be considered minimum, with states having serious problems permitted to impose more stringent standards This could lead to a proliferation of regulations at state and even local levels.

• Federal standards should be pre-emptory, tailored to meet the most extreme problem. This could impose an economic burden on areas with no auto pollution problem.

There is also some feeling that the state's pollution control efforts need reorganizing. One idea is to bring all air pollution control efforts together into one agency—either by expanding MV-PCB's scope, or creating a new agency with across-the-board control. And in April, the Waste Management and Environmental Quality Act of 1967 was introduced, with the Reagan administration endorsement, into the legislature. The law, to be administered by an Environmental Quality Board, would reorganize and consolidate all the state's effort in air, water, and waste control. Within the board would be an Air Resources Board charged with full responsibility in the air pollution control field.

Fuller says that though the measures look good, they have, in fact, been so weakened by amendments demanded by special interests that the measures have "no more teeth than a duck." There is no way to charge violators with having committed an offense, he notes, and no way to invoke penalties for noncompliance. But what is worst is that "passage would relieve the pressure of public opinion that otherwise might result in good legislation and some real progress in the fight on smog," he solemnized. And so the battle is joined again.
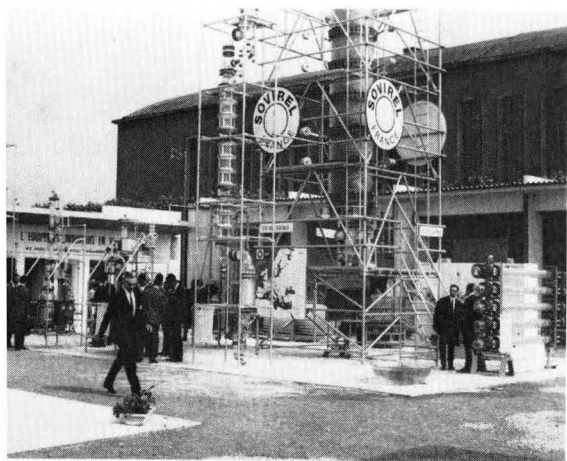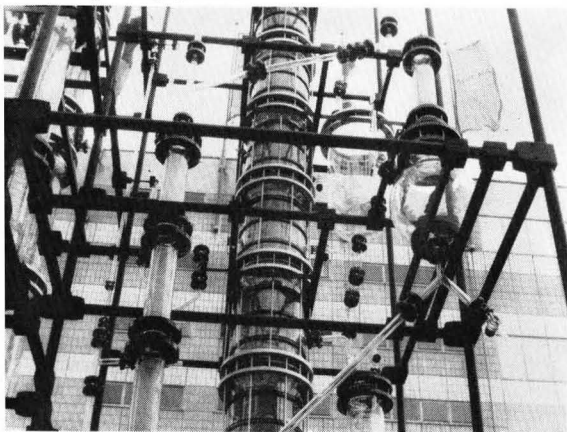
Fuller (*APCD*) *Blunted regulations*

Achema 67

Despite a long history of concern for pollution control, European manufacturers paid only scant attention to pollution control equipment at recent exposition in Frankfurt, West Germany

Glass for tough jobs...

...such as effluent streams

To Americans accustomed to being bombarded at every technical meeting with warnings about pollution, Achema 1967 came as a major surprise. In only one exhibit of the more than 2000 exhibits from 23 countries—a total of 800,000 square feet of exhibits—was pollution presented as the prime subject to attract a visitor's interest. Although effluents were obviously considered and treated by a large portion of the equipment exhibitors, they were not a featured part of the exhibits. Rather, emphasis throughout the show was on process capabilities, economics, time or labor saving possibilities, convenience, or other traditional technological considerations.

Inquiry around the fairgrounds led the American observer to an awareness that the current rash of attention given to pollution in the U. S. does not have its counterpart in today's European attitude. The basic reason for the difference is not that European managers are callous or that European citizens are uninformed. On the contrary, legislation up to 25 years old, much of which serves American lawmakers as models for their current deliberations, provides ample proof of European concern about pollution.

Rather, the reason is that most European economies are in a period of considerable slowdown compared to their frenetic growth rates of the past 15 years. Executives are tightening belts all over Europe—less travel, fewer fringe benefits, closer scrutiny of investment plans, and insistence on return in profits for money spent. And as American businessmen know, most antipollution investments either do not pay off at all or pay off at rates much lower than product or process investments.

European observers point out, however, that interest in the effects of industry on the quality of the environment continues and that investments will be resumed when the economic picture improves. The seven Achema 1967 technical papers on environmental quality—on combustion exhausts, cleanup of industrial gases by reaction or adsorption, and wastes from electrochemical processing—reflect the continuing technical efforts aimed at providing answers to the pollution problem.

ENVIRONMENTAL SCIENCE AND TECHNOLOGY was among the ACS publications on display in the Society's Achema booth, located among those of other publishers who produce a significant portion of the world's technical literature. Most of the European technical men who visited the Society display had not yet become acquainted with ES&T, which began publication in January in the throes of Europe's business slowdown.

Cyclone separator
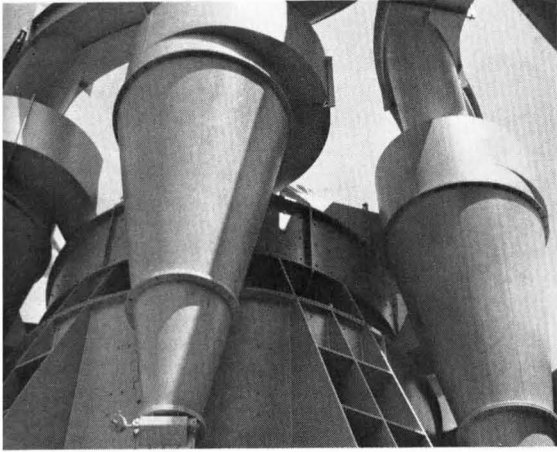
Outside displays

Air cleaner for cement grinding system
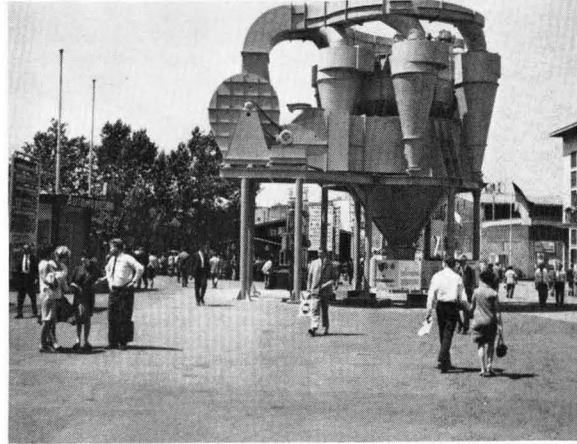
Visitors

Falling film evaporator

Exposition hall

The Sinister Side Effects of Science

In making science policy, Congress must learn to assess—in advance and in terms of human values— the consequences of technological changes

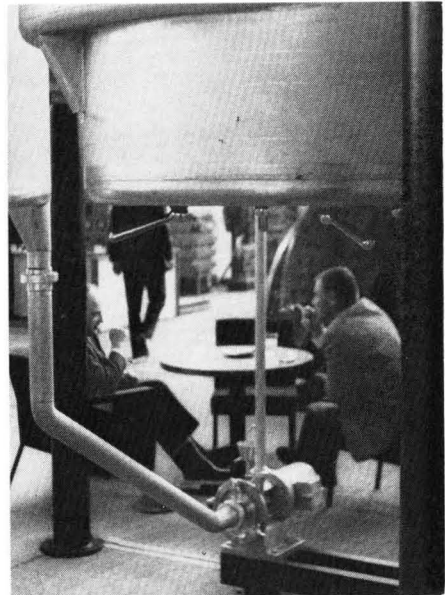Congress, today, recognizes that science and technology constitute one of the largest, most powerful, and most important forces in modern society. According to Rep. Emilio Q. Daddario (D.-Conn.), Congress is also "becoming aware of the difficulties and dangers which applied sciences may carry in its genes—and is searching for effective means to counter them."

To meet this challenge, Daddario's House Subcommittee on Science, Research, and Development plans a three-phase study of what it calls "technology assessment." The Daddario subcommittee hopes to equip Congress to make decisions on technological programs on the basis of a balanced, systematic analysis of the risks and benefits involved.

Old hands

Congress is not new at the business of assessing technology. As early as 1830 it was called on to take corrective action

after a series of boiler explosions on steamboats—the first piece of government sponsored contract research and one that was handled by the Franklin Institute in Philadelphia.

But, says Daddario, the history of the government's efforts shows that "again and again this country has moved to assess technology after some major crisis or catastrophe," the first lesson we should learn from history. He points out that "our current fight for air quality is an after-the-fact realization that the atmosphere could not be used as a convenient and inexpensive dumping place." He also cites the assessments that took place after the sinking of the submarine U.S.S. *Thresher*, the fire in the Apollo spacecraft, and grounding of the oil tanker *Torrey Canyon*.

Second lesson

History's second lesson, says Daddario, is that "technical information

needed by policymakers is frequently not available or not in the right form. A policymaker cannot judge the merits or consequences of a technological program within a strictly technical context. He has to consider social, economic, and legal implications of any course of action."

Two new factors make assessment of technological alternatives especially critical today:

• Increased population means less uninhabited area in which to conduct risky ventures. Thus, maintaining environmental quality is increasingly important.

• The powerful biological, chemical, radiation, and energy effects at man's disposal can upset the balance of the natural world. Such a widespread upset means that unforeseen consequences are less likely to be confined locally, or even detected under restriction conditions where lessons can be learned before significant and widespread damage is done.

New bill

In March of this year, Daddario introduced a bill (H.R. 6698) "to provide a method for identifying, assessing, publicizing, and dealing with the implications and effects of applied research and technology" by establishing a Technology Assessment Board. The discussions that ensued have led Daddario to believe that much more should be learned about the "how" of technology assessment before a permanent mechanism or organization can be set up. Therefore, his subcommittee plans a long-range study of the concept of technology assessment.

The study in its first phase will start with hearings and seminars on how to assess technology for congressional purposes. "The scientific and engineering community will have much to offer, for science by its very nature exposes its activities to trial and criticism," Daddario
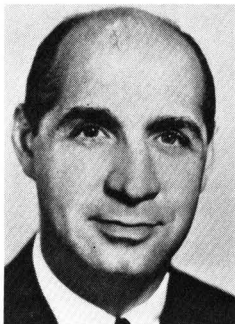
Daddario
Information not available

points out. The subcommittee will call on government and private sector technologists for opinions and operational assessment procedures. But, since assessment also considers human values, the committee will seek out testimony on social, economic, political, legal, and esthetic aspects.

The second phase of the study will involve working groups from the National Academies of Science and Engineering. The groups will:

• Arrange for pilot assessment projects on contemporary issues which call for assessment now. The assessment tasks could go to various kinds of organizations—a specially formed committee, a contract research organization, a government agency, or a professional technical society—to compare different organizational arrangements.

• Evaluate the various approaches and performances and report to Congress the most efficient and useful techniques for an eventual permanent technology assessment apparatus.

In the third phase of the subcommittee's study the Science Policy Research Division in the Legislative Reference Service of the Library of Congress will prepare an inventory of other current technology assessment projects throughout the world. However, relatively few of these assessment projects appear to exist.

A summary and analysis of historical assessment will examine such questions as: What part of society sounded the alarm? How obvious were the consequences before counteraction could be obtained? What political processes and institutions were involved in restoring the balance of benefit and deficit?

Other plans

Daddario's plan is one of several Congressional approaches to the technology assessment problem. H.R. 7796, introduced by Rep. John Dingell (D.-Mich.), calls for establishing a Council on Environmental Quality. Sen. Gordon L. Allott (R.-Colo.) introduced S. 1305 establishing a joint congressional committee on science and technology to assure that the benefits of science and technology are used most effectively in the interests of national security and the general welfare. And Sen. Edmund Muskie (D.-Me.) held hearings on Senate Resolution 68 to establish a Select Committee on Technology and the Human Environment.

QUOTE...

RUN THE SYSTEM AS A WHOLE

Mankind today has a wide range of technical and institutional options for coping with its problems of river basin development, water resource supply, waste management, and environmental quality. And I expect that, in the future, even more alternatives will be available—that current alternatives—for example, desalting—will become cheaper.

Before applying the newest machines and engineering advances, let us first ensure that we are making maximum use of the water resources presently available. The answer to our water resource problems, indeed, to all resources problems, is too often thought to be mere increase in supply of those resources. We have not thoroughly investigated nor utilized our existing water resources. We must make more efficient use, for instance, of our brackish and sea waters for irrigating crops. This is an old art and a subject receiving some attention today, but we are not making fullest use of this art.

When technical alternatives are used to solve the water problems and to meet the water needs of a particular nation, we must continually keep in mind the need to select the technical and institutional methods which are suitable to the capabilities, the needs, the goals, the values —the political, economic, and social systems, the culture and stage of development of that nation.

Just a few questions a nation or a people must ask itself before applying a technical alternative are:

• Does the technology fit the ecological conditions of the nation?
• Do economic conditions permit its application—can the technology be financed? What must be sacrificed to do so?
• Does the nation have the management capability to operate and control the technology for the good of the nation and its people?

There have been too many mistakes made in the past—in transferring technology from more to less developed nations—in transferring highly complex technology to nations unprepared to adopt it.

For example, in designing river basin, water, power, and waste management systems, we must design for a range of contingencies— for the optimist—when all works well—and for the pessimist—for the time when much goes wrong. For the test of man's technical creations is not how well they run when all parts work as designed, but how well the system runs and how great and widespread the damage when a part of the system fails.

In the United States, we have had some experience with technical systems—in our Northeast power failure which resulted when a power grid, designed to work when all went well, created potentially disastrous effects when a small part of the system failed.

Man must take care, in designing his water, power, and waste management systems, that he does not make himself, his society, and nation more vulnerable to disruption if a small element of the system which he designs does not perform perfectly.

Frank C. DiLuzio

Assistant Secretary of the Interior for Water Pollution Control, before the International Conference on Water for Peace, Washington, D.C., May 31, 1967

Water Resources: A Global Problem with Local Roots

RAYMOND L. NACE

Water Resources Division, Geological Survey,
Department of the Interior, Washington, D. C. 20242

To close the gaps in the world's knowledge of water system, to improve the training and increase the numbers of hydrologists, and to develop a better scientific base for the conservation and use of water, the nations of the world agreed to cooperate in the International Hydrological Decade

During 8000 years of historic and prehistoric management and use of water, man has yet to come of age in his relations with water and other aspects of the earth environment. Maturity in these relations will depend on improved understanding of the environment, in which water is a crucial factor. Water is rather well understood as a substance, but the behavior of this substance in the global phenomenon known as the hydrological cycle is but poorly understood. Intensive and extensive needs and plans for water management, including transcontinental diversions and distribution, will usher in a new era in history and a new order of magnitude in environmental impacts and problems.

In order to cope with these, nations of the world must cooperate to study water on national, international, continental, and global scales. The IHD provides the framework for such cooperation. Nearly 100 nations participate in this program, which is aimed to close major gaps in basic water data, promote research, and improve the rationale for water development. The program also emphasizes training and education of hydrologists and wider application of knowledge about water that is already available. The Decade's last year is 1974 but it seems likely that international cooperation will continue thereafter because of its own momentum and proved benefits.

Water and civilization

In the pre-dawn of the first morning of civilization, a man with a wooden hoe labored somewhere on the Mesopotamian plain, digging a long trench from his sown field toward the silt-laden River Euphrates, or perhaps the Tigris. A final stroke of the hoe removed the last clump of earth separating trench from river; the trench became a canal and the field became an irrigated farm. The trickle of water in the irrigation ditch has been heavenly music to men throughout the ensuing 8000 years.

The unknown farmer had planted more than the seed of grain in his field. The seed of civilization quickened there. A one-farm irrigation system requires nothing but one-man initiative. But irrigation in Mesopotamia spread within a few centuries through many hundreds of thousands of acres, based on a complicated, well-engineered system of river diversions and sluice gates, hundreds of miles of feeder canals and ditches, systematic hand dredging of silted-up canals, and maintenance of levees. Such a system required central administration and control for main-

tenance, allocation of water rights, and regulation of production. The first Chief of State may have been a river master.

A food supply assured by irrigation farming permitted the first permanent villages and in Mesopotamia it led to the first city-states and kingdoms. The subsequent spread of irrigation and ancient civilization in the Middle East, in Egypt, in India, and in China is a long story. Even longer is the story of the evolution of civilization as a whole and of its close ties to water for irrigation, navigation, sanitation, industrial and public supply, and waste disposal. During most of this 8000-year period, men simply used water where they found it, without understanding how fresh water happens to be where it is, or how it got there. As my colleague Walter B. Langbein expresses it, human water economy remained in the hunting and gathering stage during most of history and is still in that stage in the use of ground water. Many non-industrial countries are still in the hunting and gathering stage of water use.

A rude awakening

Around the middle of the present century hydrologists suddenly realized that hydrology had never found a place in the water-development industry comparable, for example, to the role of chemistry in industry. Hydrologists had been so engrossed in measuring the flow of rivers, the levels of ground water in wells, and the vagaries of precipitation that few of them had gotten into the market place and made hydrological facts and variables an integral part of water planning. They lacked even a common language for communication with economists, policy makers, and sociologists.

Awakened social consciousness among scientists is a phenomenon largely of the twenty years or so just past. This awakening contributed to the realization among hydrologists that, just as water development and planning go beyond the local area or individual river basin, so must hydrology go beyond these. Nor can it stop with multiple-basin regions or even the continents. The total amount of fresh water on the continents is only a minute percentage of all the world's water, most of which is brine or ice. Hence the flow of water in the Amazon River, for example, is important to North Americans, for a given molecule of water cannot be present in the Amazon and the Colorado at the same time.

The water cycle is a global phenomenon. Therefore, water resources are a global problem with local roots. The occurrence and movement of water in one part of the world are consequences of its occurrence and movement in all other parts of the world. At present this cycle can be described only in crudely quantitative terms which are of little help in prediction, but prediction is essential for rational water management. Controlled systematic modification of phenomena such as precipitation requires vastly improved knowledge and understanding of the water cycle on a global scale. Hydrological data are either lacking or totally inadequate for two thirds of the land area and nearly all of the water area of the world. Among the nearly blank areas are the great weather factories: polar areas, tropical areas, and major oceans. Not even the United States is rich enough or sufficiently well supplied with technical manpower to undertake studies of all the data-deficient areas of the world. How, then, can knowledge and under-

standing be achieved? The IHD (International Hydrological Decade) is an attempt to answer this quesion.

International cooperation

The IHD is a program of international scientific cooperation to close gaps in information about the world's water, to stimulate improved education and training of hydrologists, to raise the level of competence in hydrological studies, and by these means to provide a better
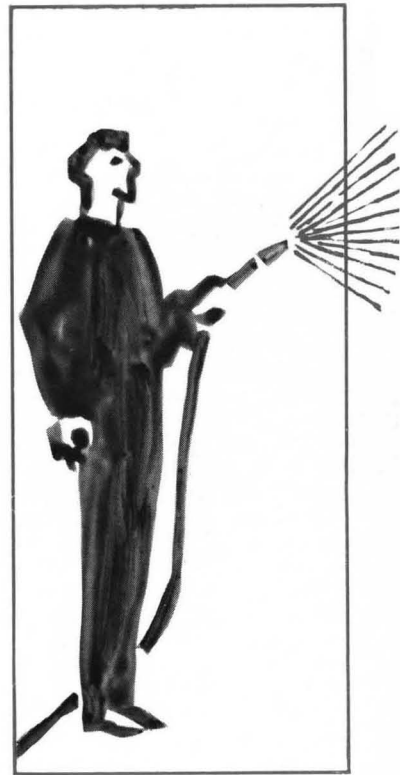
Water and water cycle are
intimately related to the daily lives of everyone

scientific base for conservation and use of water in all countries.

International cooperation in scientific ventures began as early as the 18th century, but most of these ventures involved only a few nations. One of the more recent, the IGY (International Geophysical Year, which actually spanned 18 months during 1957–58) was a specialized scientific and technological program of some 40 advanced nations, many of whom participated in special expeditions to many parts of the world. Planning and promotion of the IGY required seven years before attainment of the essentials of agreement plus money to carry it out. But international geophysical cooperation has continued during the ensuing 10 years because it proved its own value. Such cooperation may become permanent.

Ideally, the IHD should involve all the world's nations because the water cycle recognizes no national boundaries. Water and the water cycle are intimately related to the daily lives of everyone from the nomad in the Nubian Desert to the aborigine in the Amazonian rain forest, from the hunter in the Siberian tundra to the broker in the towers of Manhattan.

The program also should span a term of years because water supply is highly variable and no single year would be a sufficient time for organizing and staging useful studies. Ten years will be a useful period and is about as long as governments are willing to commit themselves, but successful essential activities will continue thereafter on their own momentum.

Discussions at national and international meetings among representatives of universities, scientific associations, government agencies, and intergovernmental agencies of the United Nations led to agreement to stage an IHD beginning in January 1965. Central planning and coordination are nec-

essary, and the 13th General Conference of UNESCO (United Nations Educational, Scientific, and Cultural Organization), the lead agency for the IHD, created a 21-member Coordinating Council to guide the activities of the 90-odd Member States that participate in the program. Other UN agencies also have important roles and responsibilities.

The WMO (World Meterological Organization) has accepted leadership for several major activities for which it can be especially effective because of its world-wide regional associations and representatives and its prior experience in catalyzing and coordinating international cooperative activities.

The FAO (Food and Agriculture Organization) is deeply interested in the IHD because of the close relation between water supply and food production. The project offices of FAO, largely in developing countries, can be especially useful in stimulating grass-roots work in those countries, where it is badly needed.

The WHO (World Health Organization) also is vitally concerned for obvious reasons. A major project of WHO in developing countries, Community Water Supplies, will benefit from and contribute to the IHD.

The IAEA (International Atomic Energy Agency) has specialized but highly important interests in the IHD because both stable and radioactive nuclides are useful as tracer tags in water studies. For example, IAEA and WMO have collaborated with various national governments in studies using bomb-produced fission and fusion products to trace the movements of atmospheric water vapor and surface water. More recently IAEA has sponsored studies to follow the tracers underground and to learn more about groundwater behavior.

The IHD is a program of Member States of the UN family, not of the

international agencies. The functions of UN agencies in the IHD are largely catalytic and supporting, because the agencies do not themselves have large operational programs. UNESCO, for example, provides a small professional staff which works full time to coordinate national action in response to recommendations of the Coordinating Council, which meets annually. The agency also stages the meetings of the Council; bears the expenses of special task forces; sends experts to advise developing countries on formulation and organization of operational activities; contributes

financial support to scientific symposia organized by international scientific associations; helps to organize and support regional advanced short courses in hydrology; provides scholarships for regular university study by candidates from developing countries, and numerous other activities. Other UN agencies have similar activities in their specialized fields.

Regional economic commissions of the UN have strong interests in the IHD. One of the more successful of these—the Economic Commission for Asia and the Far East (ECAFE)—has staged a series of successful hydrology seminars and has organized regional water studies despite disturbed political conditions in that part of the world. Southeast Asia probably is the only area in the world where guerrillas operate openly during daylight and hydrologists function surreptitiously during darkness.

