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Science & Technology

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Water,
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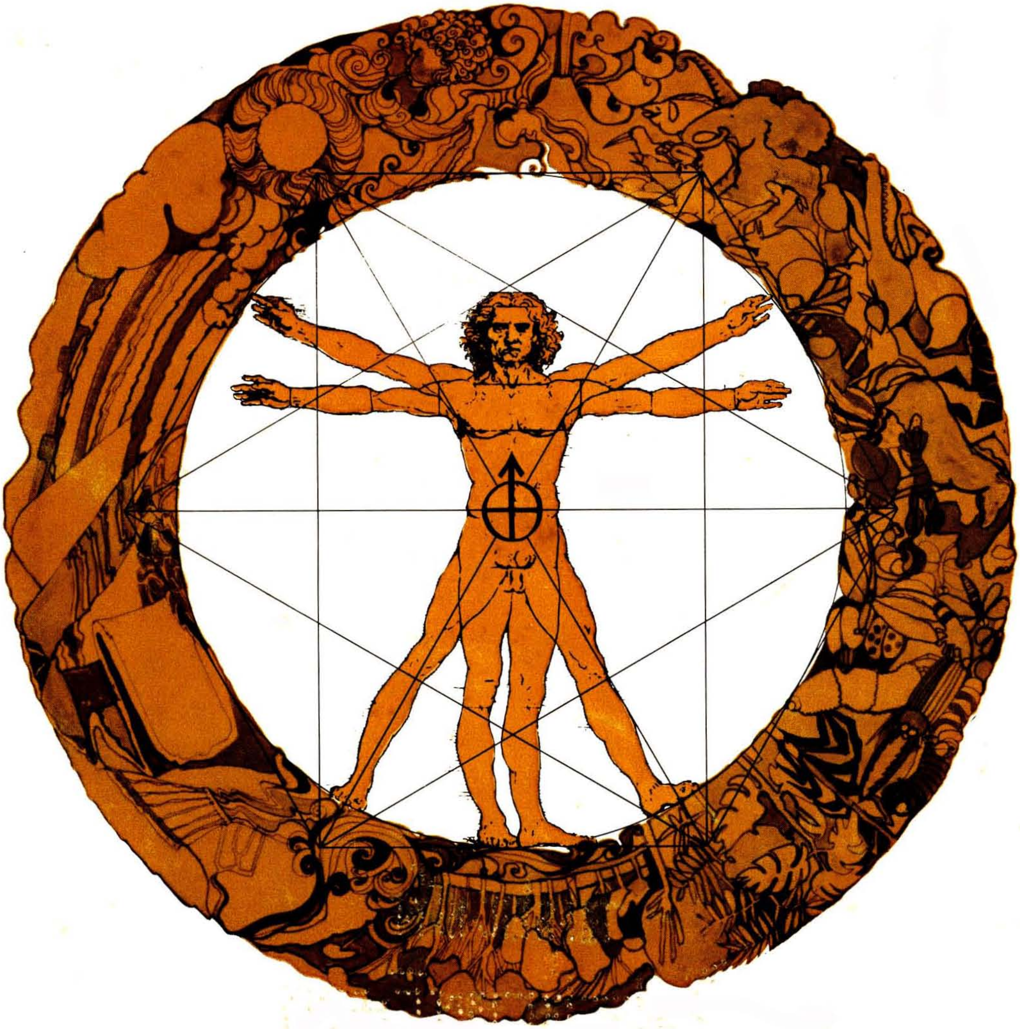
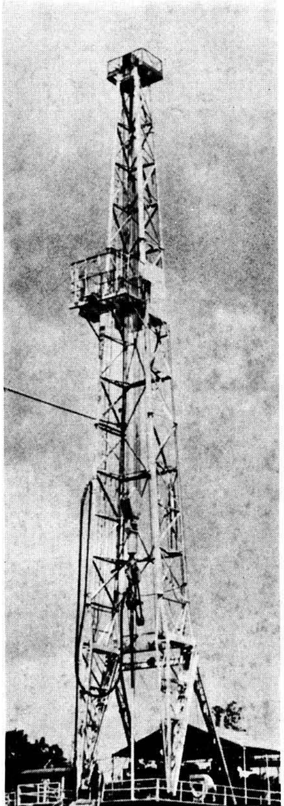
Chemistry

