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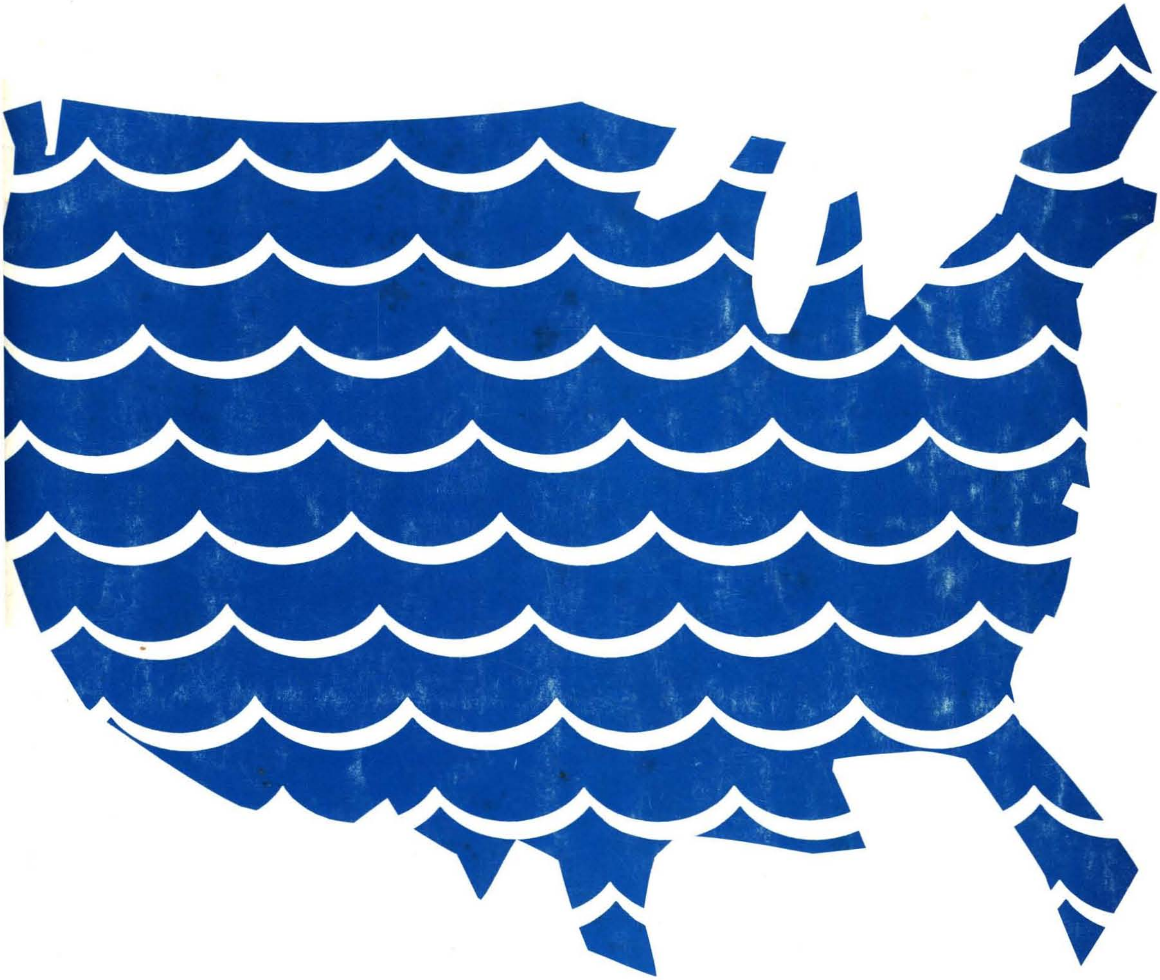
ENVIRONMENTAL Science & Technology



Protecting the nation's water

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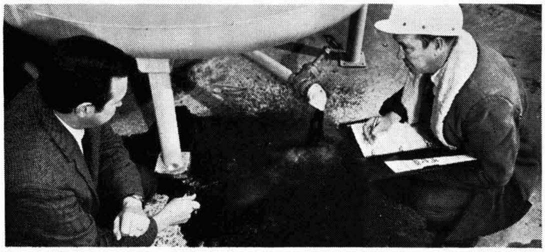

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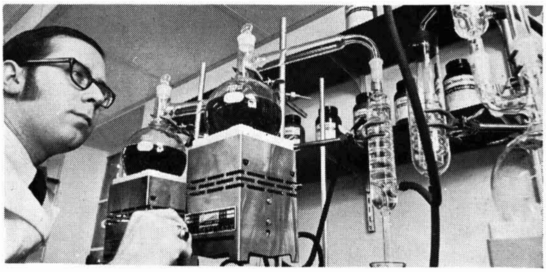

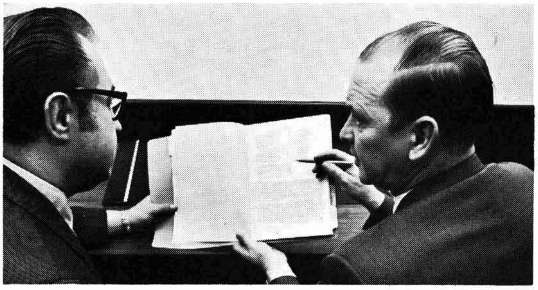

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Laboratory Park 44022
Charlotte, N. C.
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ENVIRONMENTAL
Science & Technology

ESTHAG

Volume 5, Number 2,
February 1971

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Current research

Method for determination of reaction rates of carbon dioxide with water and hydroxyl ion in seawater 127

R. F. Miller, D. C. Berkshire, J. J. Kelley, and D. W. Hood

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R. F. Vaccaro

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R. Haque and W. R. Coshow

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W. A. Glasson and C. S. Tuesday

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G. D. Blyholder and G. W. Cagle

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M. C. Goldberg, L. DeLong, and L. Kahn

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B. A. Coulehan and H. W. Lang

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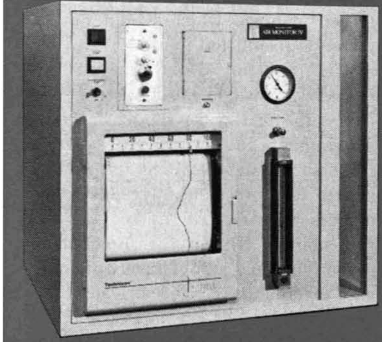

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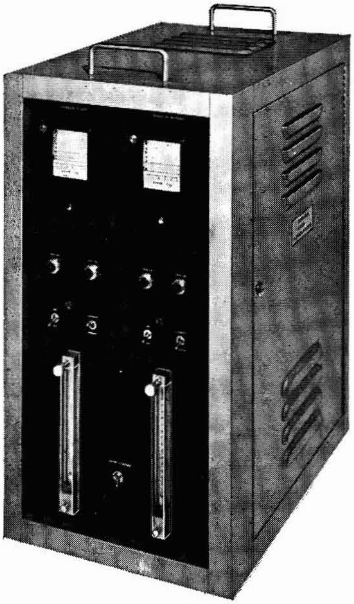


letters

Waste management economics

DEAR SIR:

Walter Spofford's article in the December 1970 issue, "Closing the gap in waste management," contains some errors which are deeply imbedded in "welfare" economics.

Environmental problems are attributed to "the failure of the private market system to allocate certain common property resources." If property owned "in common" is actually property which no one in particular owns, how is it possible for a private market to develop which will allocate the "common" property? A private market system without the exchange of private property is a logical impossibility. I think the "common property" issue is really a mirage created to subjugate the private market system to the glorified state, which can allegedly better represent "society as a whole."

Another error is the special status given to "external damages" in environmental problems. What damage imposed on some people by other people is *not* external? I can think of no "internal" damage which would not be merely self-inflicted injury.

The problem of "externalities" is necessarily outside the market system and is the reason for the existence of government. But to say that government should intervene in the market system to more efficiently allocate resources is as wrong as to say that the market system, if functioning properly, should automatically discount all "externalities." The private market system, based on supply and demand, is the only efficient allocator of resources consistent with individual freedom.

Kurt Leininger
Environmental Hygiene Agency
Edgewood Arsenal, Md. 21010

DEAR SIR:

We note with interest the article "Closing the gap in waste management" in the December 1970 issue of ES&T by Walter O. Spofford, Jr. However, we feel that we must make a correction in his reference to Bergstrom Paper Co. (page 1112).

We are not a newspaper recycling plant. In fact, in manufacturing our fine printing papers, we use no newsprint at all. We do recycle high-grade waste papers, blending various types to produce just the right paper the customer calls for. Most of the waste papers we use come from waste paper dealers who carefully sort the paper before it is sent to us. We, in turn, sort it a second time to make sure that the paper we introduce into our de-inking mill will flow smoothly through our reclaiming system.

We recognize that this is a small point in Spofford's article—which was very well done—but we just want to "set the record straight."

Henry Bickerstaff
Communication Coordinator
Bergstrom Paper Co.
Neenah, Wis. 54956

Recycling laundry wash water

DEAR SIR:

One way to fight the present problem of accelerated eutrophication of bodies of water is to use the soil as a resource renovator and to adopt the principle of "Land Disposal." This can be done, for example, by draining laundry wash water onto a lawn rather than into the sewer. Unlike municipal sewage effluent, which needs expensive treatment for medical and esthetic reasons, laundry wash water—a solution rich in plant nutrients—is free from pathogens and can be recycled and used directly for lawn irrigation. The wash water does not emit unpleasant odors and contains valuable plant food rich in nitrogen and phosphorus. The phosphates are absorbed by actively growing vegetation such as grasses, and are metabolized to organic phosphate. Under aerobic conditions, the nitrogen content of the detergent in the laundry water, when drained onto the yard of the house, is soon mineralized by the soil microbes and appears as nitrates. These, in turn, are also taken up by growing vegetation to be metabolized as organic compounds.

In the fall of 1970, my curiosity led me to study the effect of laundry wash water on the lawn grass and a few ornamental bushes in my yard. We drained the water onto the yard of the house for the irrigation of grass, camellia (*c. japonica*), azalea, chrysanthemum (*c. indicum*), etc. The soil is well-drained, loamy sand; the natural vegetation is coniferous. Soil pH is slightly on the acidic side. In our laundrying, we used Gain laundry detergent. The wash water, when drained onto the lawn, is at 40°C.

Since then, we have not noticed any unwanted or undesirable symptoms on these plants. Rather, the lawn area and ornamental plants which have been receiving laundry wash water from time to time show a better stand and healthy, vigorous green growth as compared with a surrounding area of the lawn where tap water is used for irrigation. Further research on these lines is, of course, needed.

The washing machine does not need any major modification except that the drain hose should be long enough to reach the desired area in the yard. Ordinary water hose with an appropriate diameter can meet this need. The idea is primitive—based on the old concept of "back to nature"—but seems to work well in solving the problem of eutrophication. I cannot foresee any problem that this method will create when used for aerobic sandy soils, especially if the laundry wash water is kept cool. Some housewives, who do not wish to pay ever-increasing municipal bills and taxes, may prefer to exert just a little effort to recycle the laundry waste for its profitable use in lawn irrigation.

Land disposal of laundry wash water not only reduces the labor and cost of lawn fertilization and irrigation, but it also decreases water consumption—saving on water bills and municipal taxes.

S. S. Sandhu
Professor of Chemistry
Claflin University
Orangeburg, S.C. 29115

Closing the gap in waste management

Walter O. Spofford, Jr., author of the feature article in our December 1970 issue, has brought to our attention that the article ES&T published was based on a version which had been considerably edited by ES&T and not on the final version submitted to us by him. Spofford believes that some of ES&T's editing significantly distorted economic concepts. While we, and he, agree that the general conclusions contained in the published article are correct, he feels that some of the detailed statements and reasoning leading to the conclusions are misleading to the general reader as well as to the economist. Any question one might have regarding Spofford's article may be addressed to him at Resources for the Future, Inc., 1755 Massachusetts Ave., N.W., Washington, D.C. 20036.

Effluents are tasting better and better!

As water use increases and pollution is curbed, treated wastes start to look like good sources of drinking water

According to estimates of the Water Resources Council, total U.S. water demand in the year 2000 will be 805 billion gallons per day, more than the 600 billion gallons per day presently regarded as "usable surface water." In this instance, "usable" actually means economically feasible, and more water—perhaps as much as the total U.S. freshwater supply of 1200 billion gallons per day—could be made available if the price were right. But with rapidly rising demands, the fact remains that sooner or later (more likely sooner—certainly within 100 years) water reuse will have to be practiced rather than just talked about.

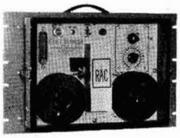
Now that the screws are beginning to be applied to water polluters all over the country (see our special report, page 120), the need to reuse water makes doubly good sense, and the signs show that many industries have seen the light. For example, if a company spends considerable sums of money to purify dirty water for plant use and still more money to clean used water for discharge, then it is clearly in its own best interest not to discharge the water, but to reuse it. Through similar reasoning, manufacturers of cooling towers have forecast a large and fast-growing market for their products. As a matter of fact, competition for water resources of finite size might by itself, even in the absence of any water pollution control laws, induce users of water to abandon the practice of once-through use.

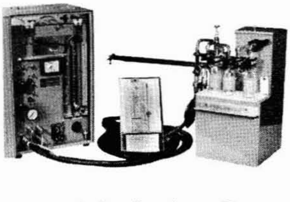
While industrial reuse of water seems reasonably assured, there is not as much reason to believe that the same thing will happen in the public sector of society. Former Assistant Interior Secretary Carl Klein was fond of describing his closing-the-loop concept (thumbs and forefingers touching to better illustrate the idea) in which domestic sewage would be purified to drinking water standards. True, Klein's ideas were not widely embraced—in fact, they were roundly declared as impractical—but "tertiary" treatment followed by chlorination could indeed produce drinkable water. Whether anyone would care to drink water so produced is a debatable matter, however. President Nixon once reportedly declined to sip water purified to Public Health Service standards at a sewage treatment plant he was visiting.

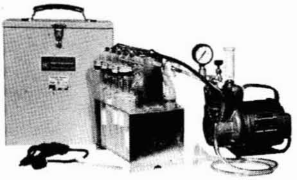
Apart from deep-rooted public fear of disease, which presumably lies at the heart of reluctance to drink treated sewage, there is the thorny problem of separate water supply and water pollution control functions to contend with. ES&T ran into this last year, in a story on drinking water supply (October 1970, page 811). While one set of officials regards production of drinking water from (generally polluted) supplies as its sole function, a second set regards pollution control as its bailiwick. Both groups—exemplified by the American Water Works Association and the Water Pollution Control Federation, respectively—advance legitimate arguments for continuing the status quo; nevertheless, I feel there are good reasons to combine the two functions.

The strongest argument for regarding water pollution control and drinking water supply as essentially the same problem will probably become apparent very soon. As stricter discharge standards are applied and enforced, the quality of discharged wastes will approach more and more closely the quality of desirable drinking water. To choose polluted river water as a basic source of drinking water in preference to treated wastes will then become manifestly illogical and, more important, uneconomical.

D. H. Michael Bowen







viewpoint

Joel A. Snow
National Science Foundation

Ecostrategies and ecotactics

Man is but a part of nature, and it is far from profound to observe that it would be unwise for man to damage the natural world on which he must depend. But elaborations and transmutations of this simple remark, supplemented with rank upon rank of potential catastrophies, have been jamming the popular media with a noise that often transcends good sense. In the course of this feverish upwelling of interest, recent popular techniques of political participation have not been neglected, whether or not they contribute to rational discourse, and a manual for participation in such ventures has even been produced—bearing the clever title "Ecotactics." What the nation more properly needs are "ecostrategies" that will ensure future compatibility between the nation's economic development and the need for keeping modern man in harmony with nature.

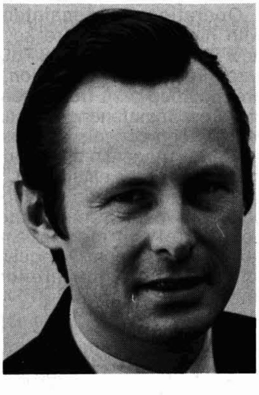
The development of ecostrategies will require expansion of the available data base, scrupulous analysis of the network of social and economic alternatives, and stimulation of new technology to extend the range of environmental options. The issues to be dealt with are complicated by wide differences in the immediate goals of the interested parties. No sensible person would wish to damage the health of his fellow citizens or to impair the stability and integrity of the natural ecosystems upon which human life ultimately depends. But matters are not that clear. Environmental health impacts are buried in an immense variety of other stresses upon the human organism, and many of the operating principles of even simple ecosystems are still primarily conjecture. The development of cogent ecostrategies is therefore very much dependent upon the willingness and flexibility of scientists and engineers to find new and broad frameworks within which to assess their work.

We must first appreciate that environmental degradation resists swift, simple solutions. There is generally no single cause that lends itself to a single cure. Rather, there is an array of causes that contribute to each problem, and the problems themselves are interrelated. We are a society with high per capita consumption based on a sophisticated technology and a complex operating network of social institutions; thus most causes do, on examination, turn out to have a common root. That is, environmental degradation arises from our *way of life*. It is this feature that has led many "ecotacticians" to attack the entire structure of our society. For those of us who wish to retain the key characteristics of our present society, it is evident that a detailed knowledge of environmental impacts is needed, and that a careful, cool-headed analysis must be made of the incentives, public and private, that can ameliorate the negative impacts so that our society can gradually evolve corrections to its excesses.

One of the most formidable obstacles to the development of ecostrategies is the absence of sufficient quantitative data and theoretical understanding of the natural environment. Yet, without adequate knowledge of the structure and resiliency of the natural ecosystems that support human life, it is hard to assess the impact of technological stresses. Particularly crucial is whether nature can find new points of stability under the stresses imposed by man, or whether modern technology must itself give way. Unraveling the complex aspects of this enormous system of trade-offs is, however difficult, one of the most essential tasks that modern man must undertake.

To remain consistent with democratic principles, the public must also be deeply involved, and raising the level of the public discourse on the environment may be a necessary precursor to any establishment of national ecostrategies. In the end, the pressures of population growth, technology, and economic development may force either a rational assessment of national choices or a descent into chaos.

Men of goodwill from the community of science shall surely prefer to work toward the former. This goal is an area in which science and technology can prove to be truly responsive to the national need.



Joel A. Snow is head of the Office of Interdisciplinary Research at NSF. *He is a physicist by training*

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WASHINGTON

Permits for new industrial discharges are required

By executive order, President Nixon established a federal permit program covering facilities that discharge wastes into U.S. navigable waters and their tributaries. Permits for new industrial discharges are required now; existing industrial dischargers must file application before July 1. Municipal dischargers are exempt from the requirement since wastes "flowing from streets and sewers and passing therefrom in liquid form" are excluded from prosecution under the Refuse Act. The permit program will involve the close cooperation between the EPA and the Corps of Engineers (see "What's the U.S. Army doing in water pollution control?" ES&T, December 1970, page 1101).

EPA and administrator Ruckelshaus are on the move

Water pollution control is in the forefront of activities of the two-month-old Environmental Protection Agency (EPA). In recent actions EPA administrator William D. Ruckelshaus: • Called for the development of a technology assessment capability to forestall further environmental degradation; • Announced four programs totaling $3.7 million for training 2600 persons as waste water operators (the programs are designed for the new personnel beginning a career in water pollution control as well as for operators already in the field to upgrade their skills); • Reconvened the Lake Superior enforcement conference to determine the acceptability of Reserve Mining Co.'s pollution abatement plan. Reserve Mining is faced with the problem of finding alternate ways to dispose of taconite tailing, some 60,000 tons daily, that they discharge into Lake Superior; • Asked the Justice Department to prosecute Armco Steel (Middletown, Ohio), Jones and Laughlin Steel (Pittsburgh, Pa.), and U.S. Plywood-Champion Paper's plant (Hamilton, Ohio) for violating water quality standards; • Awarded a planning grant to the Texas Water Quality Board for Galveston Bay. Thirty percent of all municipal and industrial waste water in Texas is concentrated in a three-county area which discharges into Galveston Bay. Ruckelshaus visited the New York office last month and plans to visit the Chicago, San Francisco, and Kansas City offices by the end of this month plus all other regional offices by mid-April.

NIPCC plans first meeting of all members

Shortly, in Washington, D.C., the National Industrial Pollution Control Council (NIPCC) will hold a meeting of all council members and members of its 30 subcouncils. The meeting promises status reports on approximately a dozen industries other than the three reported on late last year.

NSF funds environmental training for teachers

Part of the National Science Foundation (NSF) grants totaling $4.9 million goes for the training of precollege teachers on environmental problems. More than half of the NSF's Cooperative College-School Science (CCSS) Program is devoted to an interdisciplinary approach that combines several scientific disciplines. In all, more than 1000 teachers will participate in the training which involves 135 colleges and universities in 43 states and the District of Columbia. Specific CCSS environmental programs include a water pollution program for high school teachers at the University of Pittsburgh and training on water pollution, urban land use, population growth, and ecology at several other universities (see box).

Environmental training

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STATES

Minnesota loses its radioactive discharge suit

Minnesota has taken the issue of "state's rights" and "police power" to the U.S. Supreme Court. In December, a federal court ruled that the Minnesota Pollution Control Agency (PCA) was without authority to impose regulations stricter than those of the Atomic Energy Commission on Northern States Power Co.'s nuclear plant at Monticello, Minn. The plant discharges radioactive wastes into the Mississippi River, which supplies drinking water for Minneapolis and St. Paul; the PCA fears the water supply will become contaminated. Last month, attorney general Warren R. Sphannaus filed for Supreme Court action on the case, requesting state regulation of such radioactive discharges into the waterways.

Pesticides banned, waste water treated in N.Y.

The New York State Department of Environmental Conservation completely banned DDT and nine other persistent pesticides and listed 62 "restricted-use" pesticides last month. These restricted chemicals may be handled if users have been issued a "commercial" or "purchase" permit. Also, the Department has applied for a federal grant of over $1.5 million to subsidize a chemical-physical waste water treatment plant to treat industrial and domestic wastes in Waterford. The facility will treat paper mill discharges as well as raw sewage. In spite of the highly colored paper mill wastes, results of pilot studies show that the water is pure enough for most industrial purposes, including reuse by the paper mill itself.

Joint waste facilities planned in Georgia

Columbus, Ga., will be the first area in the U.S. to integrate pollution-free private industry with municipal water and waste facilities for maximum environmental control and community development. The environmental control and industrial complex will combine, under private management, the operation of a heavy water production plant (Deuterium Corp., White Plains, N.Y.) with the operation of municipal facilities for potable water production, sewage treatment, and solid waste disposal. Initially, these facilities will produce 12 million gallons of drinking water per day, treat 23 million gallons of sewage per day, and incinerate up to 1000 tons of solid waste per day.

Vermont seeks legal aid in Lake Champlain cleanup


Sen. George Aiken

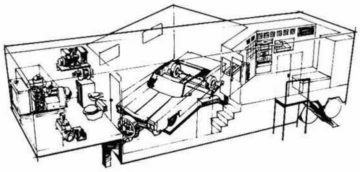
The state of Vermont is requesting U.S. Supreme Court action to force the state of New York and the International Paper Co. to remove the accumulated decaying sludge from the bed of Lake Champlain. According to Sen. George D. Aiken (R.-Vt.), the Corps of Engineers estimates that $45 million is needed to clean up the lake. Also, Vermont is considering action against the Corps for issuing a discharge permit without calling a hearing. The permit was issued to International Paper Co. in December for a new plant on Lake Champlain. These disputes are a few examples of the growing number of problems facing the newly formed EPA and its administrator Ruckelshaus.

TECHNOLOGY

Modified clinical analyzer monitors sewage effluents

A modified body fluids analyzer, developed at Oak Ridge National Laboratory (Tenn.), will be used to study sewage effluents at a federal pilot plant in Cincinnati. The analyzer uses an automatic sample injection system coupled with a high-pressure, anion-exchange resin column to determine constituents by ultraviolet or fluorometric procedures. Samples are concentrated by vacuum distillation prior to analysis, making the lower limit of detection for certain organic compounds as low as 10 ppb. Primary sewage effluents probably contain over 100 compounds, only 15 of which have been positively identified at the Oak Ridge lab.

Mobile auto emission test laboratory begins tour



GM's mobile unit

General Motors' swing-wing mobile vehicle emission testing laboratory, scheduled to hit the road early this month, will be able to analyze auto exhaust and produce test results within an hour after arriving at a new location, according to GM's director of product assurance, T. F. Nagey. Equipment on board will detect, calculate, and record mass levels of unburned hydrocarbons, carbon monoxide, carbon dioxide, and nitrogen oxides in exhaust. GM says the van is capable of running mass tests prescribed by federal requirements for 1972 as well as the current seven-mode, seven-cycle test. The 40-foot van features a swing-out center section which permits vehicles to be driven into the lab for testing under controlled temperatures.

Electrochemical particle removal is quicker, cheaper

Swift and Co. (Chicago, Ill.) has put a new twist on the conventional process for removing particles from industrial waste. Like the old process, the new technique uses flocculents to coagulate particulate matter. But then a direct current is applied to the mixture, which forces the particulate matter to the surface of a holding tank, where they can be easily removed, rather than allowing them to settle out by gravity. Swift says the electrochemical method is cheaper and quicker than conventional processes. Treatment time is about 1 hour, as compared with several days by present methods. Holding tanks need be only large enough to accommodate the amount of effluent produced in an hour, resulting in lower equipment and installation costs.

Electrocure process reduces paint spray emissions

Ford says its Electrocure process for curing paint on automobile instrument panels could result in less air pollution. The process uses a beam of electrons to cure the specially formulated paint by promoting cross-linking of acrylic polymer chains. Since the coating contains fewer volatile monomers than the solvent used in heat-cure coatings, less material is released into the air. Potential reduction could vary from 35 to 95%, the company says, depending upon the particular Electrocure coating used and the composition of the alternative heat-cure coating. The process is faster too, Ford says. Parts move past the electron beam at the rate of 15 feet per minute at room temperature. Heat-curing would require an oven time of 30 minutes at 180° F.

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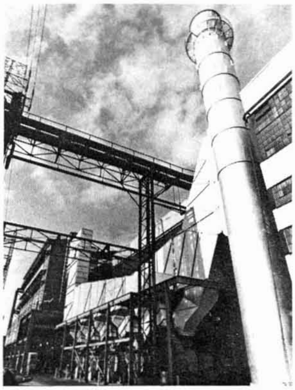
INDUSTRY

Union Carbide fences with feds over air pollution

In what promises to be an interesting test of federal muscle against industrial firms, the EPA has rejected an abatement schedule proposed by the Union Carbide Co. The schedule covers sulfur dioxide emissions from three UC Ferroally's Division power plants in Marietta, Ohio; Anmoore, W.Va.; and Alloy, W.Va. All three plants are in the federally designated Marietta, Ohio-Parkersburg, W.Va. air quality control region. UC had proposed to cut emissions 70% by September 1974, while the federal government had called for a deadline of April 1972. EPA's William Ruckelshaus has given the company until February 19 to switch to low-sulfur coal.

Henry Ford promises clean plants and products


Air controls at Ford foundry

Ford Motor Co. chairman Henry Ford II has once again pledged that his company aims to minimize pollution from its manufacturing facilities and products. Ford is spending $22.5 million on pollution control at a new casting center due to be fully operative in 1972, and is upgrading dust and smoke collection equipment at a foundry in Cleveland. The big automaker expects to spend $45 million for pollution control in 1971. Ford is also working with Koppers Co. to develop new equipment for the control of coke oven emissions, one of its most nagging air pollution problems. Ford is still committed to the internal-combustion engine, but its chairman expressed some optimism on the use of turbines for passenger cars. A continuing problem is high nitrogen oxides emissions.

Aerospace firms will find transition difficult

Suggestions that aerospace companies and personnel, who have been feeling the pinch from federal cutbacks, might move successfully into the pollution control field have fallen a bit flat. Congressional hearings held last November proceeded on the basis that aerospace technology might have some specific contribution to make in solving environmental problems. From comments made at the hearings and since, however, it appears that such hopes are weakly based. Firms already in pollution control are naturally opposed to federal assistance to aerospace firms in order to help them find their feet. The consensus is that aerospace companies do indeed have special skills, but that they should compete in the open market for the available jobs and contracts.

RESEARCH

NCAR takes lead on global air monitoring system

Scientists at the National Center for Atmospheric Research (Boulder, Colo.) have taken the first step toward what they hope eventually will be the establishment of a worldwide atmospheric monitoring network. NCAR is developing a prototype measurement station which, after field tests, will be installed at five or six locations around the world. Some substances to be measured include: particles, carbon monoxide, carbon dioxide, turbidity, persistent chlorinated hydrocarbons, sulfur dioxide, ozone, and oxides of nitrogen. NCAR's Richard D. Cadle says that the stations should be reliable enough to require attention at only two-week intervals. Strong support for the idea of a global monitoring network was given last year at a Study of Critical Environmental Problems sponsored by the Massachusetts Institute of Technology.

New blueprint emerges for air pollution controls

The Clean Air Amendments of 1970 promise clean air nationwide by the mid-70's, but only if the law is fully manned, funded, and implemented

The new year 1971, the second in the seventies—the environmental decade—came in with a new air pollution control law. Without question, the new law is tough. It is also complicated, to say the least. With more deadlines per square inch than any other piece of legislation enacted within the past 20 years, the Clean Air Amendments of 1970 is the best blueprint for clean air the nation has ever had. Bottled up in conference since before the November election but signed by the President on December 31, it extends the Clean Air Act of 1963, as amended in 1965, 1966, and 1967. (The 1967 amendments are known as the Air Quality Act.)

There are requirements and deadlines in the new law for all—for industry, the feds, and state administrators (see ES&T's calendar in box). The new law also earmarks research moneys for the scientists.

Perhaps the public was not convinced that the 1967 act did anything for clean air. With all the controls specified in the new laws, the public can only be overwhelmingly convinced that it will do the job, as long as the controls are in fact implemented and achieved. In the second half of the environmental decade, the public should begin to breathe air that is cleaner than that which it was forced to breathe in the first half.

Keyword

Standards is the keyword in the new law: emission standards for hazardous materials; national ambient air quality standards; standards of performance. These are all included in the jargon. Most terms are new.

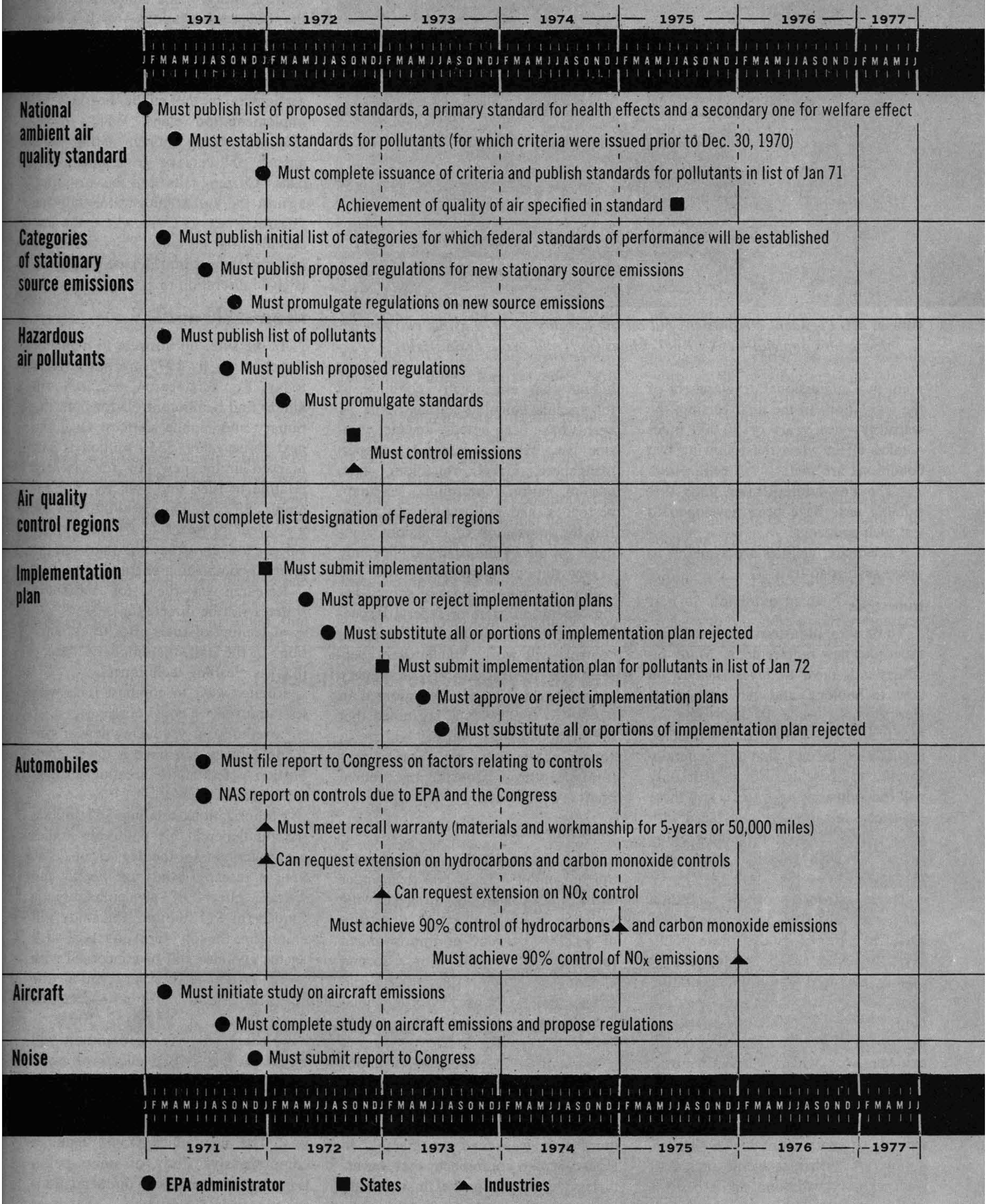
When the proposed national ambient air quality standard becomes effective, all existing, federally designated air quality regions will reset their air pollution control time clocks for clean air by mid-decade. The national ambient air quality standard is a level of air pollution burden which would protect the health and welfare of the public, including the health of particularly sensitive citizens such as bronchial asthmatics and emphysematics who, in the normal course of daily activity, are exposed to the ambient environment.

However, standards alone have no effect whatsoever on the achievement of air quality. Only when the standards are implemented and control techniques are applied will the quality of air be enhanced. Control strategies, other than emission controls for both stationary and mobile sources, may be needed to fully implement the new law. For example, during the time that automobile manufacturers are meeting the 1975 standards deadline, perhaps as much as three-fourths of the nation's traffic may have to be restricted in large metropolitan areas, if the public's health is to be protected by mid-seventies.

It is true that the deadline for automobile manufacturers is 1975. But, the National Academy of Sciences—an independent agency—will monitor their progress to determine if, indeed, the controls deadline can be met technologically. On finding that they cannot be met, the new law empowers the EPA administrator to grant a time extension to the manufacturers. However, he can grant only one extension and, in any case, the date cannot be later than Jan. 1, 1976. If the goal is not achieved by then, Congress will be faced with the problem once again.

Warranty of the control devices on automobiles was another controversial

Calendar for air pollution watchers
P.L. 91-604, signed on Dec. 31, 1970



National ambient air quality standard

- ● Must publish list of proposed standards, a primary standard for health effects and a secondary one for welfare effect
- ● Must establish standards for pollutants (for which criteria were issued prior to Dec. 30, 1970)
- ● Must complete issuance of criteria and publish standards for pollutants in list of Jan 71
- Achievement of quality of air specified in standard ■

Categories of stationary source emissions

- ● Must publish initial list of categories for which federal standards of performance will be established
- ● Must publish proposed regulations for new stationary source emissions
- ● Must promulgate regulations on new source emissions

Hazardous air pollutants

- ● Must publish list of pollutants
- ● Must publish proposed regulations
- ● Must promulgate standards
- ■ ▲ Must control emissions

Air quality control regions

- ● Must complete list designation of Federal regions

Implementation plan

- ■ Must submit implementation plans
- ● Must approve or reject implementation plans
- ● Must substitute all or portions of implementation plan rejected
- ■ Must submit implementation plan for pollutants in list of Jan 72
- ● Must approve or reject implementation plans
- ● Must substitute all or portions of implementation plan rejected

Automobiles

- ● Must file report to Congress on factors relating to controls
- ● NAS report on controls due to EPA and the Congress
- ▲ Must meet recall warranty (materials and workmanship for 5-years or 50,000 miles)
- ▲ Can request extension on hydrocarbons and carbon monoxide controls
- ▲ Can request extension on NO_x control
- Must achieve 90% control of hydrocarbons ▲ and carbon monoxide emissions
- Must achieve 90% control of NO_x emissions ▲

Aircraft

- ● Must initiate study on aircraft emissions
- ● Must complete study on aircraft emissions and propose regulations

Noise

- ● Must submit report to Congress

● EPA administrator ■ States ▲ Industries

This calendar is not to be interpreted as a complete list of legal requirements for the EPA administrator

Official act. *President Nixon signs bill on the last day of 1970 as his two top environmentalites applaud—EPA's Ruckelshaus (left) and CEQ's Train (right)*

point in Congressional development of the legislation. In the final version, the warranty—five years or 50,000 miles—takes effect when the following two conditions are met:

- The EPA administrator finds that suitable tests have been developed to test such emissions.
- Adequate facilities are available to apply such road tests.

Industries

To be sure, industries are faced with numerous new requirements. Many facilities will have to invest heavily in new technology and new processes. For example, some 19 industries are faced with the control of 14 selected agents (see below) that are generally specific to these industries. Not only will the industries have to control these emissions, but they are also faced with the problem of monitoring and keeping records of such emissions, under the new law.

Three categories of air pollution agents are specified in the new law. The first group includes those pollutants for which a national ambient air quality standard and implementation plan are to be established. They include five—SO_2, particulate matter, carbon monoxide, hydrocarbons, and oxidants—for which federal controls are already in effect, plus another five—nitrogen oxides, lead, polynuclear organic matter, fluorides, and odors. A second category contains a limited number of hazardous agents, including lead, mercury, cadmium, and asbestos.

The last category contains air pollutants that are usually confined to the specific emission source. Some 14 agents have been noted—arsenic, chlorine gas, hydrogen chloride, copper, manganese, nickel, vanadium, zinc, barium, boron, chromium, selenium, pesticides, and radioactive substances. But the imposition of emissions standards on the 19 industries applies only to new stationary sources.

Before a new stationary source begins operation, state or federal inspectors (or both) must certify that the controls will work. Standards of performance for various new stationary sources are not static; they more than likely will change. It is presumed that the new stationary sources will be in compliance with the standards of performance throughout the operational lifetime of the plant.

No compromise

Penalties for violation of the law are tougher under P.L. 91-604 than under earlier law. Conviction for a knowing violation is now subject to a penalty of $25,000 per day or imprisonment for one year, or both. For a second knowing violation, the penalty increases to $50,000 per day of the violation, imprisonment for two years, or both.

Mandatory licensing considerations and public action suits were other controversial items which were heavily endorsed by the Senate. Although these items were weakened considerably in House–Senate conference, they nevertheless survived. In the final version of the act, patents cannot be taken over by compulsory licensing, except under the most compelling circumstances and with the agreement of the attorney general and the U.S. District Court.

The public's role in air pollution control, which was a unique feature in the 1967 Air Quality Act, has been preserved but somewhat changed. Earlier, the public participated in the development of standards; now they will participate in the public hearings on implementation plans. What's more, they can bring citizen action suits against polluters or government officials. Citizen suits can be instituted against the EPA administrator only for failure to act in cases where the law specifies that he must. Suits cannot be brought against him in cases where he is given discretion to act under the law.

Research and studies

To be sure, all answers to demands for clean air by 1975 are not in hand today. For this reason, research will aim to find better controls for both stationary and mobile sources. Over the next three years, $350 million is earmarked in the new law for research relating to fuels and vehicles. For example, $89.1 million is authorized for a six-year program (1970–75) to develop a low-emissions alternative to the internal-combustion engine.

Research on fuels for stationary sources will be directed at:

- Cleaning of fuels prior to combustion. In the past, the emphasis was on flue-gas cleaning techniques.
- Better ways to combust fuels with less atmospheric emissions.
- Methods for producing new or synthetic fuels which have a lower combustion potential for creating air pollution.

Authorizations totaling $45 million for fundamental air pollution studies are contained in the legislation. The first, a research study on health and welfare effects of air pollutants, is funded for $15 million. The study will emphasize the long-term effects of such agents and also will be concerned with health effects on the very young, the aged, the infirm, and other susceptible individuals.

A second study, for $30 million, will assess the cause and effects of noise pollution. The law also calls for the establishment of an Office of Noise Pollution and Abatement within the EPA. The new office would make a comprehensive study of noise pollution and later make recommendations for appropriate legislation. SSM

A solid waste recovery system for all municipalities

The national goal of recycling could become a reality with The Aluminum Association's plant

If and when some newly authorized federal funds ($80 million for fiscal year 1972 and $140 million for fiscal year 1973, specified in P.L. 91-512—the new Resource Recovery Act) are appropriated, then state officials, sanitary engineers, and their solid waste consultants will begin to pay close scrutiny to a refuse recycling plant that literally mines today's solid wastes and makes a profit for the state or municipality over and above the disposal costs.

Basically, the plant accommodates 500 tons of trash each day (the amount generated by a municipality having 175,000 to 225,000 people), converts 60% of it to heat, and recovers the remaining 40% for recycling. Although the total plant costs $15 million in capital investments and requires 10 acres of land, it can make a profit of $22,000 to $133,000 per year.

What makes this plant so noteworthy and credible is the supportive engineering cost data which have been tagged on the separate component units by engineering personnel of The Rust Engineering Co. (Birmingham, Ala.). Flexibility is provided through options which individual municipalities can adopt or discard, depending on their particular needs and circumstances.

The coup de grace, however, is the fact that this plant has been accepted by the newly formed National Center for Solid Waste Disposal Inc., (NACSWAD) for review by its scientific advisory panel and for consideration as a potential project. A private foundation involving labor, consumer, steel, aluminum, glass, and process food manufacturing interests, NACSWAD was incorporated last August (Washington, D.C.) and opened its headquarters there last month.

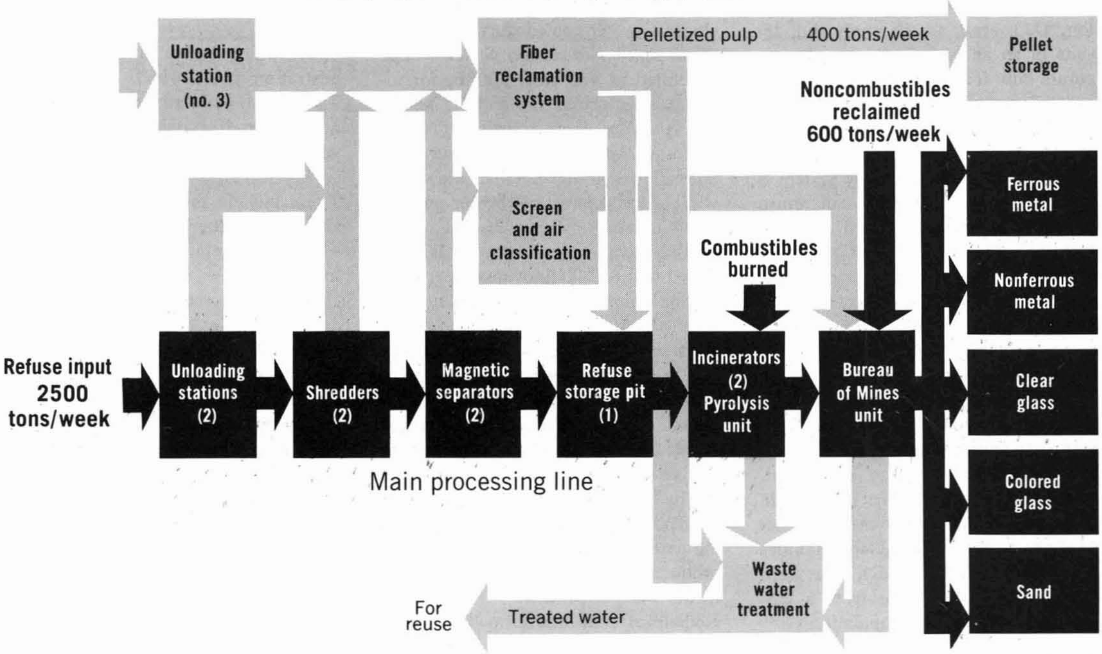
The center is a joint effort of various industries that have agreed to finance it to the tune of $2 million for calendar year 1971. Its acting director is R. T. Evans, Jr., former vice-president of Continental Can Co.; a permanent director will be appointed, perhaps as early as this month. Through the new center, state officials and their engineering consultants can get a cost estimate for their particular solid waste disposal needs.

Brainchild

This "system for all municipalities" is the brainchild of The Aluminum Association (New York, N.Y.), which represents 66 companies that are engaged in the production and fabrication of aluminum in the U.S.

As with any cost engineering study,

Municipal refuse recycling plant



Capital cost of plant

Total direct costs	$11,886,196
Indirect costs, overhead, construction fee	2,377,239
Engineering and start-up	1,315,000
Working capital	175,000
Land (10 acres)	100,000
Total	**$15,853,435**

Annual operations

$1,317,000

Annual income

Dump charge	$721,500
Glass	188,900
Ferrous	173,200
Aluminum	138,000
Steam	107,000
Paper fiber	70,434
Other nonferrous	45,800
Sand	5,500
Total	**$1,450,334**

certain assumptions were made in considering the overall costs for the system:

- The fact that disposal costs of $17 per ton in the Washington, D.C. area are the highest of anywhere in the U.S. Disposal costs range from $2 to $17 per ton, nationwide.
- The fact that construction labor costs are, again, those for the Washington, D.C. area, which are among the highest in the nation.