Ideals and realities

The IHD, now half way through its third year, presumably should be in full swing. But international cooperation, scientific or otherwise, always is cumbersome because of language barriers and other communication problems, differing national policies, and differing opinions about work priorities. Not everything important can be tackled at once in an operational program, and local and national situations influence judgments about priorities. A major problem in most Member States has been to convince ministers of finance that international cooperation is necessary or sufficiently important to be funded in competition with other activities. This was anticipated, and inducement of governments to spend money
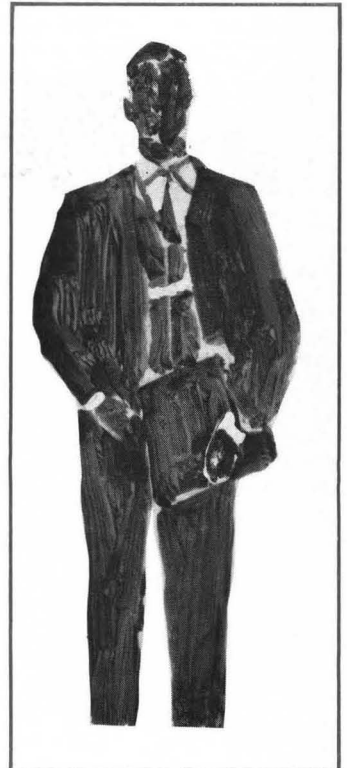
In the world as a whole, most working hydrologists are self taught

on hydrological studies, which is in itself a major accomplishment, is one objective of the program.

Many countries took no substantive action until after UNESCO's General Conference, late in 1964, set the opening of the Decade for the following January. Activity in the first two years of the Decade, therefore, has consisted largely of specific program formulation and scheduling of operations. The United States itself, where the idea originated, has had little more than a token program. The growth pains are severe.

Education and training

Many developing countries have few hydrologists or none. In the world as a whole, most working hydrologists are self taught, having been educated as geologists or engineers, with lesser numbers of chemists, physicists, mathematicians, and a few other disciplines. This has been possible because hydrology is a derived science, consisting of the application of basic sciences to the study of water. The physicist, for example, who works on a hydrological problem is a hydrologist to that extent.

In a recent manpower survey of earth sciences in the United States, only 921 out of nearly 20,000 individuals who returned questionnaires declared themselves to be qualified primarily as hydrologists. Probably about 2500 scientists and engineers in the United States actually devote most of their time to hydrological work, research, or teaching. Many hundreds more spend part or all of their time on some aspect of hydrology. Even so, the ranks of hydrology are thin and the IHD is a bootstrap operation, even for developed countries. Nevertheless, bootstrap operations have produced many important accomplishments in scientific hydrology. Geophysics was a minor discipline until after the IGY.

In 1962 a group of American universities, recognizing the critical importance of hydrology, formed an organization to improve curricula and encourage advanced education and research in hydrology and water resources. Nearly 50 member institutions of the Universities Council on Water Resources offer a wide variety of courses in hydrology and related economic and social problems. For the 1967–68 academic year, these universities have set up 15 IHD fellowships and 50 IHD research assistantships for advanced study and research in the United States. These are available to foreign nationals.

Meantime, UNESCO has a program of hydrology fellowships, already in its fourth year of operation, which currently provides fellowships for about 15 students annually. UNESCO also sponsors, in cooperation with member nations, short courses (4 to 6 weeks) in advanced hydrology. These are designed for practicing hydrologists to acquaint them with recent advances in the science and its methodology. The courses accommodate up to 30 students per course and, staged two to three times yearly, turn out 60 to 75 students per year.

Several individual countries have taken actions to improve their hydrological education and to help foreign nationals. Nations which have done so are Czechoslovakia, Hungary, Italy, Israel, the Netherlands, Soviet Union, Spain, and Venezuela.

The program of Hungary is illustrative. Hungary offers to foreign nationals a five-month international post-graduate course for 15 students annually. Fellowships for this course include monetary allowances for travel, lodging, food, cultural and social expenses, medical care, accident insurance, and other fringe benefits. During more than 100 years Hungary has been a leader in applied hydrology and prominent in European hydrological research. The kinds of instruction offered by Hungary and other eastern European countries, including Russia, are well suited to students from developing countries. The practicality of these courses is implied by the Hungarian titles "International Post-Graduate Course on Hydrological Methods for Developing Water Resources Management."

In addition to the activities noted above, WMO, FAO, IAEA, and WHO have education and training programs, parts of which concern hydrology and water management. In response to the Decade program, the water aspects of these programs have been emphasized.

Operational activities

The international program includes several major groups of activities, but space is available to summarize only a few samples.

World water balance

Study of the world water balance consists of an inventory of the total amount of water in the Earth system and its movement through the global hydrological cycle. About 97% of all water in the system is in the world ocean. Most of the remainder is frozen assets in icecaps and glaciers. Much less than 1% is present at any given time as liquid fresh water in rivers, lakes, and aquifers. The average amount of water vapor continually present in the atmosphere is a vanishingly small percentage of total water. Rivers annually discharge about 9000 cubic miles of water into the seas, but this value is merely a rough approximation, because less than 5000 cubic miles of discharge is actually measured.

The amount of water in land areas is such a small part of total earth water (326,000,000 cubic miles) that it is
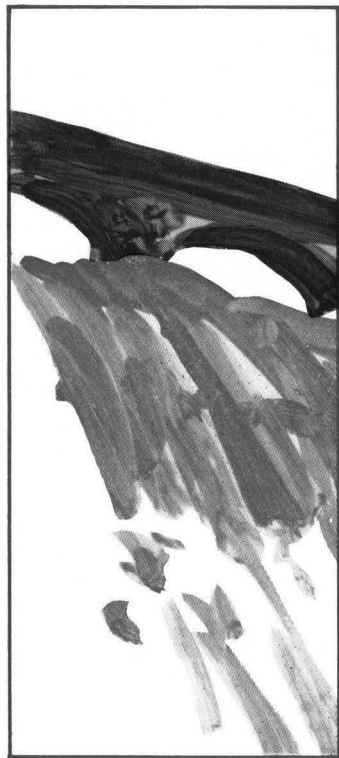
Much can be accomplished—quickly and economically—with instruments in orbiting satellites

virtually lost in the system. An explorer from space who wished to tell the home office about that curious substance, water, which covers most of the earth, probably would ignore continental water, because the amount is far less than the margin of error in estimates of the oceans and icecaps. Nevertheless, earthlings must pay increasing attention to the relatively negligible continental part of Earth's water system. This entails many problems because the water is constantly moving and means for measuring it outside the laboratory are relatively crude.

For water planning, development, and management, continuous measurement is necessary of river stages in order to calculate daily, seasonal, annual, and long-term yield. Under good conditions the flow of an ordinary river of moderate size can be calculated from measurements of depth and velocity of water with an accuracy of 95 percent or even better. But a large flood cannot be directly measured at all by any means now available. A river as large as the Amazon near its mouth requires an expedition and an ocean-going ship to make a single direct measurement of normal flow.

Ground water presents even greater difficulties than surface water because it is out of sight, its movement cannot be measured directly, and its total quantity is unknown except in a few local areas that have been studied intensively. From general geological and hydrological information, it is evident that unused ground water is available in many areas. Development of ground water has the advantage that wells can be drilled quickly for irrigation, domestic supply, public supply, and industry. Where adequate ground water is available, wells can be drilled singly or by the hundreds without awaiting construction of multimillion-dollar dams and canal systems. Thus thousands of wells have been drilled in the Gangetic Plain of India and the ground-water supply is adequate for thousands more. Ground-water is available even in some desert areas which have no other source of water. The vast Sahara Desert (nearly as large as the conterminous United States) is underlain by great thicknesses of geological formations which are abundantly water-bearing at some places. Further exploration may disclose that the Sahara contains an extensive system of aquifers that can be exploited. This, however, will require vastly more scientific knowledge about the area than is available now because ground-water management is by no means simple.

Preliminary studies have laid the ground for more intensive investigations of north Africa under international auspices, for which UN agencies will arrange scientific and technical leadership and logistical support. One such study, of the Chad Basin, already has been authorized and is getting under way with cooperation of Cameroon, Chad, Niger, and Nigeria through their Chad Basin Commission.

Evaporation from oceans and continents and total precipitation on land and sea are additional hydrological factors for which only crude or sparse data are available. But enough has been said about other aspects of the hydrological cycle, to show that it is a very large task just to inventory the average amounts of water in various environments—to derive a still picture. To go beyond that and to portray the moving picture of the water cycle in quantitative terms is a vastly greater task which will require synoptic measurements at many places throughout the world and throughout each year.

Some measurements can be made by remote-sensing, a field in which technology is advancing rapidly. Techniques include ordinary and color photography, infrared imagery and scanning, and radar scanning, to mention only a few. Remote-sensing instruments carried in airplanes can do part of the job but repetitive wide coverage by that means would be prohibitively expensive. Prospects are good that much may be accomplished quickly and economically with instruments in orbiting satellites. Examples of information that might be obtained from satellite data are maps of large flooded areas; seasonal variations in snow cover in remote areas; long-term variations in the boundaries of icecaps; boundaries and extent of oceanic currents; break-up of pack ice and shelf ice and distribution of large icebergs; extent of glaciers and perennial snow in remote areas; and many other possibilities. In addition, communications satellites may permit more efficient use of data that have been obtained by conventional methods. Stream gages, for example, can be equipped to transmit data by radio to a satellite. The satellite would relay information to a national or regional computer center, which would manipulate the data, print it out and transmit it to data users. Some highly developed regions already need such a system whether it uses a satellite or some other kind of relay.

Cold-storage lockers

Glaciers and icecaps cover 11% of the land area of the world, and most of the ice area has been mapped only crudely or on very small scales. An additional 10% of the land areas is locked in permafrost—permanently frozen ground. At any given time, 30 to 50% of the world land area is covered with snow, while 25% of the ocean is occupied by pack ice and icebergs. Worldwide, 75% of all fresh water in existence is stored as ice, chiefly

in Antarctica and Greenland, but ice and snow loom large in the water cycle in vast areas that are far more hospitable than polar regions. Cold regions contain tremendous reserves of mineral, fuel timber, water, and other resources for which human demand is increasing.

The damage done by man in temperate and tropical zones probably is small compared to what may occur in cold regions under the disordering influence of intensive "development." Environmental problems of the cold regions of the world differ widely from those in other areas.

Snow and ice studies are part of the world water balance project, but they have much additional significance, as is illustrated by data summarized by Dr. Mark F. Meier of the Geological Survey, an internationally known glaciologist. Glaciers in the state of Washington alone, covering 135 square miles, store about 42 million acre-feet of water —about equal to the combined storage of the state's reservoirs, lakes, and stream channels. During the dry months of July and August, these glaciers release about 800,000 acre-feet of water to streamflow—about equivalent to total pumpage of ground water in the state during a whole year. The principal source of streamflow in Washington and other Western States is snow and ice above 7000 feet of altitude.

Glaciers and perennial snowfields are, in effect, nonstructural water reservoirs, and the possibilities for their management merit thorough investigation. Possibilities include suppression of evaporation, suppression of melting in wet years, inducement of melting in dry years, and others. The possibilities have more than local significance. Snow, ice, and permafrost dominate the water scene in Alaska and huge areas in Canada, northern Europe, Siberia, and high mountain areas in Asia and
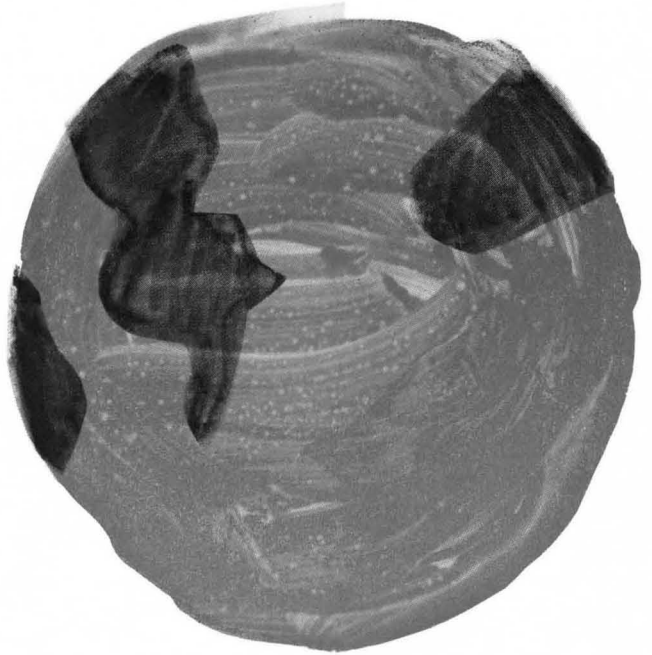
World water budget is tiny though important portion of world water supply

Water item	Volume (cubic kilometers)	Per cent of total water
SUPPLY		
Water in land areas:		
Fresh-water lakes	125,000	0.009
Saline lakes and inland seas	104,000	.008
Rivers (average instantaneous volume)	1,250	.0001
Soil moisture and vadose water	67,000	.005
Ground water to depth of 4,000 m	8,350,000	.61
Icecaps and glaciers	29,200,000	2.14
Total in land area	37,800,000	2.8
Atmosphere	13,000	.001
World ocean	1,320,000,000	97.3
Total, all items	1,360,000,000	100
BUDGET		
Annual evaporation:[a]		
From world ocean	350,000	0.026
From land areas	70,000	.005
Total	420,000	0.031
Annual precipitation:		
On world ocean	320,000	0.024
On land areas	100,000	.007
Total	420,000	0.031
Annual runoff to oceans from rivers and icecaps	38,000	0.003
Ground-water outflow to oceans[b]	1,600	.0001
Total	39,600	0.0031

[a] Evaporation (420,000 km.[3]) is a measure of total water participating annually in the hydrological cycle.
[b] Arbitrarily set equal to about 5% of surface runoff.

Note: Values in the table are approximations based on data compiled from many sources. They should not be construed to mean that any of the values is precise.

Small changes of world climate can profoundly affect water supplies regionally and locally

South America. Alaska alone contains 20,000 linear miles of glaciers storing perhaps 12 billion acre-feet of water. The extent to which reserves of snow and ice are manageable for water supply is an almost totally unexplored field.

Glaciers are highly sensitive to variations in climate. The weight of evidence seems to indicate that many alpine and valley glaciers have been shrinking appreciably during more than 100 years. However, evidence of growth during the same period is definite for certain glaciers. Whether the major ice sheets are waxing, waning, or in equilibrium is controversial among specialists, which means that not enough data are available to support firm conclusions.

It is important, however, to know current and recent trends, because small changes of world climate can profoundly affect water supplies regionally and locally. It is equally necessary to know what variations occurred during past centuries. If recurrent patterns or cycles have occurred, perhaps future ones can be predicted. Methods are available for study of past variations: ice cores are being studied to compare the water content of successive annual layers; precipitation rates can be estimated from oxygen-isotope ratios in successive layers; individual layers may be correlated from glacier to glacier and even from continent to continent on the basis of volcanic dust falls. Dust from several violent volcanic eruptions during the historical period has spread through the atmosphere of the entire globe. Glaciologists someday may find the ice-dust layer correlative with the eruption of Thira volcano, which some investigators believe destroyed Minoan Crete and perhaps ancient Troy in about 1400 B.C.

The International Commission of Snow and Ice (a scientific commission of the International Association of Scientific Hydrology) has recommended, and the IHD Council has endorsed, a world-wide network of glacial observation stations. This would include a latitudinal chain of stations extending from northern Europe and the Alps eastward to the Caucasus and through the mountains of Central Asia and the Himalaya. In North America, Canadians expect to extend one or two chains eastward across their country. A second world chain would be meridional, extending from Alaska through the coastal ranges of British Columbia and western United States and through the Andes of South America to Patagonia. These studies will be coordinated with other investigations, such as expeditions to Antarctica and Greenland and Canada's Axel Heiberg Expedition to her Arctic island of that name. Work in Canada and the United States is well underway despite shortage of qualified personnel. An American glaciologist has made two extended visits to Andean countries of South America to help plan and organize their programs. Europeans have their activities well in hand.

Research

Studies of the world water balance, including snow and ice, will require specific research to close gaps in understanding of the water cycle. An example of an important topic is the causes of the incidence and spread of continental drought. Other types of IHD research, however, concern specific hydrological processes. An example is studies of representative basins.

Small hydrological basins have been selected for special study in each continent. These are large enough to represent conditions and processes in larger areas, yet small enough to be studied intensively with adequate instrumentation. Six basins have been chosen in the United States. The hydrological characteristics and regimes of these basins will be studied in relation to climate, vegetation, soils, geology, and other factors in an effort to derive general principles. Studies of this kind can be and have been made individually in various countries without benefit of international cooperation. Few of these studies have been broadly or fundamentally definitive because isolated studies may and often do lead to wrong conclusions whose wrongness becomes apparent only when the supposed basic principles fail of application in a different and differing area. The purpose of the international project is to stimulate study in a large number of basins throughout the wide range of physical and ecological conditions from arctic tundra to searing desert, from tropical rain forest to alpine valley, and so on. Participation in this activity extends from countries in Europe and Asia to those of Africa and from North and South America to New Zealand and Australia.

Another example of important long-term research is the establishment of hydrological benchmarks. These are analogous to topographical benchmarks. Locations are chosen in isolated areas that have been disturbed little or not at all by human activity and have a chance of remaining inviolate for many years. These will be observed (runoff, precipitation, water quality, sediment movement, etc.) in an effort to relate hydrological variations with their natural causes. In most areas, man has so disturbed the environment that it is difficult or impossible to determine which hydrological variations are man-induced and which are natural. Benchmarks will aid in differentiation of causes but obviously must be operated far longer than a decade. The importance of this idea has been widely recognized but action has been slow. Undisturbed areas that will remain so are scarce or lacking in most European countries. In addition, many developing countries have not solved the problem of obtaining systematic observations in remote areas.

Water for Peace will lead to accelerated and more rational water development and use

Water facts for the future

People make decisions about water every day, but in many areas hydrologists can contribute little to the soundness of these decisions even when their advice is sought. One of the principal reasons for this is lack of basic data. Officials of FAO have emphasized to the IHD Coordinating Council that, in their agricultural development projects, they commonly have to design projects on the basis of only one to a few years of sparse hydrological data, whereas they need 20 or more years of record. The reason is that rainfall, river flow, groundwater levels and other phenomena vary widely. These variations are not just seasonal or annual. Superimposed on the short-term variations are longer ones ranging from decades to hundreds of years. Given a decade or two of streamflow records, hydrologists have methods for synthesizing and predicting probably variations during much longer periods of time.

The uses of data are so many and varied that they cannot even be summarized here. It can be stated only that water facts are crucial for the future. Many countries, therefore, are making strong efforts to improve their data networks and to establish networks where none exists. Countries that have skill in data collection and analysis are assisting less privileged countries by assisting them with network design, selection of instruments, training of personnel, and application of methods for analysis and interpretation of data.

Water for Peace

In October 1965 President Lyndon B. Johnson announced a Water for Peace program. The White House previously had endorsed the IHD and urged agencies and universities to participate. Inasmuch as the WfP announcement did not specifically mention the IHD, the relation between the two programs is not clear to everyone.

Adequate explanation of WfP would require a separate article. For the present it may be sufficient to say that the stated objectives of WfP clearly encompass those of the IHD. The IHD will improve the scientific and factual basis for water management and development. Water for Peace will embrace that objective and go farther, aiming at accelerated and improved development itself. The two programs are thus compatible and complementary.

The first substantive event in the WfP program was an *International Conference on Water for Peace* during May 23–31, 1967, in Washington, D.C. This meeting, which provided an international review and summary of principal water situations and development problems of participating nations, will lead to accelerated and more rational water development and use.

Dr. Raymond L. Nace *is a staff scientist, Water Resources Division, Geological Survey, Department of the Interior. He has been employed by Geological Survey since 1940, with a $3\frac{1}{2}$-year interlude in World War II as commander of a water-supply company. Dr. Nace received his B.S. (1935) and his M.A. (1936) from the University of Wyoming, and did graduate study at the University of Wyoming, Yale, and Columbia University before receiving his doctorate from Columbia (1960). Dr. Nace is chairman of the National Academy of Sciences' National Committee for the International Hydrological Decade, a member of UNESCO's Advisory Committee on Arid-Zone Research, AAAS, Water Works Association, Geophysical Union, and a fellow of the Geological Society.*

CURRENT RESEARCH

Theory on the Movement of Some Herbicides in Soils

Linear Diffusion and Convection of Chemicals in Soils

Fredrick T. Lindstrom, Rizwanul Haque, Virgil H. Freed, and Larry Boersma

Oregon State University, Corvallis, Ore. 97331

■ The movement of some chemicals in soils has been treated theoretically by considering for saturated conditions, the chemical diffusion coefficient, the percolation velocity of the water, the sorbtive properties of the soil, the average particle size of the soil, and the fractional number of sorbing sites. A model has been developed for the movement of chemical in saturated soil, based on Fick's law, conservation of energy, and a sorption isotherm. Theoretical curves for two different boundary conditions are given for realistic values of the water velocity in the pores and the measured diffusion coefficient.

The fate of herbicides in the soil is currently a problem of great interest. The main parameters involved in the process of herbicide movement in soils are: the soil moisture content, the percolation velocity of the water or chemical solution through the soil voids, the sorbtive properties of the soil, the particle size distribution, the ratio of the chemically active area of the soil particles to the total surface area of soil particles, and biological degradation.

Much work has been done on the movement, uptake, and degradation of chemicals which have been applied to the soil (Ashton, 1961; Burneside, Feuster et al., 1963; Freed, Vernette, et al., 1962; Harris and Warren, 1962; Hartley, 1964; Lambert, Porter, et al., 1965; Talbert and Fletchall, 1965). Most of this work has been of a qualitative nature, and though very useful by itself, it does not give the understanding of the processes involved which can be derived from the development and testing of a quantitative physical model.

Some quantitative models have been postulated (Burneside, Feuster, et al., 1963; Hayward and Trapnell, 1964), and most are based on the linear diffusion-type partial differential equation. This type of equation fails to take into account leaching or convection. Several detailed analyses of the movement of chemicals in porous media can be found in the literature. These include the early work on the adsorption of chemicals in chromatography and ion-exchange resins (Kipling, 1965; Lapidus and Amundson, 1952; Van Schaik, Kemper, et al., 1966; Vietter and Sladek, 1965), diffusion in proteins and polymers (Chao and Hodscher, 1966; Houghton, 1963; Ward and Holly, 1966) and mixing in chemical reactors (Bischoff, 1966; Bischoff and Levenspiel, 1962a, 1962b). These studies have led to several mathematical models. One early model (Kasten, Lapidus et al., 1952; Lapidus and Amundson, 1952) which has proved very useful in chromatography theory is based on the diffusional plus convective-type partial differential equation:

$$C_t + VC_x = DC_{xx} - \frac{1}{\gamma} N_t$$

where C is the concentration of chemical in the voids, U is the velocity of the carrier flowing through the voids, D is the diffusion coefficient, γ is the fractional void volume, and N is moles of solute adsorbed per unit volume of packed bed. Using the same equation, other models have been developed by Houghton (1963) and Chao and Hodscher (1966). However, these models are based on nonlinear adsorption, which may be unnecessary for many herbicides (McLaren, 1966).

Models which most closely represent the conditions of herbicide movement in soils may be found in the theory of chromatography (Kasten, Lapidus, et al., 1952; Littlewood, 1962; Purnell, 1962). Lapidus and Amundson (1952) made a great contribution along the line of chromatography. Their model assumes a constant surface concentration. Brenner (1962) improved the model postulated by Lapidus by incorporating a realistic boundary condition of fluxing at the surface. Brenner's model can be improved by adding an appropriate sorption term and a flux-plug–type input at the surface.