JUNE 1968



International Biological Program 411



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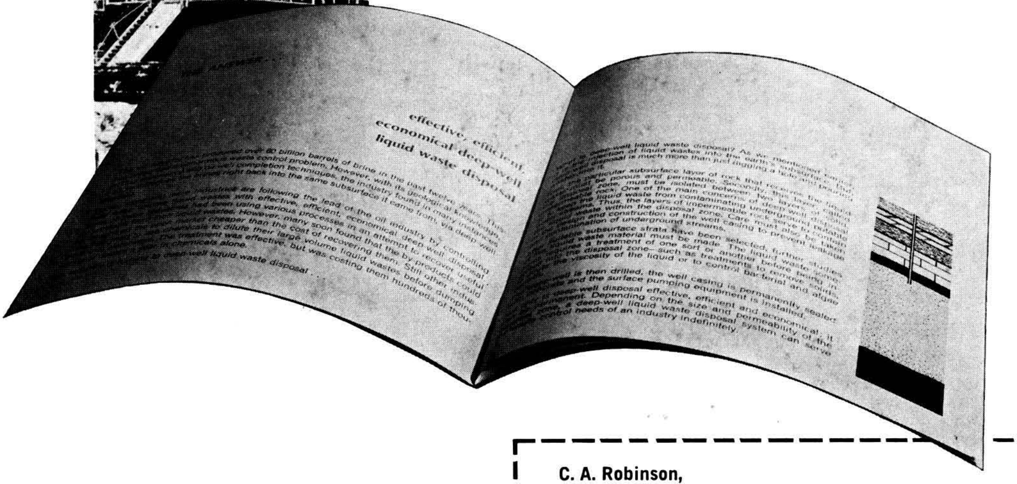

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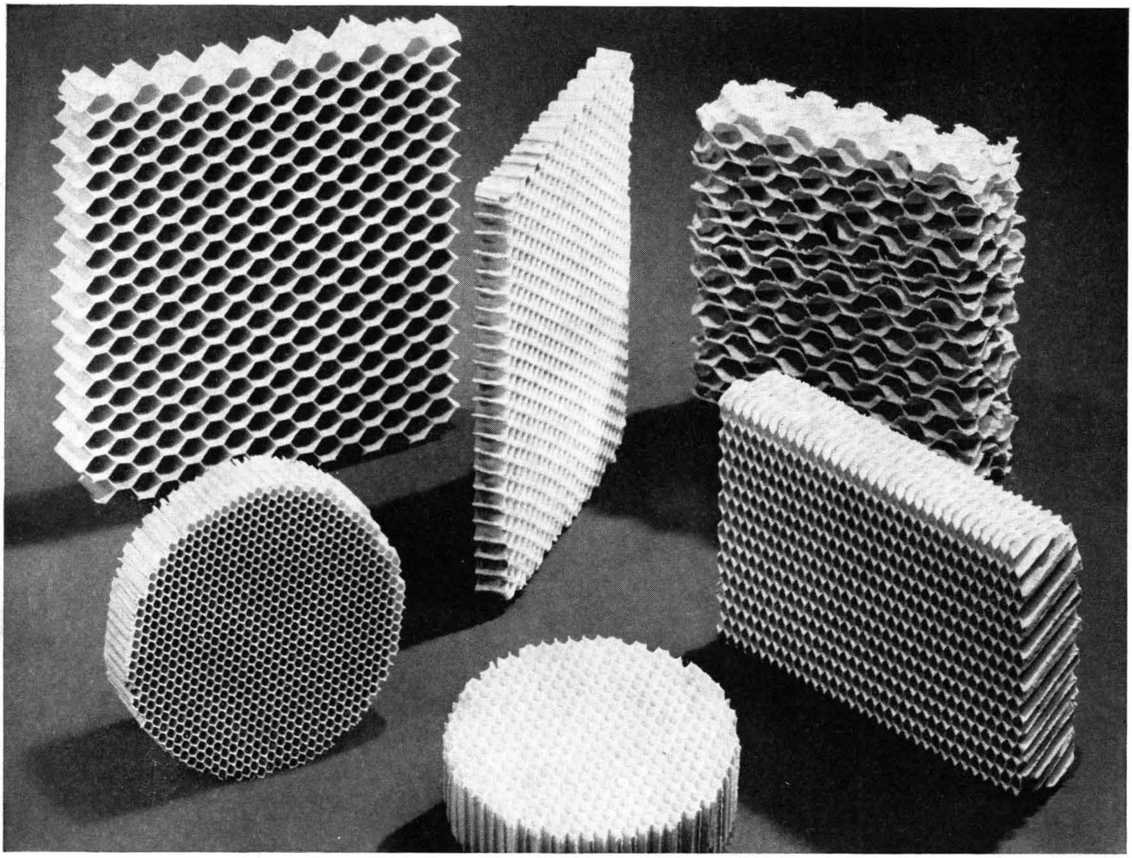