Although the costs for individual units of the system vary from city to city, basing the costs on the Washington, D.C. area, as the study did, results in an analysis that is strictly accurate only for that area. To be sure, a detailed market study should be undertaken in the area in which any plant is to be located.

So, an area-wide recovery system is now available. The system can return a reasonable revenue from recycled materials and energy from the combustion of other refuse. Although the site has not yet been selected for a demonstration plant, several urban areas, including Washington, D.C., are strong contenders.

The demonstration plant will be sufficiently versatile to test the performance and economics of a wide variety of refuse recycling equipment. Later, the plant could be installed in different combinations to meet the specific needs of individual communities across the U.S. Typically, the plant would handle the refuse from a city of 175,000 to 200,000 population.

Main engineering line

On a weekly basis, 2500 tons of trash would be handled. Sixty percent would be converted to heat; the remaining 40% would be recovered for recycling. The recovered portion would total approximately 105 tons of fiber a week (25% of the recoverable portion since the unit only operates 25% of the time) and the noncombustible material—metals, glass, and sand—would total 600 tons a week (100% of the recoverable portion).

What, then, is necessary in the way of equipment to handle the 500 tons of trash per day? The engineering report further notes that two incinerators and one pyrolysis unit, each having a capacity of 200 tons per day, are sufficient. Rather than a third incinerator, the pyrolysis unit is justified on the basis that the unit approaches the reliability of the incinerators. In addition, its operation would provide comparable engineering operating data. Capable of handling a feed of 1250 tons of shredded municipal refuse per week, the pyrolysis unit will be designed to handle the same capacity as the incinerators.

The incinerators and pyrolysis unit work best continuously, since each requires several hours for start-up and shutdown. They are therefore designed and sized for continuous operations—24 hours per day, seven days per week.

The incinerators have large furnaces with water-tube walls that heat water and generate steam. They include a water-cooled furnace and a waste heat boiler section. Steam will be generated at 400 psig, 700°F, for in-plant drive turbine use and for potential sale. The characteristics of an incinerator limit the steam pressure and temperature to levels that are unfavorable for economical power generation.

With two incinerators, it is estimated that 85,000 lb of steam per hour will be generated. Of this amount, 35,000 lb per hour will be required for in-plant turbine drive, leaving 50,000 lb of steam per hour available for sale. On the other hand, the combination of an incinerator and the pyrolysis unit produces only half as much salable steam, 25,000 lb per hour.

The basic difference between the incinerator and pyrolysis unit is that the latter produces carbon as a by-product. The carbon can be used for waste water treatment in those municipalities that desire to locate the recovery system along with their waste water treatment facility. The residue from the incinerators is processed by a materials recycling system, developed by the U.S. Bureau of Mines (College Park, Md.), that separates glass, ferrous metals, and nonferrous metals for reuse by industry. In operation, the BuMines system recovers 100% of the noncombustible portion, which represents 40% of all trash.

Here, the recoverable portion is separated into five categories of wastes:

- Glass with metallic content.
- Nonmagnetic glass.
- Nonferrous metal.
- Ferrous metal.
- Sand.

The BuMines incinerator residue recovery unit is sized to process 180 tons of wet residue per day (126 tons per day dry) from incinerator storage. The input for the BuMines unit is a mixture of noncombustible materials from either the incinerators or the pyrolysis unit. One important distinction between the two residues is that the incinerator residue must be crushed in a hammermill, whereas the pyrolysis unit residue need not be treated before sending to the unit. It consists of a series of vibrating screens (for glass), separators and classifiers (for various different-size metallic or nonmetallic wastes), and a rod mill (for particle size reduction). After separation, the different recovered materials are stored and subsequently transported to be used again in the U.S. economy.

Options

There are several units in the demonstration plant which are optional. These will be used to develop engineering and economic information which would then determine their feasibility for other locations in the U.S. These include the shredding and separation unit, the grinding and air classification system, and the fiber reclamation unit.

The report recommends that when data become available in early 1971, a grinding and classification system be considered. The system would separate activated carbon generated in the pyrolysis unit. This activated carbon could be used for tertiary treatment of sewage waste waters.

Another option, the dry fiber reclamation system, can be added later; space is allotted for the unit in the demonstration plant. In some areas of the country, the recovery of fiber—a significant portion of the total trash—

may take a lesser priority and may not be chosen. However, the system's success in actual operation in the demonstration plant is dependent upon the ability of the air classification system to make a clean separation of paper and wood materials from the mixed municipal wastes.

Wet fibers are reclaimed by the hydropulping process, by use of a Black Clawson unit. The process recovers cellulose fibers from paper cartons and other packaging materials. No preparation is needed for this unit. It can accommodate raw refuse, shredded refuse, or magnetically separated refuse. Any form of refuse can be used with this unit, which dissociates, separates, recovers, cleans, and dewaters the fibers. The product of the unit is in the form of pellets, which can be sold commercially. In fact, it can produce as much as 400 tons of salable fiber pellets each week.

Other optional items of equipment are the shredders, the dry screening unit, and the air classification unit. The shredders are two large rotary machines capable of handling appliances as large as household refrigerators and reducing them to fist-size chunks of metal. It should be noted that shredding is not required for material fed to the incinerators.

The dry screening unit accommodates shredded and magnetically separated materials. The screen effects a three-way separation—paper and plastics, food, and grit and glass. The glass is recovered as cullet and sold; other separated products are fed into the incinerators or pyrolysis unit.

The air classification unit takes the shredded material and separates it on the basis of different weights. The first fraction contains plastics and food materials, the second consists of paper and wood, a third glass. The first two are sent to the incinerators or pyrolysis unit, and the third fraction is sent to the BuMines materials recycling unit.

Clean operations

Clean air and water controls are included for all plant operations. Air pollution control equipment is provided for the incinerators, the pyrolysis unit, and ventilation of the plant in general. An electrostatic precipitator with two compartments protects the atmosphere from particulate matter emitted from the incinerators. A packed tower scrubber (in series with the precipitator) removes sulfur compounds, chlorides, and odors. The tower uses a solution of sodium carbonate, sodium hydroxide, or potassium permanganate.

Other air pollution control equipment specified in the plant design include venturi scrubbers, baghouses, and fabric filter collectors. For example, a venturi scrubber is used to remove kiln emissions from the pyrolysis unit. A baghouse prevents fine dust from floating in the plant atmosphere; the induced-draft fan of the baghouse will discharge to the atmosphere through a stack above roof level. All other areas of the plant are protected by fabric filter collectors.

A waste water treatment plant capable of treating 650 gpm can also be installed in the plant. Essentially, the system consists of a primary clarifier and a vacuum filter for sludge dewatering. Provisions have been made at the clarifier for the feed of a polyelectrolyte to promote more rapid settling of fine particles, a phosphate reducing reagent, and sulfuric acid for pH control.

Looking ahead

To be sure, many concepts for solid waste disposal have been proposed. Two, for example, are the Combustion Power Co.'s innovative approach for converting solid wastes to electricity (ES&T, August 1970, page 631) and the Hercules Inc. plant, which is Delaware's choice for a county-wide disposal facility (ES&T, September 1970, page 729).

The Combustion Power system can be categorized as innovative technology, for which federal funds have been earmarked. The Aluminum Association's plant, on the other hand, is essentially an area-wide resource recovery system for which specific federal funds have also been earmarked.

The present plant certainly merits attention, considering the fact that 100% of the trash is either recovered as resources and recycled in the U.S. economy or converted into energy. With this plant, the goal of recycling could become a reality. SSM

Potential suppliers for various units

Incinerators[a]

Barlett-Snow
(Cleveland, Ohio)

Combustion Engineering
(Windsor, Conn.)

Nichols Engineering Research
(New York, N.Y.)

Rust Engineering
(Pittsburgh, Pa.)

Pyrolysis units[b]

Monsanto Enviro-Chem Systems
(St. Louis, Mo.)

Union Carbide
(New York, N.Y.)

Fiber reclamation

Wet unit

Black Clawson
(Middletown, Ohio)

Dry unit

Bauer Bros.
(Springfield, Ohio)

Combustion Engineering
(Windsor, Conn.)

Sturtevant
(Boston, Mass.)

Air classifiers

SRI zig-zag classifier[b]
(Irvine, Calif.)

Bauer Bros.
(Springfield, Ohio)

Incinerator residue recovery unit[b]

BuMines
(College Park, Md.)

Turn-key engineering companies

Bechtel
(San Francisco, Calif.)

Brown & Root
(Houston, Tex.)

Rust Engineering
(Birmingham, Ala.)

Air pollution controls[c]

American Air Filter
(Louisville, Ky.)

Koppers[d]
(Baltimore, Md.)

American Lurgi[d]
(New York, N.Y.)

Research-Cottrell
(Bound Brook, N.J.)

Western Precipitation
(Los Angeles, Calif.)

Wheelabrator
(Mishawaka, Ind.)

Water pollution controls

Cochrane
(King of Prussia, Pa.)

Dorr-Oliver
(Stamford, Conn.)

Eimco
(Salt Lake City, Utah)

Hardinge
(York, Pa.)

[a] Standard production units
[b] Custom engineered units
[c] Including electrostatic precipitators, wet scrubbers, baghouses, and the like
[d] Not including wet scrubbers

Recycling sewage biologically

A novel use of nature's resources may effectively reclaim secondary effluent

The typical sewage treatment plant is fairly efficient in removing oxygen-demanding compounds and settleable solids. But the average plant does not remove nutrients, nor does it have a long retention time during the waste treatment process. Although effluent from the sewage treatment plant is an improvement over the untreated influent, this discharge is still rich in chemical nutrients that feed algae, bacteria, and aquatic plants that grow, die, and contribute to the eutrophication of streams, lakes, and ocean estuaries. As a result, the typical sewage treatment plant does not produce an effluent capable of beneficial recycling. Complete recycling requires more time and space, and, generally, neither is available.

In Michigan, however, a 500-acre land and water complex will present the management of waste water from a modern waste disposal plant so that nutrients and contaminants are handled as resources capable of being converted into useful products. Besides this utilization of wastes, the plan includes recreation areas that are so vital in an urban area.

Several interlocking biological recycling systems, designed as an alternative to discharging treated wastes into streams, have been developed by the Institute of Water Research (IWR) at Michigan State University (MSU). This system of recycling and reusing waste water (to be completed in September) is "not just a tertiary step" in an established system, "but is really recycling," says Howard Tanner, assistant director of IWR.

These biological systems, to be established on 500 acres of MSU property, will include a conventional waste treatment plant, an aquatic system of shallow lakes, and a land system of laboratories, wooded areas, and open field plots. The complex will handle 2 million gallons of secondary treated liquid waste per day (equivalent to sewage from 30,000 to 40,000 people). These land and water systems will be combined with a community recreation project to provide complete recycling of the waste water.

Lake system

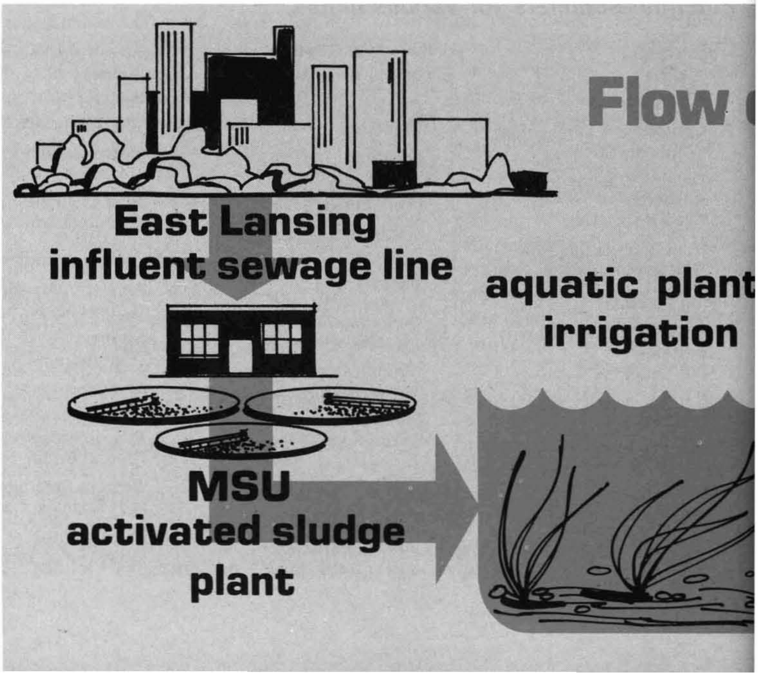
Raw sewage will be drawn from a trunk line of the East Lansing (Mich.) sewer system and will be treated by a conventional activated sludge process at the MSU-constructed sewage treatment plant. The waste solids will be returned to the city sewer system; the liquid, secondary-treated effluent, will be piped to the first of three lakes (construction to begin in March) with total surface area of 30 acres.

These three lakes (the first of five that will eventually be built) will be connected by an underground pipe, and the water will flow from lake to lake (by gravity) over a 30-day period. During this movement, the waste water will be stripped of most of its nutritional and polluting characteristics and will eventually, with additional treatment, be used in a swimming pool.

Michigan, like many other parts of the country, has soil that is sandy, which allows water seepage from lakes and ponds into the ground. In the MSU lakes, precautions are being taken to prevent infiltration or water loss into the soil. Many soil sealants are available, but few are effective and most are expensive.

A technique borrowed from agriculture will initially be utilized. An asphalt or clay emulsion will be injected under the ground to seal capillaries, providing greater water-holding capacity.

Rooted aquatic plants will be grown in these 6 to 8-ft deep lakes to maximize the removal of phosphates and nitrates from the secondary effluent. These aquatic plants, which are not algae, are selected for their adaptability to the climate, their high demand for phosphates and nitrates, and their food value. For this, plants have been collected from as far north as the Hudson Bay and as far away as New Zealand. Suitable plants have a growing season



from as early as April to as late as October, or until the lakes are covered with ice.

Of course, the first lake will be the richest in nutrient content, but each lake will support underwater plant life that will be harvested three or four times a year. The lakes are designed to facilitate harvesting of foliage.

What the harvested corp will be used for remains a question. One answer is to feed it to livestock. The nutritional value of these aquatic plants is equivalent to that of alfalfa, perhaps even higher. But they will be more costly to harvest since they have to be cut underwater. However, the cost can be partially offset by its contribution to the reclamation of the waste water. Laboratory testing has shown that the plants can be dehydrated and pelletized for future use or fed directly to livestock. Another possibility is the extraction of proteins from this material for feeding the increasing human population.

Water usage

Fish will be grown in the last two lakes, and possibly in the first lake. Forage fish that are potentially marketable as bait will be stocked in the first lake, with their use dependent upon the amount of BOD present. The last two lakes will each contain two fish populations: catfish, a high-protein source, could provide as much as 500 to 1000 lb of fish per acre per year; bluegill-bass will be a source of recreation for the sporting fisherman.

A recreational area will be an additional contribution from this reclaimed water supply. Grounds surrounding the lakes will be landscaped for public recreation. As the waste water is being purified, it will be odorless and esthetically pleasing to the eye, says Frank D'Itri, staff chemist, IWR. Thus, the area can be used for walking, boating, fishing, and picnicking.

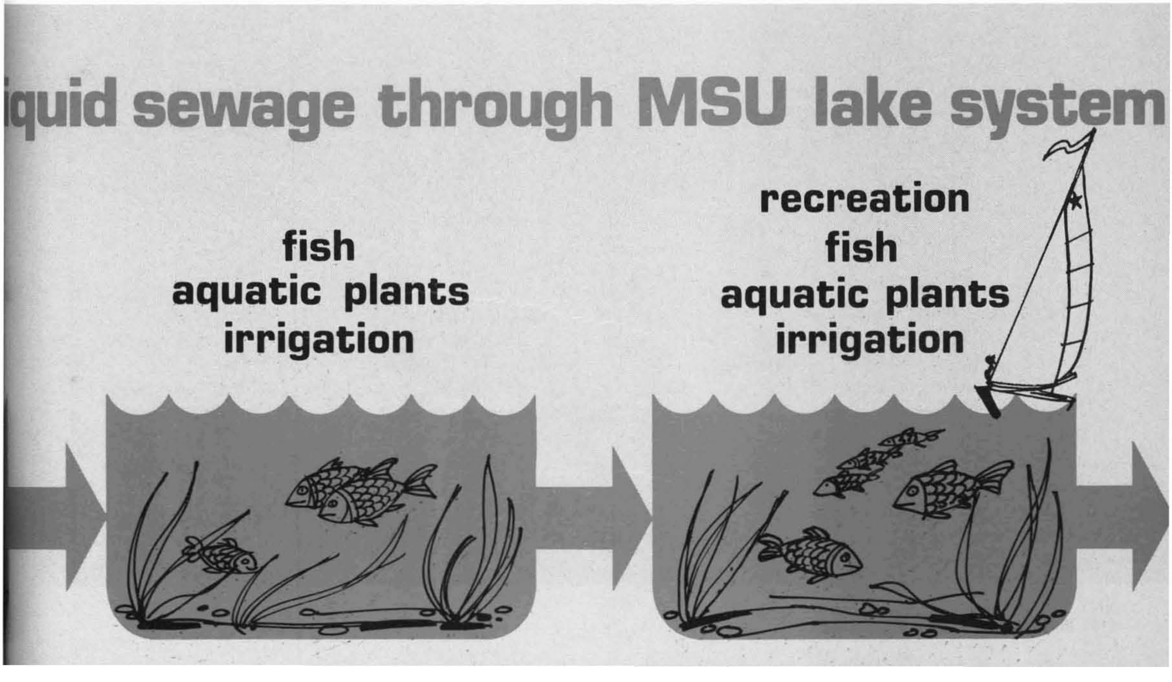
Spray irrigation on adjacent lands will also be used to strip nutrients from the water. This water will be distributed to forage crops, selected row crops, coniferous tree plantations, woodlands, and old farm lands. The increased plant growth and the effects on the soil and water will be measured after nutrient removal by the interaction of soil, sun, and vegetation. Irrigation water will be available from any of the lakes and will be used on almost every conceivable type of plant that lives in the Michigan climate. The land will be irrigated year round, perhaps with increases during the winter, when biological activity in the lakes slows down.

Another use for this "biologically cleaned" water relates to the geography of the area. Lansing and the surrounding region are above a large underground aquifer—i.e., on a large bowl of water. In 1935, before the region's population grew significantly, this underground water supply was full and often overflowed as springs. Excess water from the aquifer fed the streams and rivers. With the growth of industry and population, the large wells in this region draw heavily on the groundwater, causing a drop in the water table. The more shallow wells are now located above the table. Because of this change in the water table, not only are the people with shallow wells deprived of water, but waters from streams are now returning to the aquifer rather than being further supplied by it. Eventually, the water will be poorer in quality yet more costly to bring to the surface.

Solving such problems will take time, but this water reclamation plan offers the possibility of spraying the cleaned water over the surrounding land, where it will eventually return to the ground aquifer, thus recharging the larger underground water source. This project offers a potential closed hydrologic cycle where water is drawn from the wells, used and dirtied, cleaned, and returned to the ground to be used again after an elapsed period. Careful monitoring will assure a clean water supply for future generations.

Pioneer

When the first three lakes are completed, the final two will be added along with a swimming pool, which will make use of water from the system after additional treatment. This project, if successful, could serve as a pilot plan for communities with inadequate water treatment facilities to overcome their deficiencies. The entire country will be on watch for the outcome of this MSU "two for the price of one" system. CEK



Monitoring is at the heart of the nation's water quality management effort; without it, enforcement and cleanup programs can be of only limited effectiveness

Water quality surveillance:

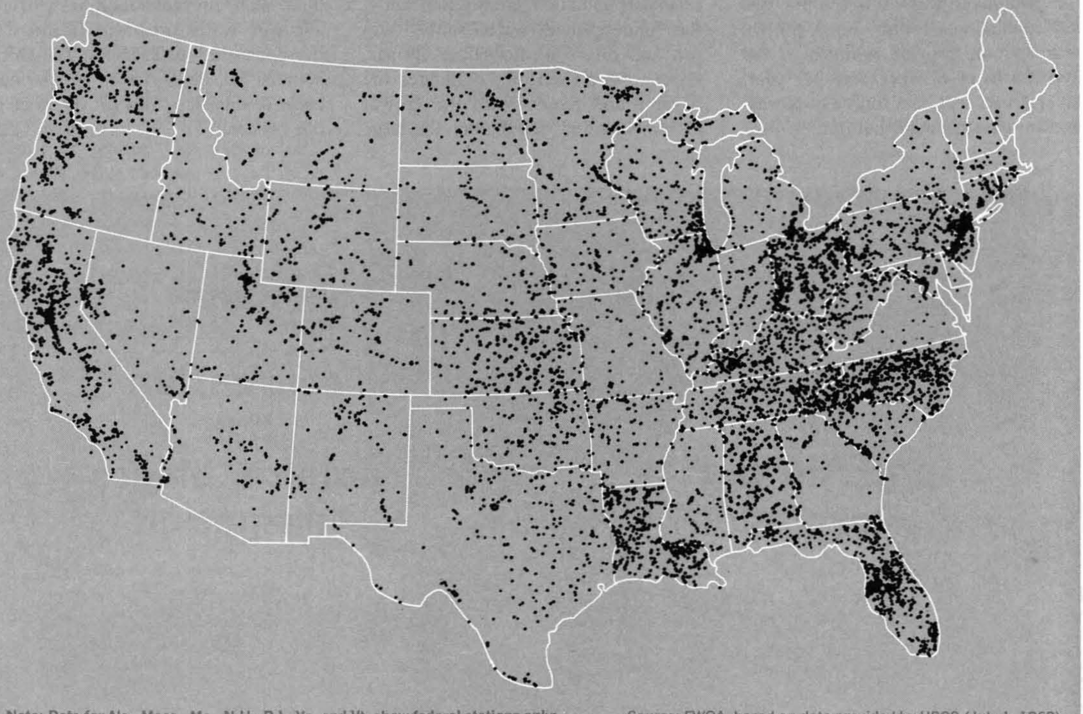
William T. Sayers
Water Quality Office,
Environmental Protection Agency,
Washington, D.C.

Within the past several years, we have witnessed an immense increase in public awareness and concern over the quality of the environment. It has become obvious that we, as a nation, must control those practices that despoil our air, water, and land. The time is long past due for us to implement the necessary steps to harmonize our technological society with our natural environment.

With respect to abatement of water pollution, efforts of various size and scope have been in practice for nearly a century. Early efforts of state and federal authorities focused on the control of waterborne diseases, such as typhoid fever. Not until 1948, however, was specific water pollution control legislation enacted. Even then, it was of a temporary nature and only a weak forerunner of the Act of 1956, the basis of our present federal water pollution control program. Amendments in 1961, 1965, 1966, and 1970 further strengthened that act to provide today's far-reaching programs in water quality management.

In passing the Federal Water Pollution Control Act, Congress recognized the primary responsibilities and rights of the states to prevent and con-

Where water quality monitoring stations are located in the U.S.



Note: Data for Ala., Mass., Me., N.H., R.I., Va. and Vt. show federal stations only; data for other states show federal and non-federal stations.

Source: FWQA, based on data provided by USGS (July 1, 1968)

the federal-state network

Parameter coverage and sampling frequency—U.S. water quality monitoring stations

No. of Stations Measuring Given Parameter at Indicated Frequency

Parameter	Continuous	Daily	Weekly	Monthly	Quarterly	Annually	Other	Total
Temperature	871	822	529	2270	832	1064	1276	7664
Specific Conductance	241	432	97	1636	491	1287	1045	5229
Turbidity	31	285	332	1053	615	57	623	2996
Color	14	87	205	939	611	1122	747	3725
Odor	9	32	14	389	406	13	248	1111
pH (Field)	77	55	156	745	372	122	721	2251
pH (Lab)	16	451	268	1914	749	1398	1111	5907
EH	18	0	0	7	0	0	1	26
Suspended Solids	0	2	48	328	213	2	45	594
Other Physical Analyses	12	19	73	146	179	41	193	663
Dissolved Solids	42	188	232	1495	624	1187	1063	4831
Chloride	10	121	118	1196	354	552	931	3282
Nutrients (Nitrogen)	14	32	243	1266	507	896	775	3733
Nutrients (Phosphorus)	23	58	135	853	609	889	918	3485
Common Ions	20	412	119	1775	555	1357	1288	5526
Hardness	6	362	225	1490	674	1310	907	4974
Radiochemical	21	3	37	339	448	31	265	1144
Dissolved Oxygen	85	45	345	1379	500	913	681	3948
Other Gases	10	86	13	34	0	5	18	166
Minor Elements	0	12	3	164	45	149	175	548
Pesticides	1	1	7	69	11	24	80	193
Detergents	0	1	85	363	463	33	114	974
Bio. Oxygen Demand	0	12	239	866	460	30	176	1783
Carbon (Tot., Diss., etc.)	0	4	4	22	0	31	4	65
Coliforms	13	240	423	1261	637	160	345	3079
Other Micro-organisms	2	13	185	252	128	4	113	697
Biologic	6	3	102	127	60	13	76	387
Sediment Conc. (Susp.)	25	291	96	269	41	9	328	1059
Particle Size (Susp.)	5	56	7	134	12	51	315	580
Part. Size (Bed Load Mat.)	0	0	0	10	2	6	33	42
Other Sediment	1	8	5	97	2	6	71	190

Source: FWQA, based on data provided by USGS (July 1, 1968)

trol water pollution. The federal role is designed primarily to supplement state activities. Major activities of the federal Water Quality Office (WQO) include:

- Providing grants for the construction of municipal waste treatment facilities.
- Assisting states in the development and administration of water quality standards.
- Administering a federal enforcement program against interstate pollution.
- Supporting research and development activities which seek better methods for controlling all forms of water pollution.
- Providing technical assistance on complex pollution problems.
- Encouraging effective river basin planning.
- Extending financial and other assistance to state pollution control agencies.

The success of water quality management efforts at all levels of government will, in the final analysis, be judged by our ability to provide adequate quantites of water of appropriate quality for all water uses.

Water quality and changes in it can be determined most effectively through

How frequently parameters are used in water quality criteria of state standards

Uniform (100%)	Frequent (99–50%)	Less Frequent (49–20%)	Least Frequent (19–0%)
Dissolved Oxygen pH Coliform Temperature Floating Solids (Oil-Grease) Settleable Solids Turbidity and/or Color Taste-Odor Toxic Substances	Radioactivity Parameters listed in Public Health Service Drinking Water Stds. Total Dissolved Solids	Arsenic Barium Cadmium Chromium (hexavalent) Fluoride Lead Selenium Silver Suspended Solids Chloride Copper Nitrate Phenols Phosphate Sulfate Cyanide Median Tolerance Limit	Bottom Deposits Chromium (trivalent) Electrical Conductance Ammonia Acidity Alkalinity Carbon Chloroform Extract Hydrogen Sulfide Pesticides Sodium Iron Plankton Foaming Substances Boron Manganese Hardness Biochemical Oxygen Demand Methylene Blue Active Substances Zinc

water quality measurement. Thus, the key to effective water quality management is the ability and capability to measure substances and to understand their behavior in water. Additionally, water quality monitoring provides the only effective yardstick for evaluating the efficiency of a water quality management program.

The surveillance network described in this article aims to assess existing water quality conditions, to determine long-term trends in water quality, and to evaluate compliance with state–federal water quality standards. This information serves to identify existing and emerging problem areas and changes in water quality with time, nationally as well as locally.

Monitoring needs and responsibilities

The effective management of water quality requires two categories of water quality monitoring. First, monitoring of individual treatment plant influent and effluent is necessary to maintain optimum treatment efficiencies. Effluent monitoring is also essential to assess the individual effects of each waste source on the waters into which they discharge. Second, the rivers, lakes, and coastal waters receiving wastes must be examined to assure attainment and maintenance of desired water quality levels consistent with criteria contained in state–federal water quality standards. Together, these two categories of monitoring will provide the information necessary for efficient management of pollution control facilities and the effective administration of water quality standards.

Monitoring of waters receiving wastes can be accomplished in two ways. One is through the operation of a vast network of strategically located long-term stations. A second approach makes use of repeated short-term surveys, each providing limited spatial coverage. Data needs can be met most efficiently by use of both approaches. A nationwide network that uses a minimal number of long-term stations can be used to identify general areas of adverse trends in water quality or violations of water quality standards. Where such conditions are found to be occurring, short-term surveys can then be conducted to define fully the extent of the problem, plus all factors contributing to the problem.

Monitoring of the individual treatment plant influent and effluent is basically the responsibility of pollution control facility managers and of local and state pollution control agencies. The enormous investment in pollution control facilities required to restore, preserve, and enhance national water quality dictates that these facilities be managed at least as conscientiously as industrial production processes representing similar investments.

Monitoring of the receiving waters to evaluate and enforce water quality standards is the primary responsibility of state water pollution control agencies. The federal government also has certain obligations here, since it may be required to enforce interstate water quality standards when a state fails to exercise its responsibility.

The interdependency of these monitoring activities and their common goals require that they be closely coordinated for maximum effectiveness. We cannot afford duplication of effort. The magnitude of the monitoring effort required demands the greatest return on each dollar expended.

Present monitoring activities

In designing a nationwide monitoring program to accomplish a specific set of objectives, all pertinent existing monitoring activities at the local, state, and federal levels should be reviewed to determine their usefulness to the proposed system. The map and table on pages 114 and 115 indicate the extent of present monitoring activities on a nationwide basis.

At the local level, most municipal water treatment facilities monitor raw water quality daily. There are about 6000 such facilities served by surface water sources. Thus, considerable information is being gathered on surface water quality in the U.S. by operators of municipal water treatment plants alone. In addition, many municipal waste water treatment programs and county agencies routinely monitor receiving waters upstream and downstream from treatment plant discharges. Many universities also regularly collect water quality data.

Most state pollution control agencies have monitoring programs for assessing surface water quality. These programs vary in scope among states and range from near-minimal to complete systems. Other water-oriented state agencies, such as conservation and geology departments, are also engaged in water data acquisition to various degrees.

More than a dozen federal agencies are engaged in the direct acquisition of water data. These activities are coordinated through the Office of Water Data Coordination of the U.S. Geological Survey, consistent with a Bureau of Budget requirement for interagency coordination to avoid duplication of effort. The budget agency (now the Office of Management and Budget) also advocates the operation of a National Network to meet the common data needs of two or more federal agencies. The U.S. Geological Survey (USGS) has been given responsibility for the management of this network. Data needs specific to any one given agency that cannot be met efficiently through the National Network will be obtained by that agency through other means.

One very significant feature of USGS's National Network will be what is referred to as its Accounting Element. This element will provide an accounting of the quantity and quality of water that flows out of 306 hydrologic basins which cover the conterminous U.S.

Surveillance network

To achieve their goal of clean water, state and federal pollution control agencies are jointly developing a surveillance network that will serve to identify:

- Compliance and noncompliance with water quality standards.
- Water quality baselines and trends.
- Improvements in water quality produced by abatement measures being undertaken—e.g., construction of waste treatment facilities.
- Emerging water quality problems, in sufficient time to effect adequate preventive measures.

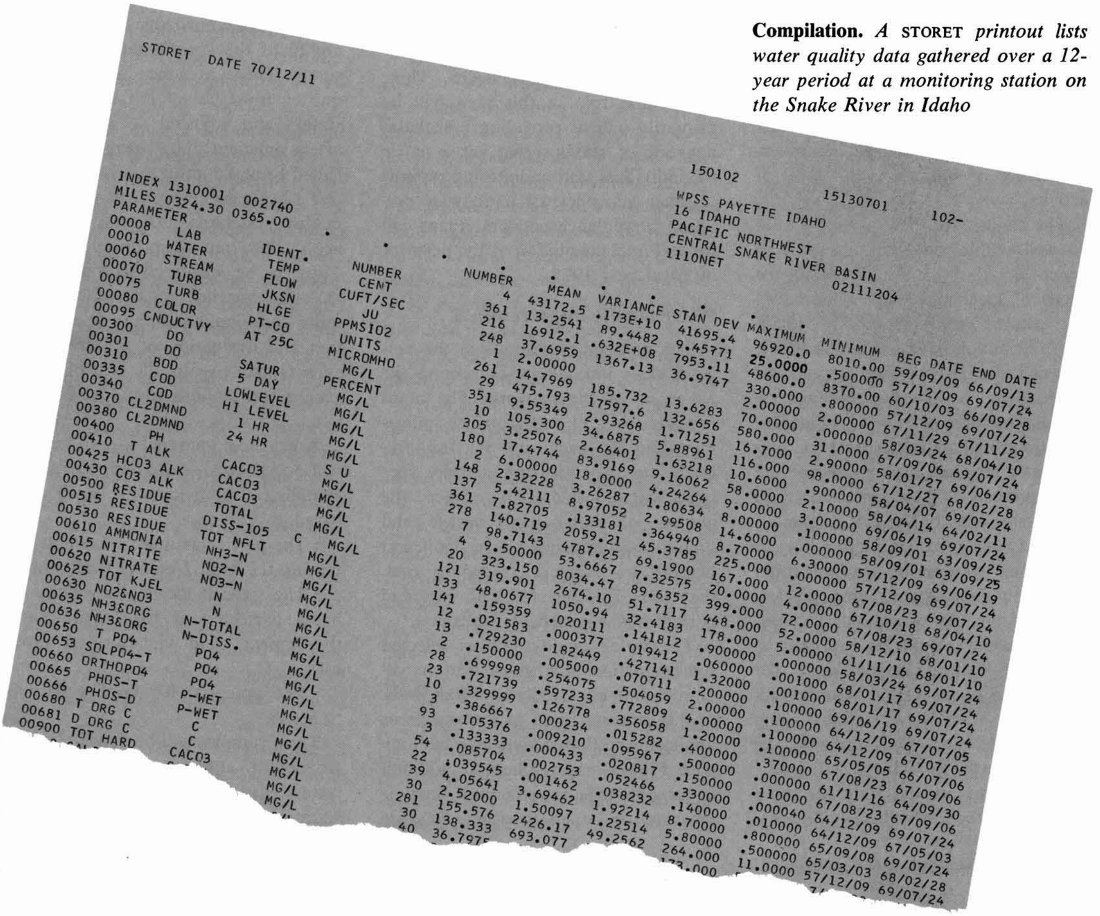
To attain these objectives as efficiently as possible, existing water data acquisition programs of all agencies will be utilized to the fullest.

The first major step in the development of this state–federal surveillance network is to complete its design. Basic steps required in the design phase are:

- Secure agreements with state water pollution control agencies on current and future monitoring locations, parameter coverage, and sampling frequencies, irrespective of political boundaries.
- Review current and proposed sampling activities of state, interstate, and federal agencies (including those of the National Network managed by USGS) to establish the need for additional stations and (or) supplementary data.
- Reach agreement among the state and interstate agencies and the federal Water Quality Office (WQO) as to which agency will take lead responsibility in funding the new stations and supplementary activities needed.

The second major step is implementation of the jointly developed surveillance network plans. This is undertaken as the design phase is completed. Implementation involves several steps:

- Completing arrangements for acquiring data in a timely fashion from various agencies collecting data of interest to state and federal pollution control agencies.
- Arranging with USGS to operate those stations that can best be handled by it and to expand parameter coverage and (or) sampling frequency at certain existing stations in the USGS network.
- Initiating new stations and expanding existing stations operated by state pollution control agencies and the WQO. In many situations, it is expected that stations will be jointly operated by state and (or) local agencies and the WQO.
- Initiating analytical quality control procedures to assure that requisite



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STORET DATE 70/12/11
                                                        150102
                                                                      15130701
                                                        WPSS PAYETTE IDAHO            102-
                                                        16 IDAHO
                                                        PACIFIC NORTHWEST
INDEX 1310001  002740                                   CENTRAL SNAKE RIVER BASIN
MILES 0324.30 0365.00                                   1110NET                02111204
PARAMETER                             NUMBER  MEAN     VARIANCE STAN DEV MAXIMUM  MINIMUM  BEG DATE END DATE
00008   LAB      IDENT.    NUMBER         4   43172.5  .173E+10 41695.4  96920.0  8010.00  59/09/09 66/09/13
00010  WATER     TEMP      CENT         361   13.2541  89.4482  9.45771  25.0000  .500000  57/12/09 69/07/24
00060  STREAM    FLOW      CUFT/SEC     216   16912.1  .632E+08 7953.11  48600.0  8370.00  60/10/03 66/09/28
00070   TURB     JKSN      JU           248   37.6959  1367.13  36.9747  330.000  .800000  57/12/09 69/07/24
00075   TURB     HLGE      PPMSIO2        1   2.00000                    2.00000  2.00000  67/11/29 67/11/29
00080  COLOR     PT-CO     UNITS        261   14.7969  185.732  13.6283  70.0000  .000000  58/03/24 68/04/10
00095 CNDUCTVY   AT 25C    MICROMHO      29   475.793  17597.6  132.656  580.000  31.0000  67/09/06 69/07/24
00300    DO                MG/L         351   9.55349  2.93268  1.71251  16.7000  2.90000  58/01/27 69/06/19
00301    DO      SATUR     PERCENT       10   105.300  34.6875  5.88961  116.000  98.0000  67/12/27 68/02/28
00310   BOD      5 DAY     MG/L         305   3.25076  2.66401  1.63218  10.6000  .900000  58/04/07 69/07/24
00335   COD      LOWLEVEL  MG/L         180   17.4744  83.9169  9.16062  58.0000  2.10000  58/04/14 64/02/11
00340   COD      HI LEVEL  MG/L           2   6.00000  18.0000  4.24264  9.00000  3.00000  69/06/19 69/07/24
00370 CL2DMND    1 HR      MG/L         148   2.32228  3.26287  1.80634  8.00000  .100000  58/09/01 63/09/25
00380 CL2DMND    24 HR     MG/L         137   5.42111  8.97052  2.99508  14.6000  .000000  58/09/01 63/09/25
00400    PH                S U          361   7.82705  .133181  .364940  8.70000  6.30000  57/12/09 69/06/19
00410  T ALK     CACO3     MG/L         278   140.719  2059.21  45.3785  225.000  .000000  57/12/09 69/07/24
00425 HCO3 ALK   CACO3     MG/L           7   98.7143  4787.25  69.1900  167.000  12.0000  67/08/23 69/07/24
00430 CO3 ALK    CACO3     MG/L           4   9.50000  53.6667  7.32575  20.0000  4.00000  67/10/18 68/04/10
00500 RESIDUE    TOTAL     MG/L          20   323.150  8034.47  89.6352  399.000  72.0000  67/08/23 69/07/24
00515 RESIDUE    DISS-105 C MG/L        121   319.901  2674.10  51.7117  448.000  52.0000  58/12/10 68/01/10
00530 RESIDUE    TOT NFLT  MG/L         133   48.0677  1050.94  32.4183  178.000  5.00000  61/11/16 68/01/10
00610 AMMONIA    NH3-N     MG/L         141   .159359  .020111  .141812  .900000  .000000  58/03/24 69/07/24
00615 NITRITE    NO2-N     MG/L          12   .021583  .000377  .019412  .060000  .001000  68/01/17 69/07/24
00620 NITRATE    NO3-N     MG/L          13   .729230  .182449  .427141  1.32000  .001000  68/01/17 69/07/24
00625 TOT KJEL   N         MG/L           2   .150000  .005000  .070711  .200000  .100000  69/06/19 69/07/24
00630 NO2&NO3    N         MG/L          28   .699998  .254075  .504059  2.00000  .100000  64/12/09 67/07/05
00635 NH3&ORG    N-TOTAL   MG/L          23   .721739  .597233  .772809  4.00000  .100000  64/12/09 67/07/05
00636 NH3&ORG    N-DISS.   MG/L          10   .329999  .126778  .356058  1.20000  .100000  65/05/05 66/07/06
00650  T PO4     PO4       MG/L           3   .386667  .000234  .015282  .400000  .370000  67/08/23 67/09/06
00653 SOLPO4-T   PO4       MG/L          93   .105376  .009210  .095967  .500000  .000000  61/11/16 64/09/30
00660 ORTHOPO4   PO4       MG/L           3   .133333  .000433  .020817  .150000  .110000  67/08/23 67/09/06
00665  PHOS-T    P-WET     MG/L          54   .085704  .002753  .052466  .330000  .000040  64/12/09 69/07/24
00666  PHOS-D    P-WET     MG/L          22   .039545  .001462  .038232  .140000  .010000  64/12/09 67/05/03
00680 T ORG C    C         MG/L          39   4.05641  3.69462  1.92214  8.70000  .800000  65/09/08 69/07/24
00681 D ORG C    C         MG/L          30   2.52000  1.50097  1.22514  5.80000  .500000  65/03/03 68/02/28
00900 TOT HARD   CACO3     MG/L         281   155.576  2426.17  49.2562  264.000  11.0000  57/12/09 69/07/24
                           MG/L          30   138.333  693.077           173.000
                                         40   36.7975
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Compilation. *A* STORET *printout lists water quality data gathered over a 12-year period at a monitoring station on the Snake River in Idaho* accuracy and precision are achieved. WQO is currently working with USGS in the development of a mutually consistent program in this area.

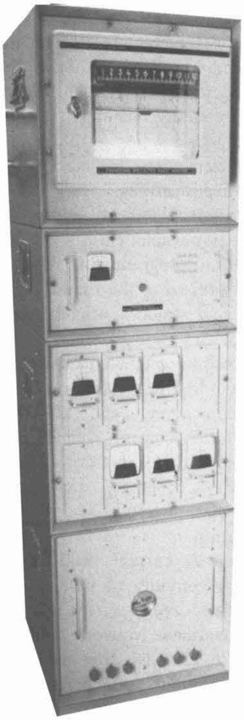
- Expanding data processing capability as necessary to permit timely evaluation of large volumes of data.

To achieve the stated objectives of the coordinated surveillance network, it is essential that the data collected be evaluated in an expeditious manner and made readily available to all users. Only in this way can appropriate follow-up actions be taken. Timely data processing and diagnosis will be achieved through the use of WQO's existing computerized data storage and retrieval system (STORET) and additional computer programs which must be developed.

A preliminary evaluation of the local, state, and federal long-term water quality monitoring effort required to provide adequate coverage of the nation's water resources indicates a need for at least 10,000 monitoring points on both interstate and intrastate waters. This may seem like a large number of stations until the length of streams, lakes, impoundments, and shoreline to be monitored is fully considered. These proposed stations, if equally spaced, would be located at 350-mile intervals. In fact, stations will be located closer together in highly developed areas and more distant in less developed areas. Obviously, there will be no overabundance of stations at this level of activity.

The majority of these stations would be well within state boundaries, and hence would most directly serve the needs of local and state water pollution control agencies. Stations providing information of key federal concern would include those along state and international boundaries, principal estuaries, mouths of major tributaries, large metropolitan complexes, and major water resource projects. There are an estimated 900 stream and 1500 open-water locations in this category.

Operational responsibility for a given new monitoring station would fall to the agency receiving greatest benefit from its operation. That is, state agencies would be expected to assume operating responsibility for most new stations within state boundaries and many new stations along state boundaries. WQO, utilizing the USGS network to achieve efficiency, would assume responsibility for those stations at the estimated 2400 locations of key federal concern. Thus, the federal role in this area will be primarily one of providing a skeleton network of stations that serve to tie the individual state monitoring systems together into one vast nationwide pollution surveillance network. Plans call for full implementation of the network by fiscal year 1975.



Robot monitor. *Information from this station on the Potomac is automatically recorded by a remote* WQO *computer*

Water quality measurements

The number of stations in the network does not, alone, determine the adequacy of the network. The number and types of water quality indices measured at each station and frequency of their measurement are very important considerations. Since the choices of parameter coverage and monitoring frequencies have significant bearing on network operating cost, they should be selected with care and periodically adjusted as warranted.

The water quality indices selected for evaluation at a given station will be determined largely by the water quality criteria listed in the standards applicable to that station (see table on page 116). Certain indices, in addition to those listed in the standards, may be measured in situations where they are considered to be of importance in establishing baseline water quality and determining trends that are required to evaluate compliance with the nondegradation clause in the water quality standards. There are still other indices that must be measured on occasion which are implicit in the standards, although not specifically listed. To thoroughly evaluate compliance with the requirement in all standards that waters be free of toxic substances, for example, would require the routine conduct of numerous tests on all samples for specific compounds known to be toxic to man, animals, and aquatic life. Obviously, the cost of doing this on even a small number of samples would be prohibitive. The plan is to evaluate all actual and potential sources of pollution in the vicinity of each monitoring station to determine which, if any, toxic substances are likely to be present, and to test for those only.

The optimum sampling frequency required to characterize water quality at a given station depends on the variability in the indices of interest. In a statistical sense, there is no answer to the question of how many samples are needed in a given time period, without foreknowledge of the variability of the constituents to be measured. Thus, a rather arbitrary frequency must be set initially for each station and adjusted at a later date, after sufficient data have been collected to make an evaluation.

To evaluate compliance with water quality standards, extreme, not average, values are of primary concern. Thus, to be *absolutely* certain that a violation has not occurred would require *continuous* sampling at each station and evaluation of *all* indices on each sample. Again, the cost of this at even a few stations would be prohibitive.

A practical approach—and one that will be followed—is to assign arbitrary sampling frequencies at each site, based on:

- The particular index of quality requiring the most frequent evaluation.
- The importance of the water uses being protected at the location and the impact of a violation on those uses.
- The potential for brief violations to occur.

Thus, samples will be collected most frequently at a station located in waters serving, for example, as a source of potable water supply for a large metropolitan area and downstream from a waste source with a potential for producing temporary violations. On the other hand, a station located in a zone subject only to minor pollution and designated for maintenance of rough fish and boating will be sampled less frequently.

Tests for those indices most subject to variation at a given station will be performed on every sample from that station. Tests for those indices less subject to variation and (or) more expensive to evaluate will be performed on alternate samples or at some other reduced frequency. Thus, the frequency of monitoring for a given water quality index may vary from continuous to four times per year, depending on the location. The frequency of monitoring at a given station will vary among the parameters being evaluated.