This paper states a mathematical model incorporating certain modified conditions of Brenner's model, states the equations, and shows solutions for certain boundary conditions of practical value.

Theory

The Model. Consider a field for which the knowledge of herbicide concentration in the soil solution, as a function of depth x and time t, is desired.

The area of the field is large enough so that edge effects can be neglected. A uniform sheet of chemical solution is applied at $t = 0$ to the surface $x = 0$. Only vertical movement of chemical and water shall be investigated.

Figure 1. Two-dimensional space for chemical movement in soil

Mathematically, this condition is represented as the negative half plane of the two-dimensional space (x,y) as shown in Figure 1.

The y coordinant is assumed to extend from $-\infty < y < +\infty$ and the x coordinant $0 \leq x < \infty$ thus generating a half plane, representing a semi-infinite slab.

Derivation of Equations. The mathematical statement of the problem will be based on the assumption that the chemical moves according to Fick's law, that no chemical is lost by evaporation, and that sorbtion on the soil takes place according to the Freundlich isotherm.

These assumptions obtain for the flux, J_x, across a boundary of a plane sheet of soil at a depth x

$$J_x = K_0(C)C_x + U_0(x,t)\,C\,(x,t) \tag{1}$$

where $K_0(C)$ is the diffusion coefficient of the chemical in the soil-water complex, U_0 is the average water velocity in the interparticle voids at depth x, and time t, and C is the concentration of chemical in the pore water.

By the law of conservation of matter for one-dimensional flow,

$$C_t = -\frac{\partial J_x}{\partial x} \tag{2}$$

which yields by substituting Equation 1 into Equation 2

$$C_t = \frac{\partial\left\{K_0(C)\dfrac{\partial C}{\partial x}\right\}}{\partial x} - \frac{\partial\{U_0(x,t)C(x,t)\}}{\partial x} \tag{3}$$

The concentration of chemical sorbed is given by the equation

$$S = RC^n \tag{4}$$

Where S is defined as the concentration of bound chemical (stationary phase concentration; grams sorbed per unit volume of soil), C is the concentration in the soil voids (mobile phase), $R = \exp(\Delta G/kT)$, n is any real number greater than -1, k is the Boltzmann constant, T is the absolute temperature, and ΔG is the free energy of sorbtion term. Let $n = 1$—i.e., a linear sorbtion isotherm. The fraction of sorbed chemical is obtained by differentiating Equation 4 with respect to t and multiplying the results by α, where α is the ratio of surface area of chemically active sites to the total particle surface area. Adding this term to Equation 3 gives

$$C_t = \frac{\partial\left\{K_0(C)\dfrac{\partial C}{\partial x}\right\}}{\partial x} - \frac{\partial\{U_0(x,t)C(x,t)\}}{\partial x} - \alpha RC_t \tag{5}$$

Combining like terms in Equation 5, one obtains

$$(1 + \alpha R)C_t = \frac{\partial\left\{K_0(C)\dfrac{\partial C}{\partial x}\right\}}{\partial x} - \frac{\partial\{U_0(x,t)C(x,t)\}}{\partial x} \tag{6}$$

which is a nonlinear second order partial differential equation. For weak concentrations—e.g., 10^{-6} to $10^{-3}M$—$K_0(C) = K_0$
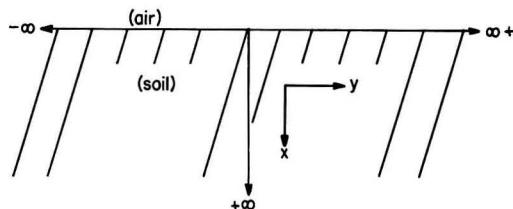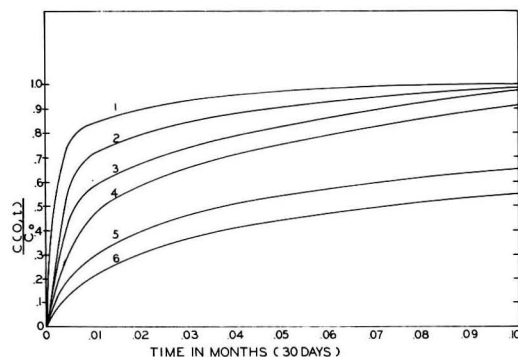
Figure 2. Relative surface concentration ratio as a function of time for various influx and free energy values

may be considered a constant for the particular soil and $\dfrac{\partial K}{\partial x}(c) = 0$. Equation 6 then becomes:

$$(1 + \alpha R)C_t = K_0C_{xx} - \frac{\partial\{U_0(x,t)C(x,t)\}}{\partial x} \tag{7}$$

Equation 7 is seen to be linear in $C(x,t)$. For saturated conditions in the soil: $U(x,t) = U_0$, a constant, and Equation 7 can be written as

$$(1 + \alpha R)C_t = K_0C_{xx} - U_0C_x \tag{8}$$

By defining the terms

$$K = \frac{K_0}{1 + \alpha R} \quad \text{and} \quad U = \frac{U_0}{1 + \alpha R} \tag{9}$$

Equation 8 becomes

$$C_t = KC_{xx} - UC_x \tag{10}$$

Solutions

The problem of interest is given by Equation 10. Two solutions to this linear second-order partial differential equation will be considered.

The first solution to be considered is for the continuous fluxing input boundary condition. The second solution to be considered is for the flux-plug–type input boundary condition. In both cases, the initial concentration in the soil is assumed to be zero.

Case 1. CONTINUOUS FLUX AT THE SURFACE. The following initial and boundary conditions apply respectively. Let

(a) $\quad C(x + 0) = 0$ $\hspace{3cm}$ (11)

(b) $\quad J_x \Big|_{x=0} = \epsilon \left\{ -K \dfrac{\partial C}{\partial x} + UC \right\} \Big|_{x=0}$

where

$$J_x \Big|_{x=0} = QC_0; \; Q = \frac{Q_0}{1 + \alpha R}$$

and where Q_0 and C_0 are respectively defined as the influx velocity (length/time) and the initial influxing concentration, and ϵ is the porosity of the medium. Note here that U_0 and Q_0 are related by the following expression

$$U_0 = \frac{Q_0}{\epsilon} \hspace{3cm} (12)$$

Equation 10 subject to Equation 11 has been solved by Mason and Weaver (1924). Brenner obtained the same solution independently in 1962. The solution given by Brenner needs to be modified for the problem under consideration to include the important sorbtion term containing ΔG. Several authors (Bischoff, 1966; Bischoff and Levenspiel, 1962a; 1962b; Houghton, 1963; Vietter and Sladek, 1965) have reported partial similar differential equations and boundary conditions without considering the sorbtion term. The solution found by laborious but straightforward Laplace techniques is given by the equation

$$C(x,t) = \frac{C_0}{2} \{ L(x,t) + M(x,t) + N(x,t) \} \hspace{1cm} (13)$$

where

$$L(x,t) = erfc \left(2 \frac{x}{\sqrt{Kt}} - \frac{U}{2} \sqrt{\frac{t}{K}} \right)$$

$$M(x,t) = \left(\frac{4U^2 t}{K\pi} \right)^{1/2} \exp\left[- \left(\frac{x}{2\sqrt{Kt}} - \frac{U}{2} \sqrt{\frac{t}{K}} \right)^2 \right]$$

$$N(x,t) = -\frac{U}{K} \left(x + Ut + \frac{K}{U} \right) \times$$

$$\exp\left[\frac{xU}{K} \right] \cdot erfc \left(\frac{x}{2\sqrt{Kt}} + \frac{U}{2} \sqrt{\frac{t}{K}} \right)$$

and where $erfc(w)$ is defined as

$$erfc(w) = \frac{2}{\sqrt{\pi}} \int_w^\infty e^{-U^2} dU$$

Equation 13 was plotted for various values of the parameters. Figure 2 shows plots of the concentration ratio $C(x,t)/C_0$ at a fixed depth x, chosen to be very near the surface of the soil, as a function of time. The six curves represent different values of the influx velocity with and without sorbtion.

The following values were used in the calculations:

$$X \cong 0; \; \epsilon = 0.4; \; K_0 = 2 \text{ in.}^2/\text{mon.}; \; \alpha = 10^{-4}$$

The values used for Q_0 and ΔG are as follows:

Curve 1. $Q_0 = 8$ in./mo.; $\Delta G = 0$ kcal./mole; no sorbtion
Curve 2. $Q_0 = 8$ in./mo.; $\Delta G = 6$ kcal./mole; strong sorbtion
Curve 3. $Q_0 = 4$ in./mo.; $\Delta G = 0$ kcal./mole; no sorbtion
Curve 4. $Q_0 = 4$ in./mo.; $\Delta G = 6$ kcal./mole; strong sorbtion
Curve 5. $Q_0 = 1.6$ in./mo.; $\Delta G = 0$ kcal./mole; no sorbtion
Curve 6. $Q_0 = 1.6$ in./mo.; $\Delta G = 6$ kcal./mole; strong sorbtion

The graphs indicate that the effect of rather strong sorbtion is to prevent rapid increase of the chemical in the soil solution over a period of time. When there is no sorbtion, the concentration in the soil solution near the surface quickly reaches the level of the input concentration. Also, Figure 2 shows that at higher velocities, the surface layer soil void concentration comes quickly up to the input concentration level.

The concentration to be expected in the soil solution at different depths after a given period of fluxing are shown in Figure 3.

Here, graphs of the concentration ratio $C(x,t)/C_0$ as a function of depth x, at the time $t = 0.05$ month are presented. The five curves represent different values of the free energy ΔG. Values of the parameters of Equation 13 used in the calculations were:

$Q_0 = 40$ inches per month; $\epsilon = 0.4$; $K_0 = 2$ sq. inches per month; $\alpha = 10^{-4}$

The values used for ΔG were:

Curve 1. $\Delta G = 0$ kcal./mole; no sorbtion
Curve 2. $\Delta G = 2$ kcal./mole; weak sorbtion
Curve 3. $\Delta G = 4$ kcal./mole; moderate sorbtion
Curve 4. $\Delta G = 5$ kcal./mole; moderate to strong sorbtion
Curve 5. $\Delta G = 6$ kcal./mole; strong sorbtion

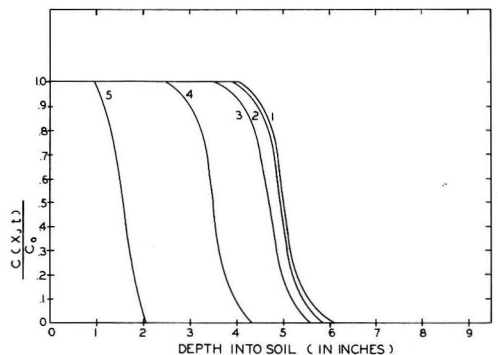Figure 3 shows that with increasing sorbtion energy the

Figure 3. Soil void concentration as a function of distance at fixed time and velocity

rather sharp front of chemical progressing into the soil is retarded in its rate of advance. The choice of the α value was based on an experiment with a sandy loam, hence the low value. For soils with higher α values the chemical fronts would shift toward the influx boundary. This emphasizes the importance of the use of the product αR in methods applied to predict the location of the advancing chemical front.

Case 2. FLUX-PLUG–TYPE INPUT AT THE SURFACE. The following initial and boundary conditions apply, respectively

$$C(x,t_0) = 0 \tag{14a}$$

$$J_x|_{x=0} = 0 \qquad t > T \tag{14b}$$

$$J_x|_{x=0} \epsilon \left(-K \frac{\partial c}{\partial x} + UC\right)_{x=0} = QC_0, \, 0 < t < T$$

The solution of Equation 11 subject to Equations 14a and 14b is

$$C(x,t) = \frac{C_0}{2} \{L + M + N\}; \, 0 < t < T, \, X \geqq 0 \tag{15a}$$

$$C(x,t) = \frac{C_0}{2} \{L(x,t) - L(x,t - T) + M(x,t) -$$

$$M(x,t - T) + N(x,t) - N(x,t - T)\}; \, t > T, \, X \geqq 0 \tag{15b}$$

Equations 15a and 15b were plotted for various values of the parameters in Figure 4. Curves of the concentration ratio $C(x,t)/C_0$ plotted as a function of depth x, are shown for several values of the sorbtive strength.

The following values were used in the calculations:

$Q_0 = 40$ in./mo.; $\epsilon = 0.4$; $K_0 = 2$ in.^{2}/mo.; $\alpha = 10^{-4}$; $U_0 = 100$ in./mo.; $T = 0.01$ month, $t = .05$ month.

The values used for ΔG were:

Curve 1. $\Delta G = 2$ kcal./mole; weak sorption
Curve 2. $\Delta G = 4$ kcal./mole; moderate sorption
Curve 3. $\Delta G = 5$ kcal./mole; moderate to strong sorbtion
Curve 4. $\Delta G = 6$ kcal./mole; strong sorption

The area under each curve shown in Figure 4 represents the mass of chemical which remains in solution in the water in the voids. As the sorbtion increases the area under each curve decreases, and the curve shifts towards the influx boundary. This illustrates the effect of increasing sorbtion energy, ΔG, for the flux-plug–type input. The stronger sorbtion by the soil takes up more chemical and reduces the mass flow of chemical in the soil voids in amount as well as in depth.

LIMITING CASES

The condition where the velocity is much larger than the rate of diffusion ($U > > K$) and the condition where the velocity of water movement is much smaller than the rate of diffusion ($U < < K$) present two interesting limiting cases.

Condition: $U > > K$. When $U > > K$, Equation 11 can be effectively written as

$$-UC_x = C_t \tag{16}$$

The initial condition (Equation 11) remains the same, but the boundary condition is changed to

$$\epsilon UC(x,t)|_{x=0} = QC_0 \tag{17a}$$

Recalling that $Q_0/\epsilon = U_0$, Equation 17a reduces to

$$C(x,t)|_{x=0} = C_0 \tag{17b}$$

Using the Laplace transform technique on Equations 16 and 17b, one obtains,

$$-U \frac{d\bar{c}}{dx} = S\bar{c} - C(x, + 0) \tag{18a}$$

$$C(0,s) = C_0/S \tag{18b}$$

The solution to Equation 18a subject to Equations 11a and 18b is given as

$$\bar{C}(x,s) = \frac{C_0}{s} \cdot \exp\left[-\frac{s}{U} x\right] \tag{19}$$

The inverse of Equation 19 as found in the tables (Erdely *et al.* 1954) is

$$C(x,t) = C_0 H\left(t - \frac{x}{U}\right) \tag{20}$$

where $H\left((t - \frac{x}{U}\right)$ is the Heaviside step function defined as

$$H\left(t - \frac{x}{U}\right) = \begin{cases} 1 & , t - \frac{x}{U} > 0 \\ \\ 0 & , t - \frac{x}{U} < 0 \end{cases} \tag{21}$$

The distribution Equation 20 is a most interesting one in that it states for large values of $U(Q_0$ large), maximum concentration in the soil is achieved almost instantaneously. This is shown graphically in Figure 5.
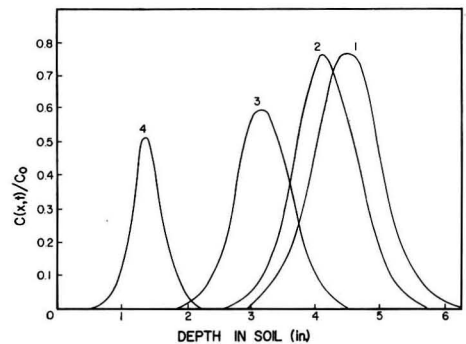

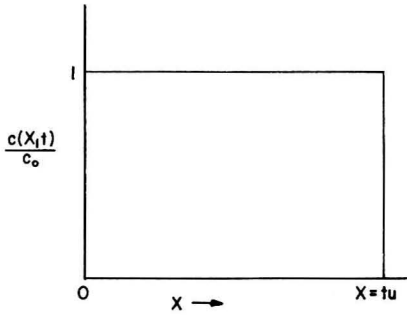**Figure 4.** Soil void concentration for influx time $T = 0.01$ month, total elapse time of 0.05 month

Figure 5. Soil void concentration for continuous input at very high velocity

Condition: $U < < K$. When $U < < K$, Equation 11 can effectively be written as

$$KC_{xx} = C_t \qquad (22)$$

Again the initial condition remains unchanged but now the boundary condition is changed to

$$-\epsilon K \left.\frac{\partial c}{\partial x}\right|_{x=0} = 0 \qquad (23)$$

since $Q_0 \to 0$ as $U_0 \to 0$.

The Laplace transform of Equations 22 and 23 are given, respectively, as

$$K \frac{d^2\bar{c}}{dx^2} - S\bar{c} = -C(x,0) \qquad (24a)$$

$$-\epsilon K \left.\frac{\partial \bar{c}}{\partial x}\right|_{x=0} = 0 \qquad (24b)$$

The acceptable solution to Equation 24a is

$$\bar{C}(x,s) = A\exp\left[-\sqrt{x\frac{s}{K}}\right]$$

However in applying Equation 24b, for all x and s, $A = 0$. Thus

$$\bar{C}(x,s) = 0 \qquad (25)$$

$$C(x,t) = 0 \qquad (26)$$

Comparing Equation 13 for small U with Equation 26, in Equation 13 as $U \to 0$

$$C(x,t) = \frac{C_0}{2}\left\{erfc\frac{x}{2\sqrt{Kt}} - erfc\frac{x}{2\sqrt{Kt}}\right\} = 0 \qquad (27)$$

thus agreement is obtained.

Now, as this model in its highly specialized form is only an approximation of what may be the actual phenomena taking place, as $U \to 0$, the actual chemical flux probably will not vanish, but it may be very small since then the movement of chemical is governed by straight diffusion phenomena with some boundary conditions other than those in Equation 11 operating. For example, if the boundary condition

$$C(0,t) = C_0, C(x, +0) = 0$$

is realized, then immediately the solution of Equation 22 is given by

$$C(x,t) = C_0 \, erfc\left[\frac{x}{2\sqrt{Kt}}\right] \qquad (28)$$

This is the standard temperature distribution-type equation in a semi-infinite media for a heat conduction–type problem which has a constant temperature maintained at $x = 0$.

Literature Cited

Ashton, F. M., *Weeds* **9**, 612 (1961).
Bischoff, K. B., *Ind. Eng. Chem.* **58**, 18 (1966).
Bischoff, K. B., Levenspiel, O., *Chem. Eng. Sci.* **17**, 245 (1962a).
Bischoff, K. B., Levenspiel, O., *Chem. Eng. Sci.* **17**, 257 (1962b).
Brenner, H., *Chem. Eng. Sci.* **17**, 229 (1962).
Burneside, D. C., Feuster, C. R., Wicks, G. A., *Weeds* **11**, 209 (1963).
Chao, R., Hodscher, H. E., *A.I.Ch.E.J.* **12**, 271 (1966).
Erdely, A., Magnus, W., Oberhettinger, F., Tricomi, F. G., "Tables of Integral Transforms," Bateman Manuscript Project, Vol. **1**, McGraw-Hill, New York, 1954.
Freed, V. H., Vernette, J., Montgomery, M., *Proc. Western Weed Control Conf.* **19**, 21 (1962).
Harris, C. I., Warren, G. F., *Weeds* **12**, 120 (1962).
Hartley, G. S., "The Physiology and Biochemistry of Herbicides," L. J. Audus, Ed., p. 111, Academic Press, London and New York, 1964.
Hayward, D. O., Trapnell, B. M. W., "Chemisorption," 2nd ed., Butterworth, London, 1964.
Houghton, G., *J. Phys. Chem.* **67**, 84 (1963).
Kasten, P. R., Lapidus, L., Amundson, N. R., *J. Phys. Chem.* **56**, 683 (1952).
Kipling, J. J., "Adsorption from Solutions of Non-Electrolytes," Academic Press, New York, 1965.
Lambert, S. M., Porter, P. E., Schieferstein, R. H., *Weeds* **13**, 185 (1965).
Lapidus, L., Amundson, N. R., *J. Phys. Chem.* **56**, 984 (1952).
Littlewood, A. B., "Gas Chromatography," Academic Press, New York, 1962.
Mason, M., Weaver, W., *Phys. Rev.* **23**, 412 (1924).
McLaren, L., Oregon State University, Corvallis, Ore., private communication, 1966.
Purnell, H., "Gas Chromatography," Academic Press, New York, 1962.
Talbert, R. E., Fletchall, D. H., *Weeds* **13**, 46 (1965).
Van Schaik, J. C., Kemper, W. D., Olsen, S. R., *Proc. Soil Sci. Soc. Am.* **30**, 17 (1966).
Vietter, W. R., Sladek, K. J., Proc. 39th Natl. Colloid Sym. of Division of Colloid and Surface Chemistry, Clarkson College, Potsdam, New York, 1965.
Ward, T. M., Holly, K., *J. Colloid Sci.* **22**, 221 (1966).

Steady-State Measurement of Krypton-85–Air Diffusion Coefficients in Porous Media

Parker C. Reist

Department of Industrial Hygiene, Harvard School of Public Health, Boston, Mass. 02115

■ To evaluate the possible use of porous underground formations for the retention and disposal of waste krypton-85, the diffusion coefficient of Kr-air mixtures within these formations is often needed. This paper reports on the design and use of a "diffusion cell" to measure these coefficients under various conditions of porosity and moisture content. It is concluded that the diffusion cell measurements represent to a good approximation the actual diffusion coefficient of air-^{85}Kr mixtures in porous media.

In investigating the possible use of porous, underground media for storage of waste krypton-85, leakage from the media by permeation and diffusion must be considered. To estimate diffusion losses, a knowledge of the diffusional behavior of krypton in the porous media is required. This behavior is generally expressed in terms of a diffusion coefficient.

Conventional methods for measuring the diffusion coefficient of a gas in a porous medium require long sampling times, as in the case of the method used by Penman (1940), or complex data treatment, with the methods used by Papendick and Runkles (1965) or Dye and Dallavalle (1958). Presented here is a simple technique for measuring this coefficient for krypton-air mixtures, based on a method used by Evans, Truitt, and Watson (1961) to measure helium and argon diffusion through large-pore graphite.

Experimental Method

Consider a porous medium of length L arranged as shown in Figure 1 with the two opposite faces exposed to separate gas streams of differing composition. When the pressure on the left-hand face (face 1, Figure 1, B) is much greater than the pressure on the right-hand face (face 2), there is a net flow of gas toward face 2. If conditions are reversed, the flow is in the opposite direction. When the pressures at the two faces are exactly equal, the gas movement, or current, from one face to the other will be mainly by diffusion, if molecule-wall collisions are assumed to be negligible compared to molecule-molecule collisions.