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New Du Pont TORVEX® used in Fume-Abatement Systems to reduce costs

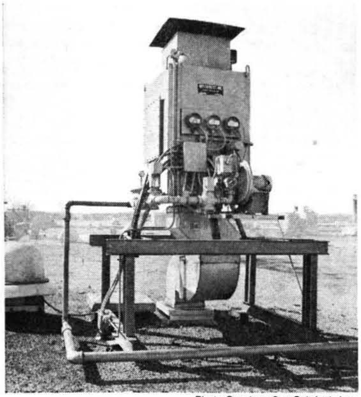

Photo Courtesy Oxy Catalyst, Inc.

The small size and weight of this odor- and fume-abatement unit at Alden Press, Chicago, Ill., is made possible by a catalytic-incineration system utilizing "Torvex" coated with a specially tailored catalyst.

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ENVIRONMENTAL Science & Technology

Volume 2, Number 6
June 1968

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J. N. Pitts, Jr., G. W. Cowell, and D. R. Burley

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B. Shleien, M. A. Wall, and D. Lutz

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D. C. MacLean, D. C. McCune, L. H. Weinstein, R. H. Mandl, and G. N. Woodruff

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Gas chromatography of pesticide residues containing phosphorus or sulfur with flame photometric detector **450**

M. Beroza and M. C. Bowman

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R. R. Claeys and H. Freund

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L. L. Medsker, D. Jenkins, and J .F. Thomas

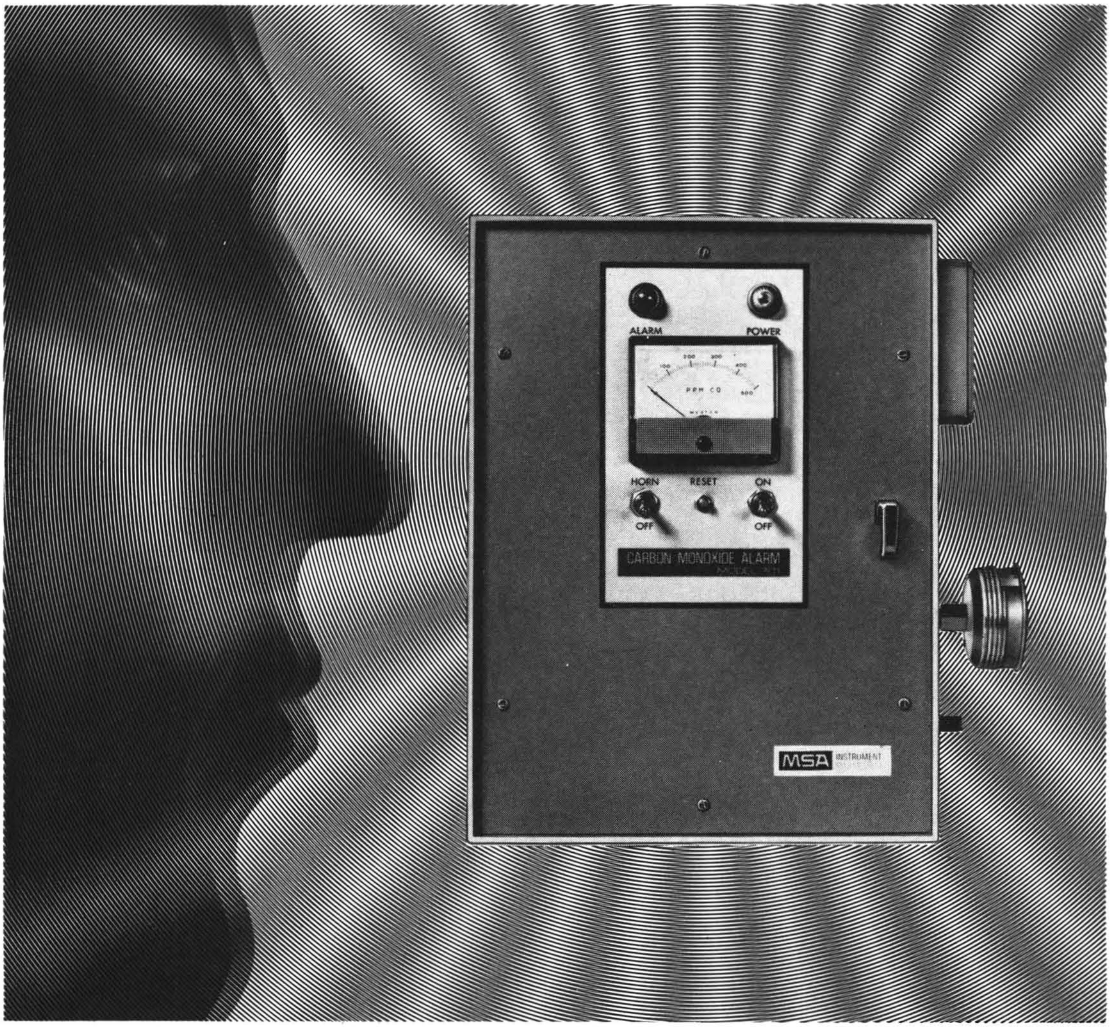
Odors in food and water supplies are traceable to the presence of the earthy-smelling compound, geosmin ($C_{12}H_{22}O$). Many actinomycetes and two species of blue-green algae produce earthy-smelling material which has been isolated by gas chromatography and has been found to have a mass spectral pattern identical with geosmin.