The proposed monitoring frequencies as well as station coverage are recognized to be near minimal. The approach being taken is to concentrate on placement and initiation of monitoring stations in the early stages of development of the surveillance network. Once the nucleus of stations is operational, greater effort will be directed toward improvement of water quality index coverage and optimization of monitoring frequencies. To assist in this endeavor, WQO has already initiated, by contract, the development of a systems analysis approach to the design of monitoring systems. This approach will include procedures for determining the optimum sampling frequency at a given location and will be applicable to streams, impoundments, and estuaries receiving any type of waste, whether from cattle feed lots, municipalities, industries, or cropland surface runoff.

Once the sampling frequency is established for a given station, the economics of manual vs. automated sample collection and (or) sensing techniques can be evaluated. In making such an evaluation, we must consider that:

- Automated devices do not completely replace field personnel since they require routine maintenance.
- Higher salaried personnel are generally required for maintenance of electronic sensors than for manual sample collection.
- Electronic sensors produce a wealth of data, which may require more elaborate and expensive data handling procedures.

Initially, perhaps as many as 15% of the stations will warrant the use of automated monitoring devices. As the population and economy continue to expand and the fixed supply of water is increasingly reused, greater and greater reliance will be placed on automated water quality sensing systems to manage water quality adequately.

To ensure the reliability of data collected by the coordinated surveillance network, an analytical quality control program will become an integral part of the overall system. All cooperating agencies will be expected to participate in such a program. The success of the pollution control effort will rest, to a great extent, upon the comparability and reliability of the information provided by the various participating agencies.

Collection of adequate quantities of accurate data is only part of the task at hand. To achieve the stated objectives, the mass of raw data received must be evaluated in a timely fashion and results made immediately available in a usable form to participating agencies for appropriate follow-up action. WQO's computerized data storage and retrieval system, STORET, is being used to meet these data handling requirements.

The STORET system, operational since 1964, utilizes many computer terminals throughout the country, all linked to a central computer. Data from four federal and about 25 state agencies are stored routinely through the remote terminals. To date, data from 30,000 stations have been stored in the central computer. The STORET system has the capability to provide a variety of statistical summaries on the stored data. When fully implemented, the STORET system will also allow comparisons, by computer, of water quality standards and the data so that apparent violations can be quickly identified for appropriate action. The system will have the capability to provide an even wider range of statistical analyses on the stored data. A variety of output formats for the raw data and statistical summaries, utilizing printers, magnetic tape, X-Y plotters, and cathode ray tubes, will be offered.

R&D needs

In the future, water resources must be managed more adequately. The ability to acquire timely information to make the necessary operating decisions on a day-to-day basis will require more sophisticated water quality sensing techniques and instruments than those now in use. Areas in which further research and development are needed to provide the necessary water quality management tools include:

- Adaptation of scientific management techniques for use in optimizing surveillance system designs.
- Development of automated instrumentation (portable and fixed) that is capable, with minimal maintenance, of accurately measuring a wide variety of water quality indices over long periods, and telemetering the data to a central location.
- Development of aerial noncontact sensing techniques for broad-scale evaluation of water quality conditions over vast geographical areas.
- Development of new, more inclusive water quality indices that can better lend themselves to automated sensing techniques.

Without these new techniques and systems for acquiring water data, true water quality management programs will not become a reality. Effort is presently underway in both WQO and the private sector to develop the much needed tools for water quality management. But this effort must be intensified if we, as a nation, wish to meet the challenges of tomorrow.

William T. Sayers *is Plans Evaluation Officer, Planning Branch, Water Quality Office (formerly* FWQA*), Environmental Protection Agency, Washington, D.C. Mr. Sayers, a C.E. (1958) and M.S. (1959) graduate of the University of Cincinnati, entered government service with the U.S. Public Health Service in 1959. He worked in Cincinnati and Dallas with the* USPHS *and was working in Minneapolis when his division became the* FWPCA. *When this article was written, Mr. Sayers was Chief, Water Quality Surveillance Systems Section,* FWQA. *The article is based on a presentation given to the* ACS *Division of Water, Air and Waste Chemistry at the Chicago National Meeting, September 1970.*

An ES&T special report

Water pollution in the states

Success for the nation's water quality program hinges on state involvement. Associate editor Stanton Miller canvassed state officials, focused on grass-roots issues, and found signs for renewed optimism

The U.S. has more than 3 million miles of streams, 88,633 miles of tidal shorelines, and millions of lakes, ponds, and bayous. Certainly, these waters cannot all be monitored, protected, and restored from Washington. So the key to success in the fight against pollution is state participation.

The action in water pollution control is at the state level. In fact, under existing federal legislation, states have the responsibility. Their programs are the crux of the nation's water pollution control effort. It is at this level that the day-to-day exchange of blows between state officials and their counterparts in industries and municipalities takes place.

Progress on water pollution abatement is being made, but certainly not at the rate envisioned by legislators when they wrote the 1965 and 1966 amendments to the Federal Water Pollution Control Act. Nor, for that matter, is it proceeding at a rate that pleases the public.

The lack of progress mainly is due to understaffing, underfunding, and undervisibility of antipollution programs. Differences of opinion between state and federal officials have developed over the last five years. Deterioration of federal–state relationship has also hampered progress.

There are numerous issues in the water pollution control game. Some are old, some are new; not one has been completely resolved. Basin planning, new financing schemes, permits, and certification requirements are a few of the new issues, while the old ones of standards, secondary treatment, enforcement, grants, and the need for new legislation are still around. Certainly, the whole list of issues affords ample opportunities for state and federal administrators to argue.

Before delving into the issues, it is important to consider the federal–state relationship. The ray of hope for improved relations between states and the federal government entered the picture only recently. But it is perhaps safe to say that, for the first time in the last five years, things are looking up.

Five years ago, the federal water pollution activity had no visibility. It then existed as the Division of Water Supply and Pollution Control in the Department of Health, Education and Welfare. Prior to the enactment of the 1965 Federal Water Pollution Control Act, the feds were accused of playing footsie with the states people. They were accused of not putting the heat on the states people to act. However, when the program was elevated in stature and moved to the Department of Interior in 1966 as the Federal Water Pollution Control Administration (FWPCA)—based on President Johnson's reorganization plan—problems began.

First, there was severe attrition of key personnel. Many of the old-time Public Health Service employees preferred to maintain their status rather than transfer and accept Civil Service status—despite the fact that practically all of the personnel were seriously committed and devoted to cleaning up water pollution.

Then, Interior had to put together its team of water pollution experts which, appropriately, was referred to as the "new, green federal team." They had little, if any, practical experience in trading blows with polluters. In those days, the state people dreaded seeing the federal officials coming.

Since then, federal efforts have been a series of faints and thrusts, most coming without warning. These unilateral actions kept the states defensive, sapped the states' manpower and efforts, and perhaps misdirected considerable attention and energies away from more mundane problems.

The feds have made the pitch for improved federal–state relations again and again. The most recent pitch was made at the meeting of the Association of State and Interstate Water Pollution Control Administrators (ASIWPCA), held in Portland, Ore., late last November.

Basin planning

Today, the biggest problem facing each state is basin planning. No administrator, federal or state, disagrees in principle that the job should be done. State administrators realize that it is a time-consuming and expensive requirement, but what plagues them now is the fact that such planning is a requirement for construction grant funds. FWQA (the Federal Water Quality Administration, formerly FWPCA, and now the Water Quality Office in the Environmental Protection

Agency) has publicly announced in the Federal Register that no funds for waste water treatment facilities would be approved unless they were tied into a comprehensive basin plan. It's a federal requirement much like an earlier requirement for secondary treatment or "no federal funds."

Certainly, state officials do not agree that the requirement for basin planning should be included as an amendment to federal law, as has been suggested by the administration. They argue that such a requirement would merely consume much of the money and manpower needed for more immediate problems, such as day-to-day work on their programs. In their opinion, the commitment of large sums of money for planning is hardly justified at this time.

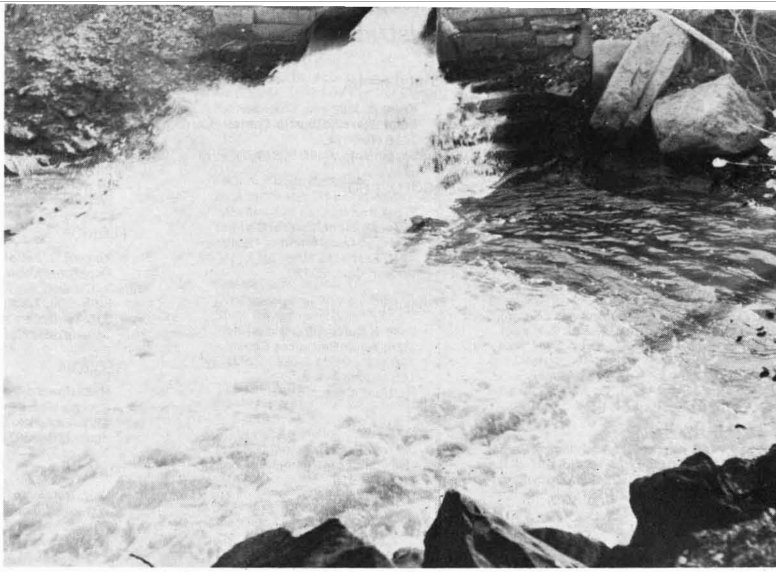
To do the basin planning job in Virginia alone would cost $15 million, says A. H. Paessler, Virginia's water control official. To do justice to the comprehensive planning that should be done is well-nigh impossible at this time, according to Paessler. Similarly, in Texas, $25 million and several years' work would be involved in the plan, estimates Joe Teller, deputy director of the Texas Water Quality Board. Nevertheless, Texas started its basin planning several years ago. The state contracted for the study and has already spent $2.5 million, but the entire basin planning job would take another 10 to 15 years, Joe Teller says.

State administrators from Arizona, Connecticut, Iowa, and New York come out unequivocally in opposition to the idea of basin planning. Others from Colorado, Missouri, New Hampshire, South Dakota, and Texas admit to the desirability of basin planning, but feel that it is a bit unreasonable at this time.

Arizona's spokesman Joseph E. Obr notes that his state does not have any problems with water pollution control that would appear to lend itself readily to the basin approach, with the exception of the salinity problem in the Colorado River Basin.

California's Kerry W. Mulligan regards river basin planning as essential. This is true, he says, whether it is on the interstate rivers, such as the Colorado and Truckee, or on California's intrastate rivers, which include the Sacramento and San Joaquin.

Although Colorado concurs that basin planning is necessary, Colorado's Frank Rozich comments that, with a total population of 25,000 still in need of adequate sewage treatment, "it seems rather asinine to ask these people now to look into basin planning." Any money could be better spent in construction of treatment facilities, says Rozich. A similar situation exists in Wyoming and New Mexico.



Outfall. *Polluted waters continuously empty into the nation's waterways*

On the positive side, Maryland's W. McLean Bingley, chief of the division of water and sewage, says river basin planning is an important part of the state's entire pollution abatement activity. In his opinion, this approach will help to solve problems that Maryland and other states may have in common (or, for that matter, that any group of political jurisdictions may have in common).

Missouri's Jack K. Smith admits that planning could help overcome some pollution problems, but he cautions that no amount of planning is going to make cooperation between cities a reality.

New Hampshire's C. W. Metcalf, director of municipal services, says that basin planning at this time will result in a slowdown of the state's program.

But a resounding voice of approval for this issue is heard from the New York official, Dwight F. Metzler. He notes that relatively small investments in comprehensive planning have yielded big dividends in improved systems at less cost, and have greatly strengthened the regional concept of solving environmental problems. New York already bases its comprehensive planning on the basin approach, according to Metzler.

Financing

Money is often the root of many arguments, and it is no exception in water pollution control. As a nation, the U.S. entered 1970 with a backlog of $4.4 billion in waste treatment needs, according to one FWQA estimate.

The federal promise of $3.4 billion to the states for construction of municipal waste treatment facilities, authorized under the 1966 amendments to the Federal Water Pollution Control Act, simply has not materialized. Slightly more than half ($1.8 billion) has been appropriated by the Congress. Considering that statutory authority for these funds expires this fiscal year, state administrators are wondering what new direction the program will take.

In addition to construction funds, federal funds have been netted out in the past—to the tune of approximately $10 million annually—for states to develop their water pollution control programs. These are provided on a matching basis. By Dec. 1, 1970, for example, some 31 states and three jurisdictions had had their programs approved by the feds; the federal contribution was more than $5.5 million.

One well-founded criticism of the federal role is that construction grant awards were made not on the basis of states' needs, but on a first-come-first-served basis. Another criticism is the lack of guarantee for prefinancing.

Surprisingly, not all states need federal funds. However, a large majority

State and interstate administrators

ALABAMA

Arthur N. Beck, Tech. Sec.
Water Improvement Commission
State Office Bldg., Rm. 328
Montgomery, Ala. 36104

ALASKA

James A. Anderegg, Comm.
Department of Health & Welfare
Pouch H
Juneau, Alas. 99801

ARIZONA

Edmund C. Garthe, Ass't Comm.
Environmental Health Services
Hayden Plaza West
4019 North 33rd Ave.
Phoenix, Ariz. 85017

ARKANSAS

S. L. Davies, Dir.
Arkansas Pollution Control Comm.
1100 Harrington Ave.
Little Rock, Ark. 72202

CALIFORNIA

Kerry W. Mulligan, Chairman
State Water Resources Control Board
1416 Ninth St.
Sacramento, Calif. 95814

COLORADO

Frank Rozich, Dir.
Water Pollution Control Div.
Colorado Department of Health
4210 East 11th Ave.
Denver, Colo. 80220

CONNECTICUT

John J. Curry, Dir.
State Water Resources Comm.
225 State Office Bldg.
165 Capitol Ave.
Hartford, Conn. 06115

DELAWARE

John C. Bryson, Acting Dir.
Division of Environmental Control
P.O. Box 916
Dover, Del. 19901

DISTRICT OF COLUMBIA

Malcolm C. Hope
Assoc. Dir. of Environmental Health
Government of the District of Columbia
1875 Connecticut Ave., N.W.
Universal Bldg., North
Washington, D.C. 20009

FLORIDA

Vincent D. Patton, Exec. Dir.
Department of Air & Water Pollution Control
Suite 300, Tallahassee Bank Bldg.
315 South Calhoun St.
Tallahassee, Fla. 32301

GEORGIA

R. S. Howard, Jr., Exec. Sec.
Georgia Water Quality Board
47 Trinity Ave., S.W.
Atlanta, Ga. 30334

GUAM

O. V. Natarajan, Administrator
Water Pollution Control Program
Public Health & Social Services
Government of Guam
P.O. Box 2816
Agana, Guam 96910

HAWAII

Shinji Soneda, Exec. Off.
Environmental Health Div.
Department of Health
P. O. Box 3378
Honolulu, Hawaii 96801

IDAHO

Vaughn Anderson, Dir.
Engineering & Sanitation Div.
State Department of Health
Statehouse
Boise, Idaho 83707

ILLINOIS

C. W. Klassen, Tech. Sec.
State Sanitary Water Board
State Office Bldg.
400 South Spring St.
Springfield, Ill. 62706

INDIANA

Blucher A. Poole, Tech. Sec.
Stream Pollution Control Board
1330 West Michigan St.
Indianapolis, Ind. 46206

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do. In fact, many have actually prefinanced the needed construction with the hope that part of the outlay would be refunded by the federal government.

Quite obviously, more funds will be needed in the future, and several estimates have been made of just how much money will be required. The Nixon administration says $10 billion is needed in the next five years. The National Association of Counties says $34 billion for the same time span, while the U.S. Conference of Mayors–National League of Cities says $33 to $37 billion over the next six years. The estimates are not directly comparable since different assumptions are made in each, but the need for considerable sums is apparent.

Most states need federal funds, but a few have more than they can use. One state, Colorado, plans to return money to the federal treasury. Another, Iowa, cannot use all the federal funds available to it. A few are satisfied with their share of federal funding. Generally, these are the small states that are neither heavily urbanized nor industrialized, such as Wyoming, South Dakota, and Utah. But most other states are not satisfied.

For heavily industrialized and urbanized areas, particularly in the coastal states—where 75% of the nation's population lives—the federal share has been too little and too late.

Many states still need federal funds to keep their water pollution control programs on schedule. Certainly, the unofficial federal goal—clean water by 1972—will not be reached.

New Hampshire's Metcalf notes that, even with his state's modest prefinancing program, federal funding continues to be inadequate. New York's Metzler says the state is not getting the authorized 30% federal participation, to say nothing of the maximum of 55% Congress had authorized. Of the 481 municipally owned waste water treatment plants in the state, 236 have been upgraded. The rub is that 358 additional plants will be needed to get the whole job done in New York.

Permits

Most states have some type of permit system. But permits differ. Are they for discharges? Construction? Operation? Or all three? For whom? Municipalities or industries, or both?

The states without permit systems include Arizona, California, Colorado, and Wyoming, for example. To say that a state has a permit system is not to imply that the system is exactly the same as that of another state. (Nor, for that matter, does it guarantee that the permit system is enforced, reviewed, or operated at the same level of excellence in any two states.)

But the one big thing that is new to state administrators is a federal requirement for them to pass judgment on construction and operations, so that their state water quality standards are not violated. The new requirement for certification by state officials was contained in the 1970 Water Quality Improvement Act. North Carolina adopted its procedure in this regard on Oct. 13, 1970; other states are in the throes of writing this language into their state laws. Although Arizona does not issue permits for industrial discharges at the present time, rules and regulations requiring permits are being considered.

Rather than a permit system, California has established requirements for waste discharges which include a monitoring program and quarterly monitoring reports. These requirements are periodically reviewed for consistency. Colorado has no type of permit system; Connecticut reviews its permits at no more than five-year intervals; Missouri reviews its permits annually.

States with actual industrial discharge permits include Iowa, Maryland, and Ohio. Others with permits include South Dakota and Texas. But many states having industrial discharge permits simply do not have the necessary manpower to make the system work.

Other states require permits for construction and operation. Florida's new permit rule, which became effective March 3, 1970, requires both construction and operation permits for new facilities and operating permits for preexisting sources of air and water pollution. Operating permits for these sources may be issued temporarily when it is found that the facility does not meet the state pollution control codes. Temporary permits are then issued, provided that the facility will take steps to meet the codes within a reasonable period, which is spelled out in the temporary permit.

In New York, construction permits are issued to an industry for a specific

IOWA

R. J. Schliekelman, Tech. Sec.
Water Pollution Div.
Iowa State Department of Health
Des Moines, Iowa 50319

KANSAS

Melville W. Gray, Chief Eng. and Dir.
Environmental Health Services
Kansas State Department of Health
Topeka, Kan. 66612

KENTUCKY

Ralph C. Pickard, Exec. Dir.
Kentucky Water Pollution Control Comm.
275 East Main St.
Frankfort, Ky. 40601

LOUISIANA

R. A. Lafleur, Exec. Sec.
Louisiana Stream Control Comm.
P.O. Drawer FC, University Station
Baton Rouge, La. 70803

MAINE

William R. Adams, Dir.
Environmental Improvement Comm.
State House
Augusta, Me. 04330

MARYLAND

James B. Coulter, Deputy Sec.
Department of Natural Resources
State Office Bldg.
Annapolis, Md. 21401

Paul W. McKee, Dir.
Maryland Department of Water Resources
State Office Bldg.
Annapolis, Md. 21401

MASSACHUSETTS

Thomas C. McMahon, Dir.
Division of Water Pollution Control
State Office Bldg.
100 Cambridge St.
Boston, Mass. 02202

MICHIGAN

Ralph W. Purdy, Exec. Sec.
Water Resources Comm.
Department of Natural Resources
Stevens T. Mason Bldg.
Lansing, Mich. 48926

MINNESOTA

John P. Badalich, Exec. Dir.
Minnesota Pollution Control Agency
717 Delaware Ave., S.E.
Minneapolis, Minn. 55440

MISSISSIPPI

Glen Wood, Jr., Acting Exec. Sec.
Air & Water Pollution Control Comm.
P.O. Box 827
Jackson, Miss. 39205

MISSOURI

Jack K. Smith, Exec. Sec.
Missouri Water Pollution Board
P.O. Box 154
Jefferson City, Mo. 65101

MONTANA

Claiborne W. Brinck, Dir.
Division of Environmental Sanitation
State Department of Health
Helena, Mont. 59601

NEBRASKA

T. A. Filipi, Sec.
Nebraska Water Pollution Control Council
State House Station, Box 94757
Lincoln, Neb. 68509

NEVADA

Ernest G. Gregory, Chief
Bureau of Environmental Health
Nevada State Health Div.
Nye Bldg., 201 S. Fall St.
Carson City, Nev. 89701

NEW HAMPSHIRE

William A. Healy, Exec. Dir.
Water Supply & Pollution Control Comm.
61 South Spring St.
Concord, N.H. 03301

NEW JERSEY

Richard J. Sullivan, Dir.
Department of Environmental Protection
John Fitch Plaza
P.O. Box 1390
Trenton, N.J. 08625

NEW MEXICO

John R. Wright
New Mexico Health & Social Services Dept.
P.O. Box 2348
Sante Fe, N.M. 87501

NEW YORK

Dwight F. Metzler
New York State Dept. of Environmental Conservation
Albany, N.Y. 12201

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project to treat a specific waste water stream. After a treatment facility is constructed, an application is made for an operation permit. The permit is issued if the facility has been constructed in accordance with the approved report and plans. It's good for five years or less, says New York's Metzler. In many cases, permits are limited to one year or less, because of the types of treatment proposed and their lack of proven success.

Standards

Water quality standards have been a perennial issue, at least since the deadline of June 30, 1967, when they were originally due. All states have standards approved, but they are laced with exceptions. Many basic issues regarding the importance of temperature and dissolved oxygen have not been settled. Consequently, exceptions in standards have not been resolved, despite the fact that resolution was a priority item slated by FWQA for completion by the beginning of 1969.

The first 10 standards were approved with reasonable dispatch. But shortly after the 1967 deadline for state standards, former Secretary of Interior Udall's team of consultants announced its guidelines for criteria (usually referred to as the green book). Then, Interior's interdepartmental task force —comprising other in-house agencies, such as its Bureau of Commercial Fisheries, Bureau of Sport Fisheries and Wildlife, and others—began to look also at state standards. With the green book in hand, Interior's "new, green team" began, in effect, to interpret the guidelines as standards. In any event, the point has been made repeatedly that the task force became the tail wagging the FWQA dog. The result was that standards were then being approved with many exceptions. The exceptions in many standards for dissolved oxygen, temperature, and salinity exist to this day.

One valid complaint of state administrators is that considerable manpower, time, and money were consumed in the discussion of these issues. Of course, during this time, state energies were directed away from the day-to-day water pollution activities.

The question that remains unanswered—if not down right impossible to answer—is how can state administrators pass judgment on certification issues until the basic issues of temperature, dissolved oxygen, and salinity are resolved? Perhaps not until basin plans are completed can we have a standard for a particular body of water. The consensus maintains that states should be permitted to set stricter standards than those indicated in the federal guidelines, perhaps with certain exceptions. Specifically, the exceptions might be in the situation where an industry is one which operates nationally, and where individual state controls would pose a nonuniform standard for the industry in certain states.

Secondary treatment

In the unending round of water pollution control gamesmanship, secondary treatment is an old issue. It stems from the now infamous (to state officials) guideline No. 8, which was only one in a series of unilateral moves that the Johnson administration took. The guideline required treatment of waste waters to a level which would not degrade the quality of the receiving stream. In practice, this has been interpreted by FWQA to mean secondary treatment. Secondary treatment subsequently became a requirement which had to be fulfilled before a state could receive federal construction funds.

Although it was a requirement for funds, secondary treatment is by no means practiced throughout the U.S. Certain coastal states, including California, Massachusetts, and Washington, are to this day exempt from the requirement.

It was the issue of secondary treatment over which the first federal enforcement action was taken against a municipal polluter. As early as 1957, a court decision ordered the city of St. Joseph, Mo., to install secondary treatment facilities for its waste waters. However, according to one official, only 50% of its municipal wastes receive such treatment today.

In an earlier review of water pollution control progress in the U.S. ("Water pollution—coast to coast," ES&T, September 1969, page 804), federal officials noted that several large cities did not provide secondary treatment for their wastes. These included Pittsburgh, Cincinnati, and Louisville. To do so would cost considerable sums of money. There are small towns in Colorado and Utah, for example, that do not presently provide secondary treatment. But on the whole, wastes from these towns are adequately treated.

NORTH CAROLINA

E. C. Hubbard, Ass't. Dir.
Department of Water & Air Resources
P.O. Box 27048
Raleigh, N.C. 27611

NORTH DAKOTA

W. Van Heuvelen, Chief
Environmental Health & Engineering Services
State Department of Health
Bismarck, N.D. 58501

OHIO

George H. Eagle
Water Pollution Control Board
State Department of Health
P.O. Box 118
Columbus, Ohio 43216

OKLAHOMA

Loyd F. Pummill, Chief
Environmental Health Services
3400 North Eastern
Oklahoma City, Okla. 73111

OREGON

Kenneth H. Spies, Dir.
Department of Environmental Quality
1400 S.W. Fourth Ave.
Portland, Ore. 97201

PENNSYLVANIA

Wesley E. Gilbertson, Deputy Sec.
Environmental Protection
Department of Health
P.O. Box 90
Harrisburg, Pa. 17120

PUERTO RICO

Ernesto Colón-Yordán, Sec. of Health
Ponce de Leon Ave.
San Juan, P.R. 00908

RHODE ISLAND

Joseph E. Cannon, Dir. of Health
Division of Water Pollution Control
Rhode Island Department of Health
335 State Office Bldg.
Providence, R.I. 02903

SOUTH CAROLINA

H. J. Webb, Exec. Dir.
S.C. Pollution Control Authority
J. Marion Sims Bldg.
Columbia, S.C. 29201

SOUTH DAKOTA

Charles E. Carl, Dir.
Department of Sanitary Engineering
State Department of Health
Pierre, S.D. 57501

TENNESSEE

S. Leary Jones, Exec. Sec.
Tennessee Stream Pollution Control Board
621 Cordell Hull Bldg.
Sixth Ave., North
Nashville, Tenn. 37219

TEXAS

Hugh C. Yantis, Exec. Dir.
Texas Water Quality Board
1108 Lavaca St.
Austin, Tex. 78701

UTAH

Lynn M. Thatcher, Exec. Sec.
Utah Water Pollution Committee
State Division of Health
44 Medical Dr.
Salt Lake City, Utah 84113

VERMONT

A. William Albert, Dir.
Water Supply & Pollution Control
Department of Water Resources
State Office Bldg.
Montpelier, Vt. 05602

VIRGIN ISLANDS

Roy A. Anduze
Virgin Islands Department of Health
Charlotte Amalie
St. Thomas, V.I. 00802

VIRGINIA

A.H. Paessler, Exec. Sec.
State Water Control Board
P.O. Box 11143
Richmond, Va. 23230

WASHINGTON

James P. Behlke, Dir.
Washington Water Pollution Control Comm.
P.O. Box 829
Olympia, Wash. 98501

WEST VIRGINIA

Edgar N. Henry, Chief
Division of Water Resources
Department of Natural Resources
1201 Greenbrier St., East
Charleston, W. Va. 25311

Colorado's Rozich notes that more than 99% of the state's population connected to some sort of municipal sewer system (1.9 of its 2.2 million people) received secondary treatment with disinfection for its waste before discharge to the streams of Colorado. At the end of 1969, 23 communities with approximately 26,000 people were not providing adequate treatment of their wastes. Other states are not so far along.

Last year, the requirement date for secondary treatment in Missouri was moved up to 1975 from an earlier commitment of 1982. Three of its four largest cities—St. Louis, Kansas City, and St. Joseph—are on the Missouri and Mississippi Rivers and must have secondary treatment by 1975.

In certain instances, secondary treatment is not meeting the Missouri water quality standards. Missouri's official Smith has found instances where effluents from secondary treatment enter underground water supplies. Advanced waste treatment, irrigation, and groundwater recharge are some possible solutions to the problem of discharging secondary treated effluents to low flow and disappearing streams.

Enforcement

If a state fails to enforce its law, then federal enforcement procedures can be applied. But these procedures are cumbersome and time consuming ("Water polluters: beware the feds!" ES&T, November 1970, page 887). There is a long delay before the federal government can come in and bring a recalcitrant polluter to terms. On the other hand, state officials can generally bring polluters to terms with reasonable dispatch, if they are so inclined.

Enforcement is only one of many priorities of the new EPA. To be sure, enforcement procedures must be firm, fair, and applied uniformly. Perhaps more important is the federal presence, the federal backup, which must become more apparent to state administrators as we move into the seventies—the environmental decade.

Enforcement may be uppermost in the minds of federal officials, but this hardly is true for state administrators. They contend that the yardstick for success of the nation's water pollution abatement effort cannot be measured by the number of enforcement actions that the federal officials file in court. Most state administrators would prefer administrative procedures to the filing of court suits. They argue that the state is the primary enforcement and coordinating agency in dealing with local governments and industry.

Most states are already involved with federal enforcement conference proceedings; nine are not. In the past year, Arizona's enforcement activities included several written orders of abatement. Three involved surface discharge of wastes from septic tank systems serving tourist facilities; others were against a copper rod and wire company, a paper mill, and a trailer park.

One state, California, has enforcement uppermost in its mind. For example, one of the key features of its Porter Cologne Act, which went into operation Jan. 1, 1970, is its strict enforcement provisions. Los Angeles' Hertler notes that the majority of his enforcement actions are secured administratively—that is, by the staff working with the discharger to perform the needed correction. When other actions are necessary, the board issues cease and desist orders, examples of which are recent orders against the Union Pacific Railroad Co. and the Saticoy Meat Packing Co.

Colorado is in the throes of setting abatement dates for violators of state laws and standards. Rozich notes that since the Colorado Water Pollution Control Commission was established in 1966, it has issued 80 to 100 cease and desist orders. It hasn't forced any industry to go out of business, but it has forced them to install adequate waste treatment facilities.

In Florida, there have been two federal–state enforcement conferences; one was called to discuss the interstate problems of Escambia and Perdido Bays in the far western portion of the state. A number of industrial and municipal sources of pollution were singled out, but many were already under notices and orders from the Florida Department of Air & Water Pollution Control. As of last September, state and federal officials were satisfied with progress being made. Satisfaction, however, is not being expressed in the second conference. The conference was called to consider the potential for thermal pollution in Biscayne Bay from a nuclear power generation facility under construction by Florida Power & Light Co. Results of this conference were inconclusive, at best.

WISCONSIN

Thomas G. Frangos, Administrator
Division of Environmental Protection
Department of Natural Resources
P.O. Box 450
Madison, Wis. 53701

WYOMING

Arthur E. Williamson, Dir.
Sanitary Engineering Services
Division of Health & Medical Services
Wyoming Department of Health & Social Services
State Office Bldg.
Cheyenne, Wyo. 82001

Interstate administrators

DELAWARE RIVER BASIN COMMISSION

James F. Wright, Exec. Dir.
Delaware River Basin Commission
P.O. Box 360
Trenton, N.J. 08603

GREAT LAKES COMMISSION

L. J. Goodsell, Exec. Dir.
5104 First Bldg.
2200 N. Campus Blvd.
Ann Arbor, Mich. 48105

INTERSTATE COMMISSION ON THE POTOMAC RIVER BASIN

Carol J. Johnson, Exec. Dir.
407 Global Bldg.
1025 Vermont Ave., N.W.
Washington, D.C. 20005

INTERSTATE SANITATION COMMISSION

Thomas R. Glenn, Jr., Dir. and Chief Eng.
Interstate Sanitation Commission
10 Columbus Circle
New York, N.Y. 10019

NEW ENGLAND INTERSTATE WATER POLLUTION CONTROL COMMISSION

Alfred E. Peloquin, Exec. Sec.
73 Tremont St., Rm. 950
Boston, Mass. 02108

OHIO RIVER VALLEY WATER SANITATION COMMISSION

Robert K. Horton, Exec. Dir.
414 Walnut St., Rm. 302
Cincinnati, Ohio 45202

Georgia's most recent enforcement action involved prosecution of a textile firm in 1969. The firm was ordered to clean up or close up. The plant elected to build an adequate treatment plant. Approximately 10 other cases have been referred to the state's attorney general by the Georgia State Water Quality Board.

Normally, the Iowa Water Pollution Control Commission takes action on four to five municipalities monthly, but its spokesman notes that the majority of improvements are made by industry and municipalities "on a voluntary basis."

Missouri's Smith comments that there is a lack of continuity in enforcement. He says that the attorney for the Missouri water pollution control board is a part-time employee of the state attorney general's office. The election of a new attorney general every four years results in the appointment of a new attorney general to work with the board.

New Hampshire's recent statewide effort to abate water pollution includes provisions in its law for review and approval of all sewage disposal facilities to be installed within 1000 ft of surface waters. In New York, assorted cases are routinely referred to the counsel's office within the New York Department of Environmental Conservation. Paper mill and cannery operations are the types of polluters most frequently singled out. These unilateral actions do not involve federal officials. Like Florida, Ohio is involved with two federal–state enforcement conferences, one on Lake Erie and the other on Mahoning River. South Dakota has not taken actions for years.

Industries

From state to state across the country, administrators' biggest headaches with specific industries vary. Pulp and paper are particularly troublesome for administrators of Arizona, California, Georgia, New York, Florida, and Oregon. In the midwest and southwest, agriculture is bothersome. Meat packing and milk processing industries were specified by the Iowa official; milk processing, along with mine processing, also was the major concern of the South Dakota official. Agricultural problems have been handled satisfactorily in Texas. Sugar refineries and canning operations are Utah's problems; steel is a big concern in Ohio, with chemicals running a close second, and the pulp and paper industry third.

The majority of Arizona's industry is located in metropolitan Phoenix and Tucson. These cities impose rigid sewer service agreements on their industries before permitting them to discharge into the municipal system. Mining, another major industry in the state, is a good neighbor. In general, the mines hoard their water very carefully with extensive recycling; none has a continuous discharge to any watercourse.

Old refineries, along with industries that handle toxic materials, present the biggest headache for California. Its personnel is working to ensure that industry pays its fair share when a municipality handles its waste.

In Florida, the entire paper industry—with the exception of one mill—the citrus industry, the phosphate mining and processing industry, and most of the chemical industries are on notices and orders of the Florida Department of Air & Water Pollution Control to correct their pollution. Progress is satisfactory, according to state officials.

Georgia's biggest headache comes from Kraft paper and pulp mills, the largest industry in the state. Most plants provide their own treatment, Howard says. Food processors and textile mills are others which present pollution difficulties.

Major industries which present problems in Iowa are the meat packing and milk products industries. Half of the meat packing industries' load (equivalent to a population of 3.8 million persons) is treated in municipal plants. But Iowa's Schliekelman says that there may be some instances in which the industry is not paying an equitable share of treatment cost.

In New York, the paper industry, as a group, is further behind on correcting its pollution than any other industry. There have been few treatment plants built to handle the waste water discharges from the paper industry. The food industry also has problems which involve the dairy and canning groups particularly. The problems arise from unsatisfactory treatment systems as well as from unsatisfactory operation of adequate systems.

Steel, chemicals, and pulp and paper are the major industrial polluters in Ohio. Most chemical companies in the state provide treatment for wastes, but none has closed its water loop.

In Oregon, the pulp and paper industry is again the number-one pollution problem. Last September, only five of the nine mills in the state had secondary treatment and chemical recovery systems. Another had chemical recovery alone. The remainder three have until July 1972 to complete installation of recovery systems and secondary treatment. Then, the overall reduction in BOD will be 90 to 94%.

Agriculture is the root of Texas' problems. But progress is noteworthy. Agricultural wastes are impounded in Texas. No discharge is made to any stream within the state.

In Utah, troublesome wastes are produced by sugar refineries, canning factories, milk processing operations, and slaughterhouse operations. Installations which discharge inorganic materials, which are generally lumped into the term salinity, also create problems for Utah officials.

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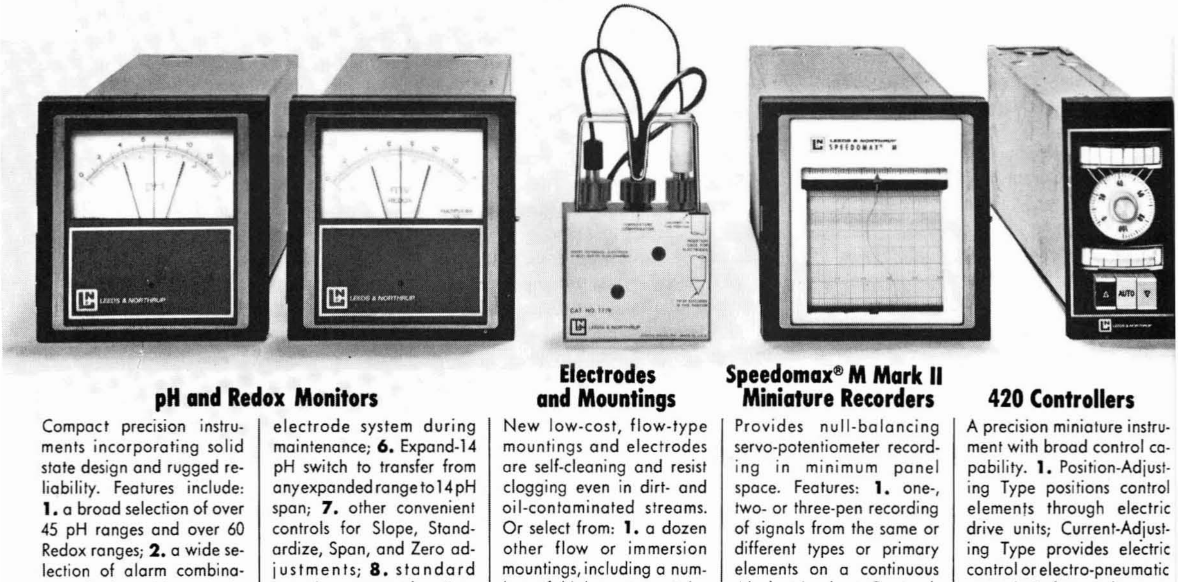

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Method for Determination of Reaction Rates of Carbon Dioxide with Water and Hydroxyl Ion in Seawater

Ronald F. Miller[1] **and David C. Berkshire**[2]
Department of Oceanography, Texas A&M University, College Station, Tex. 77843

John J. Kelley and Donald W. Hood
Institute of Marine Science, University of Alaska, College, Alas. 99701

■ The theory of the kinetics of pH change in solutions containing carbon dioxide and in contact with a gas phase is developed. A technique is described by which the rate of pH change in a vigorously bubbled sample of artificial seawater is used to calculate the rate constants for the reactions of carbon dioxide with water and hydroxyl ion in that solution. Variations in the effective constants with temperature and chlorinity are given, and the results are related to the disputed values for the second dissociation constant of carbonic acid in seawater. The rate constants suggest that the role of the hydroxyl ion reaction is more important at the ordinary pH of the sea than had previously been thought.

The kinetics of the reactions of molecular CO_2 with water and hydroxyl ions have been the subject of extensive research. It was discovered early that the hydration reaction

$$CO_2 + H_2O \underset{\kappa-1}{\overset{\kappa 1}{\rightleftharpoons}} H_2CO_3 \qquad (1a)$$

is relatively slow compared with interconversions among what we shall term the carbonate system, H_2CO_3, HCO_3^-, and $CO_3^=$. Thiel (1922) first gave an accurate estimate of the rate constant of this reaction. A second reaction, significant only at higher pH values,

$$CO_2 + OH^- \underset{\kappa-2}{\overset{\kappa 2}{\rightleftharpoons}} HCO_3^- \qquad (1b)$$

was found to be another mechanism by which molecular CO_2 could be converted into the carbonate forms. Although Koefoed and Engle (1961) have indicated the possibility of short-lived intermediates in these reactions, the simple kinetics implied in 1a and 1b have proved sufficient for most biological and physical studies. Reliable pure-water values for these two rate constants, κ_1 and κ_2, are given by Pinsent *et al.* (1956); a review of the literature is given by Kern (1960).

Unfortunately, the kinetics of these reactions in complex salt solutions have not been thoroughly investigated. Mills and Urey (1940) studied simple salt solutions and found small variations in κ with variations in ionic strength. Pinsent *et al.* (1956) published results on variations of κ_2 with variations in the ionic strength of buffer solutions. However, the fact that operational values of κ_1 and κ_2 in seawater are unknown is detrimental to studies in which conclusions are dependent upon an estimate of these constants—*e.g.*, physiological or gas-transfer work. For example, Bolin (1960), in his theoretical discussion of two-film transfer of CO_2 at sea, has assumed values in seawater equal to those in pure water. A radical alteration in the values of either of the constants might invalidate certain of his conclusions. Hood and Park (1962), in concluding the availability of molecular CO_2 to plant life in seawater of average to high pH, assumed a value for the hydration constant considerably smaller than the accepted value for pure water. Some questions were raised by Hood (1963) on work done in Batabano Bay, Cuba, in which directly measured and calculated pCO_2 values gave vastly different results, and also by Supernaw (1963), whose work with a rich *Platymonas* sp. culture in seawater suggested a possible absence of equilibrium between molecular and ionic forms of CO_2—which raises the possibility of anomalously low values for these constants in the sea.

A new experimental method involving the monitoring of pH in a portion of seawater being swept by a gas was devised to measure these constants. With sufficiently high sweeping rates, the rate of change of the pH, being a function of the rate of loss or gain of CO_2 relative to its ionic forms, could be used to determine the rates of reactions 1a and 1b. The method was chosen for several reasons. First, the necessary equipment is simple, and the method, unlike several previous

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[1] Present address, University of Connecticut, Storrs, Conn. 06268.
[2] Present address, Shell Development Co., Houston, Tex. 77001.

techniques, is easily adaptable to work with seawater. Second, when the question of maximal gas stripping arose (Hood and Park, 1962), this method offered a means for investigating the phenomenon. Third, the actual nonequilibrium interconversions between the carbonic species, when this method is used, are strikingly similar to the interconversions that would take place in a supposed boundary layer in a model of two-film transfer of CO_2 between the atmosphere and the sea; therefore this method promised to yield operational constants that could be used in actual transfer calculations.

Definitions of Symbols

(A) = activity or concentration of species A in solution

$(A)_g$ = activity or concentration of species A in gas phase

$\kappa_1, \kappa_2, \kappa_3$ = rate constants defined in 1a, 1b, and 1c, respectively

K_h = equilibrium constant for 1a

K_p = equilibrium (or partition) constant for 1c = $(CO_2)_g/(CO_2)$

K_w = ion product of water = $(H+)(OH-)$

K_1 = $[(H^+)(HCO_3^-)]/(CO_2)$, first dissociation constant of carbonic acid

K_2 = $[(H^+)(CO_3^{2-})]/(HCO_3^-)$, second dissociation constant of carbonic acid

The usual seawater definition of the "apparent K_1" is $K_1' = [(H^+)(HCO_3^-)]/[(CO_2) + (H_2CO_3)]$, because this is all that can be determined in complex solutions. It is easily shown that the constant used in this paper is related to this "apparent constant" by

$$K_1 = K_1' (1 + K_h)$$

Since $K_h \simeq 2 \times 10^{-3}$, however, K_1 and K_1' are identical within the limits of accuracy of the present technique, and were assumed to be so.

Theoretical Treatment

In any aqueous solution containing CO_2, the molecular form takes part in Reactions 1a and 1b. In addition, whenever that solution is in contact with a gaseous phase, another reaction, the transfer of molecular CO_2 between phases, also occurs

$$CO_2 \text{ (solution, liquid phase)} \underset{\kappa_{-3}}{\overset{\kappa_3}{\rightleftharpoons}} CO_2 \text{ (gas phase)} \quad (1c)$$

If the phases are thoroughly mixed, the relationship between these reactions can be schematically indicated by Figure 1, which suggests the differential equation

$$\frac{d}{dt}(CO_2) = -\kappa_1(CO_2) + \frac{\kappa_1}{K_h}(H_2CO_3) - \kappa_2(OH^-)(CO_2) + \frac{\kappa_2 Kw}{K_1}(HCO_3^-) - \kappa_3(CO_2) + (\kappa_3/K_p)(CO_2)_g \quad (2a)$$

(A) is used in the same practical sense as in the definition of K_1 and K_2. For a complex solution such as seawater, concentrations are used for the carbonic species, and activity as defined by pH measurements is used for hydrogen ion. Consequently, the rate constants derived are not to be thought of as "molecular" or "real" in any sense, but only as operative constants to be used in calculations under specific conditions—*e.g.*, the calculations in Bolin (1960). Upon rearrangement, 2a may be written

$$\frac{d}{dt}(CO_2) = -\left[\kappa_1 + \frac{\kappa_2 K_w}{(H^+)}\right]\left[(CO_2) - \frac{(H^+)(HCO_3^-)}{K_1}\right] - \kappa_3\left[(CO_2) - \frac{(CO_2)_g}{K_p}\right]$$

Defining $\phi = \kappa_1 + [(\kappa_2 Kw)/(H^+)]$, and substituting into 2b with rearrangement

$$(CO_2) = \frac{1}{(1+\phi)/\kappa_3}\left\{\frac{(CO_2)_g}{K_p} + \frac{1}{\kappa_3}\left[\frac{\phi}{K_1}(H^+)(HCO_3^-) - \frac{d}{dt}(CO_2)\right]\right\} \quad (3a)$$

which can be simplified if a quasi-steady state is assumed. That is, a glance at Figure 1 will make this clearer, if the rate of change of concentration of molecular CO_2 is small compared to the rate at which it is being produced from the carbonate forms, the last term in 3a is negligible compared to the term from which it is subtracted, and we can write

$$(CO_2) = \frac{1}{(1+\phi)/\kappa_3}\left[\frac{(CO_2)_g}{K_p} + \frac{\phi}{\kappa_3 K_1}(H^+)(HCO_3^-)\right] \quad (3b)$$

The steady-state approximation is valid if sufficient time is allowed after inception of gas contact for the rapid transient changes to go to completion and if the molecular CO_2 is only a very small fraction of the total CO_2 (ionic and nonionic) in the solution. The experimental conditions were designed to meet these specifications.