The ^{85}Kr current, $J_{Kr}(\mu Ci$ cm.$^{-2}$sec.$^{-1}$), can be considered to be the number of atoms of krypton crossing a unit area normal to the flow per unit time (Jost, 1952). The usual diffusion equation for this current can be written for a one-dimensional system in a form similar to that given by Evans, Watson, and Mason (1961) as

$$J_{Kr} = -D\frac{dC_{Kr}}{dx} + m_{Kr}J_{Kr} \qquad (1)$$

where C_{Kr} is the concentration of krypton-85 (μCi cm.$^{-3}$) at any distance x (cm.) within the medium, D is the diffusion coefficient for the krypton-air mixture (cm.^{2} sec.$^{-1}$), and m_{Kr} is the mole fraction of krypton in air. Since in our range of interest (concentrations up to several millicuries per cubic centimeter) the mole fraction of krypton in air is very much smaller than 1, the second term of Equation 1 can be neglected and Equation 1 can be written:

$$J_{Kr} \simeq -D\frac{dC_{Kr}}{dx} \qquad (2)$$

Under this condition the concentration gradient dC_{Kr}/dx at the steady-state approximates a straight line, with a slope of $(C_o - C_i)/L$ where C_i and C_o are the krypton-85 concentrations at the up- and downstream faces, respectively, and L is the thickness of the medium—i.e., the distance between the two faces. The current through the porous medium at the steady state is then:

$$J \simeq (C_i - C_o)(D/L) \qquad (3)$$

If the krypton-85 leaving the downstream face of the cell is swept away by an air stream having a flow of Q_o, the concentration of krypton-85 in the stream is $(J)(A)/(Q_o)$, where A is the total normal area through which the gas is diffusing.
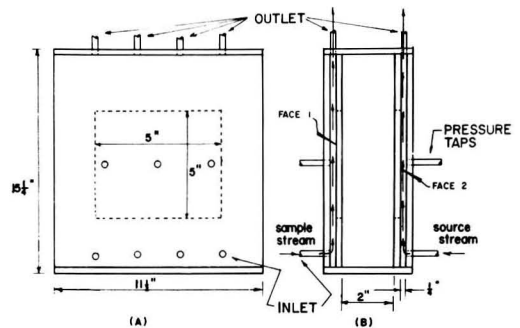

Figure 1. Design of diffusion cell

Substituting this value into Equation 3 and solving for D gives

$$D \simeq \frac{L}{A} \left(\frac{C_o}{C_t - C_o} \right) Q_o \qquad (4)$$

In a porous medium the D measured is actually a so-called "effective D," D_{eff}, which Carman (1956) considers to be related to the "true" diffusion coefficient of the gas pair (that measured outside the porous medium) by the expression

$$D_{eff}/D = \epsilon/\tau \qquad (5)$$

where ϵ is the porosity of the medium and τ is its tortuosity—i.e., the ratio of the path length through the porous medium to the direct or "crow-flight" distance through the medium. Thus two factors are taken into account in computing the effective diffusion coefficient: All of the surface area, A, is not available for diffusion and, on the average, a gas molecule must travel a distance somewhat greater than the thickness of the medium in order to pass through it.

Using the well-known transient diffusion equations, the D_{eff} described can be used to estimate the diffusion of krypton-85 within a porous medium. In addition, if for a given soil type the porosity and D_{eff} can be measured and a value of D calculated using kinetic theory, the tortuosity of the particular soil can be estimated. Such a factor is extremely important in describing the permeation characteristics of soil.

Procedure

An air stream containing krypton-85 from a large 11,000-liter reservoir was passed across sample face 1 (Figure 1),

Table I. Krypton-Air Diffusion Coefficients in Various Unconsolidated Porous Media
(Corrected to STP)

Sample Type	No. of Samples	Porosity, %	D_{av}, Sq. Cm./Sec.	Std. Dev., σ	Tortuosity
Air alone	6	100	0.134	0.021	1.0
6-mm. glass beads	9	...	0.035	0.007	...
Coarse sand, $0.0503 < d < 0.0840$ cm.	6	45.2	0.037	0.005	1.65
Fine sand, $0.0147 < d < 0.0503$ cm.	8	45.5	0.046	0.009	1.33
Very fine flint sand, $\bar{x}_g = 0.0278$ cm. $\sigma_g = 1.27$	7	49.9	0.038	0.007	1.76
Mixed const. grade sand, $\bar{x}_g = 0.044$ cm. $\sigma_g = 2.18$	5	48.2	0.037	0.004	1.77
20% coarse + 80% fine	8	45.1	0.046	0.009	1.38
40% coarse + 60% fine	5	46.4	0.037	0.002	1.68
50% coarse + 50% fine	8	44.4	0.045	0.003	1.33
60% coarse + 40% fine	6	48.1	0.041	0.003	1.48
80% coarse + 20% fine	6	45.1	0.051	0.004	1.20
Fine sand + 20% saturation	6	39.6	0.031	0.005	1.29
Fine sand + 40% saturation	8	32.8	0.025	0.003	1.29
Fine sand + 60% saturation	6	25.2	0.007	0.003	4.96

then through a rotameter, and returned to the reservoir. Since the flow was small compared with the reservoir volume, the experimental conditions were considered to be comparable to having a constant concentration of krypton-85 at face 1 at all times.

Similarly, room air was filtered, dried, and passed across face 2 of the diffusion cell. This air then passed through a Model 31 Cary 2800-cc., spherical ionization chamber where krypton activities were measured using a vibrating reed electrometer. After leaving the ionization chamber the air was discharged to a spirometer for flow measurement. When steady-state conditions were reached (usually within a few minutes), the concentration of krypton-85 on the downstream side of the sample became constant. Using the flow and up- and down-stream activities measured at this time, the diffusion coefficient of the krypton-85 through the porous medium was calculated using Equation 4.

The experimentally determined diffusion coefficient is a function of the pressure and temperature at which it is measured and so in order to compare the values of D_{eff} from different runs, it was necessary to correct all measured values to standard conditions. Pressure corrections were made using the equation

$$D_{at}P_2 = D_{at}P_1(P_1/P_2) \qquad (6)$$

and temperature corrections were made using the equation

$$D_{at}T_2 = D_{at}T_1(T_2/T_1)^{3/2}(\Omega D_{at}T_1/\Omega D_{at}T_2) \qquad (7)$$

where Ω is the collision integral. This approach follows that given by Bird, Stewart, and Lightfoot (1960).

Results and Discussion

To compare the experimental and theoretical values for D_{eff}, the diffusion coefficient was first measured when there was no sample in the cell. The value thus obtained corresponds to the diffusion coefficient for krypton in air.

Six measurements were made at various flow rates and the observed value for D was 0.134 sq. cm. per second with a standard deviation of 0.02. This compares favorably with the calculated value of 0.129 sq. cm. per second. As a result, it was concluded that the diffusion cell would provide a reasonably true indication of the diffusion coefficient of krypton in a porous medium.

Diffusion coefficient measurements were next made on three fairly homogeneous porous media samples (6-mm. diameter glass beads, graded coarse Ottawa sand, and graded fine Ottawa sand), on two samples of sand with heterogeneous particle size distributions (very fine flint sand and a construction grade beach sand), on five mixtures of various proportions of the coarse and fine Ottawa sands, all dry samples, and on the fine sand with three different moisture contents. At least five runs were made on each sample type. A value for D was then calculated and the results were averaged. The best estimate of the standard deviation for each series of measurements was computed according to standard statistical procedures (Table I).

The table shows that the diffusion coefficient for krypton in air within a dry, porous, unconsolidated medium is of the order of 0.04 sq. cm. per second or roughly 0.3 that of diffusion in free air. Investigation of the differences among the first ten samples, using the Student's t test, indicated no significant differences, although the measured values for D ranged from 0.035 to 0.01 sq. cm. per second.

The porosities of the samples were fairly uniform although they tended to be high. When water was added to the sand, however, the diffusion coefficient as well as the porosity was significantly reduced. It appears that initial reductions in the values of D_{eff} arose solely from reduced porosities available for diffusion. As the water content was increased, however, the diffusion coefficient decreased faster than could be accounted for by porosity reductions alone. Since the water filled the channels through which the gas diffused, the krypton must have been forced to take a more circuitous path in passing from one face of the sample to the other. This increase in tortuosity appears to take place in a relatively homogeneous sand somewhere between 40 and 60% saturation.

According to Rieber (1965), air injected into fine sand initially saturated with water will displace only about 50% of the water, indicating that the major flow paths through the sand take up about half of the porous space, the remainder being either "dead ends" or corners. The results from the above measurements indicate that the same thing is true for diffusion —that is, the major diffusive paths in a porous bed comprise 40 to 60% of the total bed void volume.

The results of the runs with 60% saturation indicate that krypton will diffuse through sand with this moisture content (the moisture content where some noticeable gravitational flow is beginning to take place) at a rate of about one 19th that in air alone. Thus, the addition of moisture to a porous medium greatly increases its ability to retain or retard gases trapped within it.

Effect of Small Pressure Variations

Grammakov et al. (1958) suggested that diffusion coefficients for porous media reported in the literature actually represent diffusion plus some undetermined convective flow. Since this flow would be produced by pressure differences across the sample, a rotameter was installed for monitoring the flow from the diffusion cell back to the reservoir tank under different conditions. With the inlet and outlet lines serving face 2 of the sample closed (valves V-7 and V-8, Figure 2), a certain flow (usually about 10 cc. per second) was circulated from the reservoir, across face 1 of the sample, through the rotameter, and back to the reservoir. The rotameter reading was then observed, valves V-7 and V-8 were opened, and for a given sample flow (Q_1) the face 1 exit valve (V-2) was opened or closed until the original rotameter reading was attained. This procedure was repeated until the inlet and outlet lines serving face 2 could be opened or closed simultaneously without affecting the rotameter reading. It was then considered that no pressure difference existed across the sample. It has been estimated that rotameter differences of 0.1 scale unit would arise from pressure differences as low as 6×10^{-4} inch of water. As a result, pressure differentials even less than
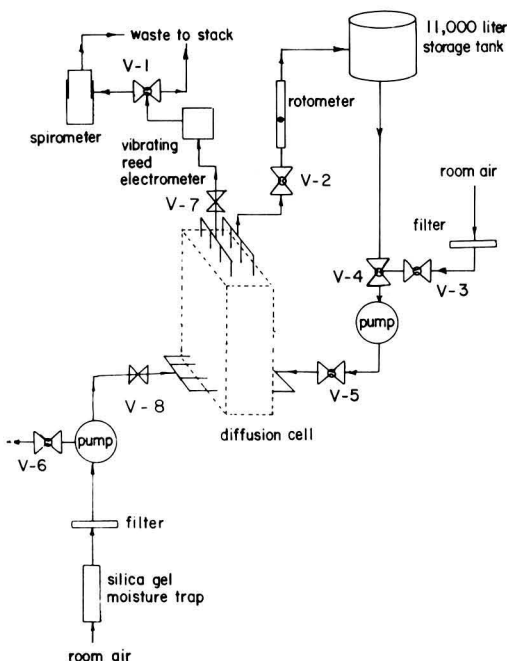
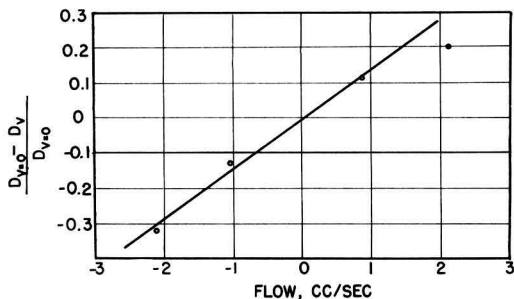**Figure 2.** External piping layout for diffusion coefficient measurements

Figure 3. Effect of small flows on diffusion coefficient measurement for air
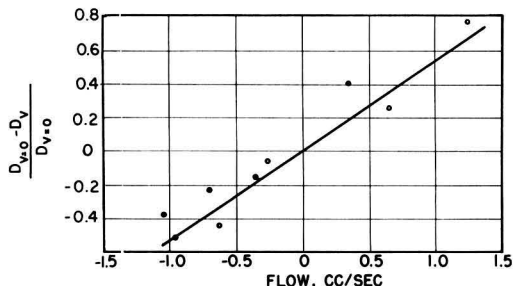

Figure 4. Effect of small flows on diffusion coefficient measurement for sand

○ Construction grade
● Coarse Ottawa

this would be indicated by slight deflections of the rotameter.

To evaluate its effect on the experimentally determined diffusion coefficient, measurements were also made in the presence of a slight convective flow, following the procedures previously outlined, and the diffusion coefficients were computed as if no convective flow existed. Runs were made on samples of air alone, coarse homogeneous sand, and a mixed, heterogeneously distributed construction grade sand. Gas flows ranged up to 1 cc. per second in the case of the two sand samples and up to 3 cc. per second when no porous sample was present.

Figures 3 and 4 show the results of these experiments. The plotted points form a reasonably linear curve for the case where air was the sample material. Although still reasonably linear for very small flows, the plotted values with sand as the sample medium are generally more irregular.

The figures show no gross anomaly in the results as the convective flow changes direction. Thus errors due to slight convective flows appear to be regular and should tend to average out in a series of runs at different rotameter settings. Since the results presented here are based on this type of experimental procedure, they are considered to represent true diffusion coefficients.

Conclusions

The diffusion cell measurements represent to a good approximation the actual diffusion coefficient of air–krypton-85 mixtures in porous media. Since gross air flows through the sample were always maintained at least below 0.15 cc. per second, measurement errors due to a pressure difference across the sample were at most less than 10% of the true value of the diffusion coefficient.

Literature Cited

Bird, R. B., Stewart, W. E., Lightfoot, E. N., "Transport Phenomena," p. 511, Wiley, New York, 1960.
Carman, P. C., "Flow of Gases through Porous Media," p. 79, Academic Press, New York, 1956.
Dye, R. F., Dallavalle, J. M., *Ind. Eng. Chem.* **50,** 1195 (1958).
Evans, R. B., III, Truitt, J., Watson, G. M., Oak Ridge Natl. Laboratory, **ORNL-3067** (1961).
Evans, R. B., III, Watson, G. M., Mason, E. A., *J. Chem. Phys.* **35,** 2076 (1961).
Grammakov, A. G., *et al.*, "Some Theoretical and Methodical Problems of Radiometric Prospecting and Survey," Proceedings of 2nd U.N. International Conference on Peaceful Uses of Atomic Energy, Vol. **2,** p. 732, 1958.
Jost, W., "Diffusion in Solids, Liquids, and Gases," p. 2, Academic Press, New York, 1952.
Papendick, R. I., Runkles, J. R., *Soil Sci.* **100,** 251 (1965).
Penman, H. L., *Intern. J. Agr. Sci.* **30,** 437 (1940).
Rieber, F., "Injection of Radioactive Gaseous Effluents," Notes on Meeting on Ground Disposal of Radioactive Gaseous Wastes at the University of California, Berkeley, Calif., 1965.

Effects of Temperature and of Ultraviolet Radition on Pyrene Adsorbed on Garden Soil

Alexander J. Fatiadi

Division of Analytical Chemistry, Institute for Materials Research, National Bureau of Standards, Washington, D. C. 20234

■ Irradiation of pyrene adsorbed on garden soil for 240 hours at 32° gave a mixture of products that could be separated by thin-layer and column chromatography. Eight compounds were formed, and five have been identified: 1,1'-bipyrene, 1,6- and 1,8-pyrenediones, and 1,6- and 1,8-pyrenediols. When the pyrene adsorbed on garden soil was stirred in the dark for 240 hours at 32°, the yield of 1,1'-bipyrene was lowered (from 4 to 6%) to 0.3%, and only traces of the two diones were formed; on treatment in the dark at 110° for only 8 hours, dione yields were increased to 2.5%. When other particulates (silica gel, alumina, Florisil, etc.) were used instead of garden soil, 1,1'-bipyrene was not formed. Experiments in which radical-capture agents were incorporated showed lower yields of 1,1'-bipyrene, indicating that the reaction with ultraviolet irradiation involves a free-radical mechanism. The yield of the diones was unchanged with these agents present, suggesting that they are formed by attack of adsorbed oxygen on photo-excited pyrene molecules. Irradiation of pyrene in the crystalline form without solvent did not produce 1,1'-bipyrene. No attempt was made to follow quantitatively the input of energy during the irradiation of pyrene on soil (a heterogeneous reaction); from the practical standpoint, however, the main objective of this study was to trace the fate of pyrene on soil, as a representative reaction of a series of polycyclic, aromatic hydrocarbons (carcinogenic and noncarcinogenic).

I n earlier work in this laboratory, it was discovered (Inscoe, 1964) that certain aromatic hydrocarbons undergo chemical changes when adsorbed on silica gel and exposed to ultraviolet light. Because pyrene (I) is a constituent of polluted air (Sawicki, 1965; Tipson, 1965), and because garden soil is a widespread, natural adsorbent, the work has been extended to a mixture of them. The purpose of the study was to determine whether pyrene adsorbed on garden soil undergoes any chemical or photochemical changes. Although pyrene shows no carcinogenic activity (Clar, 1964; Hieger, 1961), it is nevertheless representative of a class of compounds that have strong carcinogenic action. Therefore, the fate of such a compound on soil, and the nature of the products of the reactions on soil, may be of considerable practical importance.

Irradiation of I for 240 hours at 32° produces 1,1'-bipyrene (II) among other reaction products. Because of its photoinstability, II is a transition intermediate only; it decomposes rapidly when it is adsorbed on silica gel or soil and is then exposed to ultraviolet light. This demonstrates that ultraviolet radiation, which, as known, participates in the photosynthesis of vital organic intermediates in the plant world, may also share in the process of formation of organic substances in soil or similar natural adsorbents. This also may reflect on the continuous photochemical changes of aromatic air pollutants which have been resting on the surface and exposed to solar radiation, heat, and atmospheric oxygen.

+ other products
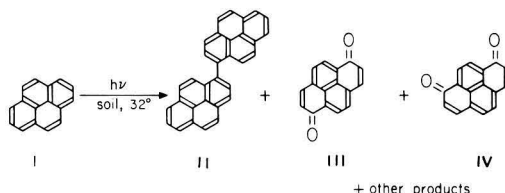
Experimental and Technique

The garden soil used came from two localities: Takoma Park, Md., and Gaithersburg, Md. The soil was dried, sieved (40- to 60-mesh), successively extracted (Soxhlet) with water, acetone, toluene, and ethyl alcohol, and dried. A 50-gram sample of this soil was mixed with a solution of 2.5 grams of I (m.p. 150–52°) in some heptane, and the solvent was evaporated. The mixture was then powdered, placed in a partially open borosilicate glass flask (250 ml.), and exposed to long-wave ultraviolet irradiation (high-pressure, mercury vapor, spot bulb, 100-watt, equipped with a 19057 Black-Ray filter; the lamp provided a concentrated beam of about 8000 μw. per sq. cm. of 3660-A. ultraviolet energy at about 30 cm.). The mixture was continuously stirred (egg-shaped magnetic bar) at 32° ± 2° for 240 hours, and then successively extracted with acetone (Soxhlet, 4 hours) and toluene (4 hours); column chromatography (Fatiadi, 1965) [silica gel, 1 to 1 (v./v.) toluene–acetic acid] of the extracts yielded unchanged pyrene and 8 to 10% (based on the original weight) of the reaction products.

Extracts from another reaction mixture were now studied by thin-layer chromatography. Examination of the acetone extract (20 × 20 cm. glass plate; silica gel G, 250 to 300 micrometers thick; 55 to 65 minutes) revealed the presence of nine compounds. The spots on the chromatogram and their corresponding R_f values, in suitable solvents or mixed solvents, were as follows:

1. Colorless to light-brown [light-green fluorescence; 18:1:1 (v./v.) heptane–toluene–acetic acid (Solvent A), R_f 0.61 ± 0.01]; unreacted I.

2. Colorless, or very pale, greenish yellow (strong blue fluorescence, Solvent A, R_f 0.41 ± 0.04); 1,1'-bipyrene (II).

3. Colorless (light-blue fluorescence, Solvent A, R_f 0.31 ± 0.04); unknown.

4. Colorless (green-blue fluorescence, Solvent A, R_f 0.25 ± 0.03); unknown.

5. Colorless (blue fluorescence, Solvent A, R_f 0.22 ± 0.01); unknown.

6. Yellow (little or no fluorescence, ethyl acetate, R_f 0.86 ± 0.02); 1,6-pyrenedione (III) (Fatiadi, 1965).

7. Orange-red (pink fluorescence, ethyl acetate, R_f 0.80 ± 0.01); 1,8-pyrenedione (IV) (Fatiadi, 1965)

8. Colorless [blue fluorescence, 18:1:1 (v./v.) benzene N,N-dimethylformamide–acetic acid (Solvent B), R_f 0.58 ± 0.02]; 1,6-pyrenediol (Volmann, Becker, *et al.*, 1937).

9. Colorless (blue fluorescence, Solvent B, R_f 0.51 ± 0.02); 1,8-pyrenediol (Volmann, Becker, *et al.*, 1937).

The colorless spots of 1,6- and 1,8-pyrenediol, when adsorbed on silica gel G and exposed to air and ultraviolet radiation, rapidly acquired a yellow and an orange color, respectively, indicating oxidation to the corresponding 1,6- and 1,8-pyrenediones; this makes detection of diols difficult.

After treatment with a small proportion of decolorizing carbon, the toluene extract of the reaction mixture, which showed a deep-blue fluorescence, was concentrated to dryness, yielding lustrous crystals (80 to 100 mg.) (m.p. 315–18°). This crude product was purified by sublimation (275°/0.05 mm.) and recrystallization from 1 to 1 (v./v.) toluene–pyridine; light-green, lustrous plates (m.p. 334–36°); λ_{max}^{MeOH} 223 sh ($\epsilon \sim 75{,}000$); 244 ($\epsilon \sim 136{,}000$); 265 ($\epsilon \sim 46{,}000$); 276 ($\epsilon \sim 86{,}000$); 292 sh ($\epsilon \sim 13{,}000$); 310 sh ($\epsilon \sim 21{,}000$); 326 ($\epsilon \sim 42{,}000$); $\lambda_{max}^{toluene}$ 301 sh ($\epsilon \sim 13{,}000$); 315 ($\epsilon \sim 25{,}000$); 330 ($\epsilon \sim 51{,}000$); 349 ($\epsilon \sim 66{,}000$); 360 sh ($\epsilon \sim 39{,}000$); 376 sh ($\epsilon \sim 19{,}000$); 382 sh ($\epsilon \sim 13{,}000$) nm; ν_{max}^{KCl} 3106 w; 1608 m; 1587 m; 1488 m; 1471 m; 1437 w; 1408 m; 1289 m; 1242 m; 1218 m; 1202 m; 1176 m; 1152 m; 1123 m; 1079 m; 982 w; 969 sh; 876 w; 853 s; 846 s; 835 s; 821 m; 812 m; 800 sh; 763 s; 729 s; 685 cm.$^{-1}$; NMR (methyl sulfoxide, 90°), four-proton symmetrical multiplet, centered at 8.31 p.p.m. (aromatic H). The product was found to be identical with an authentic sample of II (Clar, 1956) by mixture (m.p. 332–34°) and ultraviolet spectrum (Clar and Kuhn, 1956). The infrared spectrum of II shows a characteristic triplet at 853, 846, and 835 cm.$^{-1}$, not exhibited by pyrene. The yield of II after column chromatography of the acetone extract amounted to 20 to 50 mg., thus raising the total yield of II to 100 to 150 mg. (4 to 6%).

Characteristic changes appear on spraying the thin-layer chromatograms. When a chromatogram of the material from the acetone extract [18:1:1 (v./v.) heptane–toluene–acetic acid] was sprayed with a 25% solution of concentrated sulfuric acid in methanol and then heated at 110° for 2 minutes, the deep-blue fluorescent spot of II disappeared; however, the treatment simultaneously caused the spot due to I to become brown-green with a new bluish fluorescence.

When a sample of II adsorbed on silica gel G is exposed to ultraviolet illumination for 30 to 60 seconds, its deep-blue fluorescence also disappears. The latter observation suggests that the II created on soil inevitably undergoes decomposition by ring-splitting reactions, which provide nonfluorescent products (possibly carboxylic acid or carboxy-formyl derivatives). Thus, impurities were formed, and consequent losses resulted, on attempting to purify II by thin-layer chromatography.