Communication

Estimation of some atmospheric trace gases in Antarctica **464**

W. H. Fischer, J. P. Lodge, Jr., A. F. Wartburg, and J. B. Pate

The Antarctic atmosphere at some times and in some places contains nitrogen dioxide, sulfur dioxide, and aldehydes in trace quantities (concentration levels of 0.5 p.p.b.). The presence of these trace gases occurs despite a nearly total absence of the biotic conditions which might be expected to constitute a major source of these gases. Higher concentrations of these gases are found in the atmosphere of the tropics (Panama).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EDITORIAL

One-world ecology: the promise and hope of IBP

Before we can begin to manage our environment we must first understand the interrelationships of its parts

Man has throughout his history exploited the earth without too much concern for the consequences. Among his other machinations, he has burned the land, destroyed animal species, polluted the air, fouled the water. In short he has ravaged nature. Now, as the diminishing bounties of nature must be shared by ever increasing numbers of people, man is suddenly looking around himself to see what he hath wrought. Overall, he seems not too pleased. Individually, though, there are those who continue to exploit, using to their own special interests the material that belongs to all mankind.

Intuitively we know that man must—or at least that he should—renew himself regularly by reaching out, if only for a moment, to touch, inhale, and consume nature as a whole complex system. In fact, man's very survival demands that he touch, inhale, and consume many of the parts that comprise the whole we know as nature. But what do we really know about the interdependence of man and nature, or of man and the various components of nature?

Although philosophers have considered this question, and sociologists, ecologists, and others as well, we know the answer only in part or not at all. Yet, notes Rep. Emilio Q. Daddario, chairman of the House Science and Astronautics Subcommittee on Science, Research, and Development: "Until we understand through new research the environmental systems which support life on earth, we cannot know exactly what we must do in order to maintain—or regain—an environment of reasonable quality." Rep. Daddario, who made these remarks at recent congressional hearings on proposed funding for the International Biological Program (see page 411), continued: "We are dealing with the total ecosystem of our world."

As part of IBP, research workers will try to find the interrelationships and interdependences among man, animals, plants, insects, soil, water, and climate, each with the other and all together. The U.S. IBP effort has been gathering dust since its inception in 1964. But this year, if its various sponsors have their way, U.S. IBP may finally begin to move. It is "a time when . . . the thinking in both the executive and the legislative branches of the government is being directed to the quality of the environment and to what we must do to preserve and improve it," notes Dr. W. Frank Blair, chairman of the U.S. National Committee for IBP.

Fortunately, there seems to be little concern about the value of the U.S. IBP effort, which is directed to two areas of research: environmental management and human adaptability. As is often the case with such programs, the problems are organizational and monetary, but changes can be expected in both categories probably by the end of the year.

IBP involves more than 50 nations, will span at least five years, and deals with one of the crucial problems of the day: the ability of man to destroy or cause to malfunction the natural systems on which life depends. Results of these investigations, however, by describing the interrelationships of the world's ecological components could lead to an understanding of the system that, in turn, could lead to a management program for the benefit of all men.

Melvin J. Josephs

LETTERS

In other words

DEAR SIR:

I wish to commend the American Chemical Society for the quality of the new journal ENVIRONMENTAL SCIENCE AND TECHNOLOGY. I look forward to each issue. The issue for March had two very good articles, one on phosphate removal from waste water (page 182), the other on phosphates and algal growth in natural waters (page 188). On page 194 was a good article on surfactants in the Illinois River.