Examination of 2b with reference to Figure 1 shows that the first term on the right is actually the net loss or gain of molecular CO_2 through exchange with carbonate species, while the second term is the equivalent loss or gain through transfer between phases. Thus, the rate of change of the carbonate species can be written by inspection.

$$\frac{d}{dt}[(H_2CO_3) + (HCO_3^-) + (CO_3^{2-})] = \left[\kappa_1 + \frac{\kappa_2 Kw}{(H^+)}\right]\left[(CO_2) - \frac{(H^+)(HCO_3^-)}{K_1}\right] \quad (4)$$

Substitution of 3b into 4 yields, after algebraic manipulation,

$$\frac{d}{dt}[(H_2CO_3) + (HCO_3^-) + (CO_3^{2-})] = \frac{\phi}{(1+\phi)/\kappa_3}\left[\frac{(CO_2)_g}{K_p} - \frac{(H^+)(HCO_3^-)}{K_1}\right] \quad (5a)$$

This may be reduced to an equation in one free variable if the concept of alkalinity is introduced. It can be shown that if the carbonate species are in equilibrium with each other, their concentrations may be written in terms of (H^+) and carbonate alkalinity,

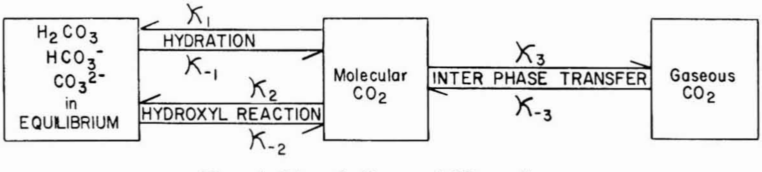

Figure 1. Schematic diagram of CO_2 reactions

$$A_c = (HCO_3^-) + 2(CO_3^{2-})$$

A full discussion of this is in Riley and Skirrow (1965) and Harvey (1957). We can write

$$(H_2CO_3) + (HCO_3^-) + (CO_3^{2-}) = A_c\left[\frac{K_h(H^+)^2 + K_1(H^+) + K_1K_2}{K_1(H^+) + 2\,K_1K_2}\right]$$

Then

$$\frac{d}{dt}\left[A_c \cdot \frac{K_h(H^+)^2 + K_1(H^+) + K_1K_2}{K_1(H^+) + 2\,K_1K_2}\right] = \frac{\phi}{(1+\phi)/\kappa_3}\left[\frac{(CO_2)_g}{K_p} - \frac{A_c(H^+)^2}{K_1(H^+) + 2K_1K_2}\right] \quad (5b)$$

This can be forced into symetrical form by introduction of the quantity $(H^+)_e$, the hydrogen ion activity that the solution would indicate were it in CO_2 equilibrium with the gas phase. Since at equilibrium

$$\frac{(CO_2)_g}{K_p} = (CO_2) = A_c\,\frac{(H^+)_e^2}{K_1(H^+)_e + 2K_1K_2}$$

5b can be written

$$\frac{d}{dt}\left[\frac{A_c}{K_1}\cdot\frac{K_h(H^+)^2 + K_1(H^+) + K_1K_2}{(H^+) + 2K_2}\right] = \frac{\phi\,A_c}{K_1[(1+\phi)/\kappa_3]}\left[\frac{(H^+)_e^2}{(H^+)_e + 2K_2} - \frac{(H^+)^2}{(H^+) + 2K_2}\right] \quad (5c)$$

If there are no salts of other weak acids present, the carbonate alkalinity is identical to the total alkalinity, which cannot be changed by contact with a gas phase containing only unreactive gases and CO_2 ("conservation of charge"). Thus, A_c can be cancelled from both sides of 5c and the expression differentiated. This yields, after noting the definition of pH and after collecting the terms on the right,

$$\frac{-d}{dt}\log_{10}(H^+) = \frac{dpH}{dt} = \frac{0.4343}{(H^+)}\left[\frac{\phi}{(1+\phi)/\kappa_3}\right]\frac{[(H^+) + 2K_2]^2}{K_h(H^+)^2 + 4K_hK_2(H^+) + K_1K_2} \times \left[\frac{(H^+)^2}{(H^+) + 2K_2} - \frac{(H^+)_e^2}{(H^+)_e + 2K_2}\right] \quad (6)$$

This final form provides a means by which we may relate a measured dpH/dt to ϕ, and so to κ_1 and κ_2, provided the rest of the terms in the expression can be determined.

Technique

An apparatus was constructed to measure dpH/dt *vs.* pH on a sample of seawater being bubbled vigorously with either bottled air (300 to 600 p.p.m. of CO_2) or CO_2 free nitrogen. A schematic drawing of the setup is presented in Figure 2.

Into a 10-cm. sintered-glass filter was poured a 50- to 200-ml. portion of artificial seawater. This water, of either 17, 19, or 22% chlorinity, was made up according to the specifications of Lyman and Fleming (1940), excluding all carbonate and borate species and all salts below KCl on their list. Carbonate alkalinity was added immediately before inception of an experiment by means of a microburet containing 0.5*M* Na_2CO_3 solution. By late addition of the carbonate, the danger of precipitation of $CaCO_3$ from the sometimes supersaturated solutions was lessened. The temperature of the water was held to ±0.2°C. excursions by placing the filter in a constant-temperature bath, and the temperature of the seawater was repeatedly checked with a 0° to 50°C. calibrated thermometer.

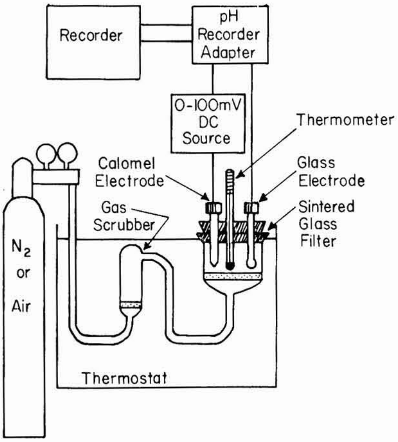

Figure 2. Schematic diagram of apparatus

Air Swept Runs. Whenever a determination of dpH/dt was desired at higher pH values, the carbonate was added to the aliquot and the solution stirred by a stream of nitrogen until a stable pH reading was attained (transferring CO_3^{2-} to OH^- by removal of CO_2). The solution was then swept by a flow of bottled air and the pH recorded continuously until the rate of change became too small for accurate measurement. After this, the bubbling was contained until the pH approached the equilibrium value, as evidenced by two successive pH measurements taken 1 hr. apart and differing by less than 0.01 pH unit. By varying the flow rate, alkalinity, and volume of solution, a series of pH *vs.* time plots were recorded.

Nitrogen Swept Runs. For a study of behavior at lower pH, carbonate was added and the solution was swept by pure CO_2 gas until the pH dropped below 6, at which time a stream of pure N_2 was passed through the liquid, and the pH recorded continuously to about pH 9. It might be expected that raising the pH by sweeping with N_2 would precipitate either $Mg(OH)_2$ or $CaCO_3$, or both. Such was the case for some runs at a very high alkalinity, but precipitation was clearly indicated by a sharp break in the pH-against-time trace. Data beyond such a point were discarded. Also, solutions were inspected for opalescence as an indication of precipitation. Since the equilibrium pH against a nitrogen gas phase would be so high, the equilibrium hydrogen-ion activity, $(H^+)_e$, in Equation 6 was assumed to be zero, and no attempt was made to achieve equilibrium. As in the case of the air-swept runs, a series of experiments at widely divergent flow rates, alkalinities, and liquid volumes was obtained at a single temperature and chlorinity.

The air and nitrogen used during the recorded pH changes were passed first through synthetic seawater in a sintered-glass gas washing bottle to bring them close to equilibrium with respect to temperature and water vapor pressure. The gas flow was always sufficient to avoid a residuum of contaminating gas in the train during actual data gathering. Water-pumped nitrogen was used and compressed air was supplied from a single bottle used throughout any one temperature–chlorinity series. With the equilibrium pH for a single alkalinity, it is possible to calculate the equilibrium pH for any alkalinity, if the gas phase remains unchanged; therefore, there exists a means for testing the various equilibrium pH values for internal consistency.

After each trace, the filter was rinsed with distilled water and dried with N_2 gas. Occasional rinsings with dilute HNO_3 dissolved any solid $CaCO_3$ that might trigger further precipitation. All pH measurements were taken with a specially designed Beckman low-temperature glass electrode, a standard palladium-junction calomel electrode, and a Sargent S-72172 pH recorder adapter. The glass electrode, a specially constructed large surface area-type, stabilized rapidly at or below 0°C. so that its response at all higher temperatures was instantaneous. The calomel electrode used was a Beckman Model 39270. Recordings of the traces were made on a Sargent SR mV recorder. The electrodes were standardized with Beckman 7 and 9 buffers [K–Na phosphates and ($Na_2B_4O_7$) solutions], and measurements were made by interpolation, setting full scale on the recorder as 1.25 pH units. A 1- to 100-mV dc source in series with the electrodes allowed excursions of greater than 1.25 pH units. Since measurements were made in a vigorously agitated medium, the familiar "stirring effect" was noticed. By measurements in alternately quiet and bubbled solutions, the effect was discovered to be +0.02 pH units, independent on the vigor of bubbling or the absolute pH range. Therefore, all pH readings were decreased 0.02 unit before processing of the data.

The slope of the pH *vs.* time curve was determined by estimation of the tangent with a straight edge. The noise concomitant with bubbling did not allow the smooth curve that would permit more sophisticated techniques of tangent estimation. Tangents were measured at close 0.05 to 0.10 pH unit intervals to minimize random errors. The only points discarded were those lying far off a smooth curve drawn through a plot of the raw data. Several observers did tangent determinations to avoid personal bias.

Preliminary Results and Data Processing

Defining $\tau = \phi/(1 + \phi/\kappa_3)$, Equation 6 may be rearranged to

$$\tau = 2.303(\mathrm{H}^+)\left(\frac{dph}{dt}\right)\cdot\frac{K_h(\mathrm{H}^+)^2 + 4K_hK_2(\mathrm{H}^+) + K_1K_2}{[(\mathrm{H}^+) + 2K_2]^2}\cdot \left[\frac{(\mathrm{H}^+)^2}{(\mathrm{H}^+) + 2K_2} - \frac{(\mathrm{H}^+)_e^2}{(\mathrm{H}^+)_e + 2K_2}\right]^{-1} \qquad (7)$$

This expression involves dph/dt and $(\mathrm{H}^+)_e$, both experimentally determinable; K_1 and K_2, constants for which values can be obtained from other work; and K_h, a constant whose size (about 10^{-8}) makes terms containing it negligible in evaluations about pH = 7. Therefore, τ can be calculated. Unfortunately, κ_3, the gas–liquid transfer coefficient, varies in an unknown manner with stirring conditions, volume, temperature, and chlorinity; hence, we cannot directly calculate ϕ from τ. Were the κ_3 sufficiently large, however, τ and ϕ would be identical, and a plot of τ *vs.* $(\mathrm{H}^+)^{-1}$ would be a straight line, the slope of which would be κ_2Kw, and the intercept, κ_1. This follows from the definition of ϕ.

To determine ϕ in actual practice, we utilize the fact that ϕ must in theory be a linear function of $(\mathrm{H}^+)^{-1}$. If variables such as temperature, gas flow, and chlorinity remain constant throughout a single trace, there must exist one κ_3 such that the ϕ's calculated from the trace

$$\phi = \frac{\tau}{(1 + \tau)/\kappa_3} \text{ rearranging Equation 7} \qquad (8)$$

lie within experimental error upon a straight line. Sample calculations showed that standard deviations for least-square fitted straight lines exhibit strong minima within narrow ranges of κ_3. For each trace, the κ_3 at which this minimum occurs is the "correct" one, and the slope and the intercept of the least-squares line corresponding to that κ_3 are assumed to be results in a determination of κ_2K_w and κ_1. Figure 3 shows the τ's calculated from a set of three traces with the corresponding best experimental ϕ's calculated by minimizing the deviations from the straight lines. Although the different traces produced τ's lying along three different curves, the corresponding ϕ's resulting from the three best κ_3's lie very close to a single straight line. Since the three traces in Figure 3 correspond to different purging rates and alkalinities, it seems unlikely that the agreement after correction is fortuitous.

The experimental conditions provided a further refinement. Under fixed temperature and chlorinity, the experiments could be divided into two subgroups of traces, one in the high pH range and one in the low. The lower pH traces, in whose range the hydroxyl reaction was negligible, were largely measures of κ_1, whereas the higher pH region traces were primarily dependent on κ_2K_w. A computer program was set up to take advantage of these differences.

After calculating the τ's corresponding to both the high and low pH traces, the computer was given a tentative value for the intercept. Singling out the high pH runs, the computer determined the slope and κ_3 corresponding to the best least squares for each trace line passing through the tentative intercept and approximating the ϕ's calculated from that trace. The computer was programmed to hunt out the best κ_3 for each trace until successive approximations had produced less than 1% change in the standard deviation of the ϕ's from the tentative lines. After all the high pH traces had been processed, the mean of the best slopes was taken. This slope was then used to calculate those intercepts and κ's which give the best least-squares lines having that mean slope and approximating the ϕ's calculated from the individual low-pH runs. The same 1% criterion was used in hunting the best κ_3's, and the mean of

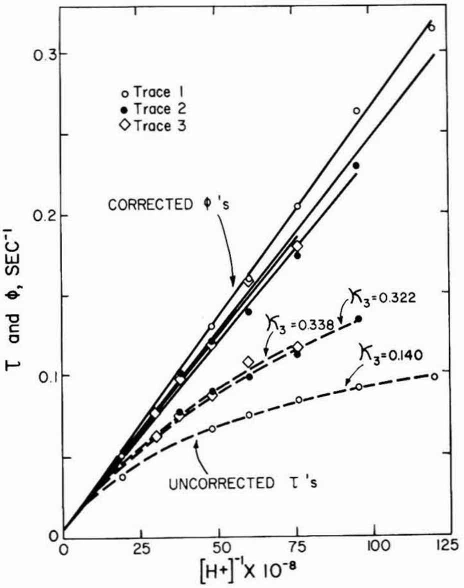

Figure 3. **Values of τ and ϕ calculated from three traces at 9.5°C. and 19% chlorinity, using the constants of Lyman**

Table I. Results of Individual Traces for Various Values of Temperature and Chlorinity

A. Temperature: 9.5°C.
Chlorinity: 19%

Average κ_1(Lyman): 0.53 × 10^{-2}sec.$^{-1}$
Average $\kappa_2 K_w$(Lyman): 0.244 × 10^{-10}sec.$^{-1}$

Average κ_1(Buch): 0.896 × 10^{-2}sec.$^{-1}$
Average $\kappa_2 K_w$(Buch): 0.255 × 10^{-10}sec.$^{-1}$

Low pH series

		Lyman			Buch		
Trace	No. points	κ_1 ×10^2sec.$^{-1}$	κ_3 ×10^2sec.$^{-1}$	Standard deviation, %	κ_1 ×10^2sec.$^{-1}$	κ_3 ×10^2sec.$^{-1}$	Standard deviation, %
1	9	0.555	0.040	4.3	0.862	0.143	3.2
2	8	0.518	0.134	4.5	0.862	2.900	4.0
3	8	0.530	0.110	5.1	0.879	2.900	4.8
4	11	0.540	2.038	3.9	0.982	2.900	6.4

High pH series

		$\kappa_2 K_w$ × 10^{10}sec.$^{-1}$	κ_3 × 10^2sec.$^{-1}$		$\kappa_2 K_w$ × 10^{10}sec.$^{-1}$	κ_3 × 10^2sec.$^{-1}$	
1	6	0.262	0.140	4.1	0.283	0.118	2.8
2	5	0.231	0.322	5.2	0.233	0.261	6.4
3	5	0.239	0.338	3.7	0.248	0.263	4.3

B. Temperature: 19.0°C.
Chlorinity: 19%

Average κ_1 (Lyman): 1.67 × 10^{-2}sec.$^{-1}$
Average $\kappa_2 K_w$ (Lyman): 0.99 × 10^{-10}sec.$^{-10}$

Average κ_1 (Buch): 2.71 × 10^{-2}sec.$^{-1}$
Average $\kappa_2 K_w$ (Buch): 1.22 × 10^{-10}sec.$^{-1}$

Low pH series

		Lyman			Buch		
Trace	No. points	κ_1 ×10^2sec.$^{-1}$	κ_3 ×10^2sec.$^{-1}$	Standard deviation, %	κ_1 ×10^2sec.$^{-1}$	κ_3 ×10^2sec.$^{-1}$	Standard deviation, %
1	6	1.71	0.352	3.3	2.78	0.818	3.0
2	6	1.63	0.385	6.8	2.64	1.081	4.6

High pH series

		$\kappa_2 K_w$ × 10^{10}sec.$^{-1}$	κ_3 × 10^2sec.$^{-1}$		$\kappa_2 K_w$ × 10^{10}sec.$^{-1}$	κ_3 × 10^{10}sec.$^{-1}$	
1	7	0.99	0.667	5.7	1.22	0.495	5.5
2	7	0.90	0.483	3.2	1.14	0.342	3.4
3	5	1.08	0.568	5.9	1.31	0.460	8.3

C. Temperature: 29.8°C.
Chlorinity: 19%

Average κ_1 (Lyman): 4.73 × 10^{-2}sec.$^{-1}$
Average $\kappa_2 K_w$ (Lyman): 5.45 × 10^{-10}sec.$^{-1}$

Average κ_1 (Buch): 7.14 × 10^{-2}sec.$^{-1}$
Average $\kappa_2 K_w$ (Buch): 7.18 × 10^{-10}sec.$^{-1}$

Low pH series

		Lyman			Buch		
Trace	No. points	κ_1 ×10^2sec.$^{-1}$	κ_3 ×10^2sec.$^{-1}$	Standard deviation, %	κ_1 ×10^2sec.$^{-1}$	κ_3 ×10^2sec.$^{-1}$	Standard deviation, %
1	5	6.36	0.609	16.9	9.49	0.712	16.5
2	6	4.25	0.902	18.3	6.43	1.012	17.4
3	6	3.58	0.983	12.7	5.48	1.087	12.2

High pH series

		$\kappa_2 K_w$ ×10^2sec.$^{-1}$	κ_3 ×10^2sec.$^{-1}$		$\kappa_2 K_w$ ×10^2sec.$^{-1}$	κ_3 ×10^2 sec.$^{-1}$	
1	6	5.20	0.688	3.4	6.85	0.699	4.3
2	5	6.04	0.684	1.9	8.05	0.682	2.3
3	7	5.11	0.900	2.2	6.65	1.001	2.4

D. Temperature: 19.8°C.
Chlorinity: 17%

Average κ_1 (Lyman): 1.56 × 10^{-2}sec.$^{-1}$
Average $\kappa_2 K_w$ (Lyman): 0.99 × 10^{-10}sec.$^{-1}$

Average κ_1 (Buch): 2.66 × 10^{-2}sec.$^{-1}$

Low pH series

		Lyman			Buch		
Trace	No. points	κ_1 ×10^2sec.$^{-1}$	κ_3 ×10^2sec.$^{-1}$	Standard deviation, %	κ_1 ×10^2 sec.$^{-1}$	κ_3 ×10^2sec.$^{-1}$	Standard deviation, %
1	7	1.43	0.890	6.2	2.41	3.350	5.1
2	9	1.57	3.350	8.0	2.72	3.350	7.8
3	9	1.68	3.350	6.6	2.87	3.350	6.9
4	9	1.55	2.091	7.9	2.66	3.350	6.7

High pH series

		$\kappa_2 K_w$ ×10^{10}sec.$^{-1}$	κ_3 ×10^2sec.$^{-1}$		$\kappa_2 K_w$ ×10^{10}sec.$^{-1}$	κ_3 ×10^2 sec.$^{-1}$	
1	10	0.96	1.808	3.5	1.15	0.826	4.5
2	11	1.02	0.998	4.4	1.24	0.574	6.6

(*Continued on page 132*)

(*Continued from page 131*)

E. Temperature: 19.8 °C. Average κ_1 (Lyman): 1.54 × 10^{-2}sec.$^{-1}$ Average κ_1 (Buch): 2.80 × 10^{-2}sec.$^{-1}$
Chlorinity: 22% Average $\kappa_2 K_w$ (Lyman): 1.40 × 10^{10} sec.$^{-1}$ Average $\kappa_2 K_w$ (Buch): 1.73 × 10^{-10}sec.$^{-1}$

		Low pH series					
		Lyman				Buch	
Trace	No. points	$\kappa_1 \times 10^2$sec.$^{-1}$	$\kappa_3 \times 10^2$sec.$^{-1}$	Standard deviation, %	$\kappa_1 \times 10^2$sec.$^{-1}$	$\kappa_3 \times 10^2$sec.$^{-1}$	Standard deviation, %
1	12	1.54	0.255	9.4	2.78	0.526	7.7
2	11	1.57	0.266	5.5	2.82	0.570	4.9
3	13	1.32	0.549	13.2	2.44	2.475	10.3
4	11	1.60	0.243	9.5	2.88	0.479	7.3
5	13	1.68	0.220	7.7	3.07	0.395	5.9
		High pH series					
		$\kappa_2 K_w \times 10^{10}$sec.$^{-1}$	$\kappa_3 \times 10^2$sec.$^{-1}$		$\kappa_2 K_w \times 10^{10}$sec.$^{-1}$	$\kappa_3 \times 10^2$sec.$^{-1}$	
1	9	1.29	0.595	3.3	1.63	0.465	4.2
2	13	1.45	0.475	4.8	1.87	0.388	7.4
3	7	1.43	1.079	4.4	1.75	0.796	5.7
4	9	1.41	0.941	4.2	1.68	0.779	5.2

the corresponding intercepts was used as a new tentative value of the intercept in the high pH-trace procedure. This cycle was repeated until successive iterations produced less than 1% change in both mean slope and intercept. The final mean slope was assumed to equal $\kappa_2 K_w$, and the final mean intercept to equal κ_1.

One fact threatens the validity of this method: The τ's are dependent on K_2, and the value K_2 in seawaters is a matter of dispute. The two most widely accepted values of K_1 and K_2 in seawaters are those of Lyman (1956) and Buch (1951). The method of this paper, being strongly dependent on K_2, suggests itself as an independent means of choosing between these values. The computer was programmed to use both sets of constants in calculating two separate sets of results.

A tabulation of some characteristic data with corresponding τ's and best ϕ's is shown in Table I. This trace corresponds to Trace 1 in Figure 3.

Results

The experimental results were consistent within the limits of error with the basic assumptions of the method. The prediction following from Equation 6 that the slope of the traces should be independent of alkalinity on the low pH (nitrogen-swept) runs was borne out: Only when alkalinity was raised above 20 meq./liter did variation occur—this undoubtedly is due to resultant precipitation of $CaCO_3$. However, a lower limit, about 0.5 meq./liter, was respected in order to avoid deviation arising from alkalinity introduced from salts of weak acids that might occur as impurities in the CP reagents used to make up the seawater. Carbonic anhydrase catalyzes Reaction 1a, a natural enzyme used to accelerate the rate of pH change, thereby demonstrating that the rate of change in pH is dependent upon interconversions between carbonate and non-carbonate forms of CO_2. Uncertainties about the effect of changing the bubbling through addition of this organic material precluded quantitative work with the enzyme.

It was decided to run a series of experiments with use of artificial seawater of chlorinities 17, 19, and 22%, and at a single temperature (about 20 °C.) to estimate the dependence of κ_1 and $\kappa_2 K_w$ upon chlorinity in the range usually found at sea. To study temperature dependence, a median chlorinity (19%) was chosen for experiments at approximately 10°, 20°, and 30 °C. Results are shown in Table I, in which individual traces are listed with results and standard deviations by using the constants of Buch (1951) and Lyman (1956). In places the N_2-swept traces do not exhibit the scatter in κ_3 that always occurs in the air-swept runs. This is attributable to the fact that the N_2 runs, having small values of τ, are only slightly dependent on κ_3. The computer discontinued its hunt after the 1% criterion was met and before κ_3 could be carried out to many decimal places.

Table II compares the temperature dependence of κ_1 at 19% chlorinity with the results for pure water in Pinsent *et al.* (1956). No such comparison is made for κ_2, since its calculation from $\kappa_2 K_w$ would involve estimation from the "apparent" thermodynamic constant of K_w, whose value is dependent on artificial definitions of activity coefficients of H^+ and OH^- ions. These are not needed in actual work since $\kappa_2 K_w$ is the constant used to determine rates under ordinary experimental or natural conditions. It is only necessary that there exist in each case some constant K_w to satisfy the ion-product relation, and the theory of this paper is unaffected. Table I compares the temperature dependence of $\kappa_2 K_w$ in seawater with that of $\kappa_2 K_w$ calculated from Pinsent *et al.* (1956). The variations of κ_1 and $\kappa_2 K_w$ with chlorinity are shown in Table II.

Calculated activation energies for reaction 1a are as follows:

This study, Lyman constants	= 16,400 cal.
This study, Buch constants	= 15,700 cal.
Pinsent *et al.* (1956), pure water	= 17,200 cal. (av.)

Aged natural seawater of 19% chlorinity was tested at 20 °C. A simple extention of Equation 6 can be made to include a correction for borate, whose concentration was estimated from the usual chloride–borate ratio. A rough calculation using Buch's constants indicated a κ_1 value of 3.2 × 10^{-2}/sec., as compared to a κ_1 of 2.98 × 10^{-2}/sec. for artificial seawater. This indicates that aged natural seawater contains no compounds capable of radically changing the values of the constants from those obtainable from artifical seawater. Therefore, all work was done with artificial seawater to avoid applying unnecessary correction factors.

Table II. Variations in κ_1 and κ_2K_w with Chlorinity and Temperature in Artificial Seawater, Compared with Results of Pinsent *et al.* (1956)

A. Temperature dependence, 19‰ chlorinity

Temp.	κ_1 (Buch) $\times 10^2$ sec.$^{-1}$	κ_1 (Lyman) $\times 10^2$ sec.$^{-1}$	κ_1 (Pinsent) $\times 10^2$ sec.$^{-1}$	κ_2K_w (Buch) $\times 10^{10}$ sec.$^{-1}$	κ_2K_w (Lyman) $\times 10^{10}$ sec.$^{-1}$	κ_2K_w (Pinsent) $\times 10^{10}$ sec.$^{-1}$
10	1.16	0.85	0.65	0.27	0.26	0.076
20	2.98	1.88	1.67	1.48	1.22	0.39
30	7.27	4.77	5.32	7.10	5.35	1.79

B. Chlorinity dependence at 20°C.

Chlorinity, ‰	κ_1(Buch) $\times 10^2$sec.$^{-1}$	κ_1(Lyman) $\times 10^2$sec.$^{-1}$	κ_2K_w(Buch) $\times 10^{10}$sec.$^{-1}$	κ_2K_w(Lyman) $\times 10^{10}$sec.$^{-1}$
17	2.66	1.56	1.19	0.99
19	2.98	1.88	1.48	1.22
22	2.80	1.57	1.73	1.40

Attempts to use this procedure in distilled water, in which the results could be checked against values from other work, failed. It was impossible to obtain a satisfactory pH *vs.* time trace because of the extreme noise produced when bubbling. We conjecture that this noise may be a result of the noticeably larger-sized bubbles produced in distilled water.

Conclusions

The method described here for measuring changes in pH is an independent means of estimating the rate constants κ_1 and κ_2Kw. The uncertainty in the values of the second dissociation constant of carbonic acid in seawater does weaken the results, though recalculation would be easy, were the values of the constant established. Allowing for this uncertainty, we found nothing to support the assumption in Hood and Park (1962) that seawater exhibits a greatly lowered hydration rate constant, although the presence of possibly large amounts of organic material associated with a biologically active system, such as the environmental conditions of Hood (1963) on the very rich algal culture of Supernaw (1963), makes it impossible to predict with assurance the CO_2 molecular-to-ionic rates in such media. Complexes and side reactions with these organics could well predominate over the simple rate picture implied in Equations 1a, 1b, and 1c.

Some further conclusions can be drawn concerning the problem of the dissociation constants. Table I shows no substantial differences in standard deviations between the results calculated according to Buch's constants and according to those of Lyman—*i.e.*, accuracy of fit does not support one set rather than the other. However, work by Mills and Urey (1940) has indicated that κ_1 is affected very little by variations in ionic strength of simple salt solutions. Our results substantiate this view: Table II shows no discernible trend in κ_1 between chlorinities of 17 and 22‰. Surely, were there a significant increase or decrease in this constant with chlorinity, the fact would be noticeable in that range, as in the case of the trend in κ_2K_w. If we conclude that κ_1 is similar for pure and seawater, a comparison of the results of Pinsent *et al.* (1956) for pure water at 20°C. with the average of the values obtained by the present method is of interest.

κ_1 [calcd from Buch (1951)] $= 2.81 \times 10^{-2}$/sec.
κ_1 [calcd from Lyman (1956)] $= 1.66 \times 10^{-2}$/sec.
κ_1 [Pinsent *et al.* (1956)] $= 1.67 \times 10^{-2}$/sec.

This comparison lends credence to the Lyman's constants.

If we ignore the question of activities and concentrations and use the formula for K_w in Sverdrup *et al.* (1942) and Buch (1938) to calculate a rough κ_2, we find that it is a factor of two or so higher than the results of Pinsent *et al.* (1956) in pure water, which is satisfactory considering the strong dependence of κ_2K_w on chlorinity in the range of 17 to 22‰. Nothing like the 100-fold greater value for κ_2, as published by Himmelblau and Babb (1958), was indicated.

We suggest that the hydroxyl-ion reaction plays a much larger role in carbon dioxide interconversions between ionic and molecular forms than had previously been suspected at the pH of ordinary seawater. Using the most likely constants, those calculated from Lyman's constants, it can be shown that, at pH 8.2, the hydroxyl-ion reaction carries about 48% of the CO_2 transferred, compared to 52% for hydration-dehydration. Its importance equals that of the hydration reaction at the pH of the sea.

Acknowledgment

The authors gratefully acknowledge the support of this work by the Office of Naval Research under contract NONR-2119(04), and by the National Science Foundation under contract NSF-G18477 with the Texas A&M Research Foundation, College Station, Tex., and ONR-N000-14-67-A-0317-001 and NSF-GB-8274 at the Institute of Marine Science, University of Alaska.

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Received for reveiew August 11, 1969. Accepted September 2, 1970. Contribution 76, from the Institute of Marine Science, University of Alaska.

Estimation of Adsorbable Solutes in Seawater with ^{14}C-Labeled Phenol and Activated Carbon

Ralph F. Vaccaro

Woods Hole Oceanographic Institution, Woods Hole, Mass. 02543

■ A ^{14}C-tracer technique is proposed whereby kinetics describing the short-term (1 hr.) uptake of labeled phenol on activated carbon provide a quantitative estimate of the adsorbable material in seawater. Adsorbent preparation, ^{14}C usage, contact period, and pH effects are considered. The method is calibrated by measuring the amounts of ^{14}C phenol adsorbed under defined conditions in seawater pretreated with activated carbon to completely remove responsive solutes of natural origin. Kinetics relating phenol adsorption to solute concentration show a saturation-type uptake pattern not unlike that described by the Langmuir equation for an equilibrium situation. For sample analysis, the degree of displacement of the phenol calibration curve is evaluated. Shipboard analyses indicative of the remote Atlantic are compared with simultaneous measurements of total dissolved organic carbon obtained with wet combustion. Since the carbon concentrations measured are similar in magnitude, the bulk of the dissolved organic carbon at locations far removed from shore appears to respond to activated carbon in a manner similar to that of phenol.

With less than 10% of the dissolved organic material in seawater identified (Duursma, 1965), there is a growing consensus among marine chemists that soluble organic heteropolymers, rather than free organic combinations, constitute the bulk of the dissolved organic carbon (DOC) of the ocean (Khailov and Finnenko, 1968). This opinion is supported by current emphasis on the importance of large molecular solutes and by elementary appraisals of *in situ* carbon:nitrogen ratios (Holm-Hansen *et al.*, 1966) obtained with improved analytical techniques for measuring both total dissolved organic carbon (Duursma, 1961, 1965; Menzel and Vaccaro, 1964) and nitrogen (Armstrong *et al.*, 1966). Some likely structural linkages being scrutinized include macromolecular polyphenols (Craigie and McLachlan, 1964) and quinones (Degens, 1965), as well as various nitrogenous compounds constructed from amino acids or urea (Degens, 1970).

Primary production by surface-oriented phytoplankton presumably provides the major source of DOC in the sea with a minor contribution from land drainage. Within the photic layer, the amount of DOC present varies with the rate of recycling, but is usually over 1 mg./liter. Here, both labile and refractory forms of carbon are prominent since organic production and degradation proceed simultaneously. At intermediate depths, further decomposition may occur following sinking or advection of organic particles but ultimately throughout the remaining and deeper portions of the water column DOC remains remarkably constant within the range 0.3 to 0.7 mg./liter (Menzel and Ryther, 1968; Menzel, 1970). Many believe that the bulk of the residual DOC present in the oceans is capable of prolonged resistance to biological decomposition (Barber, 1967), a property commonly associated with organic condensates.

Enumeration of the various organic species present in seawater and their microbiological implications would ideally resolve the validity of the above argument. However, unusually high sensitivity requirements and the abundant inorganic salts of seawater present formidable obstacles to successful analysis with routine chemical or bioassay-type analyses. On the other hand, the adsorptive capacity of surface-active inert solids such as activated carbon (AC) has been used successfully to separate responsive organic constituents, including phenol and its derivatives, from solution (Jeffrey and Hood, 1958; Morris and Weber, 1964). For this reason, we decided to evaluate adsorption as a means of providing an additional fractionation of the DOC content of seawater. Although the methodology is specifically directed toward seawater, logical extensions to freshwater and other analytical situations seem warranted.

For routine qualitative separations with AC, a simple excess of the adsorbent is the primary consideration. However, under more rigorous circumstances, such as those encountered in water supply and pollution control, economic usage dictates a more precise description of the quantitative relationships involved. Thus, Morris and Weber (1964) reported on the kinetics of phenol uptake on AC with reference to waste water purification studies. Their results suggest an application to the marine situation, in view of the proposed involvement of phenolic linkages in the organic carbon cycle of the sea. To enhance analytical sensitivity and to allow a reduction in the experimental time interval, a ^{14}C-tracer technique has been incorporated.

Theory

Sorption is an encompassing term descriptive of the overall reaction between an adsorbent such as AC and a responsive solute. Detailed kinetic studies have shown a relatively rapid initial rate (about 1 hr.) of adsorption during the early stages of contact wherein uptake is proportional to the half-power of time (Morris and Weber, 1964). Thereafter, there is a gradual approach (two or more weeks) to an equilibrium situation, during which the uptake rate pattern is essentially dependent upon the concentration gradient which controls the diffusion of solute into the internal capillaries of the carbon particles (Edeskuty and Amundson, 1952). For mixtures of competing adsorbates, the uptake kinetics are modified by the interactions dictated by the relative diffusivities which reflect the respective molecular size and cross-sectional configuration of each adsorbate (Weber, 1964).

The well-known Langmuir adsorption isotherm quantifies the long-term equilibrium situation and predicts an hyperbolic relation between the amount of solute adsorbed (per unit adsorbent) and the concentrations of solute provided. Data applicability can be tested by plotting the ratio, solute concentration:quantity of solute adsorbed *vs.* the range of solute concentrations provided. When the Langmuir equation is applicable, the points fall on a straight line and the reaction parameters can be derived from measurements of the slope and intercepts.

In our ^{14}C experiments, the amount of phenol uptake on AC (ignoring isotopic preference) has been restricted, for practical considerations, to a 1-hr. contact period, and the amount of phenol uptake was determined from

$$d' = \frac{cp'}{C\mu} \qquad (1)$$

where d' = solute adsorbed, mg. carbon per unit adsorbent; c = measured radioactivity in counts per minute (c.p.m.) of the harvested adsorbent; p' = the solute concentration of phenol initially present in mg. carbon per liter; C = the number of c.p.m. provided by 1 μCi of ^{14}C-labeled phenol corrected for geometry and self-absorbance in the counting apparatus used; and μ = the quantity of ^{14}C in μCi per sample.

Rearranging Equation 1,

$$\frac{p'}{d'} = \frac{C\mu}{c} \tag{2}$$

Materials and Equipment

The charcoal adsorbent is Fisher's Darco G-60, lot no. 732653, of lignite origin. Particle uniformity (105- to 125-μ diameters) corresponding to size no. 120/140 is achieved by passage through a U.S. Standard sieve series. Bulk quantities of the adsorbent are then heated to 650°C. for 1 hr. in a closed-muffle furnace to help standardize activity and to remove moisture and volatile contaminants. For storage, weighed quantities (10 ± 0.5 mg.) of combusted AC are deposited into fired-glass vials and kept in a desiccator, pending usage.

The reaction vessels are hard glass BOD bottles of 130-ml. capacity equipped with ground glass stoppers. These and other glassware are cleaned first with acid (50% HCl) flushed with multiple portions of distilled water, and then baked in a muffle furnace.

To ensure uniform and sufficient contact during the adsorption, all water samples are agitated with a Burrell wrist-action shaker by passage through a 3° arc at 320 strokes per min. Temperature variation during the contact period did not exceed ±2.5°C.

AC is removed from suspension on 24-mm. prewashed cellulose membrane filters, porosity, 0.45 μ or less, assisted by a vacuum not over 7 in. of mercury. Rubber cement is used to attach the filters to metal planchets before drying (1 hr., 39°C.). Beta activity on the filters is measured by end-window counting with a Nuclear Chicago Model D47 gas-flow detection apparatus of known efficiency operating within the Geiger-Mueller range.

Methods

Known amounts of analytical-grade phenol from a stock solution were added to each of 15 reaction bottles, representing three sets of five replicate subsamples with different specific activities. The actual range of concentrations selected was determined by the nature of the water being analyzed. Differences in specific activity were introduced by admixing various amounts of nonlabeled phenol with a constant amount of uniformly labeled phenol (New England Nuclear 311, 1–5 mCi/mmol.). For oceanic samples, the recommended tracer concentration is 0.625 μCi per BOD bottle, which in our case is equal to 0.0009 mg. phenol C per subsample. Final concentrations of added substrate were obtained by adding enough supplementary unlabeled phenol to extend the upper concentration limit to about 0.050 mg. C/liter, following the addition of the 50-ml. seawater sample. For calibration, the range of specific activities was extended substantially, but the recommendation for five replicate samples at each phenol concentration was retained.

Before dispensing the subsamples into the BOD bottles, 1 liter of the seawater sample is passed through a washed membrane filter to ensure removal of naturally occurring particulate material, in excess of 0.45 μ, from suspension. The filtrate is vigorously agitated in a magnetically stirred flask before 10 mg. of dry AC is added. While mixing, the 15 50-ml. subsamples are removed by siphoning into a measuring vessel, shaken by hand, and quickly transferred to the BOD bottles containing titrated amounts of labeled and unlabeled phenol. Unequal AC distributions during subsample dispensing can be minimized by discarding the residual contents of the siphon between withdrawals and by ensuring that the volume being stirred always exceeds the volume required for the subsamples by at least 25%. Subsample controls without AC are also prepared for an independent evaluation of adsorption of ^{14}C onto cellulose nitrate filter material or adventitious precipitation.

After shaking for 1 hr., samples are prepared for beta counting by membrane filtration, through 24-mm. diameter filters, rinsing and drying. Rinsing flushes out unadsorbed interstitial ^{14}C and inorganic salts, and is best accomplished by gently overlaying the denser seawater with about 5 ml. of distilled water without disturbing the natural dispersion of the activated carbon mat on the surface of the filter. Nonuniform thicknesses of the AC mat, which can markedly increase the counting errors, should be avoided.

Results

Short-Term Adsorption of ^{14}C Phenol on Activated Carbon. To define a contact period suitable for analytical purposes, the adsorption of phenol on AC was studied throughout 1 hr., AC being provided at the rate of 50 mg./liter of seawater. A minimum filtration time of about 5 min., necessary for removal of AC from suspension, ruled out observations for contacts of less than 5.5 min. Figure 1a records changes in the rates and quantities of phenol adsorption after selected time intervals. The results show that an initially rapid rate of adsorption gradually decreases during the remainder of the hour. The slow approach to the abscissa suggests that an equilibrium situation of the Langmuir-type would presumably be delayed for a very long time. Since the 50-ml. sample volumes used here contained 0.0009 mg. phenol C, appropriate conversions indicate that 48% of the initially added phenol carbon (0.44 × 10^{-3} mg.) was adsorbed after 1 hr. Over the same interval, the rate of adsorption decreased by a factor of 5.5. With use of the same data, the relation between phenol adsorption and the square root of time (Figure 1b) suggests that a linear relation between the two variables could only have occurred during the first 10 min., since at no other time does the rate parameter appear proportional to that of time. These data support 1 hr. as a logical choice for a standard contact period for short-term adsorption studies. Thus, small inequalities in contact time would have a negligible effect on the precision, since only relatively minor fluctuations in the time rate of change would result.

Adsorption of Analogous Seawater Solutes on Activated Carbon. A direct assessment of the affinity between the natural organic components of seawater and AC is difficult, since the chemical configurations of the organic solutes remain obscure. Likewise, attempts to monitor residual total carbon concentrations during a measured exposure to AC are impaired by an excessive organic carbon contamination from soluble organic components associated with AC. Accordingly, an indirect assay-type approach was used whereby chronological changes in the interference effect on ^{14}C phenol adsorption provided an estimate of the amount of adsorbable material remaining in seawater.

A large volume of Sargasso sea surface water, aged several months to stabilize microbial activity, was membrane filtered (0.45-μ porosity) and agitated with 100 mg. of suspended AC per liter. At selected intervals, a series of 1-liter samples was removed, refiltered to remove particulates, and assayed under

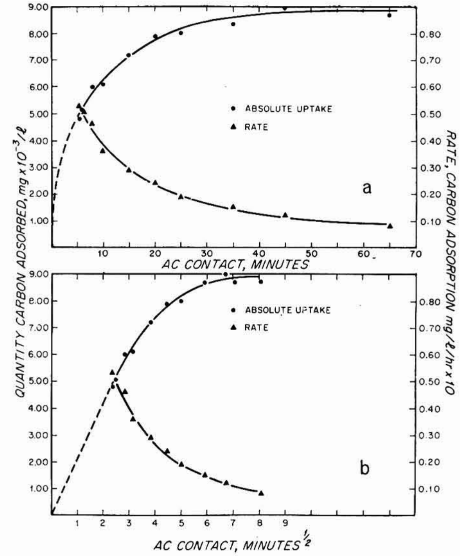

Figure 1. (a): Upaket *vs.* time for the adsorption of phenol on Darco G-60 activated carbon in seawater based on ^{14}C measurements. Each 50-ml. subsample contained 0.0625 μCi ≡ 0.90 μg. C and 2.5 mg. granular activated carbon. (b): Uptake data of (a) plotted against the square root of time, min.

standard conditions for variations in the amounts of ^{14}C phenol adsorption on freshly added AC. Such observations were repeated until the amount of ^{14}C phenol adsorbed became a reproducible and predictable quantity. The data shown in Figure 2 indicate that approximately 2.5 weeks of exposure with an excess of AC was required before a stable situation developed.

Optimum Concentration of Activated Carbon. Four different AC concentrations were used to measure the amounts of ^{14}C phenol adsorbed after a 1-hr. exposure in distilled water. The results (Table I) indicate that a 10-fold increase in AC concentration (0.50–5.0 mg./50 ml.) was required to double the amount of ^{14}C adsorbed. At the same time, an inverse relationship between the amount of AC provided and the apparent amount of ^{14}C recovered per unit weight of charcoal is also disclosed. Presumably, increasing thicknesses of the AC mats on the filter surface at higher AC concentrations has a shielding effect which significantly reduces the level of end-window counting because of a progressively greater adsorption of beta radiation among the AC particles. Hence, concentrations of AC selected for subsequent studies were standardized at 0.50 mg./50 ml. to facilitate filtration and to minimize the influence of self-adsorbance.

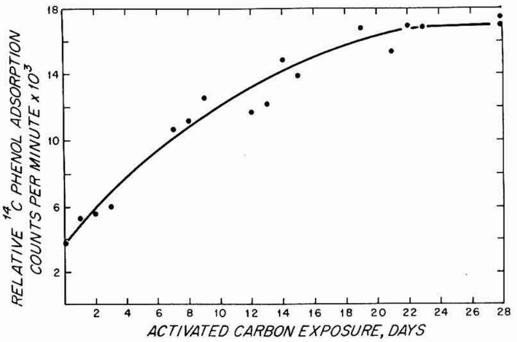

Figure 2. Extended time sequence indicative of the removal of indigenous adsorbable reactants from a sample of aged Sargasso surface water agitated with granular carbon, 100 mg./liter

pH Effects. The influence of pH on adsorptive behavior can originate from a variety of mechanisms, many of which remain inadequately understood. This uncertainty is especially applicable to seawater which represents a delicate chemical balance sustained by many inorganic bases and salts. Ideally, comprehensive studies should differentiate between direct transformations at active sites on the adsorbent surface, nonuniform changes in the original solute equilibria, and adsorptive interference from the buffering system used. Because such details are beyond the scope of this presentation, our efforts include only a limited study of the overall effect on seawater from two selected buffering systems: boric acid–sodium hydroxide and acetic acid–sodium acetate.