Reactions under Other Conditions

The relationship of the reactions observed with I to the reaction conditions employed was next examined. The adsorbate of pyrene on soil was stirred in an open flask and kept in the dark at 32° ± 2° for 240 hours. Inspection of the reaction mixture showed, unexpectedly, the presence of II, but in significantly lower yield (0.31 to 0.43%, three experiments), and traces of III and IV.

In another experiment, an unstirred, mechanical mixture of pyrene (3 grams) and soil (50 grams) was heated in air for 8 hours at 110° in the dark. The mixture was then extracted with 250 ml. of hot 1 to 1 (v./v.) toluene–acetic acid, and the extract was concentrated to dryness. Acetone extraction of the concentrate (Soxhlet, 6 hours) left a residue (250 mg.) which, on recrystallization from 50 ml. of 1 to 1 (v./v.) toluene-pyridine, yielded II (75 mg., 2.5%) (m.p. 333–35°). Column chromatography of the acetone extract yielded III and IV (2.5%). When similar reactions were performed at 110° for 72 and 200 hours, the yields of II decreased to 2 and 0.9%, respectively.

Further experiments with I and soil were conducted with heptane or toluene present as a solvent. Refluxing of soil with I in toluene in the dark produced mainly II plus traces of III and IV; but, in refluxing heptane, about equal amounts of II, III, and IV resulted.

Comparison of the yields of II (also III and IV) obtained in the experiments with and without long-wave ultraviolet irradiation, indicates that, at 32° ± 2°, the photochemical reaction is predominant in the self-coupling of I to give II. The formation of II on heating I with soil in the absence of ultraviolet irradiation can be attributed to an as-yet-unidentified heterogeneous catalyst present in soil, or to a so-called cage cation (zeolite) which is reportedly (Richardson, 1966a) able to produce radicals by abstraction of electrons (or protons) from polycyclic, aromatic hydrocarbons. General, quantitative, spectrochemical analysis of the garden soil from Takoma Park, Md., showed less than 0.001% of Ag, B, Be, Cu, Li, and Pb; 0.001 to 0.01% of Ni, Rb, Sr, V, and Zn; 0.01 to 0.1% of Ba, Ca, Cr, and Mn; 0.1 to 1.0% of K, Na, and Ti; 1 to 10% of Al, Fe, and Mg; and > 10% of Si.

The effect of temperature and ultraviolet radiation on I adsorbed on particulates other than soil was briefly examined. Heating in the dark of stirred, dry, mechanical mixtures of I with (1) silica gel G, (2) precipitated silica gel, (3) alumina (basic, neutral, and acidic), (4) silicic acid, (5) alkali carbonates, (6) Florisil (magnesium silicate), (7) industrial dust, or (8) alkaline earth carbonates, for 8 or 72 hours at 110°, did not appreciably change the starting material. Also, I did not react on heating with the particulates in refluxing heptane or toluene. In other experiments, I adsorbed on the above-mentioned particulates was subjected to long-wave, ultraviolet irradiation for 160 to 220 hours in air at room temperature. These photochemical reactions were conducted with particulates 1 to 8 as adsorbents on glass plates, with I deposited at the origin, by periodic exposure to the light source, first on one side and then on the other (to increase the efficiency of the irradiation by "double exposure"). Examination of the products by thin-layer chromatography revealed the presence of III and IV as major components. Compound II was not detected, except where silicic acid was used as the particulate; here, a minute proportion of II was observed. However, II was always formed when the garden soil was the particulate; thus, garden soil contrasts sharply with the other particulates.

In another experiment, a sample of I as a crystalline powder (80- to 100-mesh) was irradiated and then examined; no formation of II was observed. It has been reported (Calvert and Pitts, 1966; Cohen, 1965) that, on ultraviolet irradiation of certain aromatic compounds in the solid state, the corresponding photodimer is formed.

Possible Reaction Mechanisms

To shed light on possible reaction mechanisms, known (Laidler, 1965) to be complex for heterogeneous reactions, the photoreaction of I on soil was conducted in the presence of radical-capture agents or antioxidants (Scott, 1965; Gould, 1959). Equimolar quantities (0.001 mole) of I and acrylamide were adsorbed on soil (20 to 1 weight ratio), and the mixture was exposed to long-wave, ultraviolet irradiation for 240 hours at room temperature. Whereas the yield of III and IV remained unchanged (2.3%), the yield of II was 45% of that obtained without acrylamide, thus leaving about 50% of I unreacted. When 2,5-di-*tert*-amylhydroquinone was used, the yields of III and IV were again unchanged, but the yield of II was zero (two experiments). From these experiments, it may be concluded that the formation of II from I adsorbed on soil and exposed to ultraviolet radiation probably proceeds through a radical intermediate; and as the yields of the pyrenediones are not affected, their formation probably involves some other type of intermediate, possibly an ionic intermediate. Others have suggested ionic intermediates—for example, it was reported (Roberts, Barter, *et al.*, 1959; Rooney and Pink, 1961) that certain polycyclic, aromatic hydrocarbons, adsorbed on silica-alumina and heated to 500° under high vacuum, produced colored, positive ions or radical ions (Bronwer, 1961); also, reactions of hydrocarbons occurring on the surface of alumina at low temperature may involve ionic intermediates (Heldt, 1965).

When a mixture of I and soil was sealed in a borosilicate glass tube under nitrogen and then illuminated with ultraviolet light, the reaction products contained detectable amounts of II, III, and IV, indicating that the soil had contained some adsorbed oxygen. Formation of the pyrenediones may involve a direct attack of oxygen, adsorbed on the surface, on photoexcited pyrene molecules; such photooxidation (Hochstrasser, 1959; Hochstrasser and Porter, 1960), which does not involve radical chains, is well known (Laidler, p. 29, 1965; Bergman and McLean, 1941).

Without entering into a mechanistic discussion of photochemical reactions occurring on solid surfaces, the existence (by chemisorption) (Laidler, p. 258, 1965) may be postulated of a coordination complex between pyrene (a basic hydrocarbon) (Mackor and van der Waals, 1959; Streitwieser and Hammons, 1965) and the Lewis acid sites (Griggith and Marsh, 1957; Parkyns and Patterson, 1965; Parry, 1963; Scott, Flockhart, *et al.*, 1964) present in alumina embedded in silica; the necessary "third body" or catalyst, needed to promote the formation of the radicals, may be a neighboring cage-cation (Richardson, 1966b) or an as-yet-unknown sensitizer which can promote a pyrene molecule into the triplet state (Turro, pp. 86, 132, 133, 1965; Reid, 1958; Scott, p. 94, 1965; Parker, Hatchard, *et al.*, 1965). The precise nature of the chemical reactions on the surface of solids requires more study to substantiate this working hypothesis (Heldt, 1965).

This study demonstrates the unusual reactions of pyrene on soil. These may be representative of the reactions undergone by other polycyclic, aromatic hydrocarbons (constituents of the polluted air in most of our cities) (Sawicki, 1965; Tipson, 1965) exposed to solar radiation, oxygen, and heat.

Conclusions

Pyrene adsorbed on garden soil and exposed to ultraviolet radiation at 32° undergoes chemical change with the formation of 1,1'-bipyrene, 1,6- and 1,8-pyrenediones, and 1,6- and 1,8-pyrenediols, in addition to three unknown compounds. Experiments with radical-capture agents indicate that the formation of 1,1'-bipyrene involves a free-radical mechanism, whereas the formation of diones probably proceeds by attack of adsorbed oxygen on photo-excited pyrene molecules.

Literature Cited

Bergman, W., and McLean, M. J., *Chem. Rev.* **28**, 367 (1941).
Bronwer, D. M., *Chem. Ind.* (*London*) **1961**, 177.
Calvert, J. G., Pitts, J. N., Jr., Photochemistry," pp. 536–9, Wiley, New York, 1966.
Clar, E., "Polycyclic Hydrocarbons," Vol. 2, p. 124, Academic Press, New York, 1964.
Clar, E., Kuhn, O., *Ann.* **601**, 181 (1956).
Cohen, M. D., "Photochemistry of the Organic Solid State," in "Organic Photochemistry," p. 576, Butterworths, London, 1965.
Fatiadi, A. J., *J. Chromatog.* **20**, 319 (1965).
Gould, E. C., "Mechanism and Structure in Organic Chemistry," p. 708, Henry Holt, New York, 1959.
Griggith, R. H., Marsh, J. D. F., "Contact Catalysis," p. 229, Oxford University Press, London, 1957.
Heldt, W. Z., *J. Org. Chem.* **30**, 3897 (1965).
Hieger, I., "Carcinogenesis," p. 12, Academic Press, New York, 1961.
Hochstrasser, R. M., *Can. J. Chem.* **37**, 1123 (1959).
Hochstrasser, R. M., Porter, G. B., *Quart. Rev.* (*London*), **14**, 146 (1960).
Inscoe, M. N., *Anal. Chem.* **36**, 2505 (1964).
Laidler, K. J., "Chemical Kinetics," pp. 300, 312, McGraw-Hill, New York, 1965.
Mackor, E. L., van der Waals, J. H., *Trans. Faraday Soc.* **54**, 66 (1958).
Parker, C. A., Hatchard, C. C., Joyce, T. A., *Nature* **205**, 1282 (1965).
Parkyns, N. D., Patterson, B. C., *Chem. Commun.* **1965**, 531.
Parry, E. P., *J. Catalysis* **2**, 371 (1963).
Reid, C., *Quart. Rev.* (*London*) **12**, 205 (1958).
Richardson, J. T., *Abstracts of Papers*, Division of Petroleum Chemistry, 152nd Meeting, ACS, p. 23U (1966a).
Richardson, J. T., *Chem. Eng. News* **44**, No. 39, 22 (1966b).
Roberts, R. M., Barter, C., Stone, H., *J. Phys. Chem.* **63**, 2077 (1959).
Rooney, J. J., Pink, R. C., *Proc. Chem. Soc.* **70**, 142 (1961).
Sawicki, E., *Chemist-Analyst* **53**, 24 (1965).
Scott, G., "Atmospheric Oxidation and Antioxidants," pp. 61, 116–25, Elsevier, New York, 1965.
Scott, J. A., Flockhart, B. D., Pink, R. C., *Proc. Chem. Soc.* **1964**, 139.
Streitwieser, A., Jr., Hammons, J. H., *Progr. Phys. Org. Chem.* **3**, 41 (1965).
Tipson, R. S., "Oxidation of Polycyclic, Aromatic Hydrocarbons," Natl. Bur. Standards Monograph **87** (1965).
Turro, N. J., "Molecular Photochemistry," pp. 86, 132, 133, W. A. Benjamin, New York, 1965.
Volmann, H., Becker, H., Correll, M., Streeck, H., *Ann.*, **531**, 77 (1937).

Gamma Irradiation of Dilute Aqueous Alkyl Benzene Sulfonate Solutions

Marvin Fleischman and Robert H. Price

Department of Chemical and Metallurgical Engineering, University of Cincinnati, Cincinnati, Ohio 45221

■ The effects of dissolved oxygen level, pH, initial ABS concentration, iron concentration, and total dose on gamma irradiation–induced degradation and oxidation of ABS were experimentally investigated, primarily by the methylene blue and chemical oxygen demand methods. At an absorbed dose of 54,000 rads 98% of the ABS was destroyed. G values for degradation, $G(-ABS)$, increased with decreasing pH. An optimum ratio of ferrous ion concentration to ABS concentration was found at which $G(-ABS)$ increased 97% and G for oxidation, $G(-O_2$ eq.$)$, increased 52% over the values in the absence of iron at the same pH. Both G values were substantially higher in solutions containing oxygen than in deoxygenated solution. $G(-ABS)$ ranged from 0.510 to 2.46, while $G(-O_2$ eq.$)$ ranged from 0 to 67.

The Unidynamics Corp. (1963) has reported the destruction of organic refractories (compounds which resist ordinary treatment) in sewage by ionizing radiation. Bishop *et al.* (1964) have oxidized such compounds in filtered municipal secondary effluents with hydrogen peroxide. The same mechanism, autoxidation, is believed to be responsible for oxidation of organics in aqueous solution by hydrogen peroxide and by ionizing radiation. Therefore, it was felt that a more thorough study of the effects of ionizing radiation on organic refractories would be worthwhile.

An experimental investigation was made of the extent of alkyl benzene sulfonate (ABS) degradation and oxidation induced by gamma irradiation of dilute aqueous solutions. The variables studied were dissolved oxygen level, pH, initial ABS concentration, total absorbed dose, and the ratio of ferrous ion concentration to ABS concentration. Results are reported as G values—i.e., molecules reacting per 100 e.v. of radiation absorbed.

Radiation Chemistry of Aqueous Solutions

Since extremely dilute solutions ($\sim 3 \times 10^{-5}M$) were used, the direct effect of radiation on water and subsequent reaction of the irradiation products with the organic substrate must be considered (Allen, 1961; Spinks and Woods, 1964).

With radiation of low linear energy transfer (LET), such as the electrons produced by the interaction of γ-rays with water, the primary products are hydrogen and hydroxyl free radicals. Hydrogen peroxide and molecular hydrogen are produced to a much smaller extent. In the presence of oxygen, the primary radicals can initiate autoxidation of organic solutes.

$$RH + \cdot OH = H_2O + R \cdot \tag{1}$$

$$H \cdot + O_2 = HO_2 \cdot \tag{2}$$

$$HO_2 \cdot + RH = H_2O_2 + R \cdot \tag{3}$$

$$R \cdot + O_2 = RO_2 \cdot \tag{4}$$

$$RO_2 \cdot + RH = ROOH + R \cdot \tag{5}$$
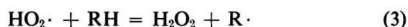
The hydroperoxides formed in the chain reaction are very unstable and decompose rapidly.

$$2RO_2 \cdot = products \tag{6}$$

$$2HO_2 \cdot = H_2O_2 + O_2 \tag{7}$$

Ferrous ions increase the yield of both primary radicals via the reactions of iron with hydrogen peroxide and the hydroperoxides and hydroperoxy radicals formed in the autoxidation chain. The reactions with hydrogen peroxide are given by Equations 8 to 10.

$$H_2O_2 + Fe^{2+} = Fe^{3+} + OH^- + \cdot OH \tag{8}$$

$$H_2O_2 + Fe^{3+} = Fe^{2+} + HO_2 \cdot + H^+ \tag{9}$$

$$HO_2 \cdot + Fe^{3+} = Fe^{2+} + H^+ + O_2 \tag{10}$$
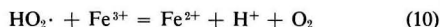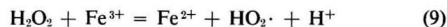
This reaction sequence can counteract Reaction 7, an autoxidation chain-ending step. Also the hydroxyl radicals produced can participate in the autoxidation chain.

The reactions of iron with hydroperoxides are

$$ROOH + Fe^{2+} = RO \cdot + Fe^{3+} + OH^- \tag{11}$$

$$RO \cdot + O_2 = RO_3 \cdot \tag{12}$$

$$RO_3H = RO_2 \cdot + \cdot OH \tag{13}$$

$$RCO_2 \cdot = R \cdot + CO_2 \tag{14}$$
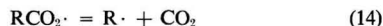
Reaction with hydroperoxy radicals is given by Equation 15.

$$Fe^{2+} + HO_2 \cdot + H^+ = Fe^{3+} + H_2O_2 \tag{15}$$
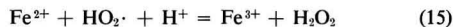
Reaction 15 could then be followed by Reactions 13 to 15.

These possible reactions with iron indicate that the net effect of ferrous ions is to increase the extent of organic decomposition.

The effects of pH can be attributed to two factors: its influence on the reactions of iron and on radicals. Decreasing pH increases the extent of the above-mentioned reactions of ferrous ions and hence should enhance the decomposition of organic solutes. As pH increases, secondary reactions involving ferric ions become prominent and the extent of organic degradation is not increased. Appreciable precipitation of ferric hydroxide occurs above pH 3.5.

Both the hydroperoxy radical (Evans *et al.*, 1952) and the hydroxyl radical (Hart *et al.*, 1952, 1955) dissociate in alkaline solution.

$$HO_2 \cdot \rightleftarrows H^+ + O_2^- \tag{16}$$

$$\cdot OH \rightleftarrows H^+ + O^- \tag{17}$$

These reactions will compete with the combination of ·OH and HO$_2$· with other radicals and/or solutes.

Below a pH of about 3 the yields of hydrogen and hydroxyl radicals increase without any corresponding decrease in the yields of molecular hydrogen and hydrogen peroxide.

Experimental

Analytical Methods. The Fricke dosimeter (American Society for Testing Materials, 1959) was used to determine the dose rate rather than direct instrumental measurement of radiation. The dosimeter is subjected to the same irradiation conditions as the test solutions, and hence the geometry factor is eliminated. Since the dose rate was fixed for all experiments, the spectrophotometric analyses for ferrous ion or ferric ion suggested for Fricke dosimetry were not used. Instead, the change in ferrous ion concentration was determined by titration of 100-ml. samples of initial and irradiated solutions with 0.004N ceric sulfate. Ferroin indicator was used to detect the end point. The experimental dose rate was 4.40 × 10^{19} e.v. or 1.41 × 10^3 rads per hour.

ABS was determined by a modified methylene blue method (Williams, 1961), the standard method for determining ABS concentration in sewage, applicable in the range 0.025 to 100 mg. per liter. The extent of ABS oxidation was determined by measuring the chemical oxygen demand (COD), the oxygen necessary for complete conversion of the organic solutes to carbon dioxide and water. This is accomplished by refluxing the sample with sulfuric acid and an excess of standardized potassium dichromate (Dobbs and Williams, 1963). In the presence of iron, the measured COD's were corrected for reduction of dichromate by residual ferrous ions.
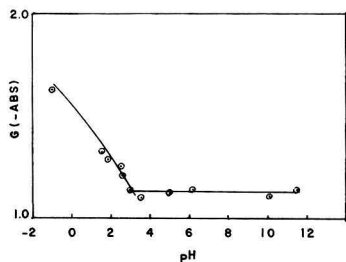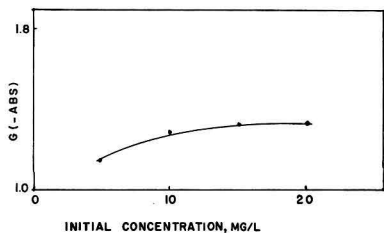
Equipment and Reagents. The reaction vessel was a wide-mouthed reagent jar, 7.75 inches high and 3.75 inches in diameter. A test tube held in the bottle by a rubber stopper, secured to the bottle by plastic tape, served as a source holder. Silicon grease was applied to the stopper to provide water repellency. The source, 2 curies of cobalt-60 sealed in a glass vial, was kept in a concrete well under 12 feet of water. A nylon string was attached to the vial to manipulate the source. A sealed light bulb unit provided light for maneuvering the source into the test tube when the filled reactor bottle was lowered to the bottom of the well.

The ABS was supplied by the Soap and Detergent Manufacturers Association, 295 Madison Ave., New York 17, N. Y. In this particular lot the ABS was a mixture of 59.5% tetrapropylene benzene sulfonate and 40.5% pentapropylene benzene sulfonate. Since the usual concentration of ABS leaving a sewage treatment plant is about 10 mg. per liter, most tests were done at this initial concentration, at which the experimentally measured COD and that calculated from the known ABS composition were both 22.9 mg. per liter.

All solutions were made with oxygen-saturated (except where otherwise noted) distilled and demineralized water. Ferrous sulfate was the ferrous ion source. pH adjustments were made by addition of concentrated sulfuric acid or sodium hydroxide. The added sulfate or sodium ions should not affect the reactions. Five hundred milliliters of working solution were used in each experiment. Most of the test solutions were irradiated for 5 hours, at a dose of 7050 rads. This period was chosen because ABS concentration changes appreciably, and the ABS is not destroyed beyond the point of detectability.

In the tests involving iron at pH 3.5 or above, ferric hydroxide precipitation was evident in the irradiated solution. To ensure uniform sampling and to avoid attributing any ABS

Figure 1.   Variation of $G(-ABS)$ with initial pH

5-hour irradiation, 10 mg. per liter initial ABS concentration

Figure 2.   Variation of $G(-ABS)$ with initial ABS concentration
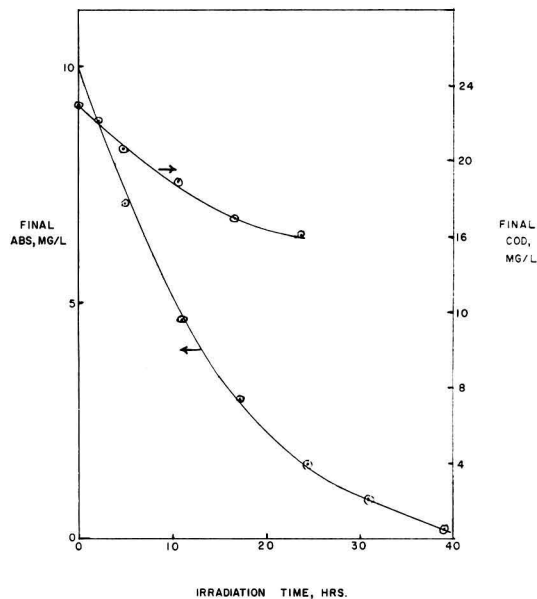
5-hour irradiation

Figure 3.   Final ABS concentration and final COD as a function of irradiation time

10 mg. per liter initial ABS concentration

or COD reduction to coagulation, the solution was clarified by adding sulfuric acid before samples were taken. This necessitated correcting the final concentrations for the volume of acid added.

It was found necessary to clean the optical cells which contained the ABS–methylene blue complex in chloroform after each spectrophotometer reading; otherwise a noticeable blue ring remained in the cell. Cleaning was accomplished with a 50–50 mixture of $3N$ hydrochloric acid and ethanol. All other glassware was cleaned with chromic acid–sulfuric acid solution and treated with sodium phosphate to eliminate ABS adsorption.

All results reported were corrected for source decay.

Results

G values for the reduction of ABS concentration, as determined by the methylene blue method, were calculated from

$$G(-\text{ABS}) = 0.375 \frac{\Delta C_{\text{ABS}}}{t}$$

where t is the duration of irradiation in hours.

In the COD procedure the amount of dichromate reduced is a direct measure of the amount of material oxidized and is expressed as oxygen equivalents. Therefore, $G(-\text{O}_2$ eq.) was defined to indicate the G value for the change in COD expressed as oxygen equivalents. These values were calculated from

$$G(-\text{O}_2 \text{ eq.}) = 85.5 \frac{\Delta \text{COD}}{t}$$

Dissolved Oxygen Level. A series of tests was run to determine whether the dissolved oxygen concentration of the solution affected the extent of ABS degradation and oxidation. The actual oxygen concentrations were not determined. Therefore, this series of tests is qualitative. Four oxygen levels were obtained by using air-saturated, oxygen-saturated, nonpreaerated or oxygenated, and deoxygenated solutions. Deoxygenation was accomplished by purging the solution with nitrogen. In one test, evacuation followed the nitrogen purge. The pH in all but one test was 5.8 to 6.0. The irradiation period was 5 hours for each test (Table 1).

A decrease was noted in both the extent of ABS degradation and the reduction of COD in the absence of oxygen. Otherwise dissolved oxygen level appeared to have no effect. Oxygen saturation provides a 17.5% excess over the oxygen required for complete conversion of the ABS to carbon dioxide and water. Air saturation provides only 35.4% of the oxygen demand. With longer irradiation periods, oxygen may become

the limiting reactant and greater G values would then be obtained in oxygen-saturated solutions. Oxygen-saturated solutions were used in subsequent experiments to avoid having oxygen become limiting.

pH. Figure 1 shows the effect on $G(-\text{ABS})$ of varying the pH. $G(-\text{ABS})$ remained constant with increasing acidity until pH 3 was reached, but below this value increased with decreasing pH. No oxidation occurred at pH 11 or above. Within the range of pH studied, the shape of the curve in Figure 1 is similar to that showing the variation with pH of primary radical yields in gamma-irradiated water (Spinks and Woods, 1964).

Initial ABS Concentration. These results are shown in Figure 2. Each experiment was conducted at pH 1.5 because of the higher G value at low pH. In the range of 10 to 20 mg. per liter initial concentration had no significant effect. However, the differences in $G(-\text{ABS})$ for 5 and 10 mg. per liter ABS are statistically significant. Since $G(-\text{ABS})$ for 5-hour and 2-hour irradiation are about equal, a concentration effect, if present, is initiated at or below 7 mg. per liter (the final ABS concentration after 5 hours' irradiation).

Total Irradiation Time (Dose). The final ABS concentration and COD after irradiation were determined for different irradiation times (Figures 3 to 5). More than 90% of the ABS was degraded within 30 hours (Figure 3). The much higher values of $G(-\text{O}_2$ eq.) indicate that a chain reaction occurs with respect to oxidation but not ABS degradation (Figure 5). The decrease in $G(-\text{ABS})$ with increasing dose could be attributed to the effect of initial concentration.

Ferrous Ion. The ratio of ferrous ion concentration to ABS concentration (moles per liter) was varied at different fixed initial values of pH. In addition, the initial ABS concentration was varied at the Fe/ABS ratio which caused the maximum ABS degradation (Figures 6 to 9 and Table II).

At the lowest pH (1.5) there was no noticeable increase of $G(-\text{ABS})$ over that in the absence of iron until Fe/ABS reached 5/10. Thereafter $G(-\text{ABS})$ increased, reaching a maximum at an Fe/ABS of about 10/1 (Figure 6). The max-
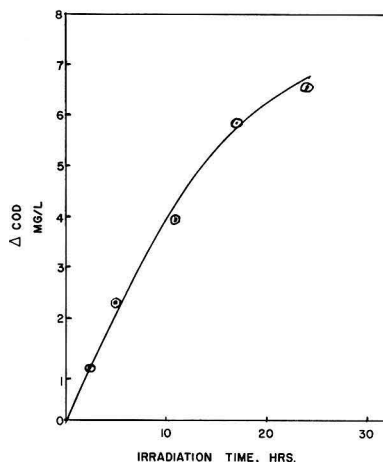
Figure 4. Change in COD as a function of irradiation time

10 mg. per liter initial ABS concentration

Table I. Dissolved Oxygen Level

State of Aeration	ΔC_{ABS}, Mg./L.	$G(-\text{ABS})$	ΔCOD, Mg./L.	$G(-\text{O}_2$ eq.)
Tap	2.9	1.1	2.8	48
Aerated	2.7	1.0	2.5	43
O_2-saturated	2.9	1.1	2.4	40
N_2-purged	1.8	0.69	0	0
	1.0	0.39	0	0
N_2 purge + evacuation	1.3	0.51	0.7	12, pH 8
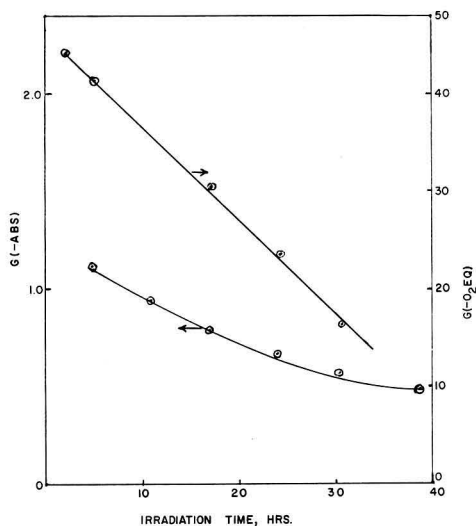
Figure 5. Variation of $G(-ABS)$ and $G(-O_2$ eq.) with irradiation time

10 mg. per liter initial ABS concentration
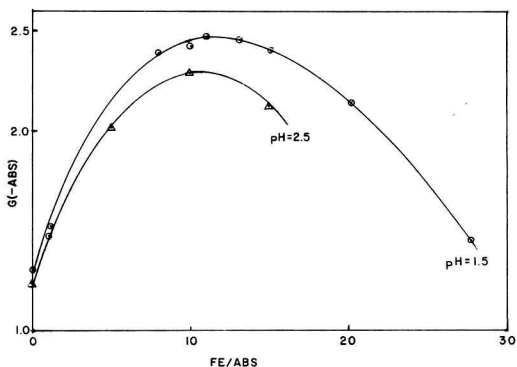
Figure 6. Variation of $G(-ABS)$ with initial ratio of molar concentration of ferrous ions to molar concentration of ABS

5-hour irradiation, 10 mg. per liter initial ABS concentration
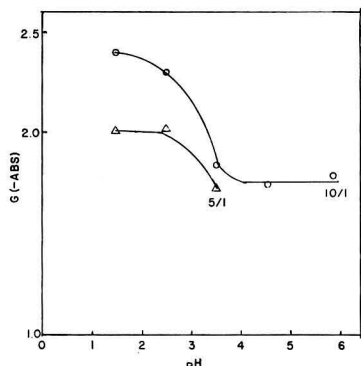
Figure 7. Variation of $G(-ABS)$ with initial pH in presence of iron

5-hour irradiation, 10 mg. per liter initial ABS concentration

Table II. Effect of Deoxygenation in Presence of Iron

(Fe/ABS = 10/1, pH = 1.5)

	Oxygen-Saturated Solution	Deoxygenated Solution
$G(-ABS)$	2.40	1.59
$G(-O_2$ eq.)	67	26

imum decrease in COD also occurred in this vicinity (Figure 8). The increases due to ferrous ion were more pronounced for ABS degradation than for oxidation.

For a fixed Fe/ABS, $G(-ABS)$ decreased with increasing pH, the maximum degradation still occurring at an Fe/ABS of about 10/1 for each pH. Above pH 3.5, tests were conducted only at 10/1, and $G(-ABS)$ was the same for all these pHs as at pH 3.5 (Figure 7).

The single test run at Fe/ABS = 10/1 and pH 1.5 in deoxygenated solution yielded much smaller $G(-O_2$ eq.) and $G(-ABS)$ values than in oxygenated solution.

$G(-ABS)$ increases with increase of initial ABS concentration (Figure 9): a 34% increase in $G(-ABS)$ with a doubling of concentration. For the 20 mg. per liter solution, ABS and COD were measured both immediately after irradiation and about 1 hour later to determine if reaction continued after removal of the radiation source. No postirradiation reaction occurred.

Comparison with Similar Investigations

The Unidynamics division of Universal Match Co., under an Atomic Energy Commission contract (U.S. Atomic Energy Commission, 1963), studied the effects of gamma irradiation on synthetic detergent solutions. Table III compares the effects of total dose on ABS degradation of this study and theirs.

Unidynamics did not indicate the ABS composition, and the differences in G values obtained in the different studies can be attributed to differences in ABS composition and structure. Reaction rate and ease of degradation should be somewhat dependent on the isomer present—i.e., point of attachment of the benzene ring to the hydrocarbon chain. Also higher $G(-ABS)$ values would be expected as the percentage of pentapropylene benzene sulfonate in the ABS mixture increased over the percentage of tetrapropylene benzene sulfonate, because chain shortening to the point where the molecule will not be detected by the methylene blue method occurs more easily with tetrapropylene benzene sulfonate.

Table III. Comparison of Results

	Unidynamics	University of Cincinnati
Dose rate, rads/min.	26.6	23.5
Dose for 50% removal, rads	10,000	15,000
Dose for 99% removal, rads	90,000	54,000 (98% removal)
$G(-ABS)$ for 50% removal	3	0.95
$G(-ABS)$ for 90% removal	1	0.60
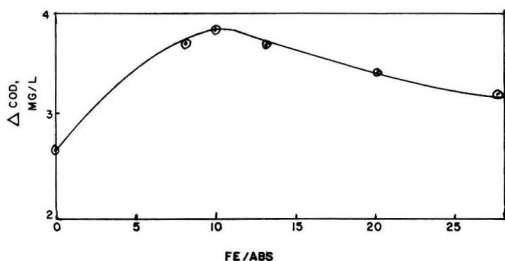
Figure 8. Change in COD as a function of initial ratio of ferrous ion concentration to ABS concentration

pH 1.5, 5-hour irradiation, 10 mg. per liter initial ABS concentration
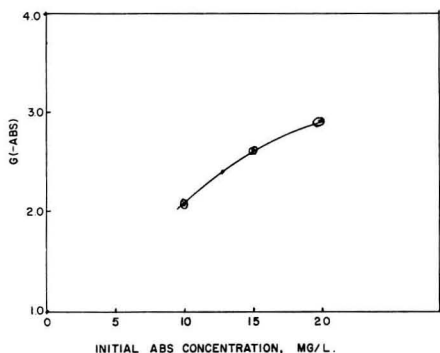
Figure 9. Variation of $G(-ABS)$ with initial ABS concentration in presence of iron

pH 1.5, Fe/ABS = 10/1, 5-hour irradiation

Unidynamics proposed a degradation scheme based on cleavage of the sulfonate group:

$$H_2O + R\text{—}\phi\text{—}SO_3Na \rightleftarrows R\phi - H + Na^+ + HSO_4^-$$
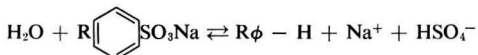
If this mechanism were effective, long-chain alkyl benzenes, which are insoluble in water, could form. A film might then exist on the surface of the water. Such an effect was not noticed in our study. However, at the low concentrations of ABS involved, the solubility of alkyl benzenes might be high enough so that a film would not form. Alternatively, desulfonation could have occurred, resulting in hydroxylated alkyl benzenes which are more soluble than the alkyl benzenes.

Discussion

The data show that for the same dose the decrease in COD is less than the decrease in ABS (both in milligrams per liter), suggesting that complete degradation of ABS requires a smaller dose and is easier to achieve than complete oxidation. However, with the analytical techniques used, a definite conclusion cannot be drawn.

The methylene blue method and COD were chosen because of their wide use as indicators of water pollution levels and for screening potential treatment processes. Neither determines the presence nor measures the amount of any specific compound. The methylene blue test will not measure carbon chains below six carbon atoms and desulfonated alkyl benzenes. Therefore, what is reported as degradation of ABS may be only the inability to measure an altered compound.

Sallee *et al.* (1956) developed an infrared technique to establish unequivocally the presence and amount of ABS in any given water sample. However, compared to the methylene blue method it is fairly complicated and time-consuming.

Benzene is not appreciably oxidized in the COD procedure, but Dobbs (1963) found that 96% of the theoretical COD for ABS is attained; 100% was found in this study. However, if the ring portion of the ABS is not oxidized in the COD analysis, destruction of all the COD may require only a change in configuration to a form not measurable by the test—e.g., desulfonation. In this case less organic material would actually be oxidized than is suggested by the reported COD reductions.

Further investigation should be directed toward identifying and measuring irradiation products and elucidating mechanisms. Swisher (1963) used gas chromatography to identify and measure the intermediates resulting from biodegradation of ABS. A similar procedure would be applicable to irradiation products. Total carbon analysis (Busch, 1967) using, for example, the Beckman carbonaceous analyzer, would determine the amount of organic material completely oxidized to carbon dioxide and water. This would measure the effectiveness of total organic destruction or removal.

Nomenclature

ΔC_{ABS} = change in ABS concentration, mg. per liter
ΔCOD = change in COD, mg. per liter
$G(-ABS)$ = G value for disappearance of ABS, molecules/100 e.v.
$G(-O_2 \text{ eq.})$ = G value for reduction of COD in terms of oxygen equivalents
Fe/ABS = ratio of molar concentration of ferrous ion to molar concentration of ABS

Literature Cited

Allen, A. D., "The Radiation Chemistry of Water and Aqueous Solutions," Van Nostrand, New York, 1961.
American Society for Testing Materials, "Method of Measuring Absorbed Gamma Radiation by Fricke Dosimeter," **ASTM D 1671-59T**, 1959.
Bishop, D. F., Stern, G., Fleischman, M., Marshall, L. S., "Hydrogen Peroxide Catalytic Oxidation of Refractory Organics in Municipal Waste Waters," 148th meeting, ACS, Chicago, Ill., September 1964.
Busch, A. W., *Analyzer* (Beckman Instruments), pp. 3–7 (February 1967).
Dobbs, R. A., Williams, R. T., *Anal. Chem.* **35**, 1064–7 (1963).
Evans, M. G., Hush, N. S., Uri, N., *Quart. Rev.* **6**, 186 (1952).
Hart, E. J., Gordan, S., Hutchison, D. A., *J. Am. Chem. Soc.* **74**, 5548 (1952); *J. Chim. Phys.* **52**, 570 (1955).
Sallee, E. M., Fairing, J. D., Hess, R. W., House, Ralph, Maxwell, P. M., Melpolda, F. W., Middleton, F. M., Ross, John, Woelfel, W. C., Weaver, P. J., *Anal. Chem.* **28**, 1822 (1956).
Spinks, J. W. T., Woods, R. J., "An Introduction to Radiation Chemistry," Chap. 8, Wiley, New York, 1964.
Swisher, R. D., *J. Water Pollution Control Federation* **35**, 1557–64 (1963).
Unidynamics Corp., *Nucleonics* **21**, 28 (1963).
U.S. Atomic Energy Commission, "Investigation of the Effects of Ionizing Radiation on Synthetic Detergents, Sewage, Colloidal Characteristics, and Sewage Sedimentation," Doc. **D63-641** (Sept. 6, 1963).
Williams, R. T., "Methylene Blue Method for Determining ABS," U.S. Public Health Service, R. A. Taft Sanitary Engineering Center, Cincinnati, Ohio (Dec. 26, 1961).

Relative Importance of Viscosity and Oxygen Solubility on Oxygen Transfer Rates in Glucose Solutions

James A. Mueller[1] and William C. Boyle

Department of Civil Engineering, University of Wisconsin, Madison, Wis. 53706

■ Oxygen transfer rates have been used to determine oxygen solubilities in glucose solutions without taking into account the viscosity effect. This study was undertaken to evaluate the effects of both viscosity and oxygen solubility on oxygen transfer rate. To accomplish this, the viscosities and oxygen saturation concentrations for distilled water and glucose solutions were measured. The results indicate that viscosity change rather than oxygen solubility is the major cause for variation in oxygen transfer rate with varying glucose concentrations. Thus, estimation of oxygen solubility for dissolved oxygen probe calibration using oxygen transfer rate data is invalid.

A method for calibrating a dissolved oxygen probe in a glucose-salts solution (Bennett and Kempe, 1964), consists of air-saturating a glucose-salts solution and using this to standardize the probe. The oxygen saturation value of this solution was calculated from data given by Solomons (1961). This method, however, is invalid, since Solomons' data are misleading and cannot be used for this purpose.

Solomons has presented a graph of solubility of oxygen expressed as oxygen transfer rate, OTR, *vs.* normality of glucose solutions. The manner of data presentation indicates that the ratio of the OTR at a given glucose concentration to the OTR in distilled water can be multiplied by the oxygen saturation value, c_e, in distilled water to obtain the oxygen saturation value in the glucose solution. However, the following analysis shows that Solomons has not taken viscosity change into account.

The oxygen transfer rate is given by Solomons as

$$OTR = 3.6D \frac{A_i}{\delta} (c_e - c) \tag{1}$$

where A_i and δ are, respectively, the interfacial area and liquid film thickness of the air bubbles, c is the oxygen concentration in the bulk liquid, and D is the diffusivity of oxygen in the solution.

The ratio of the maximum oxygen transfer rates ($c = 0$) is given by

[1] Present address, Regional Environmental Health Laboratory, Kelly Air Force Base, Tex. 78221

$$\frac{OTR_g}{OTR_w} = \frac{D_g(A_i/\delta)_g(c_e)_g}{D_w(A_i/\delta)_w(c_e)_w} = \frac{(K_{La})_g(c_e)_g}{(K_{La})_w(c_e)_w} \tag{2}$$

where K_{La} is the oxygen transfer coefficient, and subscripts g and w refer to the glucose and distilled water solutions, respectively.

Thus, to use Solomons' OTR data directly, the values of K_{La} for distilled water and glucose solutions must be equal. If the assumption is made that the interfacial area and stationary film thickness are not affected by glucose concentration, the ratio of the K_{La} values is equal to the ratio of the diffusivities. As shown in the Stokes-Einstein equation (Bird, Stewart, *et al.*, 1960), at a constant temperature, diffusivity is inversely proportional to the viscosity, μ, of the solution. Substituting this relationship into Equation 2 yields

$$\frac{OTR_g}{OTR_w} = \frac{\mu_w(c_e)_g}{\mu_g(c_e)_w} \tag{3}$$

From this equation, it is seen that the OTR ratio is a function of both the viscosity and oxygen saturation value of the solutions. Treybal (1955) states that the "diffusivity for concentrated solutions differs from that for dilute solutions because of changes in viscosity with concentration and also because of changes in the degree of ideality of the solution." To determine which of the parameters in Equation 3 has the greater effect on OTR, the viscosities and oxygen saturation values of two glucose solutions were experimentally determined.

For the viscosity determinations, a No. 100 Cannon-Fenske calibrated viscometer was used. These determinations were made at 24.2° C. on a distilled water sample and two solutions having glucose concentrations of 50 and 188 grams per liter. The results (Figure 1) indicate that viscosity increases markedly with increasing glucose concentration in the range tested.

Before measuring oxygen solubility values with a dissolved oxygen probe (Precision Scientific galvanic cell), it was necessary to determine the effect of various glucose concentrations on probe readings. This was accomplished by recording the probe reading of an air-saturated distilled water sample in an air-tight reactor, removing the probe and adding a known quantity of glucose to the reactor, immediately providing an air-tight seal by placing the probe back in the reactor, mixing the reactor contents with a magnetic stirring bar, and recording a probe reading after the glucose had dissolved.
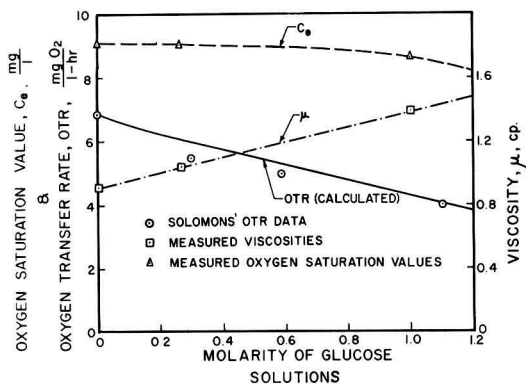
Figure 1. Relation among glucose concentration and oxygen saturation value, oxygen transfer rate, and viscosity

OTR curve calculated from Equation 3 using OTR of distilled water of 6.9 from Solomons

Since the reactor was open to the atmosphere for only a few seconds after glucose addition, insufficient time was available for the oxygen content of the glucose solution to equilibrate with the atmosphere. Therefore, the oxygen concentration in the glucose solution was substantially the same as that in the initial distilled water solution. Thus, a conversion factor, γ, can be defined by

$$\gamma = \frac{P_w}{P_{glu}} \tag{4}$$

where P_{glu} and P_w are, respectively, the probe readings for a glucose sample and for distilled water at the same dissolved oxygen concentrations. The conversion factor (Table I) decreased with increasing glucose concentrations.

Table I. Effect of Glucose Concentration on Probe Reading

Solution	Probe Reading at Dissolved Oxygen Concn. of 9.2 Mg./L.	Conversion Factor, γ
Distilled water	5.80	1.000
Glucose, 50 g./l.	5.85	0.992
Glucose, 188 g./l.	6.10	0.952

Table II. Effect of Glucose Concentration on Viscosity and Oxygen Saturation Value

Solution	Viscosity, μ, Cp.	Probe Reading, P, after Aeration Time of			c_e, Mg./L.
		0 hr.	1 hr.	2 hr.	
Distilled water	0.92	1.10	5.75	5.80	9.20
Glucose, 50 g./l.	1.04	1.10	5.75	5.80	9.15
Glucose, 188 g./l.	1.39	1.10	5.67	5.75	8.66

[a] $C_e = \dfrac{9.20}{5.80} \gamma P_{2\,hr.}$

For the determination of the c_e values, three 300-ml. flasks, each containing one of the solutions used in the viscosity determinations, were aerated at 20°C. for 2 hours. The probe readings in the flasks increased markedly in the first hour and only slightly in the second hour of aeration. Thus, the flasks after 2 hours of aeration were assumed to be saturated. Using the conversion factors, γ, from Table I, the oxygen saturation values were calculated (Table II).

The OTR curve in Figure 1 was calculated from Equation 3 using the value of OTR for distilled water given by Solomons. The slight deviation from Solomons' data may be caused by a viscosity effect on the interfacial area and film thickness. In Figure 1 there is a noticeable decrease in oxygen solubility with increasing glucose concentrations—about a 5.8% decrease in c_e from distilled water to the 188 grams per liter glucose solution. However, the viscosity, varying linearly with glucose concentration, is 51% greater for the 188 grams per liter glucose solution than for distilled water. This proves that viscosity change rather than oxygen solubility is the major cause of variation in oxygen-transfer rate with varying glucose concentrations. Thus, Bennett and Kempe's method for dissolved oxygen probe calibration using Solomons' OTR data is invalid. However, since media used in most biological studies contain glucose concentrations well below 50 grams per liter, no measurable effect will be exhibited by the glucose on either oxygen solubility or probe reading. The glucose can therefore be excluded from the media and the standard Winkler method (American Public Health Association, 1965) used for probe calibration.