Natural seawater is well buffered and its pH at locations remote from coastal areas is remarkably constant within the range of 8.10 to 8.30. However, at estuarine and other near-shore locations, much wider variations in pH occur that can increase this range from 7.50 to 9.50. Here, the effects on adsorptive behavior during our standard procedure were examined in aged Sargasso seawater (pH 8.2) buffered to pH 1.9 and 9.6. Two different concentrations of phenol adsorbate were employed, each at a different specific activity; hence, an isotope dilution effect was introduced. The results (Table II) indicate that the unmodified seawater gave significantly higher adsorption than either the more acid or basic solution. Increasing the pH from 8.2 to 9.6 caused a 30% reduction in ^{14}C uptake, while lowering the pH to 1.9 reduced the amount of uptake by 75%. The 13-fold isotope dilution factor used here consistently reduced the amount of ^{14}C-uptake activity at all three pH levels by about 65%. For more comprehensive information regarding the effects of pH on freshwater phenol adsorption, the reader is referred to the recent work of Snoeyink *et al.* (1969).

Adsorption of Representative Organic Monomers from Seawater. Known chemical entities account for less than 10% of the DOC in seawater; hence, a successful application of the procedures being discussed will largely depend on the adsorptive behavior of currently undefined chemical species. Nevertheless, we have made individual comparisons of the short-term adsorptive behavior of 11 different ^{14}C-labeled organic compounds, including some common amino acids, sugars, and organic acids. Selection was based on the previously noted involvement of these compounds in marine metabolic activity and on the possibility that their ultimate

Table I. Effects of Known Concentrations of Activated Carbon on Adsorption Measurements for ^{14}C Phenol[a]

Activated carbon added, mg./50 ml. sample	Phenol recovered, %	Adsorbed phenol C measured, mg.	Phenol C measured/ adsorbent, mg.
0.50	18	0.00016	0.00032
0.50	23	0.00021	0.00042
1.00	40	0.00036	0.00036
1.00	39	0.00035	0.00035
2.50	50	0.00045	0.00018
2.50	49	0.00045	0.00018
5.00	46	0.00041	0.00008
5.00	47	0.00042	0.00008

[a] ^{14}C phenol added = 0.0625 μCi 50 ml. = 0.00090 mg. phenol C/50 ml.; contact, 1 hr. at 22°C.

chemical modification leads to the formation of the more highly structured molecules which may constitute the bulk of the oceanic DOC. Results from this study, including observations with two different adsorbents (activated carbon and aluminum oxide), are recorded in Table III, and indicate that no significant adsorption occurred with any of these species other than phenylacetic acid. More sophisticated studies are being considered to provide a more realistic representation of the more complex organic entities characteristic of seawater.

Calibration Methods. Under more favorable circumstances, calibration of this technique would be accomplished with representative concentrations of realistically selected marine adsorbates to isolate the kinetic parameters that regulate adsorption under specified conditions. A definitive study of this type is not yet possible because of a lack of information on the true nature of seawater organic solutes. Alternatively, we adopted a provisional calibration whereby recovered amounts of beta radiation from known concentrations of pure phenol were substituted artificially in a seawater media previously stripped of all naturally incurring adsorbable material. As previously, the titrated amounts of labeled and nonlabeled phenol were so adjusted that an inverse relation between the total amount of phenol added and the recovered amount of beta radiation was assured. Phenol concentrations from 0.10 to 1.50 mg. carbon per liter led to a corresponding decrease in ^{14}C activity, which varied between 16,000 and 3000 c.p.m. The most useful segment of the curve for analytical purposes appeared to correspond to the solute range 0.20 to 0.65 mg. carbon per liter. At lesser concentrations, small differences in phenol cause excessively high variations in the adsorptive response, while at higher phenol concentrations, the technique loses sensitivity rapidly.

Calibration results relating the calculated amounts of phenol adsorbed (Equation 1) to the concentrations of phenol provided are shown in Figure 3a. The general pattern describes a saturation-type isotherm with the appearance of considerable distortion at high solute concentrations. For these data, a comparison of the ratio, solute concentration provided: quantity of solute adsorbed *vs.* the concentration of solute provided is summarized in Figure 3b. Here, the degree of observed linearity suggests that a functional resemblance to a Langmuir-type equation is an important consideration. The visually drawn line of best fit is described by

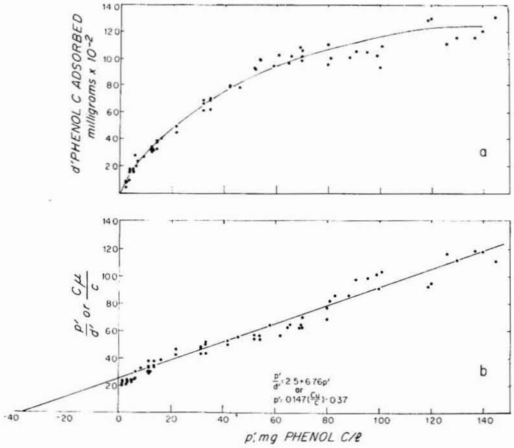

Figure 3. (a): Calibration data showing the quantities of phenol adsorbed on granular carbon (0.50 mg./50 ml.) after 1 hr. contact with known concentrations of phenol in seawater previously stripped of phenolic-type material. (b): Calibration data of (a), demonstrating the degree of linearity obtained by plotting p'/d' against p'

$$\frac{p'}{d'} = 2.5 + 6.76\, p' \tag{3}$$

which, by rearrangement and substitution according to Equation 2, can be altered to

$$p' = -0.37 + 0.147 \left(\frac{C\mu}{c}\right) \tag{4}$$

Discussion

As a potential basis for estimating adsorbable solutes in seawater, the adsorption of phenol on activated carbon has been examined. The results are encouraging; under controlled conditions, the underlying quantitative relations can be reasonably well predicted. The use of isotopically labeled phenol increases the sensitivity of the method in a manner commensurate with the low concentrations of dissolved organic matter characteristic of oceanic waters.

Table II. Effect of pH on Adsorption of Phenol from Seawater[a]

	Buffer	pH	Phenol added, μg C/liter		Response, c.p.m.[b]
			^{12}C	^{14}C	
Natural seawater	None	8.2	10	18	5116
		8.2	10	18	5130
		8.2	130	18	3290
		8.2	130	18	3520
Acid seawater	Acetic acid	1.9	10	18	1580
		1.9	10	18	1350
		1.9	130	18	930
		1.9	130	18	913
Basic seawater	Boric acid + sodium hydroxide	9.6	10	18	3680
		9.6	10	18	3410
		9.6	130	18	2340
		9.6	130	18	2240

[a] Phenol ^{14}C added = 0.0625 μCi 50 ml. = 0.00090 mg. C/50 ml. Activated carbon added = 0.50 mg./50 ml.
[b] Counts per minute.

Table III. Adsorption of Representative Marine Organic Monomers Other than Pure Phenol on Activated Carbon[a]

^{14}C-labeled substrate	^{14}C-labeled solute, mg. C/liter	Resulting ^{14}C activity, c.p.m.[b]			
		Filter control	Activated carbon	Filter control	Aluminum oxide
Phenylacetic acid	0.014	49	798	46	43
Arabinose	0.013	46	54	184	190
d'Fructose	0.025	32	66	134	148
d'Glucose	0.006	43	110	40	40
Glycine	0.003	110	213	65	66
Taurine	0.006	31	44	31	35
Sodium glycolate	0.007	48	53	158	178
Sodium lactate	0.014	104	114	75	80
Sodium acetate	0.009	40	44	77	84
Malic acid	0.002	150	197	151	179
Uric acid	0.004	44	61	58	43

[a] Medium, molecular filtered Sargasso seawater. Activated carbon added = 0.25 mg./50 ml. sample. Aluminum oxide added = 0.50 mg./50 ml. sample. ^{14}C substrate added per 50-ml. sample = 0.0625 μCi = 0.0009 mg. C.
[b] Counts per minute.

In analytical situations, the quantities of phenol adsorbed after 1 hr. at known specific activities are observed and compared with a calibration curve which defines phenol adsorption in the absence of all interfering solutes. By subtracting the amount of phenol added for analytical purposes, one is able to estimate the amount of adsorbable solute present in a given sample of seawater. Because of arbitrarily assigned experimental conditions compatible with the realities of analyses on shipboard, there is no common basis for comparing these data with adsorption studies conducted by other investigators. In our case, the equilibrium requirements apropos Langmuir adsorption did not obtain and it is generally recognized that adsorptive parameters can be highly sensitive to even slight variations in experimental conditions.

Current opinion on the nature of dissolved organic carbon in the deep ocean stresses a uniform distribution of relatively refractory material which is maintained by horizontal and vertical mixing of processes (Menzel and Ryther, 1968, 1970; Menzel, 1970). This hypothesis is consistent with evidence relating to dissolved oxygen, which suggests that after sites of low oxygen have been established due to locally enhanced biochemical activity, subsequent dispersal of the oxygen deficit is essentially controlled by mixing between neighboring water masses (Wyrtki, 1962; Menzel and Ryther, 1968, 1970). Other evidence (Barber, 1968) stresses the inability of native marine populations to utilize refractory compounds characteristic of seawater having molecular weights in excess of 500.

During the past year, we have studied the nature of DOC in surface water from the dock at Woods Hole and along an hydrographic section of over 2000 miles in the Atlantic Ocean, extending from Barbados Island eastward toward the Cape Verde Islands. These observations, from cruise no. 42 of the *R/V Atlantis II*, included measurements of the total DOC present at depths between the surface and 3000 m. at 12 locations spaced about 250 miles apart. The technique used for the DOC analyses was the wet oxidation method described by Menzel and Vaccaro (1964). At each location, replicate samples were collected from 10 m. and from the depth of the oxygen minimum to establish the fraction of DOC adsorbable on activated carbon. Water samples for total DOC were collected in Teflon-lined Nansen bottles, while a large-volume glass-Teflon sampler was used to obtain the samples for adsorption studies.

Data from this cruise (Table IV) suggest that the region covered can be divided into two: Stations 1174 to 1179 being characterized by comparatively low surface DOC concentrations, while at Stations 1180 to 1185 surface DOC concentrations increased by about 25%. However, despite this regional difference, the organic carbon values recorded by each method appear to fall within the accepted range for DOC concentrations in the open ocean (Menzel and Ryther, 1968). Quantitatively, the unexpected similarity in carbon measured by the two techniques implies that a major fraction of the DOC in this case may occur in the form of compounds which collectively behave like phenol in the presence of AC. A somewhat different situation applies to Woods Hole dock water, presumably more selectively enriched with terrestrial organic matter, where only about 25% of the total DOC responded to the AC treatment. Whether these results will be sustained by more intensive observations in the future is uncertain; however, that phenolic condensates of oceanic origin are prominent in the remote ocean, where they occupy a quasi-terminal position in the organic carbon cycle, remains a distinct possibility.

Table IV. Variation of Dissolved Organic Carbon in Seawater Samples from the Mid-Atlantic and an Intercomparison of Analytical Results from the Activated Carbon and Wet Combustion Techniques

			Carbon measured, mg./liter			
			Upper 10 m.		Depth of oxygen minimum	
Station no.	Lat., °N	Long., °W	AC[a]	Wet oxidation[b]	AC[a]	Wet oxidation[b]
1174	12°03′	57°57′	0.84	0.68	0.66	0.38
1175	12°08′	54°11′	0.61	0.73	0.31	0.42
1176	12°05′	49°59′	0.47	0.78	0.30	0.31
1177	12°06′	45°55′	0.74	0.71	0.19	0.40
1178	12°08′	41°43′	0.73	0.54	0.48	0.42
1179	12°02′	37°48′	0.77	0.61	0.43	0.47
Mean			0.69	0.69	0.40	0.40
1180	12°04′	33°42′	0.58	1.37	0.41	0.52
1181	12°59′	29°30′	1.06	0.85	0.78	0.66
1182	12°04′	25°16′	1.06	0.61	0.83	0.41
1183	12°02′	21°18′	0.88	1.31	0.67	0.53
1184	7°25′	20°35′	0.79	0.85	0.54	0.66
1185	3°30′	20°30′	0.83	0.83	0.54	0.48
Mean			0.87	0.97	0.63	0.54
Woods Hole dock water						
Mean			0.42	1.60	...	...

[a] Activated carbon analyses.
[b] Persulfate oxidation analyses.

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Received for review October 10, 1968. Accepted July 24, 1970. This work was supported in part by grants GB 7169, GB 861, and GB 5199 from the National Science Foundation to the Woods Hole Oceanographic Institution (Contribution No. 2233).

Adsorption of Isocil and Bromacil from Aqueous Solution onto Some Mineral Surfaces

Rizwanul Haque and William R. Coshow

Department of Agricultural Chemistry and Environmental Health Science Center,
Oregon State University, Corvallis, Ore. 97331

■ Adsorption of two uracil herbicides, isocil and bromacil, from aqueous solution on illite, montmorillonite, silica gel, humic acid, and kaolinite surfaces was studied. The adsorption can best be represented by Freundich-type isotherms. A humic acid surface adsorbs considerably more chemical than other surfaces. Montmorillonite and kaolinite show a concave-type adsorption, while humic acid exhibits a convex-type. From the adsorption data at two temperatures, the isosteric heats of adsorption as a function of amount of chemical sorbed were calculated. These results suggest a physical-type adsorption for most of the surfaces. At very low surface coverage there is also some hydrogen-bond formation.

Adsorption processes are important in determining the activity and persistence of many organic compounds of biological interest. For this reason there has been considerable effort expended to understand this complex process. Unfortunately, the mechanisms of adsorption for some processes are still not completely understood. This is especially true for adsorption from aqueous solution. Some of the factors that must be taken into account when studying adsorption from solution are the kinetics of the adsorption/desorption process, the energetics involved during adsorption, the nature of the adsorption (multi- or monolayer-type), and the influence of the solvent on the adsorption characteristics. Although studies dealing with the adsorption of pesticides on clay surfaces are numerous, only a few deal with the quantitative interpretation of the adsorption data. In this respect, reference could be made to the work of Frissel (1961) on the equilibrium study of several organic compounds on clay mineral surfaces, Cookson and North (1967) on the adsorption of viruses on activated carbon, Schwartz (1967) on the adsorption of various pesticides on carbon, the study of Weber and Gould (1966) dealing with the kinetics of sorption, and studies of Haque, Lindstrom, *et al.* (1968) on the kinetics and equilibrium study of the adsorption of 2,4-dichlorophenoxy acid on a variety of surfaces. Although the two uracils, isocil and bromacil, are extensively used as herbicides, little is known about their adsorption characteristics. In this paper we shall present some work on the mechanism of adsorption of isocil and bromacil from aqueous solution on a variety of surfaces.

Experimental

Materials. Isocil (3-isopropyl-5, bromo-6 methyl uracil) and bromacil (5-*sec*-butyl-5, bromo-6 methyl uracil) of the purest quality available were used in the experiments. Solutions of known concentrations of each chemical were prepared by dissolving a weighed quantity in buffer solutions of known pH. The surfaces investigated in the adsorption experiments were montmorillonite, illite, kaolinite, humic acid, and silica gel. Some of the physical characteristics of the surfaces are given in Table I. The humic acid used in this study was prepared in the laboratory by extracting the organic matter of the soil. About 150 g. of Willamette soil was shaken with 800 ml. of dilute HCl for 5 to 10 min. and allowed to stand for 30 min. The supernatant liquid was discarded and the soil was washed with distilled water. The soil sample was then reacted with 800 ml. of 0.5M NaOH under nitrogen gas for 24 hr. The extract was adjusted to pH 8, dialyzed for 48 hr. against distilled water, and then centrifuged. The soil organic matter was precipitated with $CuSO_4$, redissolved in 0.5M $Na_4P_2O_7$ solution, dialyzed against distilled water, and then evaporated to dryness. Since some of these surfaces absorb considerable amounts of water, they were first saturated with a 0.005M phosphate buffer solution of known pH value (Haque, Lindstrom, *et al.*, 1968). This process was necessary to account for the change in concentration of the adsorbate which may occur as a result of a change in the volume of the solvent. The surface material was then equilibrated with a known concentration of bromacil or isocil solution for 24 to 48 hr. This period of time was determined to be sufficient for equilibration, as was determined from an earlier kinetic study (Lindstrom, Haque, *et al.*, 1970). The amount of chemical sorbed, x, was calculated by estimating the change in the concentration of the adsorbate in the bulk solution according to the equation

$$x = \frac{(C_1 - C_2)V}{m} \tag{1}$$

where C_1 and C_2 are the original and final concentrations of the chemical, respectively, V is the volume of the adsorbate, and m is the mass of the adsorbent.

The analysis of the isocil and bromacil solutions was performed by ultraviolet techniques on a Cary Model 11 spectrophotometer at 296 mμ. Before analyzing the samples, it was determined that these compounds do obey the Beer-Lambert law. The measurements were accurate up to ±5%.

Results and Discussion

The results of the equilibrium study can best be fitted by the Freundlich-type isotherm to the equation

$$x = KC_2^n \tag{2}$$

where x and C_2 are as defined in Equation 1, and K and n are constants. A typical Freundlich-type plot for silica gel is shown in Figure 1. The values of K and n obtained from the intercept and the slope of the Freundlich plot are given in Table II.

From the slope and the intercepts of the Freundlich isotherm, qualitative information about the extent and nature of the adsorption could be obtained. The adsorption process involving the chemical and the surface S can be expressed by the chemical equilibrium

$$C_f + S \leftrightarrows C_a \tag{3}$$

If (C_f) and (C_a) represent the activity (which approaches the concentration for very dilute solutions) in free and adsorbed state, respectively, and K_e the equilibrium constant, then

$$K_e = \frac{(C_a)}{(C_f)(S)} \tag{4}$$

or

$$\frac{(C_a)}{(S)} = K_e(C_f) \qquad (5)$$

Equation 5 is a special case of the Freundlich Equation 2 where n approaches unity. By representing adsorption in terms of a power series (Equation 6) of a chemical concentration, Lambert (1967) noticed that for the adsorption of many pesticides on soils γ and higher coefficients

$$\frac{(C_a)}{(S)} = \alpha C_f + \beta C_f^2 + \gamma C_f^3 + \ldots.. \qquad (6)$$

are negligible and β is small. In other words, α approaches K_e or K. Hence the intercept, log K, of the Freundlich plot (Figure 1) is an indirect measure of the relative free energy changes, ΔG $(= -RT \ln K_e)$, of the chemical on different surfaces and could give some indication regarding the extent of binding. In every case this quantity decreases with an increase in temperature, showing the well-established exothermic nature of adsorption. The value of log K for humic acid surface is considerably higher than the others. This is due to the presence of a large number of carbon atoms, making the surface area considerably high. This is in agreement with the earlier study on the adsorption of 2,4-dichlorophenoxy acetic acid (Haque and Sexton, 1968). The slope of the log–log plot of the Freundlich equation can give information about the nature of the adsorption (Kipling, 1965). These values (n) are given in Table II. A glance at Table II indicates that montmorillonite and kaolinite surfaces give values of n that are greater than unity, indicating a concave, or S-type, isotherm. A concave-type isotherm arises from strong adsorption of the solvent, strong intermolecular attraction within the adsorbed layers, penetration of the solute in the adsorbent, and monofunctional nature of the adsorbate. The tendency of these two surfaces to absorb the solvent (Table I) may be the major factor responsible for the concave nature of the isotherm, although for the montmorillonite surface, which absorbs considerable amounts of the solvent, the penetration of isocil or bromacil into the unit layers can also produce an S-type isotherm. The value of n for humic acid surface is 0.7 which probably represents a convex, or L-type, isotherm. This kind of isotherm may arise where the competition of solvent for sites is minimum or the absorbate is a planar molecule. Since humic acid does not absorb the solvent (Table I), this scheme seems to be reasonable. The value of n for silica gel and illite surface ranges from 0.8 to 1.0, indicating an intermediate behavior between convex- and concave-type isotherms.

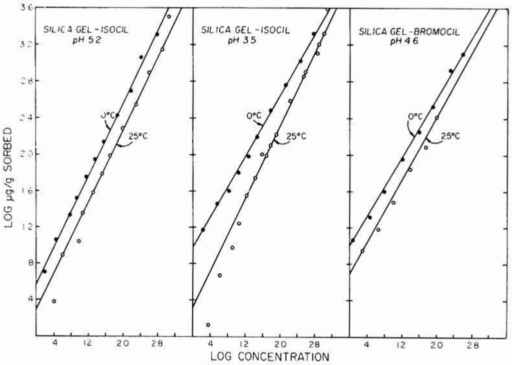


Figure 1. Freundlich plot of the adsorption of isocil and bromacil on silica-gel surface

Table I. Characteristics of Surfaces Investigated

Surface	Source	Particle size, mm.	Amount buffer required for saturation, ml.
Illite	No. 35 Fithian, Ill.	0.83	0.5
Montmorillonite	No. 25 John C. Lane Track, Upton, Wyo.	0.83	8.0
Silica gel	Grace Division Chemical, Baltimore, Md.	0.59–0.07	1.0
Kaolinite	Merck, NFV	0.24–1.68	0.75
Humic acid	Prepared in the lab	0.59–0.2	...
Alumina	Alupharm Chemical, New Orleans, La.	0.2–0.07	2.0

Table II. The Constants *K* and *n* from the Freundlich Plot

System	pH	Temp., °C.	Slope	Intercept log *K*
Silica gel–isocil	5.2	0	1.0	0.58
		25	1.0	0.31
Silica gel–isocil	3.5	0	0.8	0.97
		25	1.0	0.31
Silica gel–bromacil	4.6	0	0.8	1.03
		25	0.8	0.68
Illite–isocil	7.4	0	0.8	0.79
		25	0.9	0.3
Illite–bromacil	7.0	0	0.9	0.48
		25	0.9	0.42
Montmorillonite–isocil	6–7	0	1.1	0.49
		25	1.2	0.1
Montmorillonite–bromacil	6–7	0	1.3	−0.03
		25	1.3	−0.14
Kaolinite–isocil	6–7	0	1.1	−0.36
		25	1.2	−1.07
Humic acid–isocil	6–7	0	0.7	2.19
		25	0.7	2.05
Humic acid–bromacil	6–7	0	0.7	2.1
		25	0.7	1

An equilibrium study carried out at two different temperatures gives an opportunity to calculate the "isosteric" heat of adsorption ΔH as a function of surface coverage. If we assume that the chemical potential of the chemical in solution μ_1 is the same as in the adsorbed state μ_s, we have the following equation (Koral, Ullman, *et al.*, 1958):

$$\mu_1{}^o + RT \ln a_1 = \mu_s{}^o + RT \ln a_s \qquad (7)$$

where a_1 and a_s are the activities of the adsorbate in the liquid and in the adsorbed state, respectively. By differentiating Equation 7 we can obtain ΔH as a function of surface coverage or the amount of chemical sorbed x

$$\Delta H = Ho^s - Ho' = R\left(\frac{\partial \ln C_1}{\partial \dfrac{1}{T}}\right)_x \qquad (8)$$

Here, Ho^s and Ho' are the partial molal enthalpies of the adsorbate on the surface and in the liquid states. For a dilute solution, the activity of the chemical could be replaced by

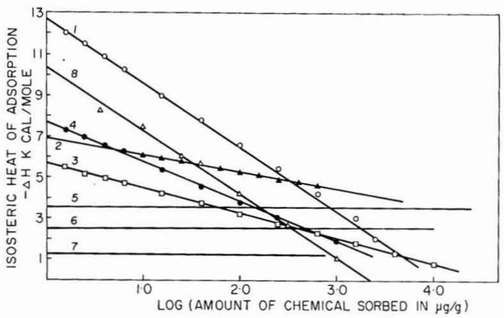
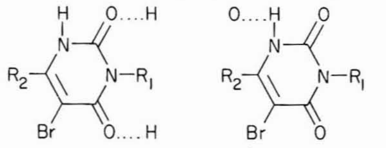


Figure 2. Isosteric heat of adsorption as a function of the amount of chemical sorbed

(1) Isocil–silica gel
(2) Bromacil–silica gel
(3) Isocil–montmorillonite
(4) Isocil–kaolinite
(5) Isocil–humic acid
(6) Bromacil–humic acid
(7) Isocil–illite
(8) Bromacil–illite

concentration C_1. The isosteric heat of adsorption, calculated as a function of chemical sorbed x, is shown in Figure 2. Some interesting conclusions regarding the mechanism of adsorption can be obtained from the thusly computed ΔH values. For most of the surfaces under investigation, the value of ΔH tends to become more positive with increasing surface coverage. This agrees with the earlier reported results. Here, as before, the behavior of humic acid surface is quite different from the others as far as the magnitude and change of ΔH is concerned. (The ΔH value is small and also its change with surface coverage is insignificant.) For most of the surfaces the probable mechanism of the adsorption is a physical or van der Waals-type adsorption as indicated by the magnitude of ΔH. However, at very low surface coverage, the value of ΔH is quite high and this indicates the possibility of some hydrogen bonding. In view of the presence of the carbonyl group in the adsorbate molecule, the possibility of hydrogen bond formation becomes quite probable whenever there are protons available on the surface material. This interaction could result in the following hydrogen bond complex:



(where R_1 and R_2 are alkyl groups)

Hydrogen bond formation could also occur through the N—H bond of the adsorbate and any electron-donating group.

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Received for review September 17, 1969. Accepted July 20, 1970. Research supported by USPHS grant no. ES-004-05 and the manuscript was issued as Technical Paper No. 2762 from the Oregon Agricultural Experiment Station.

Distribution of DDT and Toxaphene in Houston Black Clay on Three Watersheds

Allen R. Swoboda
Soil and Crop Science Department, Texas A&M University, College Station, Tex. 77843

Grant W. Thomas and Foster B. Cady
Department of Agronomy, University of Kentucky, Lexington, Ky. 40506

Ralph W. Baird and Walter G. Knisel
USDA Blacklands Experimental Watershed, Riesel, Tex. 76682

■ The movement and distribution of DDT and Toxaphene in a heavy clay soil was studied on three Blackland Prairie watersheds in Texas. Less than 16% of the DDT (total of *p*, *p*-DDT, DDE, and DDD) and less than 22% of the Toxaphene applied over a 10-year period was recovered in the top 5 ft of the soil. Between 60 and 75% of the recovered DDT was found in the top 12 in. of soil, but 90 to 95% of the Toxaphene was found in the upper 12 in. Movement of DDT into the lower soil depths was attributed to top soil being washed into the large vertical cracks of the Vertisol by rainfall. Leaching was also considered a factor in the downward movement of DDT, since a seep was found to contain from 0.2 to 1.2 ppb of DDT.

Long-time use of persistent, chlorinated hydrocarbons as insecticides and their ubiquitous occurrence as a result has prompted much public concern about the effects of these compounds on the environment. Unfortunately, the answers to many of the questions asked about the behavior of pesticides are not known.

Toxaphene and DDT residues are two of the most persistent pesticides in our environment (Allen *et al.*, 1954; Edwards, 1964; Lichtenstein, 1958). Both insecticides are relatively insoluble in aqueous solutions and it has also been generally accepted that neither are leached through soil profiles (Taschenberg *et al.*, 1961).

Edwards (1964) states that DDT persists longer than the other chlorinated hydrocarbon insecticides, with about 80% remaining after one year and about 50% remaining after three years. Woodwell and Martin (1964) suggest that DDT residues persist for substantial periods, probably longer than 10 years. Allen *et al.* (1954) applied DDT to the top 6 in. of a soil, and four years later found that 87% of the DDT residues remaining was still in the top 6 in. of soil, and that 9.5% of the residue found was at the 6 to 8-in. depth and the remaining 3.5% was found in the 8 to 10-in. depth. Lichtenstein (1958) also found that almost all of the DDT applied to a muck soil and a Miami silt loam remained in the top 6 in. of soil.

The present study was initiated to determine the fate of DDT and Toxaphene, applied in combination, on cotton in a three-year rotation with oats-clover and grain sorghum. This rotation system is common in the Blacklands of central Texas. The part of the study reported here was concerned with the distribution of DDT and Toxaphene in Houston Black clay soil as affected by rate of insecticide application, position with respect to terraces and depth of soil. The location was the Blacklands Experimental Watershed of the Soil and Water Conservation Research Division of the Agricultural Research Service, USDA, Riesel, Tex., 14 miles southeast of Waco.

Experimental

The experimental area was composed of three watersheds, Y-6, Y-8, and Y-10, as shown in Figure 1. The three watersheds have been in a cotton, grain sorghum, oats-clover rotation for 11 years. Each watershed consists of about 19 acres and are situated on a Houston Black clay soil, which contains 50 to 60% montmorillonitic clay and is strongly calcareous. Annual rainfall in the area is 33 in.

Profile samples were taken at depths of 0 to 6 and 6 to 12 in. Below 12 in., samples were collected in 1-ft increments. Each site was sampled with a 3-in. bucket auger to a depth of 60 in. The areas sampled are shown in Figure 1 numerically. The specific sites sampled are designated by small letters (*a*, *b*, *c*). The position of the site sampled in relation to terraces is also shown in Figure 1—*e.g.*, Y-10, 1 *a* indicates the profile was sampled in watershed Y-10, at site 1 and the sample was taken on top of a terrace.

All samples were taken in November 1966. They were air dried, ground to pass a 2-mm sieve, mixed by rolling on clean paper, placed in half-gallon plastic containers, and then stored for up to six months at room temperature.

The cropping sequence, the year, and amount of DDT and Toxaphene applied during the previous 11 years are shown in Tables I and II. DDT and Toxaphene were applied to the land every third year, when cotton was grown. However, no insecticides were applied in 1966 before sampling.

Extraction and Analysis of Soil Samples

Twenty grams of soil, which had been ground to less than 2 mm, was extracted with 50 ml of 1:2 benzene: isopropanol solution by shaking for 2 hr, and then filtering through a fritted-glass filter. The samples were then leached with three additional 10-ml and two 5-ml portions of extracting solution. Preliminary experiments with various extraction solutions demonstrated that 1:2 benzene: isopropanol recovered about 90% of the DDT and Toxaphene from the soil used in this study.

The collected filtrate was evaporated to approximately 20 ml and passed through a column of freshly prepared florisil (Barry *et al.*, 1963). The florisil was then leached with 200 ml of 6% ethyl ether in petroleum ether. When the 6% solution had all entered the column, the flask containing the filtrate was replaced and the column leached with 200 ml of 15% ethyl ether in petroleum ether. The two eluted solutions were evaporated to near dryness over a sand bath at 40° to 50°C, and transferred to 10-ml test tubes with petroleum ether. The samples were then evaporated to near dryness with an air stream at room temperature and then 2 ml of petroleum ether added. Five microliters of the solution was injected into a Model 5360 Barber Coleman Pesticide Analyzer equipped with a Barber Coleman electron capture detector. A 6-ft column with 10% DC-200 on Anakrom ABS was used in the chromatograph. The injector, column, and detector temperatures were maintained at 230°, 205°, and 220°C, respectively. Nitrogen, with a flow rate of 180 cc/min, was used as the carrier gas. Concentrations of DDT and Toxaphene in the samples were determined by the method described in Volume I of the "Pesticide Analytical Manual," published by the U.S. Department of Health, Education, and Welfare (Barry *et al.*, 1963). Both DDT and Toxaphene occur in the 6% ethyl ether solution. The 15% ethyl ether extract was used to check for the presence of other pesticides in the soil.

Table I. Cropping Sequence of Watersheds Used in Sampling Study

Year	Y-6	Y-8	Y-10
1964	cotton	oats-clover	sorghum
1965	sorghum	cotton	oats-clover
1966	oats-clover	sorghum	cotton

Table II. Amounts of DDT and Toxaphene Applied to Each Watershed and Years of Application

Watershed	Yr of insecticide appln	Insecticide applied, lb DDT/acre	Insecticide applied, lb Toxaphene/acre
	1957	0.5	1.0
Y-10	1960	1.5	3.0
	1963	3.0	6.0
	Total	5.0	10.0
	1958	3.0	6.0
Y-6	1961	4.0	8.0
	1964	2.0	4.0
	Total	9.0	18.0
	1959	5.0	10.0
Y-8	1962	3.0	6.0
	1965	3.0	6.0
	Total	11.0	22.0

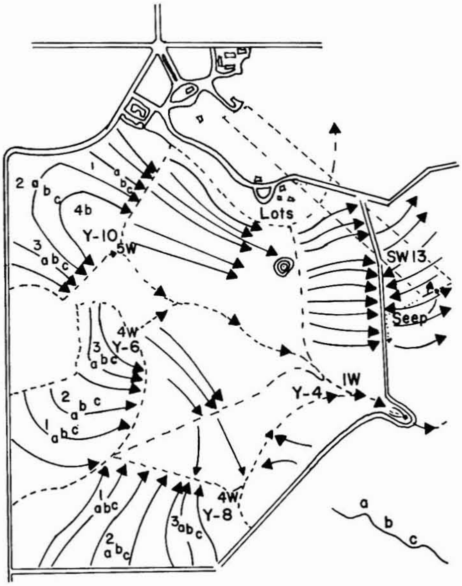

Figure 1. Map of part of the Blacklands Experimental Watershed at Riesel, Tex., with locations of sampling areas

The values reported for DDT are a summation of *p,p*-DDT, DDE, and DDD. DDE and *p,p*-DDT occurred in about equal quantities, whereas only very minute quantities of DDD were extracted from the soil.

Thin-layer chromatography was not used to confirm the identification of DDE, *p,p*-DDT, DDD, or Toxaphene by gas chromatography because of the low concentration of the compounds in most samples. The retention times of the identified gas chromatography peaks for the different compounds were checked with use of two different column packings.

Results and Discussion

DDT. The total amounts of DDT found in the 60-in. profiles of Houston Black soil are given in Table III. The amounts given are averages of nine profiles from each watershed.

There was little difference in the amount of DDT found in the soils where 9 or 11 lb of DDT per acre had been applied, but both were much higher than where 5 lb of DDT per acre was applied. The recovery of DDT in the 60-in. profiles ranged from 11.5 to 16.1% of that added in the past 11 years. Less than 10% of the DDT applied was recovered in the top 12 in. of the profiles. Only about 60% of the DDT in fields Y-6 and Y-10 was concentrated in the top foot of soil (Table III). About 74% of the DDT recovered in field Y-8 was found in the top foot of soil. Field Y-8 received 3 lb of DDT per acre the year before sampling. This probably explains the higher percentage of DDT found in the top foot of soil.

Although the total DDT in the top 5 ft of soil showed little difference between the 9 and 11 lb rate, the distribution did show a large difference. Plots of the average DDT concentrations found in the profiles taken at location *a* in the three watersheds are shown in Figure 2. The amount of DDT in the upper foot of soil was much lower where 5 lb of DDT had been applied than with the other two treatments. Where 11 lb of DDT had been applied, there was a much higher concentration of DDT in the 0 to 6-in. layer and a lower concentration below that depth than where 9 lb of DDT had been applied. This higher concentration of DDT in the upper part of the soil is no doubt a reflection of the higher total DDT applied and the more recent application to that field (Table II). The higher proportion of DDT with depth where DDT was applied earlier (1963 or 1964 *vs.* 1965) suggests that there is a fairly steady and indicative movement of DDT out of the top foot of soil.

The soil position, with respect to terraces (Figure 1), did not have any effect on total DDT in the soil profile. Means for positions *a*, *b*, and *c* were 0.49, 0.45, and 0.44 ppm, respectively. There was no position *X*-rate interaction. The distribution of DDT with depth also was not statistically different between positions.

The amount of DDT found below 1 ft was significant (Figure 2). Previous experiments (Allen *et al.*, 1954; Edwards, 1964; Lichtenstein, 1958) showed that almost all of the DDT residue in soils could be recovered in the upper 6 in. of the soil profile. The watersheds studied here are situated on a Vertisol (Houston Black clay), which consist of 50 to 60% clay and which is predominately montmorillonitic. Since Vertisols are known for their cracking and "self-mulching" action, it is believed that a large part of the DDT found at the lower depths of the profiles is a result of rainwater washing top soil into the cracks. However, some of the DDT found at the deeper profile depths is probably a result of leaching, since water from a nearby seep was analyzed for DDT and Toxaphene and was found to contain significant concentrations of DDT. Normal concentration in the seep water was about 0.2 ppb of DDT, although when initial flow began in the fall a maximum concentration of over 1 ppb was detected.

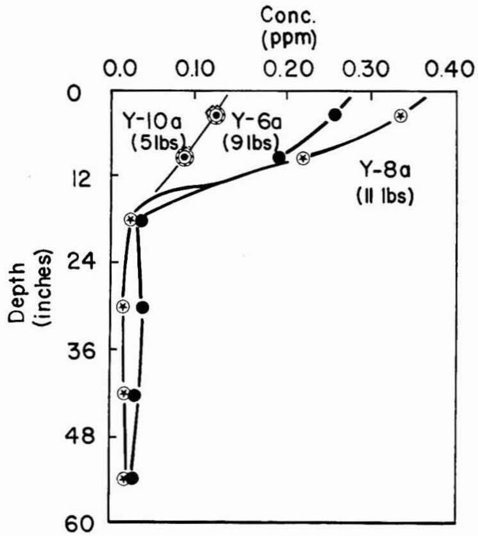

Figure 2. DDT concentrations in profiles of Houston Black clay from three watersheds receiving different amounts of DDT during an 11-year period

Some of the applied DDT may have been lost by volatilization. This may account for the low recoverable DDT found in these soils. Surface soil temperatures of 60 °C have been measured in central Texas. Lahser and Applegate (1966) and Baker (1970) have also reported low recoverable quantities of DDT in soils from Presidio, Tex., and have indicated that volatilization was a major contributor to the loss of DDT.

Toxaphene. The amount of Toxaphene found in the three watersheds was relatively small in comparison to the amount applied (Table IV). Fields Y-6 and Y-8, which received 18 and 22 lb of Toxaphene per acre, respectively, during the past 10 years, contained about the same amount of Toxaphene in the upper 5 ft of soil. Field Y-10, which received only 10 lb, was found to contain a significantly lower amount of Toxaphene, indicating that the quantity recovered was related to the amount applied. A higher percentage of the applied insecticide was recovered in the field receiving the low rate of Toxaphene than in the two fields receiving the higher rates. This was true for both the top 12 in. and the entire profile. The reason for

Table III. Quantities and Percent of DDT (*p,p*-DDT, DDE, and DDD) Found in Profiles of Houston Black Soil

Field	DDT applied, lb/acre	Last appln of DDT	DDT found, lb/acre		Applied DDT recov, %		DDT in top 12 in., %
			0–12 in.	0–60 in.	0–12 in.	0–60 in.	
Y-10	5	1963	0.446	0.754	8.9	15.1	59.2
Y-6	9	1964	0.840	1.388	9.3	15.4	60.5
Y-8	11	1965	0.939	1.267	8.5	11.5	74.1

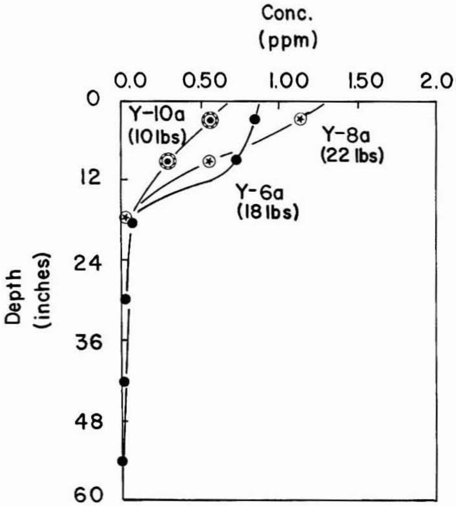

Figure 3. Concentrations of Toxaphene in profiles of Houston Black clay from three watersheds receiving different amounts of Toxaphene during a 11-year period

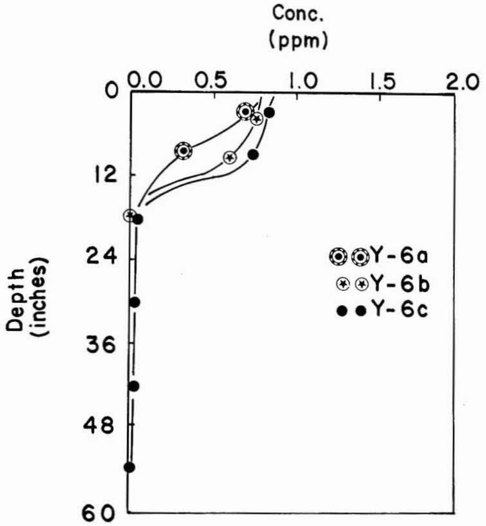

Figure 4. Concentrations of Toxaphene in soil profiles at different locations in field Y-6, which received 18 lb of Toxaphene during the previous 11 years

this difference in percent recovery is not known, especially since Toxaphene was last applied in field Y-10 three years before sampling and the other fields had received more recent applications.

The distribution of Toxaphene varied with rate in somewhat the same way as DDT (Figure 3), but the interaction was not significant at the 5% level. The 22-lb rate (most recently applied) had much higher recoverable Toxaphene in the top 6 in. than did the other two treatments, whereas the 18-lb rate showed a higher concentration in the 6 to 12-in. layer. The relative distribution suggests that more recently applied Toxaphene is closer to the surface. Unlike DDT, however, there is no appreciable Toxaphene at depths greater than 1 ft. On the average, about two-thirds of the recoverable DDT was found in the top foot, while about 90% or more of the Toxaphene was in the top foot of soil (Table IV). The complete lack of Toxaphene in drainage water taken from a nearby seep also suggests that Toxaphene does not move very deeply.

The effect of terrace position on total Toxaphene recovered was not significant, but there was a trend toward a higher concentration at the highest position (*a*). The average values were 1.42 ppm at position *a*, 109 ppm at position *b*, and 1.14 ppm at position *c*.

The distribution of Toxaphene with depth was different between positions *a* and *c* at the 10% level (Figure 4). As in the case of DDT, this suggests that movement of Toxaphene from the 0 to 6-in. layer to the 6 to 12-in. layer is occurring at position *a* (high on the terrace), because the soil is drier most of the time and cracking and sloughing of the soil occurs more frequently than at position *c*.

The behavior of DDT and Toxaphene in a swelling cracking soil was similar. The major difference was that more DDT was found deep in the soil and that a smaller recovery of applied DDT was obtained. The average DDT and Toxaphene distributions shown in Figures 2 and 3 show this conclusively.

These figures strongly imply that DDT is moving down the soil profile by soil "churning," or with water, and probably both. It seems significant that measurable quantities (>1.0 ppb) of DDT were found in water draining from a seep near the sampled fields, whereas no Toxaphene was found. Because of these findings, it is concluded that some DDT move completely through these heavy clay soils into shallow, localized groundwater. The total quantity of DDT that has been lost by leaching as water soluble DDT in 10 years, assuming 6 in. of water percolation yearly and an average DDT concentration of 1.0 ppb, is only 0.014 lb per acre. This, of course, does not include any DDT that is lost from solution in the chalk below the soil depth measured.

Other losses of DDT and Toxaphene can be expected from spray drift, removal in harvested portions of plants, and by volatilization from the soil. Since the soil surface contains most of the pesticides and the Houston Black clay reaches temperatures of 140°F almost daily in the summer, it seems reasonable that large losses of both compounds by volatilization can occur.

In any case, losses of DDT and Toxaphene of the order of 70 to 80% in a 11-year period are higher than those reported by workers in other climatic regions (Edwards, 1964; Lichtenstein, 1958; Taschenberg *et al.*, 1961). However, Randolph *et al.* (1960) reported large losses of DDT from Texas soils. We

Table IV. Quantities and Percent of Toxaphene Found in Top 60 in. of Houston Black Soil

Field	Toxaphene applied, lb/acre	Last appln of Toxaphene	Quantity found, lb/acre		Recov, %		Toxaphene in top 12 in., %
			0–12 in.	0–60 in.	0–12 in.	0–60 in.	
Y-10	10	1963	1.90	2.14	19.0	21.4	88.8
Y-6	18	1964	2.60	2.73	14.4	15.2	95.2
Y-8	22	1965	2.52	2.71	11.5	12.3	93.0

suggest that the higher losses are primarily a result of high leaching losses (with DDT, at least), movement with soil particles, and volatilization due to high soil temperatures.

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Received for review February 17, 1970. Accepted July 6, 1970.

Carcinogenic Air Pollutants in Relation to Automotive Traffic in New York

Joseph M. Colucci and Charles R. Begeman

General Motors Research Laboratories, Warren, Mich. 48090

■ Particulates and carbon monoxide were sampled at five metropolitan New York sites to relate polynuclear aromatic hydrocarbons [benzo(a)pyrene and benz(a)anthracene] to automotive traffic. Carbon monoxide and lead indicated automotive air pollution sources, and vanadium and sulfate nonautomotive combustion sources. Pollutant concentrations were highest at Herald Square, lowest in suburban Scarsdale. Benzo(a)pyrene concentrations ranged from 0.1–9.4 $\mu g/1000$ m^3, were higher during the day than at night, and highest in autumn and winter. For all data, the correlation coefficient for BaP and carbon monoxide was 0.65; for lead, 0.74; for vanadium, 0.54; and all were statistically significant. At individual sites, however, only some of these correlations were significant. BaP in air, even in heavy-traffic areas, appears related to both automotive and nonautomotive sources. BaP at the central New York sites was lower than that measured in central Detroit, even though New York traffic was greater. BaP in New York was lower than that of most other U.S. cities, and much lower than BaP in European cities.

Air was sampled in New York City to determine the atmospheric concentrations of certain polynuclear aromatic hydrocarbons and the relationship of these substances in air to automobile traffic. With use of equipment in a mobile laboratory, sampling was done at five street-level sites. The polynuclear aromatic hydrocarbons determined were benzo(a)pyrene (BaP), a strong carcinogen; and benz(a)anthracene (BaA), a weak carcinogen. These relatively nonvolatile organic compounds are considered to be in the air as solids, most likely associated with carbonaceous or other polymeric substances, as well as with inorganic solids. Sampling of the air was, therefore, by filtration. A benzene extract of the filter yielded a "tar" containing the polycyclic hydrocarbons. Tar in air derives from the combustion or pyrolysis of any carbonaceous matter, and is not specifically related to a particular combustion source.

Carbon monoxide and lead were measured as general indicators of automotive air pollution (U.S. Department of Commerce, 1967; Colucci and Begeman, 1969a). Two other air pollutants, generally considered to derive principally from nonautomotive sources, were also measured. Sulfate was determined as a rough index of pollution from the combustion of fuels for nonautomotive power (U.S. Department of Health, Education, and Welfare, 1958) inasmuch as most other fossil fuels contain much more sulfur than does gasoline (Rohrman and Ludwig, 1965). Nonautomotive sources—mainly those that burn residual fuel oil—have been estimated to contribute 99% of the sulfur compounds emitted to New York air (U.S. Department of Health, Education, and Welfare, 1967). Vanadium was determined as an index of pollution caused by the combustion of petroleum residual fuel (Smith, 1962). Residual fuel oils used in New York, mostly from Venezuela, are especially high in sulfur (Council of the City of New York, 1965) and vanadium (Costanides *et al.*, 1959).

Apparatus and Procedures

Sampling equipment and procedures have been described in detail (Begeman and Colucci, 1962; Colucci and Begeman, 1965) so that only very brief descriptions are included here. A large "absolute" filter, containing 26 m^2 of all-glass filter paper, was mounted about 1.5 m above ground in a truck, which was parked with the engine off during sampling operations. Air was drawn through the filter at 140 m^3/min; the volume filtered in a sampling period ranged from 92,000 m^3 to 816,000 m^3. About 2% of the filter paper was used in analyses for lead, vanadium, and sulfate. The other 98% was extracted with benzene + methanol (4 to 1), and the benzene-soluble portion reduced to tar. The tar was analyzed for benzo(a)pyrene and benz(a)anthracene at the Sloan-Kettering Institute for Cancer Research by column chromatography and reversed-phase paper chromatography in conjunction with ultraviolet spectrophotometry (Hoffmann and Wynder, 1962a,b).

Carbon monoxide was measured continuously during particulate sampling periods with a nondispersive infrared analyzer (Colucci and Begeman, 1969a).

Sampling sites are described in Table I. Automobile traffic at the five sites ranged from very heavy (Herald Square and Columbus Circle in Manhattan) to very light (suburban Scarsdale). The sites are classified according to the predominant nature of the immediate area—*e.g.*, commercial, freeway, or residential.

Table I. New York Area Air Sampling Sites

Site	Type	Specific location	Distance from nearest traffic
Herald Square, Manhattan	Commercial	On Broadway, between 34th and 35th Sts.	6 ft from Broadway traffic lane, about 100 ft north of 34th St.
Columbus Circle, Manhattan	Commercial	Within the circle drive, in the southeast quadrant	10 ft from circle drive
Queens Expressway Interchange	Freeway	On 134th St., first street southeast of interchange parallel to Van Wyck Expressway, south of Union Turnpike	About 250 ft from Van Wyck Expressway, 6 ft from residential traffic
Queens residential	Residential	On northeast corner of 185th St. and 90th Ave.	6 ft from 185th St. traffic
Scarsdale, Westchester County	Residential	On shoulder adjacent to Murray Hill Rd.	6 ft from Murray Hill Rd.

Table II. Annual Average Pollutant Concentrations

Site	CO, ppm	Lead	Vanadium	Sulfate	Tar	BaP	BaA
		$\mu g/m^3$				$\mu g/10^3m^3$	
Herald Square	10.3	8.3	1.06	56	59	3.9	5.6
Columbus Circle	6.8	5.1	1.20	67	29	1.3	2.5
Queens Expressway Interchange	4.0	4.1	0.83	36	23	1.3	2.5
Queens residential	3.3	2.7	0.23	26	19	0.6	1.2
Scarsdale, Westchester County	2.1	1.7	0.17	25	7	0.3	0.6

Table III. BaP and BaA Levels in New York Air

Site	Benzo(a)pyrene, $\mu g/10^3m^3$			Benz(a)anthracene, $\mu g/10^3m^3$		
	Annual av	Minimum	Maximum	Annual av	Minimum	Maximum
Herald Square	3.9	0.5	9.4	5.6	1.0	16.0
Columbus Circle	1.3	0.5	2.6	2.5	0.4	5.1
Queens Expressway Interchange	1.3	0.1	3.5	2.5	0.1	4.7
Queens residential	0.6	0.3	0.8	1.2	0.6	1.7
Scarsdale, Westchester County	0.3	0.1	0.6	0.6	0.1	1.2

Air was sampled from April 1962 through February 1964 on a prearranged quarterly schedule to study seasonal variations in pollutant concentrations. At Herald Square, Columbus Circle, and Queens Expressway Interchange, sampling was divided into daytime and nighttime periods, with the changeover at about 7 a.m. and 7 p.m., to correspond with changes from heavy daytime automobile traffic to lighter nighttime traffic. At the residential sites in Queens and Scarsdale, samples were taken over 24-hr periods.

Results

Annual average pollutant concentrations at each site are shown in Table II. All pollutant concentrations were highest at Herald Square, except for vanadium and sulfate, which were highest at Columbus Circle. Pollutant concentrations at Scarsdale, where the air was least contaminated, were generally 10 to 25% of the concentrations at Herald Square. BaP and BaA concentrations were highest at sites with highest concentrations of both automotive-derived pollutants (CO and lead) and nonautomotive-derived pollutants (vanadium and sulfate), and BaP and BaA were lowest at sites with lowest concentrations of automotive and nonautomotive pollutants. This implies that atmospheric carcinogens derive from both automotive and nonautomotive sources.

Average, minimum, and maximum BaP and BaA concentrations are given in Table III. BaA concentrations were generally one and a half to two times those of BaP.

At the Manhattan commercial sites (Herald Square and Columbus Circle), the air was more polluted during the day than at night (Figure 1). The higher carbon monoxide and lead concentrations in daytime, when traffic was heavier, were expected inasmuch as automobiles are considered the primary source of these pollutants. The fact that tar, BaP, and BaA were also higher in the daytime might indicate that these materials also derive from automobiles. However, vanadium (presumably from nonautomotive sources) was also higher in daytime.

At the freeway site in Queens, daytime and nighttime concentrations of all pollutants were essentially the same, even though automobile traffic was presumably higher in the daytime. At this site, the sampling truck was 250 ft from the expressway in a residential area so that expressway traffic had little effect, and less than expected.

Seasonal concentrations of the pollutants and meteorological data are shown in Figure 2. Generally, pollutant concentrations were either highest or second highest in the autumn, and lowest in the spring or summer. The greater pollution in the autumn was most likely a result of the lower-than-average wind speed, together with the more frequent thermal inversions during this season (U.S. Department of Health, Education, and Welfare, 1967). Conversely, the lower pollution in the spring was likely related to the characteristic higher-than-average wind speed for this season.

Atmospheric BaP and BaA concentrations in the winter

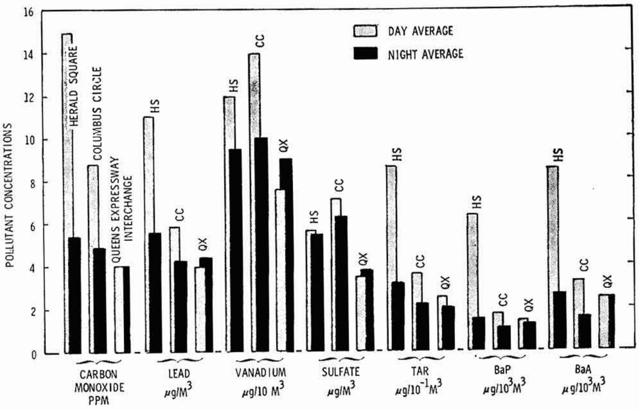

Figure 1. Annual average day and night pollutant concentrations in New York City

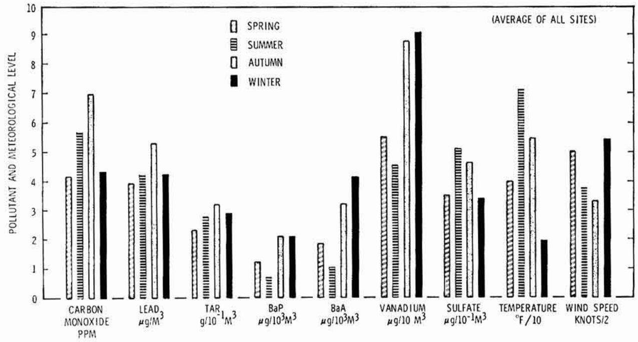

Figure 2. Seasonal pollutant concentrations and meteorological measurements in New York City

were about double the summer concentrations. Although tar-in-air concentrations were nearly constant throughout the year, tar obtained during winter contained the highest concentrations of BaP and BaA, indicating that combustion sources active in winter emitted tar relatively richer in carcinogens. Vanadium concentrations in winter were also about double those in summer, indicating a relationship between carcinogens in air and the combustion of residual fuels. Another factor contributing to the lower atmospheric BaP and BaA levels in summer, as compared with winter, might be their more rapid destruction in air during summer (Tebbins *et al.*, 1966; Thomas *et al.*, 1968).

Generally, seasonal differences in carbon monoxide, lead, tar, and sulfate concentrations were not large.

Discussion

Correlation coefficients among the pollutants are summarized in Table IV.

Since we assumed that both carbon monoxide and lead originate primarily from automobiles, the correlation between these pollutants was of special interest (Colucci and Begeman, 1969b). The correlation coefficient for these pollutants for all samples at all sites, 0.90, is significantly nonzero with 99% confidence. Correlation coefficients for Herald Square, Columbus Circle, and the Queens Expressway Interchange (Table IV) are nearly as high. Thus, because the relationship between CO and lead is good, only carbon monoxide will be used as an index of air pollution from automobiles in

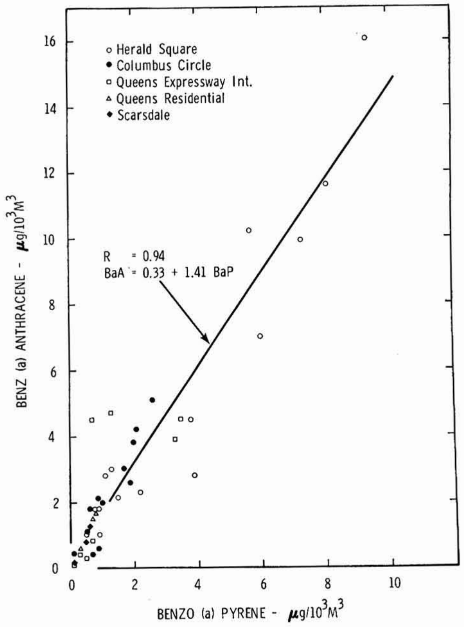

Figure 3. Atmospheric BaA *vs.* BaP in New York

Table IV. Correlation Coefficients among Pollutants

Variables	Correlation coefficients All data	Herald Square	Columbus Circle	Queens Expwy Int.
CO–lead	0.90[a,b]	0.84[a,b]	0.81[a,b]	0.92[a,b]
BaP in air–BaA in air	0.94[a,b]	0.96[a,b]	0.91[a,b]	0.72[a,b]
BaP in air–CO	0.65[a,b]	0.47	0.57	0.94[a,b]
BaP in air–lead	0.74[a,b]	0.60[a]	0.42	0.92[a,b]
BaP in air–vanadium	0.54[a,b]	0.47	0.38	0.72[a,b]
BaP in air–sulfate	0.12	−0.32	0.37	0.24
BaP in air–tar	0.79[a,b]	0.71[a,b]	0.32	0.79[a,b]
BaP in air–temp.	−0.09	−0.25	0.33	−0.09
BaA in air–CO	0.57[a,b]	0.36	0.63[a]	0.58
BaA in air–lead	0.68[a,b]	0.52[a]	0.48	0.70[a]
BaA in air–vanadium	0.61[a,b]	0.56[a]	0.65[a]	0.77[a,b]
BaA in air–sulfate	−0.02	−0.28	−0.09	0.04
BaA in air–tar	0.73[a,b]	0.62[a]	0.48	0.69[a]
BaA in air–temp.	−0.22	−0.37	0.30	−0.65
BaA in tar–temp.	−0.23	−0.50	0.03	−0.07
BaA in tar–temp.	−0.52[a,b]	−0.66[a,b]	−0.06	−0.76[a,b]

[a] Coefficient significantly nonzero with 95% confidence.
[b] Coefficient significantly nonzero with 99% confidence.

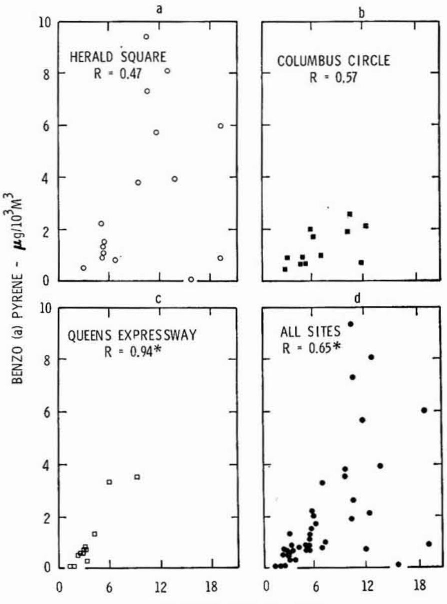

Figure 4. Atmospheric BaP *vs.* carbon monoxide at New York sampling sites

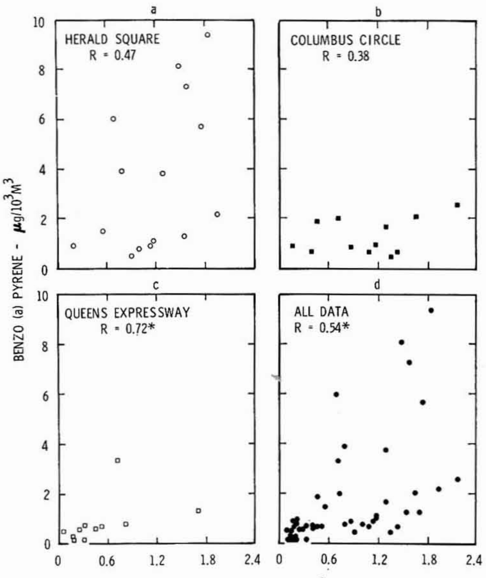

Figure 5. Atmospheric BaP *vs.* vanadium at New York sampling sites

discussing the relationships of other pollutants to automobiles.

It is evident that BaP and BaA are closely related (Figure 3). The correlation coefficient for all sites combined, 0.94, is significantly nonzero with 99% confidence. Correlation coefficients for Herald Square, Columbus Circle, and Queens Expressway individually ranged from 0.72 to 0.96, and all were significantly nonzero with 99% confidence. It will be sufficient, therefore, to illustrate other relationships involving these polynuclear aromatic hydrocarbons using BaP only.

The correlations of BaP with carbon monoxide at the three sites for which sufficient data are available individually are shown in Figure 4 (a,b,c). Only at Queens Expressway is the correlation coefficient statistically significant. However, when data for all five sites are combined (Figure 4d), the correlation coefficient between CO and BaP, 0.65, is statistically significant. Similarly, the correlation coefficient between lead and BaP is 0.74 for all five sites combined.

In a similar manner, BaP is correlated with vanadium

(Figure 5). The correlation coefficients at Herald Square and Columbus Circle are not significant, whereas the correlation coefficient at the Queens Expressway site is significant. When data from all sites are combined, the BaP–vanadium correlation coefficient, 0.54, is significantly nonzero with 99% confidence.

Thus, when all sites are considered together, BaP is significantly related to both automobile-derived pollutants (CO and Pb) and to a nonautomotive-derived pollutant (vanadium).

BaP did not correlate with sulfate (Table IV). This is not surprising considering the anomalities involved in sampling for sulfate by filtration (Lee and Wagman, 1966; Corn and DeMaio, 1965). Even though sulfurous emission is about three times higher in winter than in summer (Council of the City of New York, 1965), sulfate in air was indicated to be slightly lower in winter (Figure 2). A similar situation was observed in Detroit (Colucci and Begeman, 1965).

Concentrations of BaP and BaA in air were not significantly related with ambient temperature (Table IV) although the coefficients were generally negative, which, because of greater fuel usage in cold weather, might be expected. However, correlations of BaA in tar, for two of three individual sites and for all data combined, were significant. Correlations of BaP in tar with ambient temperature were not significant. These differences may be due to the relative stabilities in air of these hydrocarbons.

Atmospheric concentrations of BaP in U.S. and foreign cities for which seasonal data are available are summarized in Table V. Concentrations range from 0.1 μg/10³m³ at several sites of this study to 388 μg/10³m³ in Hamburg, Germany (Hettche, 1964). BaP concentrations in European cities were, on the average, much higher than in U.S. cities, very likely because of the extensive use of coal for space heating (Hangebrauck *et al.*, 1965). Winter BaP levels in U.S. and European cities were generally about four times greater than summer levels. Winter levels of BaP in 94 U.S. cities (Sawicki *et al.*, 1960), not included in Table V, ranged from 0.4–61 μg/10³m³, and averaged 10.6 μg/10³m³.

BaP concentrations at the New York City sites ranged from 0.1–9.4 μg/10³m³. These concentrations were lower than those reported for most other cities (Table V). No other reports were found for BaP in New York City air so that, unfortunately, the measurements given in this paper cannot be compared with others for New York.

Only at one of the five New York sampling sites, Herald

Table V. Benzo(a)pyrene Content of Urban Air

Investigators	City	Benzo(a)pyrene, μg/10³m³ Spring	Summer	Fall	Winter
Colucci and Begeman, this report	New York:				
	commercial	0.5–8.1	0.7–3.9	1.5–6.0	0.5–9.4
	freeway	0.1–0.8	0.1–0.7	3.3–3.5	0.7–1.3
	residential	0.1–0.6	0.1–0.3	0.6–0.8	0.5–0.7
Colucci and Begeman, 1965	Detroit:				
	central sites commercial	7.2	. . .	. . .	5.0–17.0
	central sites freeway	. . .	4.0–6.0	3.4–7.3	9.2–13.7
	residential	. . .	0.2	. . .	0.9–1.8
Sawicki *et al.*, 1960	Atlanta	2.1–3.6	1.6–4.0	12–15	2.1–9.9
	Birmingham	6.3–18	6.1–10	20–74	23–34
	Cincinnati	2.0–2.1	1.3–3.9	14–18	18–26
	Detroit	3.4–12	4.1–6.0	18–20	16–31
	Los Angeles	0.4–0.8	0.4–1.2	1.2–13	1.1–6.6
	Nashville	2.1–9.0	1.4–6.6	30–55	25
	New Orleans	2.6–5.6	2.0–4.1	3.6–3.9	2.6–6.0
	Philadelphia	2.5–3.4	3.5–19	7.1–12	6.4–8.8
	San Francisco	0.8–0.9	0.2–1.1	3.0–7.5	1.3–2.4
DeMaio and Corn, 1966	Pittsburgh	. . .	0–23	2.9–37	8.2
Hettche, 1964	Hamburg, Germany	14–72	10–26	66–296	94–388
Waller, 1952	London, England	25–48	12–21	44–122	95–147
	Sheffield, England	20–44	21–33	56–63	64–78
	Cannock, England	4–16	6–11	27–31	27–32
Waller *et al.*, 1965	London (in traffic)	20	11	57	68
	London (background)	11	1	38	42
D'Ambrosio *et al.*, 1958	Milan, Italy	12	3	25	150
Campbell and Clemmesen, 1956	Copenhagen, Denmark	6	5	14	15
Skramovsky, 1963	Prague, Czechloslovakia	. . .	13–36	. . .	53–145
Saringer, 1963	Budapest, Hungary	. . .	17–32	. . .	72–141
Louw, 1965	Pretoria, South Africa	. . .	10	. .	22–28
	Johannesburg, South Africa	. . .	. . .	. . .	22–49
	Durban, South Africa	. . .	. . .	. . .	5–28
Watanabe and Tomita, 1966	Osaka, Japan				
	commercial	5.7	2.7	9.4	14
	residential	3.3	1.4	3.8	6.7
Cleary and Sullivan, 1965	Sidney, Australia	0.6–2.4	0.6–1.8	2.5–7.4	3.8–8.2

Table VI. Average Air Pollutant Concentrations in Central Detroit and Central New York

Site	CO, ppm	Lead	Tar	BaP		BaA	
		μg/m^3		μg/10^{3}m^3	Tar, ppm	μg/10^{3}m^3	Tar, ppm
Detroit:							
John Lodge-Edsel Ford Freeway Interchange	6.2	8.2	32	5.8	195	11.2	388
Grand Circus Park	2.9	2.8	23	6.9	305	13.7	630
New York:							
Herald Square	10.3	8.3	59	3.9	66	5.6	95
Columbus Circle	6.8	5.1	29	1.3	45	2.5	85

Square, did the BaP concentration for any sample exceed 3.6 μg/10^{3}m^3. At Herald Square, the highest concentration was 9.4 μg/10^{3}m^3. These concentrations are lower than those for many other U.S. cities, and much lower than in most foreign cities, even though automotive traffic was probably higher in New York.

It is likely that some of the BaP levels given in Table V, especially those determined before 1960, are erroneously high due to the inclusion of either benzo(k)fluoranthene or benzo(g,h,i)perylene in the determination of benzo(a)-pyrene (Dubois *et al.*, 1967; Sawicki *et al.*, 1967). This may explain, in part, some of the relatively high concentrations reported.

BaP and BaA concentrations in air at the two Manhattan commercial sites were generally less than half the concentrations at two central sites in Detroit (Colucci and Begeman, 1965) (Table VI), even though tar concentrations in air were higher at the New York sites. The BaP content of the tar at these New York sites was only about 0.2 as great as in tar obtained at the Detroit sites. Thus, even though automobile traffic on Manhattan was denser than in central Detroit and sampling was closer to the traffic lanes (as indicated by higher concentrations of carbon monoxide and lead), polynuclear aromatic hydrocarbon concentrations were much lower in New York. It is apparent, therefore, that the higher polynuclear aromatic hydrocarbon concentration in Detroit air is most likely due to nonautomotive sources. This conclusion was previously reached on other evidence (Colucci and Begeman, 1965). The nonautomotive sources in Detroit are probably associated with space heating, especially with coal as fuel. Coal consumption in Detroit was five times greater per square mile than in New York (Council of the City of New York, 1965; Sterling, 1965).

Acknowledgment

The authors appreciate the assistance of John Neff, formerly of the Research Laboratories Fuels and Lubricants Department, in carrying out the filter extraction and tar concentration procedures; Richard Loranger and William Lee, of the Chemistry Department, in making the vanadium and sulfate analyses; and Kay Kumler, of the General Motors Industrial Hygiene Department, in making the lead analyses. We are also indebted to Ernst Wynder, Dietrich Hoffman, and their staff at the Sloan-Kettering Institute for the determinations of BaP and BaA in tar. We also appreciate the assistance of public officials in New York City and Scarsdale for granting permission to park in restricted areas.

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Received for review August 22, 1969. Accepted July 20, 1970. Presented at the 61st Annual Meeting of the Air Pollution Control Association, St. Paul, Minn., June 1968.

Reactivity Relationships of Hydrocarbon Mixtures in Atmospheric Photooxidation

William A. Glasson and Charles S. Tuesday

Fuels and Lubricants Department, General Motors Research Laboratories, Warren, Mich. 48090

■ The use of individual hydrocarbon reactivity data for estimating the reactivity of various emissions requires a knowledge of reactivity relationships in hydrocarbon mixtures. The nitric oxide photooxidation rate, used as the measure of hydrocarbon reactivity in this study, was determined with binary and quaternary hydrocarbon mixtures with use of long-path infrared spectrophotometry. Observed rates were compared to rates calculated by summing individual rates extrapolated from rates measured at 1.0 p.p.m. hydrocarbon to the concentrations in the mixture (linear rate) and by summing rates measured at the concentrations of the individual hydrocarbons in the mixture (combined rate). The data obtained at a total hydrocarbon concentration of 1.0 p.p.m. indicate that the linear rate is in agreement with the observed rate, which is less than the combined rate.

Reactivity of individual hydrocarbons is an important consideration in controlling photochemical smog formation (Caplan, 1965; Hurn *et al.*, 1965; McReynolds *et al.*, 1965). Hydrocarbon reactivities in the atmospheric photooxidation of nitric oxide (Glasson and Tuesday, 1970a) have recently been used (Jackson, 1966) to estimate the effectiveness of various exhaust control methods in reducing photochemical smog.

The use of individual hydrocarbon reactivity data to estimate the reactivity of hydrocarbon mixtures requires knowledge of the effects of reaction variables, as well as the reactivity relationships in hydrocarbon mixtures.

The effects of certain reaction variables on hydrocarbon reactivity in nitric oxide photooxidation have recently been reported (Glasson and Tuesday, 1970b). This study indicated that, even though reactivities are nonlinear functions of hydrocarbon concentration, the total reactivity of complex hydrocarbon mixtures (gasolines) at a hydrocarbon concentration of 1 p.p.m. can be predicted by using linear extrapolations of individual hydrocarbon reactivity data obtained at the same hydrocarbon concentration. An understanding of this phenomenon and of the effect of hydrocarbon mixtures on reactivity in general is the object of this investigation.

The rate of nitric oxide photooxidation was studied with various binary hydrocarbon mixtures and some quaternary mixtures using hydrocarbons with different structures and reactivities.

Experimental

Apparatus. Analyses were performed with a 3-m. base-path multiple-reflection cell used in conjunction with a modified Perkin-Elmer Model 21 infrared spectrophotometer. Analyses were made with a pathlength of 120 m. Irradiation was supplied by a number of black-light fluorescent bulbs mounted in the long-path cell which also served as the reaction vessel. Details of the cell and the irradiation system are given elsewhere (Tuesday, 1961).

Chemicals. Mesitylene, (1,3,5-trimethylbenzene) 2,3-dimethyl-2-butene, 2,3-dimethyl-2-hexene, and *trans*-4-octene were API standard samples. The other hydrocarbons used were Phillips Research Grade materials. Nitric oxide (Matheson) was purified by passage through a bed of Ascarite, followed by repeated bulb-to-bulb distillations. Nitrogen dioxide was prepared, as needed, by the thermal oxidation of nitric oxide, as described previously (Tuesday, 1963).

Procedure. The long-path cell was evacuated to a pressure of 10 μ Hg before each run. Nitric oxide and nitrogen dioxide at known pressures were expanded into the cell from an attached glass vacuum system. Hydrocarbons with high vapor pressures were individually expanded into the cell from the vacuum system. Hydrocarbons with low vapor pressures at room temperature were added from an electrically heated stainless steel manifold containing several high-vacuum valves and a silicone rubber septum. The required volume of hydrocarbon was injected into this manifold with either a 10- or 50-μl. syringe, depending on the amount required, and then expanded into the cell. Where more than one hydrocarbon was injected for a mixture, separate syringes were used. The manifold was flushed briefly to ensure quantitative hydrocarbon addition. To avoid contamination, a new septum was used for each mixture. Nitrogen was then added to the long-path cell to a pressure of about 600 mm. Hg. After the addition of 155 mm. Hg oxygen, the final pressure was brought to 760 mm. Hg with the small amount of additional nitrogen required.

Light intensity was measured by photolyzing very low concentrations of nitrogen dioxide in nitrogen, and is expressed as the first-order rate constant for photolysis $Kd(NO_2)$.

The following conditions were used for all experiments in this investigation: 155 mm. Hg oxygen; 760 mm. Hg total pressure; a light intensity corresponding to $Kd(NO_2)$ equal to 0.29 min.$^{-1}$; and a temperature of 79°F. ± 1°.

Since the time from the addition of oxygen to the start of irradiation was only 2 min., the thermal oxidation of nitric oxide occurring in the cell prior to irradiation was insignificant (Glasson and Tuesday, 1963).

The formation of nitrogen dioxide was followed by measuring the absorption at 6.15 μ. A portion of the spectrum containing this wavelength was scanned repeatedly throughout the photooxidation. The spectral range covered depended on the nitric oxide photooxidation rate. For very fast reactions, the 6.15-μ absorption was monitored continuously.

For most runs, the water vapor absorption was monitored at 6.4 or 6.8 μ, and the absorption at 6.15 μ corrected for any changes in the water absorption at that wavelength.

The nitrogen dioxide formation rate is expressed as the average rate to the half-time ($t_{1/2}$)—*i.e.*,

$$\text{Average NO}_2\text{ formation rate} = \frac{(\text{NO})_0}{2t_{1/2}} \qquad (1)$$

where $(\text{NO})_0$ is the initial nitric oxide concentration and $t_{1/2}$ is the time necessary to convert one-half of this concentration to nitrogen dioxide. The rate is given in the units p.p.b. (v./v.) per min. (p.p.b. min.$^{-1}$).

Results

Nitric Oxide Photooxidation. Two binary hydrocarbon mixtures were used in a preliminary exploration of the atmospheric photooxidation of nitric oxide. The mixtures contained 2-methyl-2-butene and either propylene or mesitylene. The total hydrocarbon concentration was maintained at 1.0 p.p.m., the individual hydrocarbon concentrations varying from 0 to 1 p.p.m., while the concentrations of nitric oxide and nitrogen dioxide were kept at 0.38 and 0.02 p.p.m., respectively. The results are given in Figures 1 and 2.

The observed nitric oxide photooxidation rates are compared graphically (Figures 1 and 2) with two calculated rates—the combined rate and the linear rate.

The combined rate is defined as the sum of the rates measured for each hydrocarbon at the concentration of that hydrocarbon in the mixture, but in the absence of any other hydrocarbon. For example, for a mixture of 0.5 p.p.m. of 2-methyl-2-butene and mesitylene, the rates obtained with 0.5 p.p.m. 2-methyl-2-butene alone (8.7 p.p.b. min.$^{-1}$) and 0.5 p.p.m. mesitylene alone (4.2 p.p.b. min.$^{-1}$) are added to yield the combined rate (13 p.p.b. min.$^{-1}$).

The linear rate is defined as the sum of the rates for each hydrocarbon linearly extrapolated from the rate measured at 1.0 p.p.m. of the individual hydrocarbon to the concentration of that hydrocarbon in the mixture. For example, referring to the mixture cited above, the rates of 1.0 p.p.m. of 2-methyl-2-butene and mesitylene are 19 and 5.1 p.p.b. min.$^{-1}$, respectively. Linear extrapolation to 0.5 p.p.m. of each hydrocarbon gives the individual rates 9.5 and 2.55 p.p.b. min.$^{-1}$, which are summed to yield the linear rate, 12 p.p.b. min.$^{-1}$

The data in Figures 1 and 2 show that the observed rate is lower than the combined rate. Further, the combined rate is always greater than, or equal to, the linear rate within the experimental error, which is estimated to be approximately 10%.

To assess the validity of these observations, data were obtained for numerous hydrocarbon mixtures. Since the maximum difference between the observed rates and calculated rates for the mixtures of 2-methyl-2-butene with either propylene or mesitylene occurred for the 50-to-50 mixture, this composition was selected for study. The results are given in Table I, together with the appropriate data of Figures 1 and 2.

Of the 15 binary mixtures at a total hydrocarbon concentration of 1.0 p.p.m., 14 have observed rates less than the corresponding combined rates, while 13 have observed rates equal to the corresponding linear rates, within experimental error. The consistent nature of these trends demonstrates the usefulness of the linear rate in estimating the reactivity of, at least, binary hydrocarbon mixtures.

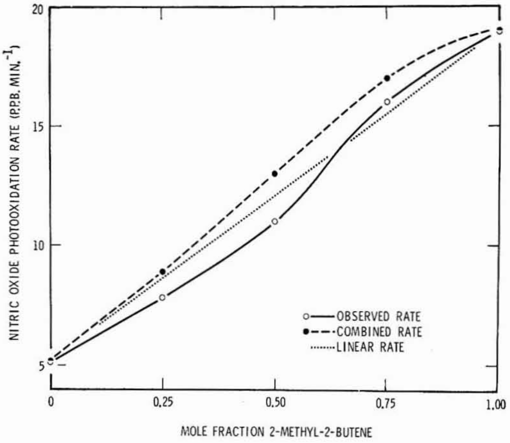

Figure 1. Nitric oxide photooxidation with hydrocarbon mixtures; 1.0 p.p.m. (mesitylene + 2-methyl-2-butene), 0.38 p.p.m. nitric oxide, 0.02 p.p.m. nitrogen dioxide

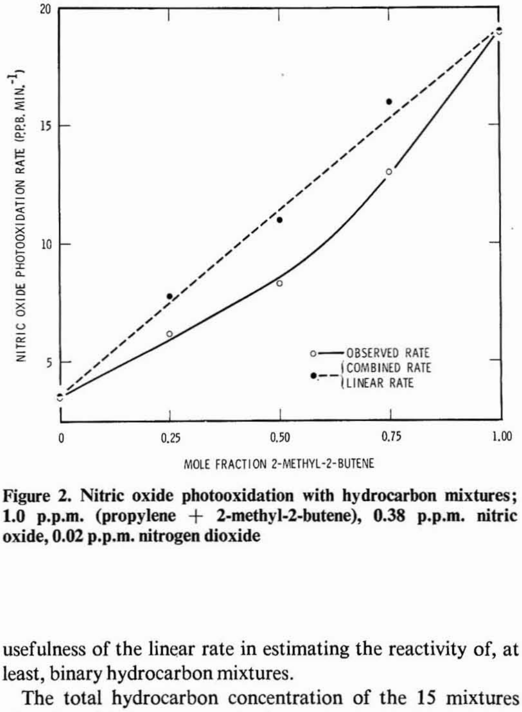

Figure 2. Nitric oxide photooxidation with hydrocarbon mixtures; 1.0 p.p.m. (propylene + 2-methyl-2-butene), 0.38 p.p.m. nitric oxide, 0.02 p.p.m. nitrogen dioxide

The total hydrocarbon concentration of the 15 mixtures given in Table I was maintained at 1.0 p.p.m., the concentration used as the reference point for the calculation of the linear rate. To determine the applicability of linear rates to hydrocarbon mixtures in which the total hydrocarbon concentration is different from 1.0 p.p.m., several runs were carried out at a total hydrocarbon concentration of 0.5 p.p.m. The results are also given in Table I.

In all cases, the observed rates are less than the combined rates, but in contrast to the other data of Table I, the linear rate is not generally equal to the observed rate. This inequality, however, was only found in the two mixtures containing mesitylene.

Table I. Observed and Calculated Rates for the Atmospheric Photooxidation of Nitric Oxide with Binary Hydrocarbon Mixtures[a]

Hydrocarbon pair	Total (HC)$_0$, p.p.m.	Rate,[b] p.p.b. min.$^{-1}$ Observed	Combined	Linear
Ethylene + propylene	1.0	2.5	3.1	2.6
o-Xylene + propylene		3.2	3.9	3.1
2-Methyl-1-pentene + toluene		2.0	2.9	1.8
m-Xylene + propylene		3.9	4.5	3.6
Mesitylene + *o*-xylene		4.1	6.0	3.8
2,3-Dimethyl-2-butene + 2-methyl-2-butene		33	45	39
2,3-Dimethyl-2-hexene + 2-methyl-2-butene		27	26	27
n-Hexane + ethylene		1.5	1.7	1.3
2-Methyl-2-butene + mesitylene		11	13	12
2-Methyl-2-butene + propylene		8.3	11	11
Toluene + *n*-hexane		1.2	1.6	1.1
n-Hexane + 2,3-dimethylbutane		1.0	1.3	1.0
Ethylene + isobutene		2.8	3.7	2.6
Propylene + mesitylene		4.3	6.3	4.3
n-Hexane + *trans*-4-octene		2.2	2.5	2.1
Propylene + mesitylene	0.5	3.4	3.8	2.2
Propylene + *o*-xylene		1.6	2.1	1.5
o-Xylene + mesitylene		2.7	3.5	1.9

[a] The experiments were performed with equal amounts of each hydrocarbon, 0.38 p.p.m. NO and 0.02 p.p.m. NO_2.

[b] The observed, combined, and linear rates are defined in the text. The individual rates at 0.5 p.p.m. of the given hydrocarbon are (p.p.b. min.$^{-1}$): ethylene, 1.0; propylene, 2.1; *o*-xylene, 1.8; 2-methyl-1-pentene, 2.0; toluene, 0.90; *m*-xylene, 2.4; mesitylene, 4.2; 2,3-dimethyl-2-butene, 36; 2-methyl-2-butene, 8.7; 2,3-dimethyl-2-hexene, 17; *n*-hexane, 0.66; 2,3-dimethylbutane, 0.68; isobutene, 2.7; and *trans*-4-octene, 1.8. Those at 0.25 p.p.m. are: propylene, 1.2; mesitylene, 2.6; and *o*-xylene, 0.90.

As a further check on the effect of total hydrocarbon concentration on the correlation between linear and observed rates, rates were also calculated by linear extrapolation from the individual measurements at 0.5 p.p.m. These rates were then summed to yield a calculation rate analogous to the linear rate based, however, on a reference concentration of 0.5 p.p.m. hydrocarbon rather than 1.0 p.p.m. These rates are (p.p.b. min.$^{-1}$): propylene + mesitylene, 3.2; propylene + *o*-xylene, 2.0; and *o*-xylene + mesitylene, 3.0. Comparison of these rates with the data of Table I indicates that a better correlation between observed and "linear" rates is obtained when the reference hydrocarbon concentration is the same as the total hydrocarbon concentration of the mixture.

Two quaternary hydrocarbon mixtures were also studied. The concentration of each hydrocarbon was 0.25 p.p.m. for a total hydrocarbon concentration of 1.0 p.p.m. The remaining experimental variables were the same as those used in the studies described above. The results in Table II indicate that the observed rates are considerably lower than the combined rates in both cases, but are equal to the linear rates within experimental error.

These results are consistent with the data of Table I and further demonstrate the successful application of linear rates in estimating the reactivity of hydrocarbon mixtures in the atmospheric photooxidation of nitric oxide.

Discussion

The results of this investigation can be summarized briefly as follows: (*a*) nitric oxide photooxidation rates observed with

Table II. Nitric Oxide Photooxidation with Quaternary Hydrocarbon Mixtures[a]

Mixture	Rates, p.p.b. min.$^{-1}$ [b] Observed	Combined	Linear
n-Hexene *trans*-4-Octane Propylene Mesitylene	3.0	5.0	3.2
Isobutene Ethylene 2-Methyl-1-pentene Toluene	2.3	3.4	2.2

[a] The quaternary mixtures contained equal amounts of each component at a total hydrocarbon concentration of 1.0 p.p.m. The initial concentration of nitric oxide and nitrogen dioxide were 0.38 and 0.02 p.p.m., respectively.

[b] The average rate to the half-time.

binary and quaternary hydrocarbon mixtures are consistently less than the rates calculated from independent experiments with the single hydrocarbon systems; (*b*) rates calculated from linear extrapolations of data obtained with 1.0 p.p.m. of the individual hydrocarbons agree closely with the observed rates for the mixtures.

A plot of rate *vs.* hydrocarbon concentration from a previous study (Glasson and Tuesday, 1970b) is reproduced in Figure 3 for convenience in this discussion. The hydrocarbon is mesitylene and the experimental conditions are the same as those in Table I.

The less-than-linear hydrocarbon dependence shown in Figure 3 is consistent with increasing inhibition of nitric oxide photooxidation with increasing hydrocarbon concentration. In a mixture of hydrocarbons, this inhibition will be a function of the total hydrocarbon concentration. The reactivity of an individual component of a mixture will, therefore, be reduced relative to the reactivity measured in the absence of other hydrocarbons but at the same concentration as that in the mixture. Thus, the combined rate will be higher than the observed rate.

On the other hand, the rates used to calculate the linear rates are obtained by linear extrapolation from the rate at 1.0 p.p.m. hydrocarbon. The extrapolated rates will be less than or equal to the actual individual rates at individual hydrocarbon concentrations less than 1.0 p.p.m., subject to the degree of nonlinear dependence shown by the particular hydrocarbon (Figure 3). The linear rate will, therefore, be less than or equal to the combined rate. Since, for hydrocarbon mixtures, the observed rate is consistently less than the combined rate, the linear rate will be a better approximation to the observed rate than the combined rate.

The limited data in Table II suggest that the linear rate is not a good approximation to the observed rate for binary hydrocarbon mixtures at a total hydrocarbon concentration of 0.5 p.p.m. The degree of hydrocarbon inhibition of the nitric oxide photooxidation rate decreases with hydrocarbon concentration in a nonlinear manner, while individual rates obtained by linear extrapolation from 1.0 p.p.m. hydrocarbon include a degree of inhibition relevant to 1.0 p.p.m. hydrocarbon. At 1.0 p.p.m. hydrocarbon, the compensation provided by the linear extrapolation is sufficient to attain agreement between the observed and linear rates. However, at 0.5 p.p.m. hydrocarbon, where inhibition is less dominant, linear extrapolation from 1.0 p.p.m. results in overcompensation of the inhibition,

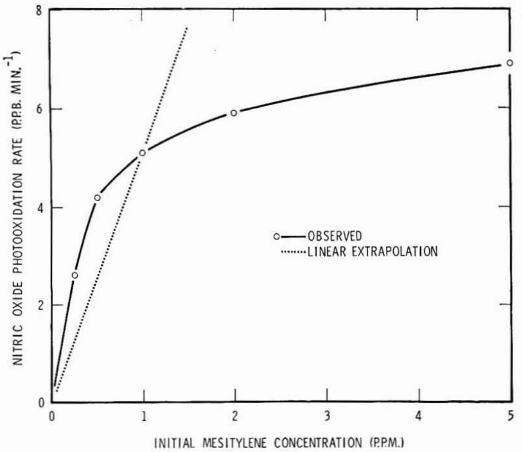

Figure 3. Nitric oxide photooxidation rate as a function of mesitylene concentration; 0.38 p.p.m. nitric oxide, 0.02 p.p.m. nitrogen dioxide

and thus the linear rate is lower than the observed rate. Linear extrapolation from 0.5 p.p.m. hydrocarbon, however, avoids this overcompensation of hydrocarbon inhibition so that the extrapolated results are in better agreement with the observed results.

The results of this study demonstrate the applicability of individual reactivity measurements in estimating the nitric oxide photooxidation rate in binary and quaternary hydrocarbon mixtures using linear extrapolations of individual rates. The use of such a computational method to predict nitric oxide photooxidation rates of emission samples under atmospheric conditions is still subject to experimental verification. Varying conditions of reactant concentrations, light intensity, temperature, and relative humidity as found in the atmosphere make the use of hydrocarbon reactivity values, obtained under vastly different experimental conditions, of uncertain value. There are some data in the literature, however, that make the method seem more promising, even under atmospheric conditions. This method was successfully applied to a series of complex hydrocarbon mixtures (Glasson and Tuesday, 1970b). Further, some of the hydrocarbon reactivities used in this study were also measured in the GM Smog Chamber (Heuss and Glasson, 1968). The two sets of values obtained for 26 hydrocarbons correlated well (correlation coefficient, 0.995). The smog chamber results were obtained under conditions of temperature and humidity which were substantially different from those used in the long-path infrared cell. The nitrogen oxides concentration in the smog chamber was about 2.5 times that used in the long-path cell, while the hydrocarbon concentration in the smog chamber was twice that in the cell. The hydrocarbon to nitrogen oxides ratio was 2.0 in the smog chamber and 2.5 in the cell. Agreement of hydrocarbon reactivity values under such diverse conditions suggests that application of such hydrocarbon reactivity values to atmospheric systems would be justified.

The results of this study offer evidence for the utility of a computational method for predicting nitric oxide photooxidation rates in the presence of hydrocarbon mixtures. Evidence has been found, however, indicating that computations by this method should be restricted to systems at a total hydrocarbon concentration of 1.0 p.p.m. In practice, normalization of composition data to a total hydrocarbon concentration of 1.0 p.p.m. will permit valid comparisons between different hydrocarbon mixtures.

Acknowledgment

The authors express their gratitude to Jerome Zemla for his invaluable assistance in obtaining data and preparing the manuscript.

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Received for review January 13, 1970. Accepted July 29, 1970 Presented in part at the 153rd Meeting, ACS, Miami Beach Fla., April 1967. Division of Water, Air, and Waste Chemistry.

Suspended Particulate Matter: Seasonal Variation in Specific Surface Areas and Densities

Morton Corn, Thomas L. Montgomery, and Nurtan A. Esmen
Department of Occupational Health, Graduate School of Public Health, University of Pittsburgh, Pittsburgh, Pa. 15213

■ Suspended particulate matter was collected at a sampling site on the roof of the Graduate School of Public Health, University of Pittsburgh, with use of a high-volume air sampler and glass-fiber and membrane filters. Specific surface areas of samples were measured by the Brunauer-Emmett-Teller method with nitrogen and krypton gas as adsorbates after sample degassing at 25° and 200°C. Specific density was measured by micropycnometer with ethylene glycol. The arithmetic mean of sample specific surface areas and densities varied with season of the year from a low of 1.90 ± 0.36 m.^{2} per gram (spring) to a high of 3.05 ± 0.38 m.^{2} per gram (winter) for samples degassed at 25°C. Higher values of specific surface were measured after sample degassing at 200°C. Arithmetic mean values of sample specific densities were 1.8 ± 0.2 g./cm.^{3} (spring) and 2.1 ± 0.5 g./cm.^{3} (winter).

The interaction of suspended particulate matter and pollutant gases in the atmosphere has been a continuing subject of investigation (Smith and Wagman, 1969). In addition to the chemical-physical phenomena involved, the biological effects associated with inhaled particles has received widespread attention. The biological response of an aerosol in combination with a pollutant gas in air is often greater than (synergism) or less than (antagonism) the response of the organism to either agent alone. The synergism and antagonism associated with gas particle mixtures are not well understood, despite their great implications for judging the hygienic quality of urban air.

One mechanism proposed to explain the enhanced effects observed when certain combinations of gases and particles are inhaled is that the gas is adsorbed by the particle, with subsequent high local concentration of gas at the site of deposition of the particle in the respiratory tract (Goetz, 1961). Specific surface area is an important parameter required to characterize the capacity of suspended particulate matter to adsorb gases. Preliminary data related to specific surface areas and densities of suspended particulate matter in Pittsburgh air has been reported (Corn *et al.*, 1968). Additional data are now reported for an entire year of air sampling at the same site. These data and those originally reported provide the only information available relative to specific surfaces and densities of an urban aerosol.