Literature Cited

American Public Health Association, New York, "Standard Methods for Examination of Water and Waste Water," 12th ed., 1965.
Bennett, G. F., Kempe, L. L., *Biotech. Bioeng.* **6,** 347–60 (1964).
Bird, R. B., Stewart, W. E., Lightfoot, E. W., "Transport Phenomena," Wiley, New York, 1960.
Solomons, G. L., "Aeration and Agitation in Continuous Culture," in Continuous Culture of Microorganisms, Monograph **12,** pp. 233–53, Society of Chemical Industry, London, 1961.
Treybal, R. E., "Mass Transfer Operations," McGraw-Hill, New York, 1955.
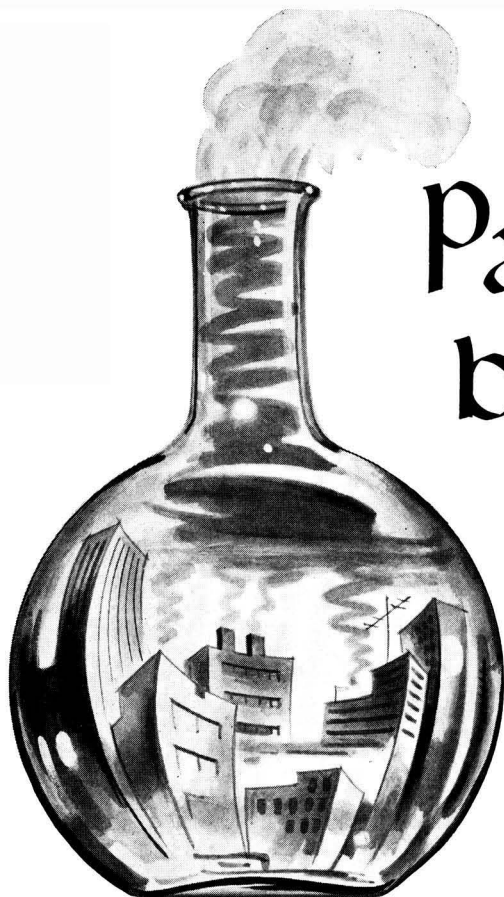
Pandora's bottle

MEET THE CHALLENGE WITH GASFLOW INSTRUMENTATION & STANDARDS FROM ⓒ
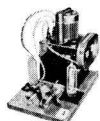
GAS MIXING PUMP Provides standard gas concentrations for calibrating instruments. 0.05% accuracy.	**WET & DRY GASFLOW METERS** Many ranges available. Accuracy from 0.1%.	**INFRARED GAS ANALYZER** Rapid, accurate, with full scale ranges from 0.01% to 100% (by volume).	**ULTRAGAS 4** Batch or continuous CO, CH_4, CO_2 measurement. Includes electronic circuitry. Ranges: 0-100 ppm, 0-500 ppm. Accurate to 1.0 ppm.
GAS CALIBRATION CART Delivers one gas stream with up to 4 constituents for instrument calibration. 0.167 ppm accuracy.	**GAS ANALYZER** Quick determination of CO, CO_2, O_2 and other atmospheric gases. Accurate to 0.02%.	**CALIBRATION GAS SERVICE** Cylinders, all sizes, custom filled to order. Accuracy cross checked.	**ULTRAGAS 3** For atmospheric SO_2 by conductivity measurement. Scale ranges: 0.56 ppm, 1.7 ppm, 3.5 ppm. Runs 30 days. Remote sampling and reading.
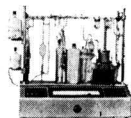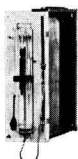
Write or call for complete details.

Ⓒ CALIBRATED INSTRUMENTS, INC.

17 WEST 60th STREET, NEW YORK, N.Y. 10023 ■ (212) 245-5590

Circle No. 3 on Readers' Service Card

NEW PRODUCTS DIGEST

pH Meters

An industrial pH monitor combines indication transmission and control/alarm in a single unit. Three standard types are available in pH ranges of 0–14 pH, 2–12 pH, and ± 500 mv. Separate 100 μA/pH output is provided for remote indicators, recorders, electropneumatic converters, and other controllers. Also available: an industrial pH electrode selector, a device enabling up to six electrode assemblies to be selected and connected, in turn, to a single pH monitor. W. G. Pye & Co., Ltd. **61**

Spectrophotometers

Model SP800 automatic recording spectrophotometer is a double-beam instrument based on the optical null-balance principle. Spectra are drawn on an integral flat-bed recorder with a linear absorbance scale. Model SP90 atomic absorption spectrophotometer is designed for the rapid determination of trace elements in a wide variety of samples. It can be fitted with an autosampler enabling it to analyze 32 samples unattended. Model SP20 recorder, a new strip-chart unit for analytical applications, has six speeds, full span zero control, alarm contacts, and provision for remote control. The recorder can be used with any of the Company's spectrophotometers. Unicam Instruments, Ltd. **62**

Aerosol Photometer

This forward-scattering aerosol, smoke, and dust photometer is available in console and portable models. The self-contained unit measures, records, and controls dust and smoke concentrations over a wide range. Phoenix Precision Instrument Co. **63**

Wafer Butterfly Valve

A TFE-protected, wafer-type butterfly valve is available for use in corrosive environments, at pressures up to 150 p.s.i. and temperatures up to 400° F. Garlock, Inc. **64**
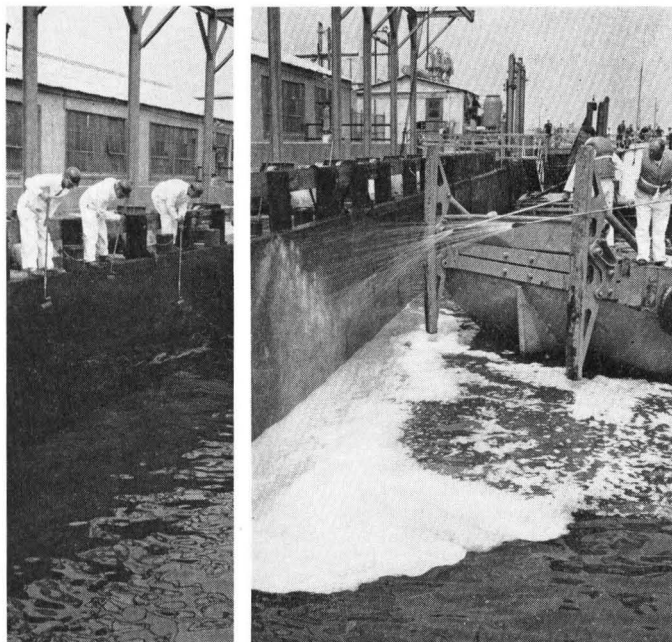
Oil Spills—One Company's Remedy

In the wake of the *Torrey Canyon* incident, research on solubilizers and dispersants for oil spills has gained an urgency that was not present before the accident. Chemical companies have stepped up research and oil transport concerns have accelerated their testing programs for effective oil-pollution remedies.

The chemical product sought must be effective in removing oil from water and sand, and from bulkheads. It must form a biodegradable residue. Most important, it must be completely soluble and nonirritating to human skin or animal life. Another important attribute must be its relative concentration or power, since one probable use would be stockpiling on oil-transport vessels for use in accidental oil spills on the high seas.

Recently Sun Oil Co. gave a public demonstration of such a product, Polycomplex A solubilizer manufactured by Guardian Chemical Co. The product proved effective in water, sand, and bulkhead tests in dispersing a domestic naphthenic crude oil of 23 API gravity. One gallon Polycomplex A per 10 gallons crude produced a microdispersion which company spokesmen claimed was readily degradable and nonirritating to plant and animal life.

In one demonstration, crude was smoothed over a bulkhead (left) and then sprayed with Polycomplex A to show the chemical's cleaning power (right). Guardian Chemical Co. **60**

Activated-Carbon for Air Conditioners

Grade 164 activated carbon adsorbs up to 25% of its weight of nitrogen dioxide or 20% of sulfur dioxide, and is highly efficient in adsorbing other airborne gaseous pollutants. It has no affinity for carbon monoxide and ethylene. The material is made from controlled-process hydrocarbon feedstock, and is produced in coarse granular form (6 × 12 U.S. Sieves size). Witco Chemical Co.   65

New Phosphate Polymer Material

A synthetic, organic polymer designed for boilers with feedwater hardness levels up to 25 p.p.m. has been tested for sludge conditioning, scale control, and foam control with good results. Extremely stable, the polymers show no corrosion potential (even in steam blanketed areas), may be used in high pressure applications (up to 1200 p.s.i.), and require no special feeding procedures. Nalco Chemical Co.   66

Drive System

A variable torque a.c. adjustable speed drive system for applications requiring constant pressure, level, flow, or temperature control, the Tri-Clad VT-700 consists of a silicon controlled rectifier static control panel and a high-slip, Type KXA motor. The unit automatically maintains wet-well level within ±2% of the prescribed level. General Electric Co.   67

Air Pollution Reagents

An air pollution reagents list, drawn up from HEW's *Selected Methods for the Measurement of Air Pollutants*, includes several procedures for sulfur dioxide, for nitrogen dioxide and nitric oxide, and for oxidants determination; and a single method for various other procedures. CAMP reagents are supplied in dry form. Harleco.   68

Waste Water Treatment

Packaged waste water treatment systems automatically neutralize acid or alkaline wastes, and break down chromate and cyanide wastes. Units may be added or rearranged as needs change, and are available in 2500-, 6250-, and 12,500-g.p.h. capacities. Sethco Manufacturing Corp.   69

Butterfly Valves

A line of butterfly valves, in sizes ranging from 1 to 72 inches i.d., used to control the flow of gases as well as liquids, is available. Rockwell Manufacturing Co.   70

Hand-Held Pipetter

A compact unit furnished with an integral, 250-ml. reagent reservoir, the Jet-Pipet is available in 5-ml., 1-ml., and 0.25-ml. dispensing volumes. The unit operates as rapidly as the trigger mechanism can be squeezed. Volumes are adjustable and reproducible within ±0.15% F.S. Setting scale is accurate within ±0.5%. Since liquids contact only glass and Teflon, corrosive acids and organic solvents can be handled. York Instrument Co.   71
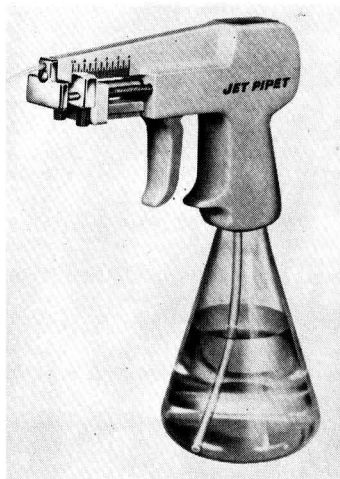
Computerized Water Management System

A computerized management system designed specifically for water utilities handles both on-line and off-line functions. The equipment costs about half as much as other available computer equipment for water utilities. The unit is equipped with warning lights and audible alarms for emergency conditions. Accounting, billing, meter monitoring, forecasts, and other operations can be handled. Badger Meter Manufacturing Co.   72

Relative Humidity Indicator

Model AB-167 hygrometer uses a Durotherm element to move the red-tipped pointer over a dial calibrated from 0 to 100% relative humidity. Carefully calibrated before shipping, the hygrometer is accurate to 230° F. and has a direct-reading dial. Abbeon, Inc.   73
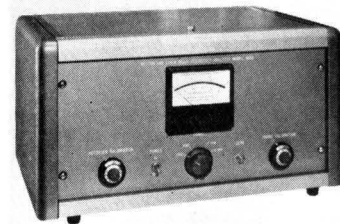
Dissolved Oxygen Analyzer

The Model 400 dissolved oxygen analyzer determines trace concentrations of dissolved oxygen in liquids through the parts per billion range. A specially designed polarographic probe is separated from the sample by a semipermeable membrane. The solid state circuitry may be either a.c. or d.c. powered. The unit features fast response, low drift, high accuracy and reproducibility, and long life. Weston & Stack, Inc.   74

Conductivity Bridge

Model PM-70CB solid-state conductivity bridge measures conductivity (0.1 micromho to 0.1 mho) or resistivity (100 ohms to 10 megohms) over a wide pH range. A digital scale readout is provided with the compact, lightweight, battery-powered bridge. Barnstead Still and Sterilizer Co., Inc.   75

NEW LITERATURE DIGEST

Instrument News. Volume 17 No. 3 of *Instrument News*, covering new developments in the broad field of instrumental analysis, is available. Subjects covered include: gas liquid chromatography, infrared spectroscopy, polymorphic forms, and a new system which permits atomic absorption analysis of undissolved samples. Perkin-Elmer Corp. **77**

Chromatography products. Catalog No. 11 lists, in its 52 pages, information on gas chromatography, thin layer chromatography, lipids, calibration standards, and other topics. Applied Science Laboratories, Inc. **78**

Chemicals films. A 23-page film guide on chemicals, chemistry, and the chemical industry (1967–68 edition) is available. Manufacturing Chemists' Association, Inc. **79**

Smog research. An 8-page booklet summarizes the smog research at the University of California. Entitled *The Polluted Air*, the illustrated report quotes UCLA Meteorologist Morris Neiburger as saying, "Humanity may only have another 100 years or so before it becomes extinct, the passive victim of a smoggy doom." University of California. **80**

Ground water. The Ground Water Resources Institute offers a 27-slide series on ground water and local water system problems, suggesting that underground water is overlooked and underused. Reasonable quantities of the script are free; the slides cost $15.00 per set for GWRI members, $25.00 for nonmembers. Ground Water Resources Institute. **81**

Pneumatic controllers. Bulletin 500-3, Bailey pneumatic control engineering, application, and product information, describes the company's single-loop, cascade, feedforward, and ratio control pneumatic controller systems. Bailey Meter Co. **82**
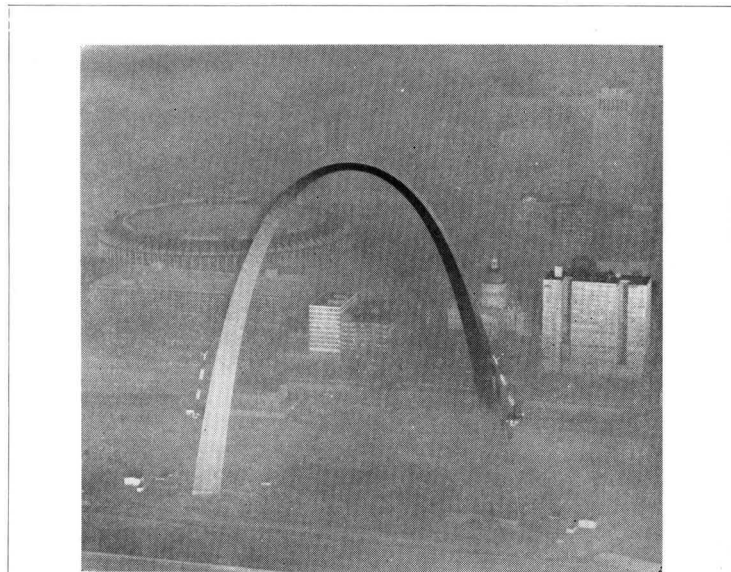
Air Pollution Films

"Fourteen professionally-produced films that illustrate the serious problem of air pollution, and what to do about it!" are available for loan, without charge, from the Public Health Service, according to PHS Publication No. 1264. Bearing such titles as *Something in the Wind* and *Air of Disaster*, the 16 mm. films range from 5 to 50 minutes long and have optical sound channels. All but four films are available in color. Single copies of the pamphlet describing the films are available free from the Public Health Service. **76**

Chromatography products. 3010 DB 8-2 is an 8-page folder on the chromatographic products and accessories available in the 5000 Series Selecta-Systems for research applications. Information is included on routine, quality control chromatographs, and liquid chromatography. Barber-Colman Co. **83**

Smoke chart. A factsheet is available from the Bureau of Mines, Department of the Interior, concerning the reissuance of the Ringelmann Smoke Chart (Information Circular 8333). Instructions for use of the chart are included; single copies may be obtained without charge. Bureau of Mines. **84**

Atmospheric water resources. Research Report No. 5 in the Water Resources Technical Publications series by the Bureau of Reclamation is *Park Range Atmospheric Water Resources Program*, *Phase I*. Park Range is one of 25 weather modification or cloud seeding programs administered by the Bureau. 75 cents. Bureau of Reclamation. **85**

Deep-well disposal services. A 4-page folder outlines the kinds of wastes that can be disposed underground, cost of deep-well disposal, successful applications of deep-well disposal, and deep-well services offered by the company. Dow Chemical Co. **86**

Will new air pollution laws catch you unprepared?

They're coming—at all levels of government. New laws are underway to curb industrial waste in the air.

Without proper monitoring equipment, you won't be able to tell how serious the problem is in time to protect yourself.

Research Appliance Company designs and manufactures a complete line of precision air sampling equipment, including the nationally-accepted A.I.S.I. Sampler. We have one exactly the right size, the right price for your operation. For our catalog, contact us.
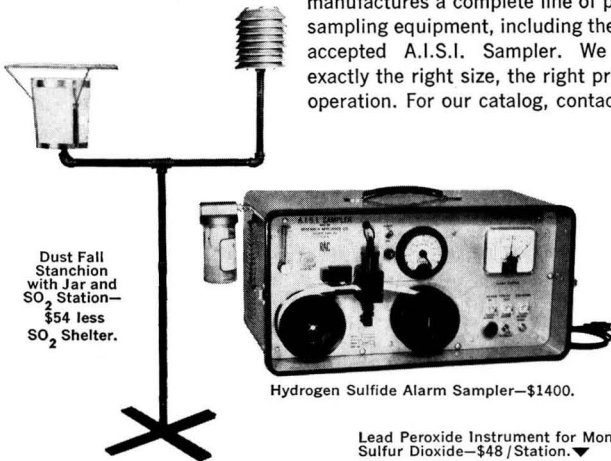
Dust Fall Stanchion with Jar and SO₂ Station—$54 less SO₂ Shelter.

Hydrogen Sulfide Alarm Sampler—$1400.

Lead Peroxide Instrument for Monitoring Sulfur Dioxide—$48 / Station.▼

A.I.S.I. Sampler with built-in Evaluator and Recorder—$748 to $858.

Battery Operated Midget Air Sampler. Lightweight, Compact, Versatile—$260.▼

Research Appliance Company
Route 8, Allison Park, Pennsylvania
Pittsburgh District (412) 961-0588

Skimming equipment. Bulletin No. 315-71 describes the use of Rex skimmers in industrial and municipal water and waste treatment applications for removing floating oil, scum, and sludge. Rex Chainbelt, Inc. **87**

Wastewater treatment. A 16-page brochure, *Evaluation*, describes how to select wastewater treatment systems and equipment. Yeomans Brothers Co. **88**

Pressure filter system. Bulletin No. 67DDY02 is a 4-page explanation of a pressure filter system that removes solids and oils from waste water from hot rolling mill and continuous casting systems. Dravco-Doyle Co. **89**

Laminar flow equipment. A 16-page monograph, *Laminar Flow Equipment Selection Guide*, is a treatise on the principles and applications of laminar air flow filtration. Techniques design, applications, and products are discussed. Envirco, Inc. **90**

Sewer pipe. A 4-page booklet gives details on an asbestos-cement nonpressure sewer pipe. The illustrated flyer includes tables of dimensions and tolerances, and emphasizes new design and performance features. Certain-teed Products. **91**

Germanium and gallium extraction. Methods for extracting germanium and gallium from coal fly ash are detailed in Bureau of Mines Report of Investigations 6940, *Extraction of Germanium and Gallium from Coal Fly Ash and Phosphorus Furnace Flue Dust*. Bureau of Mines. **92**

Acid mine waters. *Mine Water Research, Neutralization*, tells how Bureau of Mines research workers have shown that inexpensive and plentiful coarse limestone will neutralize sulfuric acid and remove undesirable iron from mine waters in a sustained reaction. The report, written by Maurice Deul and E. A. Mohok, is Report of Investigations 6987. Bureau of Mines. **93**

Air pollution. *A Primer on Air Pollution* is a 20-page booklet explaining the contribution of fuels to atmospheric pollutants, and discussing various solutions to the fuel contamination problem (electric vehicles, gas turbine engines, other fuels). Mobil Oil Corp. **94**

California's Calamity or How to Mismanage Water

By Robert Haveman

This volume is a detailed and comprehensive treatment of a set of regional production processes and institutions, largely in the public sector, which the authors call "the water industry." In this oversized volume, each level of production, from the release of ground water or the tapping of stream flows to final water use, is empirically analyzed through the economist's "structure, conduct, and performance" model, a criterion usually reserved for the analysis of conventional industries in the private sector.

The authors state that their ultimate aim "is to measure or appraise the composite performance of the industry's members with respect to the development of water resources, the timing and sequence of this development, the allocation of water among uses, and the technical efficiency they attain in fulfilling their functions—and to evaluate this performance in terms of appropriate criteria of optimal economic efficiency." Other aims are to relate the quality of the industry's performance to its structure and behavior and from these relationships to establish guides for public policy.

Structure

The first part of the book (close to 230 pages) is devoted to a description of the structure of the industry. Without question, the most important discussion here deals with the framework and application of the law to both water rights and the operation of federal, state, and local water agencies. The thesis is that the legal framework has spawned an uneconomic allocation of water rights and water usage and has precluded active and viable markets for water and water rights.

Other chapters in this section deal with the hydrologic and geographic characteristics of the region, the patterns of integration and concentration in the capture, wholesaling, and retailing of water, the determinants and elasticity of the various demands for water, and the cost and supply characteristics of the capture and transportation of water, all in the context of Northern California. From this analysis, the water industry is shown to have the distinctive characteristics of:

• A population of agencies with the traits and motivations of users' cooperatives.

• Virtual insularity (or absence of competition) among the member entities.

• No organized or continuous markets for the exchange of the product.

Conduct

The second part of the book (nearly 300 pages) treats the behavioral (or conduct) characteristics of the industry. Issues of historical development, pricing and allocation practices, and investment decisions of wholesale and retail entities, urban and agricultural suppliers, and federal, state, and local agencies are described and analyzed in nearly overwhelming detail.

From the behavioral characteristics described in this section, a rather severe and disturbing pattern of resource misallocation—at nearly every margin— is evident. The patterns of conduct displayed by the members of the industry and the institutions which support these patterns have precluded the possibility of economically efficient resource development and allocation. In this section, the discussions of special merit and originality are, first, the analysis of water as a scarce commodity and, therefore, a commodity to which a positive "opportunity price" must be attached even in the absence of an observable market price; and, second, the analysis of the relevance of external (or spillover) effects in the attainment of allocative efficiency in both pricing and investment decisions.

Performance

In the third part of the book, the performance of the industry is evaluated. On the basis of both statistical evidence and inferences drawn from patterns of behavior, the authors analyze a number of resource allocation problems. Among them are:

• General overdevelopment of water facilities and water usage because of (among other things) the persistent tendency of agencies to overestimate benefits and underestimate costs and to neglect the external effects of water development.

• Subsidization of irrigation and consequent overdevelopment of facilities for the supply and transportation of irrigation water relative to other uses.

• Excessive transfers of water from winter to summer use.

• Excessive interbasin transfers.

• Overallocation of water to consumptive use at the expense of in-stream uses, such as recreation activities, fish hatcheries, and pollution abatement.

• Premature development of many long-lived and enormously expensive capital facilities.

Indeed, the authors claim evidence of significant resource misallocation at all of the relevant margins—misallocation among investment periods, among uses, among seasons, among regions, among groups of users, and among individual water consumers.

Policy

In the final part of the book, the authors submit a set of policy recommendations to correct the tendencies

toward resource misallocation. These proposals center on the legal framework within which the industry operates. Proposal I suggests the establishment of a board or commission at both the state and national levels which would be independent of the operating agencies. This board would assume the project authorization function now held by Congress and the legislature and would make authorization on the basis of a rigorous set of economic criteria.

Proposal II entails the repeal of existing preferential treatment provisions which subsidize agriculture and irrigation. Proposal III recommends a thoroughgoing reform of reimbursement and user charge policy, aimed at breaking the political alliances leading to excessive and uneconomic investments in water facilities.

Proposal IV entails changes that must be made in the laws if we are to encourage the development of markets for water and water rights. Additional proposals deal with legal changes necessary to account for external effects imposed by agency investments in water facilities.

None of these recommended institutional changes is particularly novel or original; all of them have been given substantial attention in the water resources literature. Indeed, Proposal I differs only in detail from the recommendations of the Hoover Commission, offered some 15 years ago.

Critique

While the volume presents a competent and detailed description of the many facets of the industry, it is disappointing in two major respects. First, most of the analysis of difficult empirical problems rests on basic research by other writers. A disappointingly small amount of new, empirical evidence is presented. For example, the chapter on the elasticity of demand for water consists of a recounting of the statistical difficulties encountered in trying to estimate demand elasticity, a retelling of the statistical results presented by others, and a seat-of-the-pants estimate of the elasticity range in Northern California. One suspects that a significant net increment to knowledge would have resulted from additional efforts in statistical elasticity estimation relative to the approach chosen by the authors.

The length of the volume seems quite unwarranted. Elimination of some of the elaborate and detailed descriptions, the repetition, and the excessive verbosity would have left a tight 300-page volume with a potential for readership and policy impact far greater than the potential of the present encyclopedic volume.