Methods

Samples were collected from October 1967 through October 1968 on the roof of the Graduate School of Public Health, Oakland, Pittsburgh, Pa. Particulates were collected on filter paper (Corn *et al.*, 1968) with a high-volume sampler (USPHS, 1962a). The filter paper used was either the membrane, type-SC, 8-μm pore size, (Millipore Filter Corp., Watertown, Mass.) or the glass fiber, Type-1106B (Mine Safety Appliances Co., Pittsburgh, Pa.). Stations of the National Air Sampling Network normally collect samples during a 24-hr. period and use glass-fiber filters, but this study required larger samples for analyses; therefore, sampling time was one to two weeks at flow rates of approximately 0.85 to 1.4 m.^{3} per minute. For analyses, 1-g. samples were obtained by brushing off the top layer of removable dust from the filter; data on particulate concentration (μg. per m.^{3}) for this site are available (USPHS, 1962b) and will not be reported here.

The specific surfaces of samples were measured by the Brunauer-Emmett-Teller (BET) method (Faeth, 1962); both nitrogen and krypton were used, as indicated in Tables I and II. The specific surface of each sample was measured twice, once after degassing for 8 hr. at 25.2° ± 1.0°C., and again after degassing for 4 hr. at 200°C. Effective cross-sectional areas occupied by the adsorbates were assumed to be 16.2 and 19.5 Å per molecule for nitrogen and krypton, respectively (Faeth, 1962).

The bulk density of samples was determined by placing a small amount of each sample in a capillary column (2-mm. i.d.) of known weight and volume, and closed at one end. The tube was tapped gently on a hard surface during and after introduction of the sample, until gentle tapping did not decrease the height of the sample above a predetermined level in the tube.

The densities of the particulate samples were determined by placing a weighed sample in a weighed micropycnometer of about 1-cm.^{3} volume (May and Marienko, 1966). While the samples were under vacuum, ethylene glycol was introduced by syringe until it was covered. The weight per unit volume of dust was calculated from glycol density and by assumption that the volumes of glycol and particulate sample were additive.

Results and Discussion

Table I summarizes our results of specific surface area and density measurements for samples collected on glass-fiber and membrane filters.

Table I. Specific Surface Areas, Bulk Densities, and Densities of Suspended Particulates in Pittsburgh Air

Sampling period	Specific surface area, m.²/g.				Density,[a] g./cm.³	
	Adsorbate	25° C.	Adsorbate	200° C.	Bulk	Specific
Samples collected on Type-1106B MSA fiber-glass filters						
10/13–10/20/67	Kr	1.80	Kr	4.22	0.69	2.1
10/25–11/3	Kr	2.36	Kr	3.49	0.63	1.5
11/7–11/22	N	2.86	N	3.58	0.57	2.0
11/22–12/7	N	2.96	N	4.97	0.59	2.1
12/7–12/21	N	3.32	N	5.50	0.53	3.0
12/21/67–1/5/68	Kr	3.10	N	4.41	0.57	2.3
1/5–1/19	Kr	3.39	Kr	5.11	0.51	2.4
1/19–2/5	Kr	3.10	Kr	5.36	0.54	2.0
2/5–2/19	N	2.92	N	5.04	0.64	2.2
2/20–3/4	Kr	3.13	N	4.70	0.55	2.0
3/4–3/18	N	2.42	N	3.47	0.57	1.5
3/18–4/4	N	2.54	N	3.64	0.61	1.9
4/4–4/22	N	2.33	N	3.78	0.58	2.0
4/22–5/8	N	2.82	N	4.29	0.57	1.7
5/8–5/27	N	2.18	N	2.81	0.62	1.8
5/29–6/19	N	1.91	N	3.46	0.57	1.5
6/20–7/9	N	2.26	N	2.67	0.64	2.0
6/8–8/7	N	1.55	N	2.32	0.63	2.3
7/24–8/7	N	1.89	N	3.02	0.66	2.1
Arithmetic means		2.57		3.99	0.59	2.0
Arithmetic standard deviation		0.59		0.95	0.047	0.36
Samples collected on Type-SD (8-μm pore size) membrane filters						
10/23–11/3/67	N	3.68	N	5.65	0.67	1.5
11/7–11/22	N	3.23	N	5.65	0.52	1.8
11/22–12/7	Kr	3.33	Kr	5.23	0.51	2.1
12/7–12/21	N	3.26	N	4.92	0.64	2.8
12/21/67–1/5/68	N	4.36	N	6.75	0.54	2.3
8/7–8/14	Kr	1.43	Kr	3.86	0.65	2.2
8/14–8/21	N	2.16	N	2.59	0.57	2.2
8/21–8/30	N	1.90	N	3.39	0.62	2.1
8/30–9/6	Kr	1.78	Kr	2.84	0.56	2.2
9/6–9/13	Kr	1.64	Kr	2.91	0.66	2.2
9/13–9/23	N	1.62	N	3.10	0.60	2.4
9/23–10/3	N	2.66	N	3.81	0.59	2.7
10/4–10/13	Kr	1.72	Kr	3.18	0.52	2.7
Arithmetic means		2.52		4.14	0.59	2.2
Arithmetic standard deviation		0.95		1.34	0.06	0.36

[a] Density values are averages of two determinations for each sample.

The data have been grouped to obtain seasonal averages (Table II).

The specific surface data of Table I are shown in Figure 1. Figure 2 shows the variation of seasonal averages.

Previously reported preliminary data (Corn *et al.*, 1968) suggested the trend of data presented here. There is a difference between the specific surface of suspended particulate matter when the determination follows sample degassing at 25°C. and degassing at 200°C. In all cases, samples degassed at 200°C. are associated with higher specific surface areas. The amounts of material vaporized during the higher temperature measurements were estimated to be about 10% of initial sample weight. High-resolution mass spectrometric analyses have been performed by the U.S. Bureau of Mines on the condensate collected above the degassing chamber of the BET apparatus (Sharkey *et al.*, 1969). The most intense peaks in the mass 76 to 266 range were attributed to anthracene, pyrene, benzanthracene, benzopyrene, and benzo(g,h,i)-perylene.

The specific surfaces of samples measured after degassing at 25° C. are probably associated with gas-solid phase chemical reactions occurring at the particle surfaces in the atmosphere. The higher specific surfaces measured after degassing at 200° C. are probably associated with liquid-solid phase reactions after particle deposition in the lung. Pylev (1967) demonstrated that leaching of 3,4-benzopyrene adsorbed on carbon black particles occurs over a period of 30 to 50 days in rat lungs. The available particle specific surface after leaching of organics by lung fluids may be analogous to the surface area measured after degassing at 200° C.

The variation in concentrations of suspended particulate matter (in urban areas) with season of the year is well documented (Corn, 1968). The seasonal variation of specific surface area and density of suspended particulate matter in an urban area is reported here for the first time. Data collected at this single sampling site suggest that the specific surface area of suspended particulate matter is highest in the winter and lowest in the summer. The fall is associated with specific surfaces lower than those of winter samples, but higher than those of spring samples. The data suggest also that there is less seasonal variation in the bulk density of suspended particulate matter than in the specific density, as these parameters are defined here. It must be noted that these are generalizations with regard to seasonal averages; examination of Figures 1 and 2 reveals that certain individual samples are exceptions to these generalizations.

To compare results for specific surface with values of specific surface which may be calculated from other independent measurements at this sampling site, we performed the following calculations. Other data collected at this sampling site resulted in assigning an average value of 1.78 to the ratio between the mean projected area diameter (d_p) and the aerodynamic equivalent diameter (d_e) of particles collected in a horizontal elutriator (Stein *et al.*, 1969). The average specific density of samples reported here (Table II) is 2.2 g. per cm.³ Thus, as an approximation

$$\epsilon = \left[1 - \left(\frac{\rho_{d_p/d_e}}{\rho_s}\right)\right] \qquad (1)$$

where ϵ = average fraction of voids in particles; ρ_s = density measurements reported here (2.2 g. per cm.³); and $\rho_{(d_p/d_e)}$ = density measurements of individual particles (1.8 g. per cm.³). Thus, $\epsilon = 0.18$.

The average weight concentration (C) of suspended particulate matter at this site is 130 μg. per m.³, and the average particle number concentration (N) is 2×10^7 per m.³ The average particle volume diameter (d_v) is estimated to be

$$d_v = \left(\frac{6C}{\pi N \rho_{d_p/d_e}}\right)^{1/3} = 1.9\ \mu\text{m}. \qquad (2)$$

d_v can also be calculated from Andersen Impactor data reported for this sampling site (O'Donnell *et al.*, 1970). The mean particle aerodynamic equivalent diameter (d_e) of approximately 2.6 μm. can be converted to d_v, according to Stokes law, in the following way:

Table II. Seasonal Variations in Specific Surface Areas and Densities of Suspended Particulate Matter[a]

			Av. specific surface area, m.²/g.		Av. density, g./cm.³		
			Arithmetic mean ± S.D.		Arithmetic mean ± S.D.		
Season	Sampling period	No. samples	25° C.	200° C.	Bulk	Specific	Sampling filter
Fall	9/23–12/21/67	5	2.66 ± 0.59	4.35 ± 0.87	0.60 ± 0.06	2.1 ± 0.5	Fiber glass
Winter	12/22/67–3/20/68	9	3.05 ± 0.38	4.85 ± 0.75	0.56 ± 0.06	2.1 ± 0.3	Fiber glass
Spring	3/21–6/21/68	5	2.36 ± 0.35	3.59 ± 0.54	0.59 ± 0.06	1.8 ± 0.2	Fiber glass
Summer	6/21–9/22/68	3	1.90 ± 0.36	2.67 ± 0.35	0.64 ± 0.02	2.1 ± 0.2	Fiber glass
Fall	9/23–12/21/67	4	3.38 ± 0.31	5.36 ± 0.36			Membrane
Fall	9/23–12/21/67	6			0.57 ± 0.07	2.3 ± 0.5	Membrane
Winter	12/22/67–3/20/68	1	4.36	6.75	0.54	2.3	Membrane
Summer	6/21–9/22/68	6			0.61 ± 0.04	2.2 ± 0.1	Membrane
Summer	6/21–9/22/68	2	1.80 ± 0.52	3.22 ± 0.90			Membrane

[a] Samples collected on roof of Graduate School of Public Health.

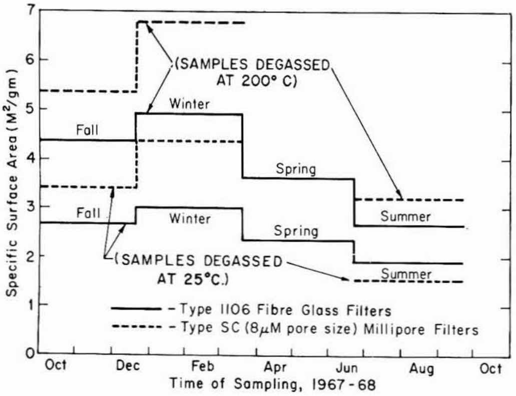

Figure 1. Variation of specific surface area of suspended particulate matter samples

Samples collected on roof of Graduate School of Public Health (1967–68)

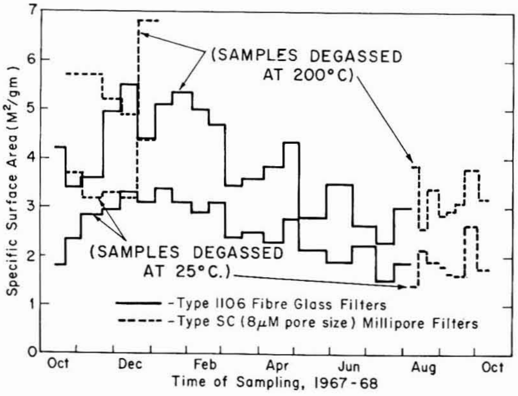

Figure 2. Seasonal averages of specific surface areas of suspended particulate matter

Samples collected on roof of Graduate School of Public Health (1967–68)

$$d_v = d_{e,\mu\text{m.}} \sqrt{\frac{1 \frac{\text{g.}}{\text{cm.}^3}}{\rho_{d_p/d_e}}} = \frac{2.6}{\sqrt{1.8}} = 1.9\ \mu\text{m.} \tag{3}$$

It is now possible to estimate the average specific surface of these particles by assumption of a model for particle shape. Consider the particles to be smooth spheres with two small cylindrical holes of diameter D drilled to their center (Figure 3). Then the area of the particle which is exposed to air is

$$A = \pi d_v^2 + \pi D d_v \tag{4}$$

The spatial volume within the particle is approximately

$$\left(\frac{\pi D^2}{4}\right) d_v = \frac{\epsilon \pi d_v^3}{6} \tag{5}$$

Hence,

$$D = \left(\frac{2\epsilon}{3}\right)^{1/2} d_v \tag{6}$$

Substituting the value of D from Equation 5 into Equation 3 yields

$$A = \left[1 + \left(\frac{2\epsilon}{3}\right)^{1/2}\right] \pi d_v^2 \tag{7}$$

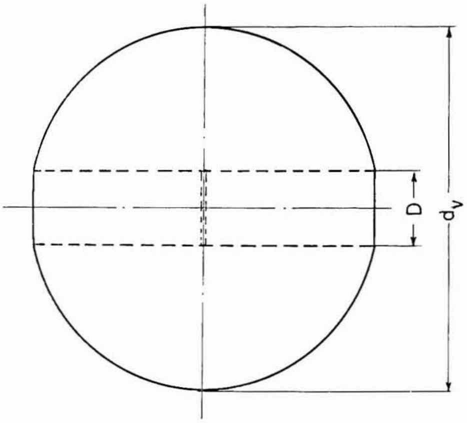

Figure 3. Model for particle surface area

$A = \pi d_v^2 + \pi D d_v$

The specific surface area is

$$S_v = \frac{6\left[1 + \left(\frac{2\epsilon}{3}\right)^{1/2}\right]}{(\rho_{d_p/d_e})(d_v)} \quad (8)$$

The experimental values of $\epsilon = 0.18$, $\rho_{(d_p/d_e)} = 1.8$ g./cm.³, and $d_v = 1.9$ μm. lead to a value of $S_v = 2.4$ m.² per gram. This value of S_v compares favorably with experimental values reported in Table II.

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Received for review December 19, 1969. Accepted August 18, 1970. This investigation was supported by PHS research grant AP 00431-04, National Air Pollution Control Administration.

Infrared Spectra of H_2S, CS_2, SO_2, CH_3SH, and C_2H_5SH Adsorbed on Fe and Ni

George D. Blyholder and Gordon W. Cagle
Department of Chemistry, University of Arkansas, Fayetteville, Ark. 72701

■ Infrared spectra over the spectral range 4000 to 450 cm.⁻¹ of the stable surface species formed at 25° C. by the exposure of evaporated Fe and Ni to H_2S, CS_2, SO_2, CH_3SH, and C_2H_5SH were recorded. No infrared bands for adsorbed H_2S and CS_2 were detected on either Fe or Ni. For ethyl mercaptan on both Fe and Ni bands at 1240, 1045, and 965 cm.⁻¹ are interpreted as indicating the C—C—S chain is intact in the adsorbed species. Interaction of SO_2 with Fe and Ni surfaces produces SO_4 surface species.

The study of the properties of adsorbed sulfur compounds is of interest for the light it can shed on sulfur compound poisoning of catalytic processes, the role of sulfur compounds in air pollution, and the catalytic removal of sulfur compounds to prevent catalyst poisoning and air pollution. Sulfur compounds have been known for some time to play a major role in air pollution (Stern, 1962). Much of the sulfur in the atmosphere is initially injected as H_2S, which is subsequently oxidized to SO_2 (Amer. Chem. Soc., 1969). Relatively little is known about how these sulfur compounds react in the atmosphere and on surfaces.

A fundamental understanding of surface processes requires a knowledge of the detailed nature of surface species. When it can be obtained, infrared spectral data have proved to be effective in obtaining structural information about adsorbed species. Previous infrared work with adsorbed sulfur compounds is quite limited. The effect of CS_2 on the spectrum of adsorbed CO has been examined, but no infrared bands for adsorbed CS_2 were found (Garland, 1954). Infrared spectra of some organic sulfur compounds adsorbed on minerals have been reported (Eyring and Wadsworth, 1956). From work in this laboratory, the infrared spectra of surface species resulting from the exposure of silica-supported Ni to H_2S, mercaptans, thioether, and thiophene have been reported (Blyholder and Bowen, 1956). The silica support limits the infrared region to the range of 4000 to 1350 cm.⁻¹ so that carbon—hydrogen bond vibrations, but not carbon and sulfur skeletal vibrations, could be observed. The adsorbed species were shown to have undergone considerable C—H bond rupture from the original molecules, but information about the breaking of C—C and C—S bonds was not available.

In this laboratory a technique for obtaining the spectra of gases adsorbed on evaporated metal particles over the wide spectral range from 4000 to 400 cm.⁻¹ has been developed. The spectra of the stable surface species formed at 25° C. by the interaction of Fe and Ni metal particles with H_2S, CS_2, SO_2, CH_3SH, and C_2H_5SH are reported here.

Experimental

The wide spectral range experimental technique, described in detail elsewhere (Blyholder, 1962), consists of evaporating metal from an electrically heated tungsten filament in the presence of a small pressure of helium. Metal particles form in the gas phase and then deposit in a hydrocarbon oil film on the salt windows of an infrared cell. The gas to be studied is then admitted to the cell, and the spectrum of the chemisorbed species obtained. Spectra are recorded before and after admission of the gas to the cell. Five minutes of pumping has been found sufficient to remove all spectra caused by gas-phase molecules. For three and four carbon atom molecules, 30 min. of pumping may be required to remove molecules dissolved in the oil film.

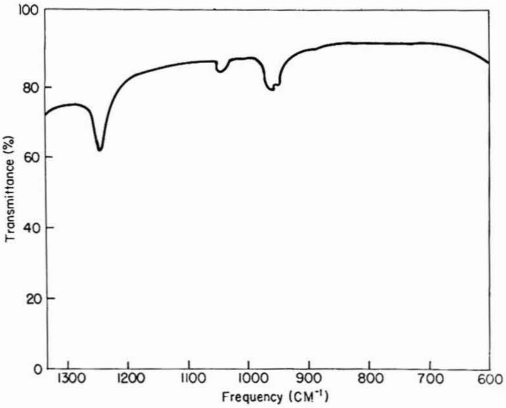

Figure 1. Infrared spectrum of ethyl mercaptan adsorbed on Fe at 25° C.

The spectra were obtained using a Perkin-Elmer Model 337 spectrophotometer, a grating instrument which can scan the region from 4000 to 400 cm.$^{-1}$ Normal spectrometer settings were used.

The adsorbates were obtained as reagent-grade chemicals from commercial sources. They were degassed by repeated freeze–thaw cycles in the vacuum system. The CO was passed through an activated charcoal trap cooled with liquid air.

This technique has the advantage that a wide infrared spectral region is available for study. It has the disadvantage that the metal surface is covered with oil. This oil is apparently only weakly adsorbed since many gases have been found to chemisorb readily on the metal. Essentially, the oil is regarded as a solvent which has weak interactions with the systems of interest. Having a wide spectral range available aids greatly in attempts to determine structure.

Spectra and Interpretation

Interaction of H_2S and CS_2 separately with both the Fe and Ni surfaces produced no observable infrared bands. Subsequent exposure of the surfaces to CO, which produces intense bands for chemisorbed species on both Fe and Ni, produced no infrared bands. This is interpreted as indicating H_2S and CS_2 do interact with the surface, but dissociate in the process so that no infrared bands are observed for the surface species. Formation of a surface metal sulfide would not produce bands in the infrared region covered by our instrument.

Adsorption of ethyl mercaptan produced the results shown in Figure 1 and listed in Table I. Since the oil matrix blocks out the C—H stretching and bending regions, these types of bands are omitted from the table. Comparison of the adsorbed species spectra on both Fe and Ni to the gas-phase molecular spectrum of C_2H_5SH leads to the conclusion that the C—C—S skeleton is intact and that only the sulfur atom is bonded to the surface. This conclusion is reached because the skeletal vibrations, including the CH_3 rock, for the surface species are very little changed from those of the molecular species. In fact, the agreement is so good that one may wonder why substituting a metal atom for an H atom does not have more effect on skeletal vibrations. This agreement is due to both the H and the metal having little effect on the skeletal vibrations. The H atoms have little effect because, while the S—H force constant is large, hydrogen is too light to affect greatly skeletal vibrations. In the case of metal atoms, the metal–sulfur bond has a relatively low force constant. It is a well-known principle that where there is a large separation in force constant or vibration frequencies, the modes of motion are fairly independent (Wilson, Decius, *et al.*, 1955). A case similar to this one is the agreement between alkoxide spectra and free alcohol spectra that has been found for the infrared spectra of Al and Ti alkoxides (Bell, Heisler, *et al.*, 1953; Guertin, Wiberley, *et al.*, 1956; Kriegsmann and Licht, 1958; Wilhoit, Burton, *et al.*, 1962).

The possibilities of some other structures were considered and discarded for a variety of reasons. Structures containing hydrogen atoms attached to unsaturated carbon atoms were eliminated because of the absence of C—H stretching vibrations above 3000 cm.$^{-1}$ While the oil blocks out the saturated C—H stretching region, bands for unsaturated C—H groups that usually occur near 3100 cm.$^{-1}$ should be clearly visible. Two-point or more attachment to the surface in which both a carbon–metal and a sulfur–metal bond are present is eliminated because of the presence of the CH_3-rocking band at 1045 cm.$^{-1}$ and because multiple attachment is expected to perturb the skeletal vibrations more than is observed. Failure to observe a band does not mean that a structure is necessarily completely absent but rather that its concentration is too low to give observable spectra with our technique.

Adsorption of CH_3SH on Fe produces weak bands at 1300 and 950 cm.$^{-1}$ The most intense bands in the spectrum of gas phase CH_3SH are at about 2900, 1450, 1335, and 1060 cm.$^{-1}$ There are much less intense bands at 2600 and 710 cm.$^{-1}$ For our adsorption experiments, bands near 2900 and 1450 cm.$^{-1}$ would be obscured by the adsorption of the oil matrix. We propose to assign the bands for the adsorbed species at 1300 and 950 cm.$^{-1}$ to a symmetrical CH_3 deformation mode and a C—S deformation mode respectively corresponding to the assignment of the 1335 and 1060 cm.$^{-1}$ bands of the gas-phase molecule to these modes (Thompson and Skerrett, 1940; Sheppard, 1955). These assignments suggest that the surface species have the structure M—S—CH_3, so that methyl mercaptan behaves analogously to ethyl mercaptan on Fe. The interaction of CH_3SH with Ni produced no observable bands.

In Table II is shown a comparison of the infrared spectra of the surface complexes formed by the interaction of SO_2 and Fe or Ni surfaces with the spectra of gas-phase SO_2, SO_3, the free sulfate ion, and complexed sulfate ion. The spectra of the surface complex do not at all resemble those of SO_2 or SO_3. It does, however, match the expected spectrum of a complexed sulfate ion with the three main bands shifted to lower wave numbers. The band positions for a complexed sulfate ion

Table I. Infrared Spectra of C_2H_5SH Adsorbed on Fe and Ni at 25°C

Surface species on Fe		Surface species on Ni		Gas phase C_2H_5SH		Assignment
1240 cm.$^{-1}$	(m)	1240 cm.$^{-1}$	(m)	1270 cm.$^{-1}$	(g)	C—S—C
1045	(vw)	1045	(vw)	1090	(w)	CH_3 rock
965	(w)	965	(w)	970	(m)	C—C—S

Table II. Comparison of the Spectra of Some Oxides of Sulfur with the Spectra of the Surface Species Produced by SO_2 on Fe and Ni at 25°C. in the Region 1400 to 500 Cm.$^{-1}$

Compounds	Frequencies (cm.$^{-1}$)				
SO_2 (Herzberg, 1945a)	1361 (s)	1151			519
SO_3 (Herzberg, 1945b)	1330 (s)	1069		652	552
$SO_4^=$ (Nakamoto, 1963a)	1110 (s)		983	622	
$SO_4^=$ complexed (Nakamoto, 1963b)	1120±	1040±	980±	620±	
SO_2 on Fe surface	1055 (s)	955 (s)	865 (s)	630 (m)	
SO_2 on Ni surface	1060 (m)	960 (m)	880 (m)	640 (m)	

given in Table II are average positions marked with ± signs because complexes have been found to have band positions varying considerably from these average positions. The broad nature of the bands for the surface complex is shown in Figure 2. The surface complex being formed by oxidation of a neutral SO_2 group on the metal surface may be expected to have an electron density less than that of a complexed sulfate ion with the consequence that the bonding is weaker and the frequencies lower. The overall similarity of the surface complex spectra to that of a coordinated sulfate ion seems most consistent with the surface complex being a SO_4 group. The results for Fe and Ni are quite similar with respect to band positions but the intensities are quite different. The much lower intensities for the SO_4 complex on Ni from those on Fe indicate a lower stability for the complex on Ni.

Discussion

Previous work has indicated that exposure of a Ni surface for a few minutes to 4 mm. of H_2S does not completely poison the surface for CO adsorption (Blyholder and Bowen, 1956). Here we find that longer exposure (1 hr.) of either an Fe or Ni surface to a higher pressure (10 mm.) of H_2S does poison the surface for CO adsorption. We have demonstrated that just a coordination bond of an oxygen atom to Fe or Ni surfaces does not form a stable bond for adsorption of oxygen containing molecules (Blyholder and Neff, 1966 a,b). Because sulfur is much less electronegative than oxygen, it seemed quite possible for it to behave differently in this respect. However, since there are no observed S—H stretching frequencies for adsorption of H_2S on Fe and Ni, the interaction is presumed to be dissociative. While the S—H band intensity is generally low, an appreciable number of adsorbed species with H—S bonds would be expected to be observable. This indicates that, for H_2S, simple coordination of a lone pair of electrons on a sulfur atom without dissociation of other bonds is not the most favorable way of interacting with Fe and Ni metal surfaces.

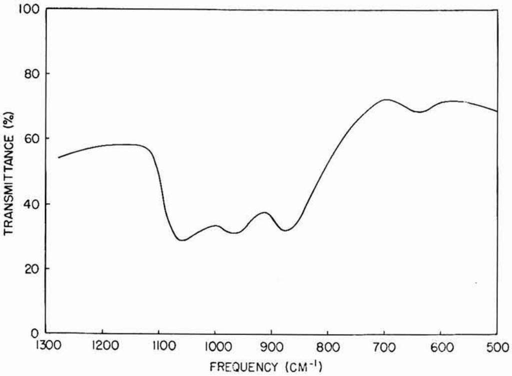

Figure 2. Infrared spectrum of the surface species produced by the interaction of SO_2 with a Fe surface at 25° C.

For H_2S adsorption on oxide surfaces the only infrared data we are aware of are for H_2S adsorption on Fe_2O_3 (Blyholder and Richardson, 1962). In this case the results were interpreted as indicating that one of the S—H bonds dissociated with the resultant formation of an OH^- group and a SH^- group on the Fe_2O_3 surface. Thus, our experimental results demonstrate that H_2S in the atmosphere should be expected to interact dissociatively with both metallic and oxide surfaces of particles in the atmosphere. The ease with which H_2S interacts with the different kinds of surfaces suggests that heterogeneous reactions could play a major role in the oxidation of H_2S in the atmosphere.

Having found the S—H bond to be readily broken in surface interactions, we next looked at C—S bonds as found in mercaptans. Ethyl mercaptan adsorbed on Fe and Ni indicates that C—S bonds are more stable in surface interactions than S—H bonds. A marked difference is found in the behavior of ethyl mercaptan from its oxygen analog, ethanol. Whereas on Fe both S and O compounds maintained the integrity of the skeletal chain (Blyholder and Neff, 1966a), on Ni the oxygen compound undergoes C—C bond cleavage (Blyholder and Neff, 1966b, 1963) while the C—C—S skeleton remains intact. Again the spectra are interpreted as indicating that attachment to the surface results from S—H bond cleavage rather than simple coordination of the S atom to the surface.

Much of the SO_2 put into the atmosphere is presumed to end up as sulfate. The data obtained here give direct experimental evidence for the formation of SO_4 groups from SO_2 on metal surfaces. While SO_4 formation fits in well with sulfate formation from SO_2 in the atmosphere, it may seem surprising in view of the ready catalytic oxidation of SO_2 to SO_3, a much used commercial process. While the commercial catalysts may not behave like the surfaces examined here, a SO_4 surface group could well be an intermediate in SO_3 formation. In the catalytic oxidation of CO to CO_2, there is evidence that the surface reaction proceeds through a CO_3 complex. Thus, in both cases the surface promotes the formation of a surface complex similar to the highest anion oxide, which then can decompose to give a gas-phase oxide with a lower oxygen to other atom ratio than the surface complex. This suggests that because the stability of a surface complex similar to the highest anion oxide is promoted by the ability of the surface to complex with it, one may find in general that oxidation of nonmetal elements over transition metals occurs through this kind of surface complex.

Having determined the structures of the surface species formed from some pure compounds containing sulfur, we now plan to examine the effect of other gases on the surface species and then to investigate their reactions.

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Received for review December 15, 1969. Accepted May 13, 1970. This investigation was supported in part by PHS Research Grant No. AP 00818-01 from the National Air Pollution Control Administration and in part by a grant from the National Science Foundation for an Undergraduate Research Participation Program.

COMMUNICATIONS

Continuous Extraction of Organic Materials from Water[1]

Marvin C. Goldberg and Lewis DeLong

U.S. Geological Survey, Denver Federal Center, Denver, Colo. 80225

Lloyd Kahn

Federal Water Quality Administration, Edison, N.J. 08817

■ A continuous liquid solvent extractor, designed to utilize organic solvents that are heavier than water, is described. The extractor is capable of handling input rates up to 2 liters per hour and has a 500-ml. extractant capacity. Extraction efficiency is dependent upon the *p*-value, the two solvent ratios, rate of flow of the aqueous phase, and rate of reflux of the organic phase. Extractors can be serially coupled to increase extraction efficiency and, when coupled with a lighter-than-water extractor, the system will allow the use of any immiscible solvent.

Naturally occurring organic solutes and organic colloids in environmental surface and groundwaters are present in low concentrations. These quantities are usually less than 100 mg. per liter in freshwater supplies. Detailed laboratory examination of these materials, however, is facilitated by having sample weights in the order of 100 mg. To obtain this sample weight, the original organic load must be concentrated. One good method of concentration is liquid–liquid, solvent extraction.

When dealing with naturally occurring organic materials, a first consideration of the analyst is maintaining the sample in its original form, from the time of collection to the final analysis. Solvent extraction allows the analyst to deactivate the organic molecules through choice of the proper extraction solvent and thus prevent biological or physical degradation. It is a gentle technique and one that is rarely implicated in degrading organic solutes. Many solvents are available which can retard biodegradation and inhibit most chemical reactions. Careful sample handling will prevent photochemical or thermal activation.

Solvent extraction from an immiscible phase can be made as complete as desired, depending on the *p*-value (defined in Equation 1) for the reaction. Solvent *p*-values for pesticides, for example, can be calculated from the data given by Beroza and Bowman (1965). Equation 1 (Laitinen, 1960) shows that at any given *p*-value, *n* extractions will result in any specified extraction efficiency.

$$f_n = \left(1 + p\frac{V_o}{V_w}\right)^{-n} \tag{1}$$

where f = fraction remaining unextracted; n = number of successive extractions; $p = X_o/X_w$; X = mole fraction; V = volume; X_o = organic mole fraction; and X_w = aqueous mole fraction.

There are some inherent suppositions to the application of Equation 1 to this extractor:

The volume of water in the extractor is constant.
The volume of solvent in the extractor is constant.
At any given time, an equilibrium condition exists for the organic solute distribution between V_o and V_w. It is assumed that the flow rate of the aqueous phase is slow enough to approximate the equilibrium condition.

Two limiting factors in solvent extraction are the solvent saturation capacity and the volume of liquid available for extraction. Both limitations have been partially removed from the extractor described in this text. In addition to continuous rather than batch operation, this extractor makes available an almost-pure solvent as the extraction agent during the entire time of operation. It is also portable, inexpensive to

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[1] Publication authorized by the director of the U.S. Geological Survey.

fabricate and operate, and it allows selective extraction of dissolved solutes.

The extractor apparatus is similar to that described by Kahn and Wayman (1964), but it is designed to operate with heavier-than-water solvents. When this extractor is coupled with a lighter-than-water solvent extractor, the total system can use any immiscible solvent as the extracting agent.

Apparatus

The extractor (Figure 1) consists of a 1000-ml. Erlenmeyer flask (4) containing a side arm flask (6) with a reflux condenser (1) mounted on top. The side arm flask penetrates the side of the Erlenmeyer flask and has an opening at the bottom which contacts the organic solvent. Inside the side arm flask is a funnel (5) held in position by glass struts at the top of the funnel. An adapter (7) with ground joints on both ends enters a 500-ml. round-bottomed flask (8), which rests in a heating mantle (9). The Erlenmeyer flask has two glass tubes (2 and 3) which extend into the flask. At the bottom of this flask (4) is a glass-lined magnetic stirring bar (10).

Operation

The extractor combines two cyclical systems, each immiscible in the other. The first system is an aqueous system and contains the material to be extracted. The second system is a nonaqueous system and acts as the extractant. Since the aqueous system is passive, it needs only to circulate through the extractor. The aqueous solvent enters tube (2) under a constant pressure and is conducted to the bottom of the Erlenmeyer flask, where it mixes with the organic solvent to form an emulsion. By properly regulating the stirring rate, the emulsion can be formed by relatively large water bubbles in the organic solvent. These bubbles rise to the surface of the solvent to add to the aqueous solution. A carefully regulated siphoning action will pull the aqueous layer out of flask (4), exiting through tube (3). While the aqueous solution contacts the organic solvent, the extraction process takes place.

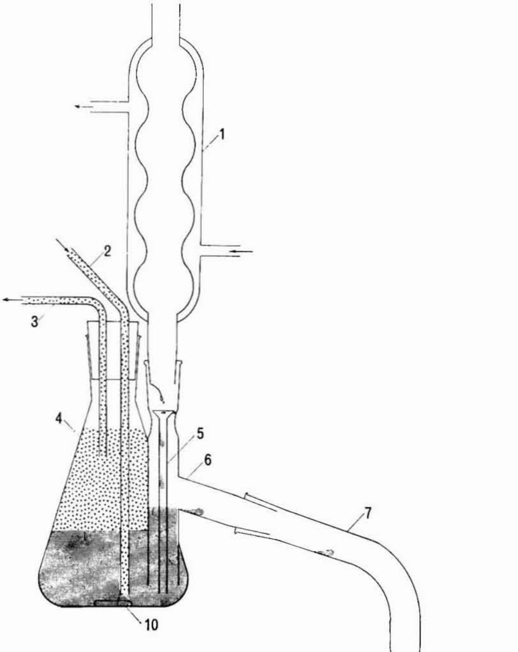

Figure 1. Continuous organic heavier-than-water solvent extractor

1, reflux condenser; 2, water inlet; 3, water outlet; 4, extraction flask; 5, dropping funnel; 6, reflux side arm; 7, adapter; 8, 500-ml. round-bottomed boiling flask; 9, heating mantle; 10 glass-lined stirring bar

Variation in contact time is regulated by aqueous pumping rate and stirring rate. A typical pumping rate is 2 liters per hour.

The second system is the organic system composed of the organic solvent at the bottom half of flask (4) and half of the round-bottomed boiling flask (8). The usual charge in the flask (8) is 500 ml. The organic solvent is represented by heavy shading in Figure 1. Nonaqueous solvent cycling is done by heating the solvent in flask (8) with heating mantle (9) to the boiling point. Vapor rises into adapter (7) through the side arm (8) and around the funnel into the reflux condenser (1). After condensation, it is conducted by a lip at the end of the reflux condenser into the funnel (5) and back into the organic solvent reservoir in flask (4). The condensate, being pure solvent, replenishes the extraction agent. Solvent already stored in flask (4) undergoes hydraulic lift, overflows side arm (6), and returns to boiling flask (8), completing the cycle.

A second important variable, in addition to *p*-value, is residence time of the aqueous solution in the extraction flask (4). This variable is controlled through regulation of the flow rate into the influent tube (2) along with pressure-head adjustment, at the output (3) of the last extractor in the series.

For optimum utilization, these procedures should be followed:

Where use of multiple extractors is desired, a connection between extractors is best effected by the use of ground-glass ball joints; the influent into the first extractor should be stored in a reservoir that can be elevated above the extractor in such a way that any desired static hydraulic head may be maintained.

Even though the solvents are immiscible, a small volume of influent water will be collected with the extraction solvent. This solution will accumulate in the boiler (8). For aqueous organic systems, the volume of the aqueous portion will usually be less than 10% of the total extractant volume collected in flask (8). This small aqueous volume can easily be separated by passing the extractant through a separatory funnel, then treating with anhydrous sodium sulphate.

Once the influent water has been extracted, the organic solvent can be stripped from the solute. First, the organic extractant is concentrated in a Kuderna-Danish concentrator to bring the solvent volume to a few milliliters (the original solvent volume is usually 500 ml. and the final solvent concentrate volume is below 5 ml.); second, a preparative gas chromatograph is used to strip off the organic solvent.

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Received for review March 4, 1970. Accepted August 14, 1970.

Rapid Determination of Nitrogen Oxides with Use of Phenoldisulfonic Acid

Barbara A. Coulehan and Helen W. Lang

U.S. Bureau of Mines, Safety Research Center, Pittsburgh, Pa. 15213

■ A rapid, quantitative batch procedure for analysis of atmospheric nitrogen oxide samples ($NO + NO_2$, commonly referred to as NO_x) from mines, tunnels, and raw or dilute diesel exhaust is described. This modification of the phenoldisulfonic acid nitration procedure eliminates the time-consuming evaporation step and two transfer steps of the original procedure. Samples are collected in evacuated bottles containing an absorbent solution and hydrogen peroxide to completely oxidize the gas-phase NO_x to nitric acid. After destruction of excess oxidant, an aliquot of the absorbed sample is added to the phenoldisulfonic acid reagent in a 25-ml. volumetric flask which is used as the reaction vessel for subsequent nitration and neutralization. This modified method can double or triple the number of analyses per day by the original method.

The phenoldisulfonic acid nitration procedure (Beatty *et al.*, 1949) has long been considered a reliable method for determining NO and NO_2, commonly referred to as NO_x. The NO_x gas-phase mixture is oxidized completely to nitric acid by hydrogen peroxide, followed by ring nitration of 1-phenol-2,4-disulfonic acid and visible spectrophotometric determination of the trialkali salt formed on neutralization.

The phenoldisulfonic acid (PDSA) method is not as sensitive as the Saltzman (1954) procedure and other modifications of the Griess-Ilsovay reaction. The latter methods use diazotization and coupling to form azo dyes and are particularly useful for the low levels of nitrogen oxides encountered in air pollution work. The PDSA method, however, can be readily used for the NO_x levels found in raw diesel engine exhaust (50 to 2000 p.p.m.) or atmospheres resulting from the use of explosives (10 to 200 p.p.m.).

Chlorides and organics are major interferences in the determination of nitrates by the PDSA method (Boltz, 1958; Scott, 1930). Both materials are likely to be present in auto exhaust. However, in the Bureau of Mines schedule testing program we found that the level of total organic compounds or chlorides is very low (in the part per million range) in the exhaust of a properly adjusted diesel engine. Removal of both chlorides and organics from samples prior to analysis is detailed by Boltz (1958). Dimitriades (1968) reported that tetraethyl lead (TEL) in amounts equivalent to 2 ml. per gallon produces auto exhaust containing 25 p.p.m. (Cl + Br). Assuming an NO_x content of 1500 p.p.m., the halide interference is equivalent to a -1.7% error in the nitrate determined. Organic matter interferes mainly through the off-colors imparted to the original sample solution. Additional decomposition of organic substances may be caused by charring the residue during evaporation or by the strongly acidic PDSA reagent.

The PDSA procedure requires lengthy absorption and evaporation steps and careful attention to avoid spattering losses. For this reason, it is often supplanted by modifications of the Saltzman procedure even for the higher ranges of NO_x concentration. In most cases, a factor must be used since side reactions are known to occur (Koshlov and Ulitin, 1966; Murphy, 1967; Shaw, 1967).

However, a modification of the Saltzman procedure, developed by Davis and O'Neill (1966), provided quantitative results only under the very specialized conditions such as those in the testing of diesel engines for suitability for safe underground operation. Here, the gas issues from the exhaust with the oxides almost entirely in the form of nitric oxide. Samples are taken almost immediately under conditions where nitrous acid forms exclusively due to the very high ratio of nitric oxide to nitrogen dioxide, thus promoting the overall reaction $NO + NO_2 + H_2O \rightarrow 2HNO_2$. The available diazotization-coupling reagent acts very rapidly to consume the nitrous acid nearly as fast as it is formed.

A relatively rapid, quantitative batch procedure was sought for the analysis of nitrogen oxide samples obtained from mines, tunnels, and raw or dilute diesel engine exhaust. Modification of the PDSA method by eliminating the evaporation step was thought to be the best approach.

Experimental

Reagents. A solution for absorption of gas samples is prepared containing 1.5 ml. of 30% hydrogen peroxide per liter of $0.1N$ sulfuric acid, which is stable for at least 12 months (Beatty *et al.*, 1949). A standard $0.0025M$ potassium nitrate is prepared by using the absorbent solution for dilution. The standard is equivalent to that obtained by absorption of 224 ml. of 1000^{V}_{V} p.p.m. NO_x (10 μmoles) in 4.00 ml. absorbent solution at STP. The PDSA reagent is available (Hartman-Leddon Co., Philadelphia, Pa.) as phenoldisulfonic acid, APHA, Item 1913. Water used for dilution should be distilled and passed through a double ion-exchange bed to eliminate nitrates and other ions.

Equipment. An electrically operated rotator is used which is capable of holding several 250-ml. Bureau of Mines air sample bottles (Beatty *et al.*, 1949). These are round-bottomed tubes, approximately 150-mm. long and 55 mm. in diameter, which are evacuated and sealed after the addition of 4 ml. of absorbent solution. An ultraviolet-visible range spectrophotometer is used with matched quartz 1-cm. cells for measurement of absorbance.

Summary of Preliminary Experiments. Time studies were made to determine the effect of agitation upon the gas sample absorption and oxidation. In the nitration of phenoldisulfonic acid reagent, the maximum amount of aqueous dilution that could be tolerated was measured to determine whether the neutralization and evaporation steps could be eliminated. Conditions under which the reaction mixture could be heated to provide for rapid color formation without charring were studied.

Procedure. Prepare a calibration curve by using 4.00 ml. of standard nitrate solution. Destroy excess peroxide present in the standard by adding 3 to 4 drops of $0.6N$ potassium permanganate. Remove excess oxidant and manganese dioxide which is present as a brown precipitate (MnO_2 results from reduction of $KMnO_4$ by H_2O_2) by adding 1 to 2 drops of $0.6N$ oxalic acid. This operation results in a colorless solution. If only 3 drops of permanganate or only 1 drop of oxalic acid is required, add one drop of water in either case to provide a total volume close to 4.30 ml. The volume of the drop may vary, depending on the type of dropper used; therefore each dropper should be calibrated. The use of drops in place of accurately measured volumes does not contribute significantly to error. This method of addition is preferable to making up to a definite volume since it avoids an unnecessary transfer step and is sufficiently accurate. Add small aliquots of the resulting solution up to a maximum of 2.00 ml. (4.66 μmoles) to 2 ml. of PDSA contained in 25-ml. volumetric flasks which are cooled under cold running water and shaken to prevent local overheating. Heat each flask for 10 min. on a steam bath, then cool. Make flasks up to volume by slowly adding 1:1 NH_4OH. Flasks should be shaken and cooled during neutralization. Measure the absorbance against a reagent blank at 410 nm. Draw a calibration curve of absorbance *vs.* μmoles NO_x. This curve is linear up to at least 2 μmoles and has a slope of approximately 0.00240.

Collect gas samples in evacuated air sample bottles containing 4.00 ml. of absorbent. If immediate analysis is required, rotate bottles for 1 hr. After destruction of excess peroxide in the bottles, add 0.50- to 2.00-ml. aliquots of absorbed sample to the PDSA reagent, according to the expected concentration range. Perform nitration, neutralization, and absorbance measurements as with the standard. Determine NO_x levels from the calibration curve after making suitable pressure, volume, and temperature corrections. Use the accurately known volumes of the individual gas bottles (measured by water displacement) in the calculations.

Comparison with PDSA Method. The modified PDSA method was compared directly with the currently used PDSA method. Three nitric oxide standards, nominally 600, 1100, and 1600 p.p.m., were used. In addition, exhaust gas samples taken from a one-cylinder CFR engine were compared directly by both methods to check accuracy.

Results and Discussion

Absorption and oxidation of 600 to 1600 p.p.m. of nitric oxide in a gas sample was found to be complete after the sample bottles were rotated for 1 hr. Total absorption was also obtained when sample bottles were allowed to stand for 24 hr. In contrast, only 90% of the maximum absorption was obtained after 3 hr. of standing.

The reaction also could be safely carried out by heating on a steam bath. When a hot plate was used, charring occasionally resulted.

In the dilution studies varying amounts of standard nitrate solution were added to 2 ml. of PDSA reagent. It was determined that a maximum of 2-ml. aqueous standard nitrate could be used to ensure completion of the reaction at 100° C. Thus, a maximum aliquot of 2 ml. of the 4.3 ml. of an absorbed gas sample can be taken, since the reaction will not go to completion with an acid concentration of less than 50%.

The modified method eliminates the time-consuming evaporation step of the original procedure. Two transfer steps, with attendant rinsing, are avoided by adding a sample aliquot directly to a volumetric flask which is used as the reaction vessel. The 10 to 12 samples normally handled per day with the original method can be increased two to three times by this modified procedure. Since none of the basic chemical reactions of the original method have been changed by the suggested modifications, the rapid method is suitable for any type of samples which would normally be analyzed by the PDSA method. The sensitivity is comparable to the original method.

No interference studies were made since it had been our experience that neither chlorides nor charable organics, two major interferences in the PDSA method, are found in the exhaust from properly adjusted diesel engines. To apply this method to auto exhaust samples, however, studies of such interferences would be required.

Table I. Precision of Modified PDSA Method

Mean concn, p.p.m.	Standard deviation	Coefficient of variation, %
557	24	4.3
1117	50	4.5
1630	65	4.0

Table II. Comparison of PDSA Methods to Determine Accuracy

Test no.	NO_x, p.p.m. PDSA	NO_x, p.p.m. Modified PDSA
1	896	925
2	1071	1063
3	948	902
4	520	474
5	839	792
6	594	512
7	938	974
8	470	490

The precision of the modified PDSA method was estimated by using 20 replicate samples of each of three nitric oxide standards. Sampling was carried out on two days, and the results obtained by two chemists using both 1-hr. rotation and 24-hr. standing absorption. A 0.50-ml. aliquot of the treated solution was taken in each experiment. Results are given in Table I.

Previously determined precision of the conventional PDSA method was of the same order.

Eight pairs of samples were taken under varying conditions over a period of several days directly from the exhaust of a CFR engine. Results are given in Table II. Each sample pair was taken simultaneously.

Based upon the data in Table II, a regression line (Crow *et al.*, 1960) was obtained with a slope of 1.0506 and an intercept of −57.6957. A standard deviation of $Sy/x = 45.35$ and a correlation coefficient of 0.98 indicate that the methods can be readily interchanged without significant loss of precision or accuracy.

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Received for review March 28, 1969. Accepted August 24, 1970.

Chemical Separations Corp. (Oak Ridge, Tenn.) has concluded a demonstration contract with two Long Island, N.Y., communities in which it successfully reduced nitrate levels in a 5000-gallon sample of contaminated well water below those necessary to meet PHS drinking water standards. In Chem Seps tests, water with as much as 50 ppm nitrate was purified to less than 10 ppm, the PHS standard.

Kelley Co., Inc. (Milwaukee, Wis.) will enter the solid waste disposal field with what it claims is an economical, all-purpose, smoke-free incinerator. Design of the unit combines a self-proportioning air system with high-temperature combustion. The company claims that no auxiliary scrubbers, etc., are needed to abate emissions.

Havens International (San Diego, Calif.) has dedicated a 20,000-gpd plant which uses reverse osmosis to produce pure water directly from raw sewage. The plant feed is sewage from the metropolitan San Diego system. The purified water will not be drunk, but will be used as boiler feed water.

Universal Oil Products Co. has developed a new process to remove sulfide pollution problems from numerous industrial processes. The new process, called Sulfox, has up to 100% efficiency in recovering elemental sulfur from streams bearing hydrogen sulfide. The process is claimed to cause no air pollution, to produce a liquid effluent that is low in sulfur compounds, and to offer recovery of ammonia in either anhydrous or aqueous forms.

Dravo Corp. (Pittsburgh, Pa.) has agreed with Mono Pumps (Engineering) Ltd. (London, England) to design and sell Mono's Minipack, a compact sewage treatment plant, in the U.S. The compact unit can be built in capacities from 1200 to 12,000 gpd; it will supplement Dravo's existing line of packaged treatment plants, which are rated from 10,000 to 2 million gpd. The Minipack features a plastic filter medium.

The Carborundum Co. (Hagerstown, Md.) has installed a multimillion-dollar baghouse system to control air pollution at a specialty foundry of the Ford Motor Co. (Dearborn, Mich.). The system has a 16-compartment Pangborn cloth collector and treats both hot and ambient gases, removing up to 6 tons of dust and fumes per hour. The discharged air is clean enough to meet any emission standards presently in force, Carborundum claims.

B. F. Goodrich Chemical Co. has started operation of new liquid waste treatment facilities at its Henry, Ill., PVC resin plant. The new plant, which cost $300,000, will remove up to 95% of all suspended solids from the wastes. The system is rated a 750 gpm. (For more on waste treatment at a PVC plant, see ES&T, August 1970, page 637.)

Browning-Ferris Industries (Houston, Tex.), a division of which operates solid waste management systems in 11 major metropolitan areas, has acquired Reitzloff Cos. (Detroit, Mich.). Reitzloff has more than 500 customers for solid waste services in the Detroit area, among them the big three auto makers. Reitzloff's sales run over $2 million per year.

Ovitron Corp. (E. Stroudsburg, Pa.) has been awarded a $400,000 contract by the City of Chicago for the installation of an air pollution control system on the city's new Calumet incinerator. Ovitron will supply a Linac separator, a wet scrubber, and associated equipment to reduce particulate matter. The system will also include plume suppressing equipment. (For more on the Linac separator, see ES&T, September 1969, page 806.)

Hittman Associates (Columbia, Md.) has been awarded a $96,452 contract by the WQO to investigate the relationship between the way treatment plants are operated and maintained and their overall efficiency. The firm has also been awarded a contract for $87,681 by the APCO to evaluate techniques for reducing SO_2 emissions from stationary sources.

CIP Research Ltd. (Hawkesbury, Ont.) has developed a new sulfite pulping process that is claimed to be odor-free. The process, which CIP says is economically competitive with Kraft (sulfate) pulping, will undergo trials at a plant in Quebec. SO_2 in the process is kept in the liquid phase and sulfides are not used, hence no odors.

The Slick Corp. will undertake a multimillion-dollar expansion of its manufacturing facilities in West Germany. Slick's German subsidiary, MikroPul GmbH, has experienced an annual sales growth of 30% in recent years, and the new plant will expand capacity to manufacture dust collectors, product recovery units, and grinding mills.

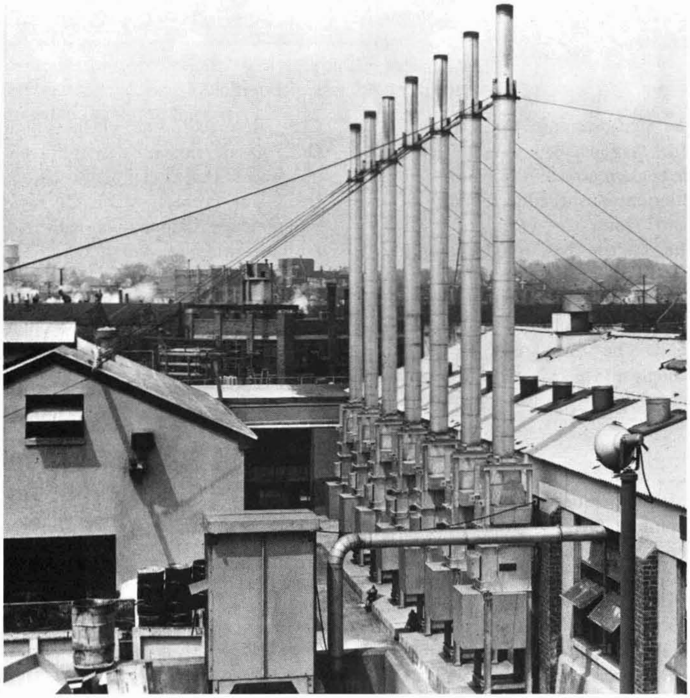
Certain-Teed Products Corp. (Valley Forge, Pa.) has completed tests of a $125,000 catalytic incinerator at the fiber-glass manufacturing plant of a subsidiary in Mountaintop, Pa. The incinerator burns off excess gases and fiber-glass particles discharged by manufacturing ovens. The incinerator was installed as part of a $250,000 air pollution control program.

C&I/Girdler Inc. (Louisville, Ky.) will engineer and construct a 2-million gpy solvent recovery facility for Standard Gravure Corp. in Louisville. The facility will remove 98% of the hydrocarbon solvents contained in gases leaving rotogravure printing plants. Activated carbon adsorption is the heart of the removal process.

Resource Control, Inc. (West Haven, Conn.) has entered into an agreement with Degussa, the West German metals and chemicals manufacturer, whereby Degussa will have, in effect, exclusive rights for RC's cyanide water pollution control device. The agreement covers all European Common Market countries and extends through mid-1971.

Combustion Engineering (Windsor, Conn.) has granted the U.S. government a royalty-free license to use a system for firing solid wastes as fuel in steam generating units. CE has a patent on the system, which will be demonstrated under an EPA grant at a power station in St. Louis.

(continued on page 166)



(continued from page 165)

Copeland Process (Canada) Ltd. (Montreal, Que.) has been awarded a contract by Great Lakes Paper Co. (Thunder Bay, Ont.) for a fluid-bed waste disposal system. The unit will dispose of up to 180 tons of scrap wood, sawdust, etc. per day, and will burn the suspended waste solids at 70% water without supplemental fuel supply. Over 4000 gpm of hot water will be produced; this will be used in a closed cycle to raise water temperature in the wood-room operation.

Envirotech Corp. (Palo Alto, Calif.) has acquired the assets and know-how of EcoloTech Research (New York, N.Y.), the group that developed the physical-chemical method of waste water treatment known as the Z-M process. The acquisition was made for an undisclosed amount of Envirotech stock. The Z-M process, which was heavily touted about a year ago, is claimed to be cheaper than conventional secondary plus tertiary treatment.

The Firestone Tire & Rubber Co. has opened a new waste water treatment facility at its rubber and latex plant in South Akron, Ohio. The unit removes suspended solids from waste water; the discharged water contains only 50 ppm of ss. Cost of the unit was $320,000.

Rollins-Purle, Inc. (Wilmington, Del.) has opened its new $1.6 million central waste disposal plant in Baton Rouge, La. The plant, which will operate on a continuous basis, is capable of handling 250,000 gpd of heavy industrial wastes produced in the Baton Rouge area by a wide variety of industries. A similar plant is in operation in New Jersey, and another is being built in Houston, Tex.

Armstrong Cork Co. has begun construction of a $1 million secondary treatment facility at its plant in Macon, Ga. The new facility will work in conjunction with a primary facility now nearing completion. The system is rated at 3 million gpd and is designed to facilitate expansion, should output at the building products plant increase.

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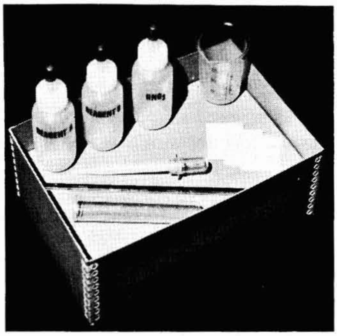
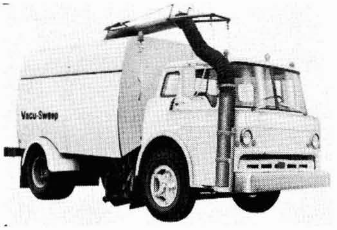
Oil analysis

A system for the continuous analysis of ppm oil in refinery effluent water has been introduced for pollution control. This system is also utilized in monitoring the oil content of boiler feed water as low as 0 to 1 ppm full scale. This sampling system permits analysis of the total oil content exclusive of soluble organic compounds not considered oil. A highly reliable all solid-state, dual-beam, compensating ultraviolet analyzer featuring plug-in electronics is the sensing device. Teledyne Analytical Instruments **62**



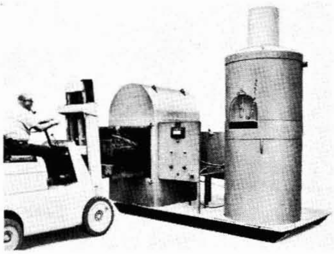
Mercury detection

A new low-cost test kit for mercury pollution in water is sensitive to 0.1 ppm, which is five times more accurate than the approved maximum limit of 0.5 ppm. The kit is easy to use and offers positive identification of mercury contamination in about 1 min. The test can be made by nontechnical personnel in this line of work. Koslow Scientific Corp. **63**



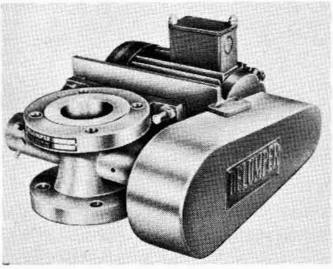
Road cleaner

The new Vacu-Sweep street cleaning vehicle gives a new approach to street pollution control. Besides the high cleaning performance, versatility, and low maintenance factors of the Vacu-Sweep, it can meet every challenge in urban environment by use of its high-velocity suction effect and compacting unit. Ecolotec Inc. **64**



Pollution-free incineration

This incinerator is initially manufactured for salvage operators. The unit consumes all fly ash and disintegrates all smoke. It gives a Ringleman reading of zero with a warranty that emissions (which are invisible) are acceptable to all pollution control specifications as presently defined. Uses for this system include stack smoke elimination, car salvage burning, complete systems for incineration of trash, garbage and other waste materials, and the waste disposal of rubber and plastic products that are impossible to burn without severe pollution contamination. United Corp. **65**



Pipeline delumper

Rags, stringy material, and large chunks flow unimpeded in the new rugged Pipeline Delumper Comminutor. New design improves the performance of the machine in the processing of all types of sewage and waste water. Effluent flows free at the full capacity of the pipeline system. This highest power unit available requires no open pit, is sanitary, and is fully supported by the pipeline system itself. Patented clog-free action utilizes a massive impeller/crusher/cutter mechanism to both comminute the toughest solids and to maintain the internal structure clean and free-flowing. Frankline Miller, Inc. **66**

Silver recovery

Rotex Silver Recovery Systems can be used in recirculating installations by prolonging the useful life of the hypo bath. Facilities using as little as 2 gal. of hypo per week can profitably install a Rotex system, which is also available for even the largest processing operation. Silver ions in spent hypo solutions pose a serious problem for waste water treatment plants. Rotex systems can profitably recover the silver and aid in solving the pollution problem. Snook Corp. **67**

(continued on page 170)

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

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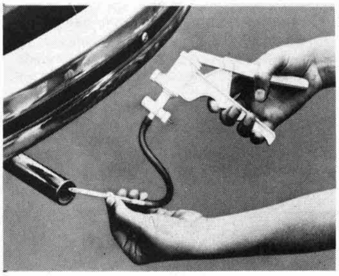
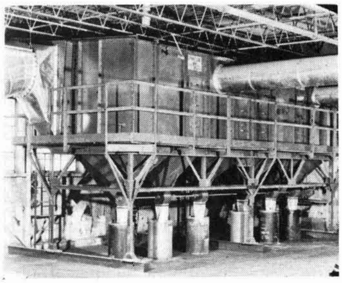


Air pollution tester

Tester no. 71,349 includes two ampoules each to test carbon dioxide, carbon monoxide, hydrogen sulfide, nitrogen dioxide, and sulfur dioxide. This light-weight and portable unit can be useful on field trips, sampling the air at industrial sites, discovering the chemicals in the atmosphere, and experimenting with the effect that chemicals have on plants. Depending upon the concentration, this supply is sufficient to test two to four times for each gas. Kit features a plastic air-sampling pump, scales for determining results, coupling tubes, break-tip ampoules, and instructions. The hand-operated pump draws air through an ampoule containing an impregnated chemical specific to the pollutant. The length of the stain appearing inside the ampoule indicates the concentration of gas in the air. Edmund Scientific Co. **68**

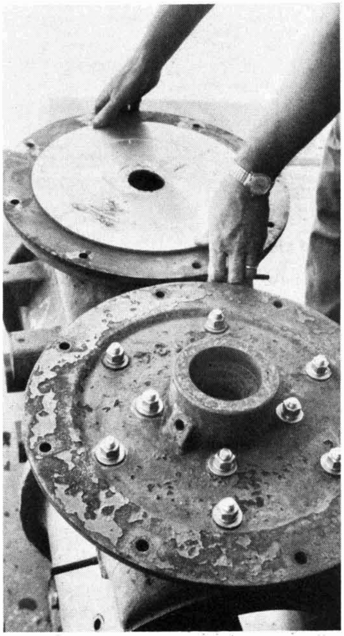


Dust filters

Multiseal automatic bag cleaning allows Dynaclone Dust Filters to operate continuously, without shutdown, providing continuous suction at all dust sources. Low-velocity collection protects bags from abrasion. These filters can be installed indoors or outdoors with capacities from 1122 cfm up, and can handle temperatures up to 250°F. Collection efficiency is guaranteed to be 99.9% on particulate matter over 0.5μ in size. W. W. Sly Mfg. Co. **69**

Electronic air cleaner

E-Z-BREATH removes dust, dirt, pollen, smoke, grease, and other airborne particles from the air, down to 1/2.5 millionth of an inch. It is to be used for rooms, including offices and conference areas, up to 15 ft × 25 ft in size, and is effective in reducing discomforts caused by smoke, smog, asthma, hayfever, emphysema, and other respiratory illnesses. Volume Marketing Corp. **70**



Stainless steel fasteners

Stainless steel fasteners facilitate equipment repairs and reduce maintenance costs in waste water treatment plants. Wear plates on sludge-drying air locks need frequent replacement. Because stainless steel resists heat and corrosion, stainless fasteners dissemble quickly and easily, and they can be reused. As a result, time and material can be saved by use of economic Type 304 or 316 stainless steel fasteners. Basford, Inc. **71**

Centrifugal fan

A new laboratory fan rapidly removes potentially dangerous vapors and corrosive fumes from fume hoods and various industrial applications. Model HCLV-8 laboratory fan delivers up to 1700 cfm and up to 1.75-in. static water gauge pressure. Heil Process Equipment Corp. **72**

Liquid clarifier

The Barrett Clarifuge (R) removes solids from liquids at flow rates compatible with most industrial applications, making it readily adaptable for closed (reuse) or open (reclamation) processing systems. The most prominent feature is the glass fiber reinforced polyester housing, combining light weight, high strength, and better corrosion resistance. The Clarifuge has clarified contaminated water to the point where it could be reused in noncritical areas. The machine was designed to be a high-production centrifugal clarifier for profitable reclamation of both used industrial liquids and their suspended solids. Leon J. Barrett Co. **73**

Water monitor

The Model 3660 Water Quality Monitor was designed for on-site field measurement and digital readout of water temperature, pH, dissolved oxygen, conductivity, and depth. This completely portable instrument comprises a ruggedly constructed deck readout unit and a submersible probe assembly containing sensors for five parameters. The monitor is powered by a rechargeable battery supply that includes a built-in charger. Model 3660 features waterproof packaging in a fiber-glass case and removable electronic modules for each of the measured variables. Benthos, Inc. **74**

Swagelok® Tube Fittings

SWAGELOK Tube Fittings are available in sizes from 1/16" through 1¼" in virtually every conceivable body, shape or style. Materials include: Brass; Stainless steel; Steel; Monel; Nylon and many other machineable metals and plastics. In addition to trouble-free SWAGELOK Tube Fitting connections, fittings can be furnished with SWAGELOK to male or female pipe; SWAGELOK to butt or socket weld; SWAGELOK to tube adapters; SWAGELOK to AN; SWAGELOK to O-Seal straight thread or pipe thread connections.

Whatever your system may require, there is a SWAGELOK answer to your problem.

MONEL, TM International Nickel
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CRAWFORD FITTING COMPANY
29500 Solon Road, Solon, Ohio 44139
Crawford Fittings (Canada), Ltd., Ontario, Canada

Circle No. 3 on Readers' Service Card

MERCURY

ANALYSIS

During the past eight months ArRo Laboratories, Inc. has analyzed hundreds of compounds for mercury including grains, water, fish, food products, pharmaceuticals, sewerage, gases, etc.

Send your samples to the experienced people for analysis and prompt service. Cost per sample for Hg analysis is $20 for water, and $30 for all others.

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P. O. Box 686
Joliet, Illinois 60434
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KIT

For analysis by

FLAMELESS ATOMIC ABSORPTION

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0.2 ppb

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Custom fabricated glassware, quartz cells, tubing, chemicals, standards, procedures, etc.

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P. O. Box 863
Joliet, Illinois 60434
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Circle No. 22 on Readers' Service Card

no "sea clutter"

with metrodata's mr 17

The MR 17 meteorological receiver has found applications in a variety of marine uses. The versatile MR 17 serves as a transponder receiver for interrogating data buoys. The replies send position as well as meteorological information. The MR 17 is also used as a telemetry receiver for meteorological data transmitted from buoys. Operation in parallel with the radar scope presents only the transponder data, with no "sea clutter". Two companion modules are the RD 5 for converting radiosonde signals to a DC voltage suitable for recording, and the PD 15 demodulator for detecting pulse-position modulated signals. All units operate on small amounts of 50-400 Hz power.

SPECIFICATIONS

MR 17

Tuning Range, MHz	395-410 and 1672-1688
Detection Modes	AM, FM and pulse
Sensitivity (pulse mds), uV	0.5 or better (-115 dbm)
IF rejection, db	60
Image rejection, db	36
Noise figure, db	6
Band width, MHz	4
Outputs	
Video (1 to 2 usec pulse), V	10 (pos or neg)
Video, shaped (0.25 usec), V	15 (pos or neg)
Power requirements, watts	20 (50-400 Hz)
Size, inches	6½H, 11W, 11D

RD 5

Signal output, VDC	0-5*
Output impedance,	10
Power requirement,	20 watts (50-400 Hz)
Size, inches	6½H, 5½W, 11D

PD 15

Signal output, VDC	0-5*
Output impedance, ohms	1
Power requirement,	20 watts (50-400 Hz)
Size, inches	6½H, 5½W, 11D

*Other ranges available.

For additional information write or call Metrodata Systems, Inc.

metrodata systems, inc.
Box 1307 Norman, Okla. 73069 405 329-7007

Circle No. 24 on Readers' Service Card

new literature

Foundries. Bulletin FY-184 describes the charging system at the Dalton Foundries of Warsaw, Ind. The 72-in. diameter water-cooled cupola illustrated in the bulletin is typical of what the melting operation could utilize to reduce the cost of pollution abatement equipment by 40%, compared to that of a conventional cupola of comparable size and capacity. The Dalton Foundries have also experienced a 35% reduction in power consumption for the gas-cleaning operation. Whiting Corp. **91**

Test kits. Aquatic ecology and pollution studies are the subjects of a new 22-page catalog of simplified test kits for detergents, nitrogen, phosphate, and many other similar tests. This "Buyer's Guide of Simplified Test Kits for Aquatic Ecology and Pollution Studies" also describes a convenient and accurate means for testing water in the field. Hach Chemical Co. **92**

Metering chemicals. "Case History No. 85" describes the metering of a controlled and predictable amount of chemicals into a water-softening system. The result is that boiler feed water is more pure than city drinking water. The metering equipment uses controlled vibration to accomplish in minutes what in the past took two man-hours per shift to accomplish by hand. An oil removal system is also designed to be incorporated into the system. Vibra Screw Inc. **93**

Filtration system. Bulletin KL-4520 describes two new "Recla-Mate" systems designed for advanced waste treatment and offering consistent high-quality performance from new or already existing secondary systems. The Recla-Mate filtration system treats waste through package or custom filtration, using mixed-media filters without chemicals. The Recla-Mate SWB system is used where consistently high-quality effluent or phosphate removal is necessary. These two units may be altered to meet the flow requirements of the installation by addition of concrete basins and other design alterations. Neptune MicroFLOC, Inc. **94**

Solid waste disposal. "A Pledge & a Promise" describes an Anheuser-Busch system's approach to the problem of solid waste disposal. The publication details the company's stand on solid waste and research team of specialists in materials engineering, physical ecology, regional science, sanitation engineering, and government. Anheuser-Busch, Inc. **95**

Industrial noise. A new eight-page brochure enables the reader to understand and analyze industrial noise problems. Bulletin 10.8 also simplifies the selection of practical, economical solutions to the problems of reducing noise from manufacturing and processing equipment, as well as protecting personnel from severe noise environments. Certified test data, loudness reduction curves, absorption coefficients, dimensions, assembly methods, materials, and construction details are included in the publication. Barry Controls **96**

Mechanical aeration. Bulletin 315-131 R describes Oxy-Treat, a mechanical floating surface aerator for biological treatment processes, including aerated lagoons and activated sludge plants. It is equally applicable to chemical oxygen processes and to other areas requiring rapid oxygen transfer. The Oxy-Treat aerator is available in sizes from 5 to 75 hp. The unit requires little or no maintenance. Rex Chainbelt, Inc. **97**

Pollution-free cars. "Progress towards Pollution-Free Cars" provides a brief background of the air pollution challenge and a progress report on what has been done during the past decade to reduce automotive pollution. It also discusses current General Motors development programs designed to achieve essentially pollution-free cars as soon as possible. General Motors Corp. **98**

Mineral recovery. Bulletin M7-F118 presents the problem of recovering mineral values at a coarse size as soon as freed, and eliminating slime losses or increasing the overall recovery of an all-gravity concentration plant. The publication presents four flow sheets describing washing operations and recovery of minerals from the slurry. Joy Mfg. Co. **99**

Garbage. The packaging industry's role in litter and solid waste disposal problems has become a controversial and emotional issue. Convenience-food packaging has been singled out as a major contributor to both problems. In "Everything You Always Wanted to Know About Garbage . . . But Were Afraid to Ask," a leading authority on solid waste discusses these problems and suggests some practical steps toward solving them. Reynolds Metals Co. **100**

Solid waste literature. The importance of collecting and making available the information pertaining to solid waste-related research, demonstration projects, and other activities was emphasized in the Solid Waste Disposal Act. The Bureau of Solid Waste Management compiled report SW-58.8, which lists publications collected or published by the Bureau in response to the act. Publications Distribution Clerk, Bureau of Solid Waste Management, 5555 Ridge Ave., Cincinnati, Ohio 45213 (Write direct)

Pesticide pointers. The U.S. Department of Agriculture is distributing a new publication designed to increase safety in the selling of pesticides to farmers, industrial users, and home owners. "Safety Guide for Pesticide Dealers" is aimed at preventing accidents related to pesticides and pollution and attempts to expand public knowledge on the safe handling and use of these chemicals. Safety Guide, PA-943, Office of Information, U.S. Department of Agriculture, Washington, D.C. 20250 (Write direct)

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

The Environment: A National Mission for the Seventies. Editors of *Fortune.* 220 pages. Harper & Row, Inc., 49 E. 33rd St., New York, N.Y. 10016. 1970. $1.25, paper.

Originally, the contents of this book appeared in *Fortune* magazine. "The most important news in this book is that environmental reform is going to be harder to achieve than many of its advocates suggest," say the authors. Almost every article in this book questions the adequacy of our present decision-making processes. This publication sets forth the proposition that the U.S. must start inventing political, economic, and intellectual processes that will give today's society and the individuals in it a more realistic choice on how they want to live. ■

The Practice of Sanitation in Its Relation to the Environment. Edward Scott Hopkins, W. McLean Bingley, George Wayne Schucker. x + 550 pages. Williams & Wilkins Co., Baltimore, Md. 21202. 1970. $24.50, hard cover.

The authors of this volume hope to provide a reference on the mechanisms and techniques of sanitation. This text has been developed as a guide in environmental sanitation for the training of physicians qualifying as health officers, sanitarians, nurses, students in sanitary engineering, and others working in the field. The book represents an attempt to bring together, in one volume, the pertinent facts comprising sanitation practice as it is today in the U.S. ■

Decontamination of Nuclear Reactors and Equipment. J. A. Ayres, Ed. xvi + 825 pages. The Ronald Press Co., 79 Madison Ave., New York, N.Y. 10016. 1970. $22.50, hard cover.

As a reference on the currently valid information on decontamination of nuclear reactors and associated equipment, buildings, and environs, and directed to engineering, management, and operational personnel concerned with nuclear reactors, the book presents basic information necessary for development of procedures for removing unwanted radionuclides from surfaces in various types of nuclear reactor systems. The book also gives detailed descriptions of actual experience in decontaminating systems and decontamination after widespread release of radiation to the environment. Unsuccessful as well as successful experiences are described. Also discussed are methods of cleaning, safety, and waste disposal. ■

Use and Conservation of the Biosphere. 272 pages. Unipub, Inc., P.O. Box 433, New York, N.Y. 10016. 1970. $6.00, paper.

As the 10th volume in the Natural Resources Research series, the proceedings of the Intergovernmental Conference of Experts on the Scientific Basis for Rational Use and Conservation of the Resources of the Biosphere in 1968 are presented. This volume deals mainly with the terrestrial part of the biosphere, including inland waters and coastal areas. This publication contains the 10 background papers and the official report of the conference, including a summary of the discussions, conclusions, and recommendations. ■

Nitrogen Oxides: An Annotated Bibliography. iii + 633 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1970. $2.75, paper.

The primary objective of this book, researched by the National Air Pollution Control Association, is to collect, condense, and organize existing literature on the nitrogen oxides. Abstracts of more than 1500 documents are presented. The documents were collected from many sources, and all are included in the in-house information and storage and retrieval system of the Air Pollution Technical Information Center (APTIC). ■

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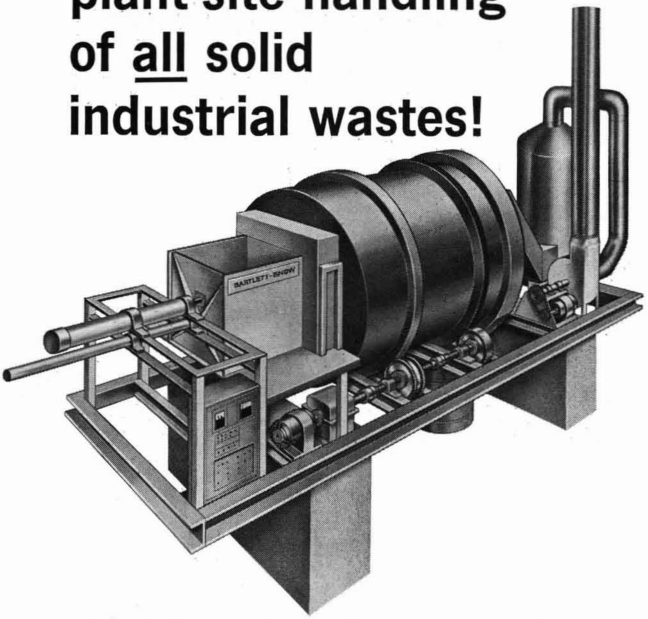

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Disposal of Plastics Waste and Litter. J. J. P. Staudinger. xvi + 100 pages. Society of Chemical Industry, 14 Belgrave Square, London SW1, England. 1970. 2£, hard cover.

A detailed analysis of plastics in domestic refuse is covered in this report. One chapter deals with the analysis of the future situation and its dimensions in respect of production, home demand, and applications areas. Packaging developments are reviewed in some detail. Also included is a review of the effects of plastics on various waste management techniques—collection, disposal by sanitary landfills, composting, pulverization, incineration, compaction, and on-site disposal. This is a matter of concern to plant manufacturers, local authorities, waste disposal contractors, and appropriate government laboratories. ■

Air and Water Depollution: Roles of Industrial Property, Innovation and Competition. iii + 135 pages. PTC Research Institute, George Washington University, Washington, D.C. 20006. 1970. $5.00, paper.

Four major areas of discussion are presented in the published proceeding of this special conference: incentives for innovation and invention; solving air and water depollution problems; technological competence of the private entrepreneur; and antitrust factors involved in joint and cooperative activities among private parties. Also covered are key factors involved in coordination among government, industry, and the universities, and cooperation between managers and technical men. ■

Physiology, Environment, and Man. Douglas H. K. Lee, David Minard, Eds. xv + 239 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1970. $11.00, hard cover.

A modern approach to environmental physiology by discussing the absorption, metabolism, and excretion of environmental agents, their mechanisms of action, and the processes of adaptation from the subcellular level to that of the total organism is presented in this book. As a scientific account necessary to understand the actions of the environment on man, this publication can be used by physiologists, biologists, and those working in environmental health agencies in federal and state governments. ■

meeting guide

February 8 and 9

University of Missouri-Rolla

Symposium on Technology for the Future Control of Industrial and Urban Wastes

Rolla, Mo.

Educators and industrial representatives will discuss technological methods for urban pollution control, prospects for recycling of natural resources, problem waste products of the future, and ways by which the educational institution and industry can work together effectively to combat pollution. Contact: UMR Centennial Events Office, UMR Library, Rm. 316, Rolla, Mo. 65401

February 10–12

Cornell University

Agricultural Waste Management Conference

Syracuse, N.Y.

Conference will emphasize the application of current concepts, research results, and field experiences to the operational problems of agricultural waste management. Contact: Prof. Fred N. Swader, Conference Chairman, 149 Emerson Hall, Cornell University, Ithaca, N.Y. 14850

February 15 and 16

Illinois Environmental Protection Agency, and the Department of Civil Engineering, U. of Ill.

13th Water Quality Conference

Urbana, Ill.

This conference is planned for engineers and scientists in education, government, industry, and private practice, and for water and waste water works managers and operators. For more information, contact: V. L. Snoeyink, Assistant Professor of Sanitary Engineering, 3230 Civil Engineering Bldg., University of Illinois, Urbana, Ill. 61801

February 15 and 16

The Royal Society of Canada

Mercury in Man's Environment

Ottawa, Ont.

This international symposium will present the current state of scientific knowledge on environmental contamination by mercury. Write: The Royal Society of Canada, 395 Wellington St., Ottawa 4, Ont., Canada

February 21–26

Engineering Foundation of the United Engineering Trustees, Inc.

1971 Engineering Foundation Conference

Pacific Grove, Calif.

"Environmental Engineering in the Food Industry" and "Stack Gas Emissions and Measurements" are two of the conference themes. Attendance, limited to approximately 100 persons, is by invitation or application. Fee: $160. Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

February 22–24

Technical Association of the Pulp & Paper Industry (TAPPI)

1971 Pulp & Paper Exhibit, and 56th Annual Meeting of TAPPI

New York, N.Y.

Over 250 exhibit booths are planned with such features as equipment for air and water treatment. Over 19 technical sessions are scheduled. Contact: Technical Association of the Pulp & Paper Industry, 360 Lexington Ave., New York, N.Y. 10017

February 23

Toronto Section, Chemical Institute of Canada

Source Sampling of Atmospheric Contaminants

Toronto, Canada

Symposium features the "how-to-do-it" of source sampling, the measurement of stack velocity, and collection and analytical procedures for the characterization of particulate and gaseous emissions. Contact: Dr. H. G. McAdie, Ontario Research Foundation, Sheridan Park, Ont., Canada

February 28–March 2

American Public Works Association

National Conference on Solid Waste Disposal Sites

Washington, D.C.

Primary purpose of the conference is to develop an action program to facilitate the acquisition of the land required to dispose of solid wastes generated in urban communities in a safe, sanitary, and economic manner. Contact: American Public Works Association, 1313 E. 60th St., Chicago, Ill. 60637

February 28–March 3

American Gas Association, and Institute of Gas Technology

National Conference on Natural Gas Research and Technology

Chicago, Ill.

Pollution control session topic will cover gas-fired combustion systems, incinerators for fumes, liquids, and solid wastes, and new applications of gas to solve pollution problems of other fuels. Contact: Jack Reid, Institute of Gas Technology, 3424 S. State St., Chicago, Ill. 60616; or Lou Sarkes, American Gas Assoc., 1515 Wilson Blvd., Arlington, Va. 22209

February 28–March 4

American Institute of Chemical Engineers

68th National Meeting and Sixth Petrochemical and Refining Exposition

Houston, Tex.

Featured is an environmental session with papers and discussions. Contact: E. L. Ekholm, Bechtel Corp., P.O. Box 2166, Houston, Tex. 77001

March 4 and 5

City of Santa Clara, and the Engineering Dept. of San Jose State College

Third Annual Solid Waste Symposium

San Jose, Calif.

The main theme will be directed to the creation and solution of the solid waste problem and what is being done along these lines within the various industries. Contact: S. M. Cristofano, Director of Public Works/City Engineer, Santa Clara, Calif. 95050

March 7–10

National Service to Regional Councils

1971 Conference of Regional Councils

New Orleans, La.

Sessions on environmental quality—solid waste disposal, air pollution control, and water quality—will be included. Conference fee: $55 to $95. Write: Annual Conference, National Service to Regional Councils, 1700 K St., N.W., Suite 1306, Washington, D.C. 20006

March 7–11

Society of Toxicology

Annual Scientific Meeting of the Society of Toxicology

Washington, D.C.

Meeting aims to promote the extension of knowledge in toxicology and to facilitate the exchange of information among members and investigators of other sciences. For more information, contact: Dr. Joseph F. Borzelleca, Dept. of Pharmacology, Medical College of Virginia, Richmond, Va. 23219

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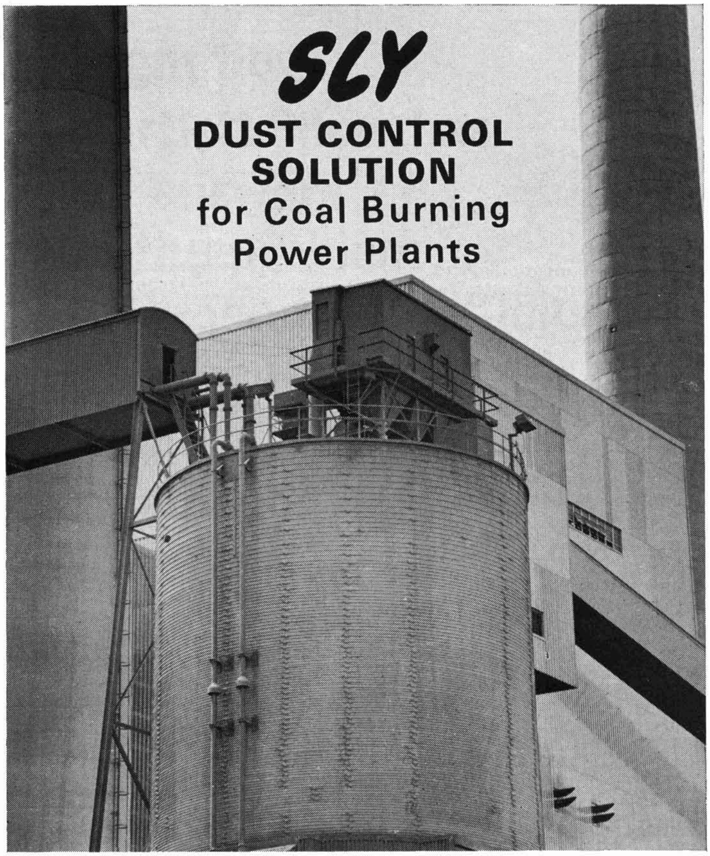

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March 8–12

American Society for Metals, and Society of Manufacturing Engineers

WESTEC Pollution Control Exposition and Conference

Los Angeles, Calif.

Conference is designed to meet the challenges of the metal working industries in western U.S. Contact: Jane Rehm, Information Services, Society of Manufacturing Engineers, 20501 Ford Rd., Dearborn, Mich. 48128; or Ronald J. Seman, News Bureau, American Society for Metals, Metals Park, Ohio 44073

March 23–26

Pacific Northwest Water Laboratory, Water Quality Office, EPA

Second National Symposium on Food Waste Treatment Research

Denver, Colo.

Discussions include waste treatment methods for all types of food processing wastes. Contact: J. R. Boydston, Chief, National Waste Treatment Research Program, Pacific Northwest Water Lab., EPA-WQO, 200 S.W. 35th St., Corvallis, Ore. 97330

March 24 and 25

Chemical-Biological Division of the American Ordnance Association

Second Annual Environmental Pollution Symposium

Edgewood Arsenal, Md.

This technical program will have presentations by several states, industry, Department of Defense, WQO, NAPCA, Environmental Protection Agency, and the Bureau of Solid Waste Management. Contact: Commander A. D. Sullivan, USN (Ret.), American Ordnance Association, Union Trust Bldg., 15th and H Sts., N.W., Washington, D.C. 20005

March 24–26

Midwest Benthological Society

19th Annual Meeting

Notre Dame, Ind.

Contact: Cornelius I. Weber, Secretary, WQO, 1014 Broadway, Cincinnati, Ohio 45202

March 29–31

University of Calif., and others

Third Annual Air Pollution Workshop

Riverside, Calif.

Meeting will cover various aspects of pollution damage to vegetation as well as sponsor a field trip to examine smog injury. Contact: Dr. Norman Lacasse, 226 Chemical Engineering II, Center for Air Environment Studies, Penn. State Univ., University Park, Pa. 16802

April 1 and 2

Dept. of Environmental Sciences and Engineering at the Univ. of North Carolina, and others

20th Southern Water Resources and Pollution Control Conference

Chapel Hill, N.C.

Conference to feature presentations and discussions on the technology of water resources and water quality management, particularly in reference to the southeastern U.S. Write: Dr. Charles M. Weiss, Chairman, Operating Committee, 20th SWRPC Conference, Dept. of Environmental Sciences and Engineering, Univ. of N.C., Chapel Hill, N.C. 27514

April 5–8

Technical Association of the Pulp & Paper Industry (TAPPI)

TAPPI 1971 Water & Air Conference

Boston, Mass.

Features air pollution presentations. Besides technical papers on such aspects of air pollution control as monitoring, computer control, and government regulations, there will be a discussion of odor problems by a panel of top mill experts. Write: M. J. Williams, TAPPI, 360 Lexington Ave., New York, N.Y. 10017

April 6–8

Air Pollution Control Institute, Calif. Air Resources Board, and Calif. State Dept. of Public Health

12th Conference on Methods in Air Pollution and Industrial Hygiene Studies

Los Angeles, Calif.

Current practices and new methods for source testing will be discussed. Intended for the technical staff of health departments, air pollution control districts, educational institutions, instrument manufacturers, and others concerned with air pollution problems. Contact: Edward Jeung, Air and Industrial Hygiene Laboratory, California Dept. of Public Health, 2151 Berkeley Way, Berkeley, Calif. 94704

Courses

Institute for Environmental Technology and Occupational Safety and Health, Inc.

Master Course

This correspondence course covers air resources, water quality management, in-plant noise control, survey of the use of radiation in industry and hazards associated with its use, theories and techniques of industrial safety, and environmental legislation. Fee: $300. Contact: William D. Hurley, Institute for Environmental Technology and Occupational Safety and Health, Inc., 1001 Connecticut Ave., N.W., Suite 701, Washington, D.C. 20036

February 22–26

Manitoba Dept. of Health and Social Development

17th Annual Wastewater School

Winnipeg, Man.

Annual training school in water/waste treatment. Write: G. D. Balacko, Manitoba Dept. of Health and Social Development, 300-419 Graham Ave., Winnipeg 1, Man., Canada

March 1–5

NUS Corp.

Utility Workshop on Fuel Management

Rockville, Md.

Discusses the technical and economic decisions associated with planning, purchase, operation, and disposal of fuel for nuclear power plants. Fee: $600. Contact: W. V. Macnabb or F. C. Duvall, NUS Corp., 4 Research Pl., Rockville, Md. 20850

March 22–24

Dept. of Civil Engineering, Univ. of Mass. at Amherst

Short Course on Joint Municipal-Industrial Waste Treatment

Amherst, Mass.

Purpose is to disseminate knowledge about technology in sampling, treatability studies, laboratory and pilot plant investigation, solids handling, and economics. Contact: Dr. E. Ernest Lindsey, School of Engineering, Univ. of Mass., Amherst, Mass. 01002

Call for papers

April 1 deadline

Southwestern Radiological Health Laboratory, USPHS, and the Univ. of Nevada

Tritium Symposium

Las Vegas, Nev.

Topics include tritium detection, measurement, monitoring, ecological aspects, isotope effect, kinetics, and biological effects. Send 100 to 200-word abstract to: Dr. A. Alan Moghissi, Chairman, Program Committee, Southwestern Radiological Health Laboratory, P.O. Box 15027, Las Vegas, Nev. 89114

CLASSIFIED SECTION

IMPORTANT NOTICE

Various state laws against discrimination and the Federal Civil Rights Act of 1964 prohibit discrimination in employment because of sex unless based on a bonafide occupational qualification. Help wanted and situations wanted advertisements on these pages are for readers' convenience and are not to be construed as instruments leading to unlawful discrimination.

POSITIONS OPEN

ENVIRONMENTAL SYSTEMS

Our clients, highly successful NON-DEFENSE industry leaders, Mid-Atlantic locations have several hi-level career opportunities immediately available. Starting salaries $17,000–$24,000 plus benefits. Interviewing, relocation expenses paid by the client companies. Requirements include M.S. or Ph.D. Chem/Ch.E., etc. + exp. in one of the following areas: Ecology, Ecology Investigations, Environmental Effects or Sciences, Pollution Control or Monitoring, Program Mgt., Weather Systems. Please send resume in confidence indicating current earnings to

Mr. Richard Guerin,
Everett Kelley Associates, Inc.,
20th Floor, 121 South Broad St.,
Phila., Pa. 19107

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Environmental Scientists. Positions with Environmental Defense Fund, a coalition of scientists and lawyers, which takes legal action to alleviate environmental degradation. Must be or become conversant with one or more broad areas of environmental concern such as water treatment, power generation, agriculture, or air pollution. Establish panels of experts in a field and serve as liaison between the teams and EDF lawyers. Participate with other scientists and lawyers in formulation of EDF policy. One or two year sabbatical or temporary appointments welcome. Work in offices at Long Island, Washington, D. C., or possibly San Francisco. Economists, biologists, physicists, engineers, M.D.'s, etc. Send resume, interests and salary requirements to **Dr. Paul P. Craig, EDF, 162 Old Town Road, East Setauket, New York 11733.** Please indicate past activities demonstrating concern and self-actuating qualities in the field of environment.

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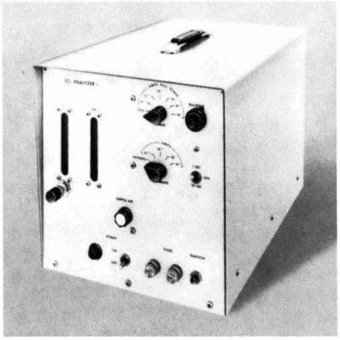

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