In short, the allocation of resources in the research and production of the volume appears to diverge from the optimum: the breadth of the study and the length of the volume are overdeveloped relative to the opportunities for depth of measurement and analysis. Consequently, the contribution of the study, while significant, is not as great as it could have been.

Annual Report of Progress on Engineering Research-1965. U.S. Department of the Interior. ix + 177 pages. U. S. Government Printing Office, Washington, D. C. 20402. 1967. 70 cents, paper.

The booklet is Research Report No. 6 in the Water Resource Technical Publication group; it summarizes the status of 140 investigations in 17 categories of water resources research. Report No. 6 includes chapters on water conservation, water quality of reservoirs and streams, atmospheric water resources programs, hydraulics, soils engineering, bituminous materials, protective coatings and sealers, plastic materials, metals and corrosion, applied chemistry, physics and petrography, electric power, and desalination of sea and brackish water.

Advances in Water Pollution Research (3 vols.). International Association on Water Pollution Research. Water Pollution Control Federation, Washington, D. C. 20016. 1967. $15.00 each or $40.00 for the set, hard cover.

The three volumes are the proceedings of the Third International Conference on Water Pollution Research held in Munich in 1966. Volume I is Freshwater Pollution; Volume II is Waste Treatment; and Volume III is Marine Disposal. Paper, formal discussions, and authors' replies are included.

Standards of Performance for Film Badge Services. Donald E. Barber. Public Health Service Publication No. 999-RH-20. viii + 47 pages. U. S. Government Printing Office, Washington, D. C. 20402. 1967. No charge for single copies, paper.

MEETING GUIDE

August 13–16
Soil Conservation Society of America
22nd Annual Meeting
  Hotel Fort Des Moines, Des Moines, Iowa

The theme of the symposium is Soil and America's Future. Sessions will be directed to land management, resource conservation problems, soil erosion, sediment and nitrates in soil and water management, and managing the environment for quality living.

August 23–25
American Society of Civil Engineers (Sanitary Engineering Division)
National Symposium on Estuarine Pollution
  Stanford University, Stanford, Calif.

Designed to satisfy the needs of sanitary engineers and scientists concerned with the effects and control of pollution in estuaries, the symposium will cover recent studies on the effects of municipal, industrial, and agricultural pollutants on water quality and aquatic life, as well as the distribution of such pollutants by tidal action, wind, sunlight, temperature, and other physical, chemical, and biological factors. Also planned are discussions on forecasting techniques, model studies, and recent developments in water quality management.

August 28–30
Environmental Engineering Intersociety Board and American Association of Professors of Sanitary Engineering
Second Conference on Environmental and Sanitary Engineering Education
  Technological Institute, Northwestern University, Evanston, Ill.

Sessions will focus on the curriculums for environmental engineering students, planning of environmental engineering systems, and the criteria and mechanism for accreditation of programs in environmental engineering, among other topics.

August 29–30
Water Conditioning Association International, Water Conditioning Foundation, and Water Conditioning Research Council
3rd Annual International Water Quality Symposium
  Conrad Hilton Hotel, Chicago, Ill.

Water management, economics, supply, treatment, and quality will be examined, with emphasis on health, productivity, and aesthetics.

September 6–9
Society of Mining Engineers of AIME, and Rocky Mountain Minerals Conference
SME Fall Meeting
  Las Vegas, Nev.

Technical papers will be presented on solid fuel in pelletizing shaft furnaces, sulfur recovery from coal and flue gases, methane monitoring in coal mines, and acid mine drainage, among other topics.

September 10–15
American Chemical Society
154th National Meeting
  Chicago, Ill.

The Division of Water, Air, and Waste Chemistry will present, in joint efforts with other divisions, discussions of scientific information resources for the water researcher; water resources; and adsorption from aqueous solutions. For detailed program, please see pages 591–2, this issue. Other programs of interest planned are **Foam Fractionation** by the Division of Industrial and Engineering Chemistry and **Microbial Waste Treatment** by the Division of Microbial Chemistry and Technology.

September 11–14
Instrument Society of America
22nd Annual International Instrument-Automation Conference
  Chicago, Ill.

Concurrent with the conference are symposia on data handling and computation, measurement standards, and physical and mechanical measurement instrumentation. The conference will highlight the areas of automation, biomedicine, and food.

September 12–14
Polytechnic Institute of Brooklyn and Naval Applied Science Laboratory
Materials-Key to Effective Use of the Sea
  Statler Hilton Hotel, New York, N.Y.

Current research and development programs and materials problems will be emphasized the first day; the behavior of materials in ocean environments will be summarized the second day; and materials technology in the ocean engineering field will be discussed on the third day.

September 18–22; 25–27;
October 2–December 11
Cleveland State University
Water Pollution Control
  Stilwell Hall, Cleveland State University, Cleveland, Ohio

Designed to assist people who have had some technical training in better understanding the problems and developments in water pollution control, three separate programs have been set up at Cleveland State University. The Sept. 18–22 session will feature biological and chemical laboratory procedures in water pollution control. Fee: $75. The Sept. 25–27 session will feature an institute on technical aspects of water pollution control (lectures only). Fee: $50. The session beginning on Oct. 2 and continuing on Monday afternoons through Dec. 11 is a seminar series on selected topics in water pollution control. Seminar fee: $50. For further information contact Dr. Paul Olynyk, Chemistry Dept. Cleveland State University, Cleveland, Ohio 44115.

September 21–22
Illinois Basin Section of the Society of Petroleum Engineers of AIME
Midwest Regional Meeting
  McCurdy Motor Hotel, Evansville, Ind.

Technical papers will be presented on new logging techniques, new tools to be used in gas storage, automation in oil field operations, and the application of oil field technology to industrial fluid disposal problems, among others.

September 24–27
American Institute of Chemical Engineers and Instituto Mexicano de Ingenieros Quimicos
2nd Joint Meeting
  Hotel Maria Isabel, Mexico City, Mex.

There will be symposiums on air and water pollution as well as on the prediction of thermodynamic and transport properties, separation and purification by crystallization from the melt, on-line computer control, and others.

August 27–September 1
American Institute of Biological Sciences
18th Annual Meeting
  Texas A&M University, College Station

The plenary session will include discussions on gradual and sudden changes in the environment, and protection and management of the environment. Symposiums will be on the subjects of environmental measurements, the role of phosphorus in plant growth, development of cytoplasmic organelles, ecological response to environmental stress, and related subjects.

October 2–6
National Institutes of Health
17th Annual Instrument Symposium and Research Equipment Exhibit
National Institutes of Health, Bethesda, Md.
The instrument symposium will include discussions of holography, laboratory computer usage, ultramicroanalytical techniques, new frontiers in spectroscopy, thermoanalytical methods, low-temperature luminescence, and molecular separation by size and charge. The exhibit (which ends Oct. 5) will include examples of the latest types of research equipment available from instrument manufacturers.

October 8–13 and 15–18
Water Pollution Control Federation
40th Annual Conference
Hotel Americana, New York, N. Y. (Oct. 8–13)
Puerto Rico Sheraton Hotel, San Juan, Puerto Rico (Oct. 15–18)
The meeting will take place in two sessions. The first will take place in New York City from October 8–13; the meeting will reconvene in San Juan, Puerto Rico, from October 15–18. The New York sessions will include a special symposium on water quality analysis as well as sessions on water quality standards, industrial wastewater research, estuary problems, nutrient removal, and like topics. The Puerto Rico sessions will be concerned with refinery waste treatment, refinery wastes effect on marine biology, open-pit mines, rum distillery wastes, and other problems.

October 9–12
Association of Official Analytical Chemists
81st Annual Meeting
Marriott Motor Hotel, Washington, D.C.
Methods, instrumentation, and techniques for analysis of feeds, fertilizers, pesticides, food additives, hazardous substances, and other materials, will be discussed. There will be a special symposium on drugs.

October 23–24
Metropolitan Engineers Council on Air Resources (MECAR)
New Developments in Air Pollution Control
Commodore Hotel, New York, N.Y.
The two-day technical symposium will emphasize major developments in the areas of recovery of sulfur oxides from stack gases, control of noxious gaseous emissions, control of particulate emissions, and control of solvent emissions. Attendance is limited and will be by preregistration only, $15.00 per person. Contact Robert A. Fox, P.O. Box 607, Grand Central Post Office, New York, N.Y. 10017.

October 23–24
1967 Cleaner Air Exposition
Commodore Hotel, New York, N.Y.
The exposition is held in conjunction with the nationwide observance of Cleaner Air Week, October 22–28. It will feature exhibits by manufacturers of air pollution control equipment, publishers of air pollution control literature, consulting and engineering services, and air pollution control agencies.

November 6–8
American Water Resources Association
National Symposium on Ground Water Hydrology
Mark Hopkins Hotel, San Francisco, Calif.
The symposium will include sessions on occurrence of ground water in different geologic environments; ground water movement and well hydraulics; sea water intrusion, artificial recharge, and surface water-ground water relationships; and model and radio-isotope techniques in ground water investigations.

November 27–30
Entomological Society of America
1967 Annual Meeting
Hotel New Yorker, New York, N.Y.
The implications of insecticide choice, and pesticide movement and degradation in soils, among other topics, will be discussed.

January 22–26, 1968 (Tentative)
Instrument Society of America
Fourth Marine Sciences Instrumentation Symposium
Melbourne, Fla. (Tentative)
The theme of the symposium will be directed to the problems of marine instrumentation, especially data recording, handling, and processing. Those who wish to participate in the symposium are invited to send a letter of intent to submit a paper (including title and abstract) to: Mr. H. W. Dubach, National Oceanographic Data Center, Washington, D.C. 20390.

June 23–28, 1968
American Society of Testing and Materials
Materials and Their Performance in the Marine Environment
San Francisco, Calif.
Sessions are planned on the performance of materials in deep sea and coastal waters and at environmental interfaces; structures in the sea and the stress and fatigue which they undergo; new materials in sea applications; and high pressure environmental testing facilities. Those wishing to contribute papers should submit titles and abstracts no later than Sept. 1, 1967, to: Mr. H. W. Dubach, National Oceanographic Data Center, Washington, D.C. 20390.

Symposiums on Water Problems Set for September

Symposiums on two different aspects of water problems are planned for the 154th National ACS Meeting in Chicago. One, a joint session between the ACS Divisions of Water, Air, and Waste Chemistry and Colloid and Surface Chemistry, is directed at the topic of Adsorption from Aqueous Solution. The second, a joint program between the ACS Divisions of Water, Air, and Waste Chemistry and Chemical Marketing and Economics, is directed at Technical and Economic Aspects of Water Management

SYMPOSIUM

Adsorption from Aqueous Solution

Division of Water, Air, and Waste Chemistry and
Division of Colloid and Surface Chemistry

Co-Chairmen:

WALTER J. WEBER, JR.
College of Engineering, Dept. of Civil Engineering
University of Michigan, Ann Arbor, Mich. 48104

EGON MATIJEVIĆ
Institute of Colloid and Surface Science
Clarkson College of Technology, Potsdam, N.Y. 13676

THURSDAY MORNING (SEPT. 14)

General Topics on Adsorption from Aqueous Solution

W. J. Weber, Jr., Presiding

9:00 Introductory Remarks, **W. J. Weber, Jr.**

9:05 **F. C. Goodrich,** The Use and Abuse of Gibbs Conventions in Capillary Thermodynamics

9:35 **J. M. Smith,** Kinetics of Adsorption

10:05 **M. de Heaulme, Y. Hendricks, A. Luzzati, and L. Ter-Minassian-Saraga,** Two-Dimensional, Monomolecular Ion Exchangers. Kinetics and Equilibrium of Ion Exchange

10:35 **F. Helfferich,** Chromatographic Behavior of Interfering Solutes

11:05 **E. Matijević, L. J. Stryker, and R. V. Lauzon,** Adsorption of Hydrolyzed and Non-Hydrolyzed Metal Ions on Hydrophobic Colloids

11:35 **M. Mirnik,** Thermodynamics of an Ionic Solid-Electrolyte Solution System

THURSDAY AFTERNOON (SEPT. 14)

Adsorption of Inorganic Ions at Solid-Aqueous Solution Interfaces

E. Matijević, Presiding

2:00 Introductory Remarks, **E. Matijević**

2:05 **T. W. Healy, R. Cooper, and R. O. James,** The Mechanism of Transition Metal Ion Adsorption at the Silica-Water Interface

2:35 **Y. G. Berube and P. L. DeBruyn,** Specific Adsorption of Alkali Cations on Rutile as a Function of pH

3:05 **E. A. Jenne and C. J. Lind,** Kinetics of Cobalt Sorption by γ-MnO_2

3:35 **D. W. Fuerstenau, T. W. Healy, and D. J. Murray,** The Adsorption of Group I, II, and Transition Metal Ions at the Manganese Dioxide–Water Interface

4:05 **F. J. Hingston, A. M. Posner, and J. P. Quirk,** Adsorption of Selenite by Goethite

4:35 **F. A. Blanchard and P. H. Cardwell,** Adsorption and Measurements by a Streaming Current Detector

FRIDAY MORNING (SEPT. 15)

Adsorption of Inorganic or Organic Species at Solid-Aqueous Solution Interfaces

T. W. Healy, Presiding

9:00 Introductory Remarks, **T. W. Healy**

9:05 **H. Hahn and W. Stumm,** The Role of Adsorption in the Kinetics of Coagulation by Hydrolyzed Al(III)

9:35 **W. Heller,** Some Effects Resulting from Macromolecular Adsorption on Colloidal Systems

10:05 **E. J. Clayfield and A. L. Smith,** Adhesion and Detachment of Solid Colloidal Particles in Aqueous Ionogenic Surfactant Media

10:35 **W. J. Weber, Jr. and V. L. Snoeyink,** Hydrated-Proton Reactions at the Carbon–Water Interface

11:05 **F. G. Greenwood, G. D. Parfitt, N. H. Picton, and D. G. Wharton,** Adsorption and Wetting Phenomena Associated with Graphon in Aqueous Surfactant Solutions

11:35 **J. M. Corkill, J. F. Goodman, and J. R. Tate,** Adsorption of Non-Ionic Surface-Active Agents at the Graphon-Solution Interface

FRIDAY AFTERNOON (SEPT. 15)

Adsorption of Organic Species at Solid-Aqueous Solution Interfaces

W. Heller, Presiding

2:00 Introductory Remarks, W. Heller

2:05 **K. M. Van Dolsen and M. J. Vold,** Analysis of the Composite Isotherm for the Adsorption of a Strong Electrolyte from its Aqueous Solution onto a Solid

2:35 **W. J. Weber, Jr. and T. M. Keinath,** The Solution-Solid Phase Transfer of Dinitro-o-sec-butyl-phenol in a Continuous Flow System

3:05 **D. W. Fuerstenau and T. Wakamatsu,** The Effect of Hydrocarbon Chain Length on the Adsorption of Sulfonates at the Solid-Water Interface

3:35 **A. H. Herz, R. Danner, and G. Janusonis,** Adsorption of Dyes and their Surface Spectra in Aqueous Dispersions

4:05 **A. Rondeau and J. Pouradier,** The Effect of Superficial Crystal Defects on the Adsorption of Gelatin on Silver Halide

4:35 **F. R. Eirich,** The Effects of Polymer Adsorption and the Stability of Dispersions

Papers in absentia **Y. M. Glazman and J. G. Blashtchuk,** Adsorption of Some Surface Active Agents from Aqueous Solutions on Arsenic Sulfide Powder
K. Shinoda and M. Fujihira, The Determination of the Relative Adsorbability of Counterions at the Charged Interface by Radio Tracer Technique

SYMPOSIUM

Water Management

Division of Water, Air, and Waste Chemistry and Division of Chemical Marketing and Economics

WEDNESDAY MORNING (SEPT. 13)

Symposium on Water Management

F. M. Middleton, C. H. Kline, Presiding

9:00 Introductory Remarks, F. M. Middleton

9:10 **D. R. Dykes, T. S. Bry, and C. H. Kline,** The Availability and Cost of Water

9:35 **A. C. Printz, Jr.,** The Impact of Water Quality Standards

10:05 **B. M. Putman,** Chemicals for Use in Water Management

10:40 **T. W. Lesperance,** Equipment Markets and Marketing in Water Management

11:05 **J. C. Vaughn,** Tastes and Odors in Water Supplies

11:30 **E. W. Palmer and R. S. Robertson,** Conditioning and Handling of Biological Solids in Municipal Waste Treatment Plants

PROFESSIONAL CONSULTING SERVICES

if you have an industrial waste pollution problem . . .
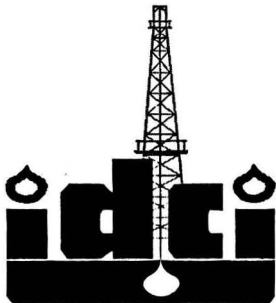
has the answer!

Many industrial companies find that the injection of wastes into a disposal well has provided a permanent, low-cost solution to their problem. This is known as "deep-well" waste disposal. IDCI combines the 25 years of drilling experience of Lohmann-Johnson Drilling with the geological and engineering know-how of Mitchell and Stanonis, Inc. into an organization capable of providing:

○ Geological feasibility studies for injection in your plant area
○ Studies to determine the necessary pre-injection surface treatment of your material
○ Engineering design and contract installation of the entire surface and subsurface systems
○ Continued supervision of the operation and maintenance of the fluid injection system

For more information, write (on your Company letterhead, please) to International Disposal Contractors, Inc., 355 Permanent Savings Bldg., Evansville, Indiana, 47708. Or phone (812) 425-1349.

INTERNATIONAL DISPOSAL CONTRACTORS, INC.
Subsurface Industrial Waste Disposal Systems
Suite 355 Permanent Savings Bldg.
Evansville, Indiana 47708

BRANCH OFFICES

|	
1806 Clark Bldg.	881 High Street
Pittsburgh, Pa. 15222	Worthington, Ohio
740 Elueden House	1734 Wichita Plaza Bldg.
Calgary, Alberta, Canada	Wichita, Kansas

Circle No. 21 on Readers' Service Card

▼ ▼ ▼

Now, a complete water quality program.

Measure 1, 2, or any 12 water pollutants…automatically, continuously and specifically.
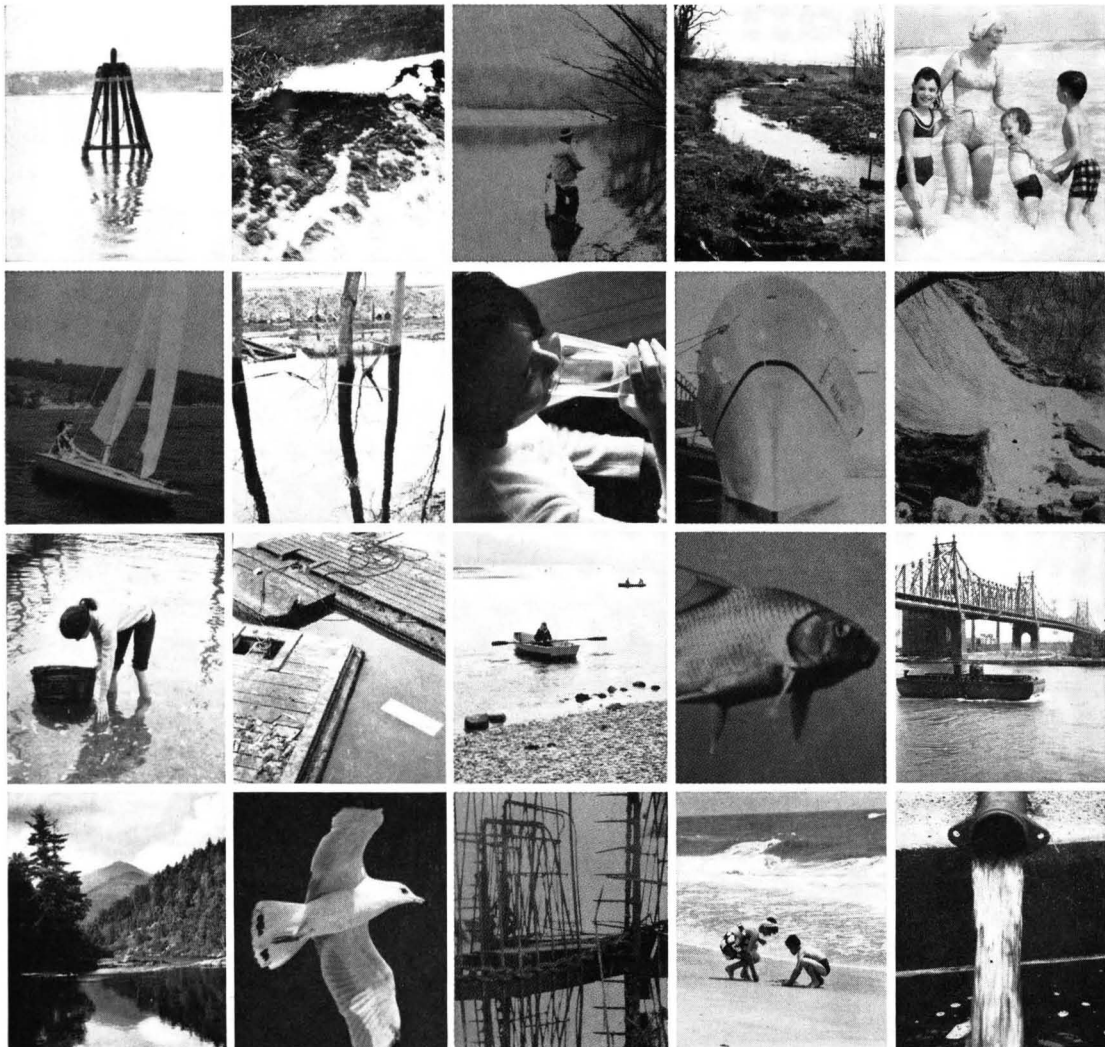
You may want to quantitate COD, phenols, cyanide, ammonia nitrogen, or any one of a host of pollutants. You may even want to quantitate 12 at one time. Technicon® AutoAnalyzer® systems, employing Standard Methods, give you this flexibility, as well as accuracy and specificity. Around-the-clock watch on vital water quality measurements can be returned within 15 minutes. Low maintenance enables a network of these monitors to be established at extremely low cost. The Technicon brochure CSM-12 explains how the limitation of exactly measuring the many possible pollutants is removed by continuous on-site monitoring. Write for it. Dept. G, Technicon Corporation, Ardsley, New York 10502.

Circle No. 19 on Readers' Service Card
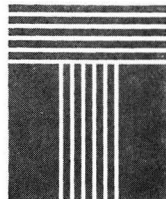
compare
us WITH OTHER MANUFACTURERS OF AIR POLLUTION CONTROL EQUIPMENT

- ☐ electrical precipitators
- ☐ centrifugal collectors
- ☐ wet scrubbers
- ☐ catalytic incinerators
- ☐ thermal incinerators
- ☐ fabric filters
- ☐ adsorption systems
- ☐ dust level indicators

- ☐ source testing
- ☐ heat exchangers
- ☐ stack gas and emission analysis (both particulates and gases)
- ☐ product and energy recovery studies
- ☐ design, fabrication, field start-up
- ☐ trouble-shooting
- ☐ planning and equipment modernization services

You'll find that from UOP you get the best, most efficient and economical job . . . with complete air correction service, as well. Check us out today. UOP Air Correction Div., Universal Oil Products Company, Greenwich, Connecticut 06830. The company where environmental engineering is important.