These are very well written articles and the data on phosphate removal at Lake Tahoe is well described. However, as a member of this branch or section of the Society for many years, and as a consultant in this field, I wish to object to the prominence given in the subtitle "and the cost is moderate—less than 5 cents per 1000 gallons" (ES&T, March, page 182).

This cost really is $50 per million gallons and is more than the total operating costs of present secondary treatment plants of any other size except the very small ones, in which case the costs are much higher. The most recent published results from Lake Tahoe are in an article by R. L. Culp [*J. Am. Water Works Assoc.*, **60**, 84–94 (1968) which summarizes the costs as follows]:

Process	Cost per million gallons Capital	 Operation	 Total
Lime treatment for PO_4 removal	$11	$52	$63
Filtration after lime	17	24	41
SUBTOTAL	**28**	**76**	**104**
Ammonia stripping	6	9	15
Activated carbon adsorption	18	12	30
TOTAL estimated costs at Tahoe	**52**	**97**	**149**

Please note that the total cost of lime treatment and filtration is given as $104 per million gallons which is almost the same figure as the one given in ES&T on page 185 (that is 10.46 cents per 1000 gallons or $104.60 per million gallons).

My objection is not to the accuracy of your reporting but to the impression given by the headlines and the early table in the article, which dwells on how cheap 5 cents per 1000 gallons is. The total cost of PO_4 removal as given by your article for a 10-m.g.d. plant is:

$$10.46 \text{ cents} \times 1000 \times 10 = \$1046 \text{ per day}$$

$$\$1046 \times 365 = \$382{,}000 \text{ annually}$$

This cost is almost twice the annual

cost of operating a standard 10 m.g.d. secondary treatment plant. Thus, when such advanced treatment is necessary it will triple the cost of present secondary treatment.

The Dow Chemical treatment, which so far has shown a 70–80% removal, is perhaps cheaper. But I have seen no place where they have given the additional cost due to additional sludge handling, increased sludge digestion tanks, or incineration costs. At least one third of the cost of sewage treatment is in the handling of the sludge which is produced.

The article by Ferguson on algal growth and nutrients (page 188) is an excellent summary and is an article which does not give any false propaganda about the terrible condition of our surface waters. Algal blooms in our lakes have existed before phosphates were ever used in our detergent mixtures and some of the present publicity is propaganda with very little scientific background. It is doubtful if the removal of 90% of the phosphorus in sewage effluents will sufficiently reduce algal growth to be worth the cost.

William D. Hatfield
Decatur, Ill.

Myopia or short term

Dear Sir:

I feel compelled to write to you to voice objection to the title of Mr. Ferguson's paper, "A Nonmyopic Approach to the Problem of Excess Algal Growth," in the March issue (ES&T, page 188).

The title infers that a host of people who have spent many years of their lives in study of the problem are suffering from myopia simply because they are attempting to do something constructive to relieve the situation.

There is always room for a difference of opinion, but there is not room for "headline hunting" titles in professional publications.

There is an element of sense in Mr. Ferguson's paper, but to suggest that we postpone all preventive action because there may be a few isolated cases which do not seem to fit the general pattern is to "beg the question." Many of these result from "fair weather" or short term investigations which lead to unjustified conclusions. In my experience, every study has pointed to nitrogen and/or phosphorus as the prime nutrients, regardless of their origin.

In my opinion, if we are to be accused of myopia, it should be because we are attacking phosphorus alone and not both phosphorus and nitrogen. I predict the latter will be within five years, also.

Clair N. Sawyer
Boston, Mass.


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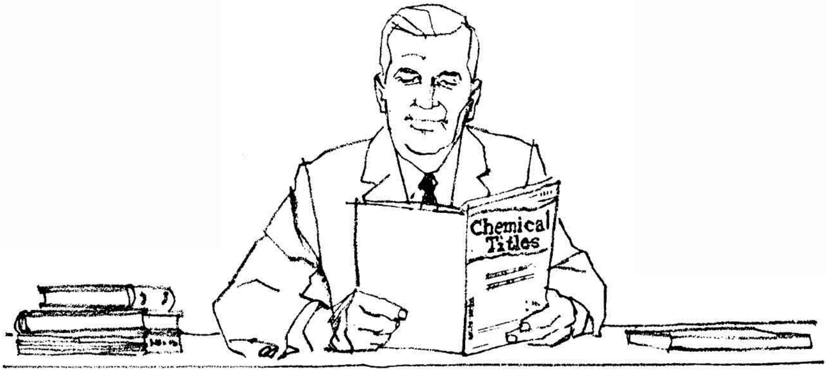

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ENVIRONMENTAL CURRENTS

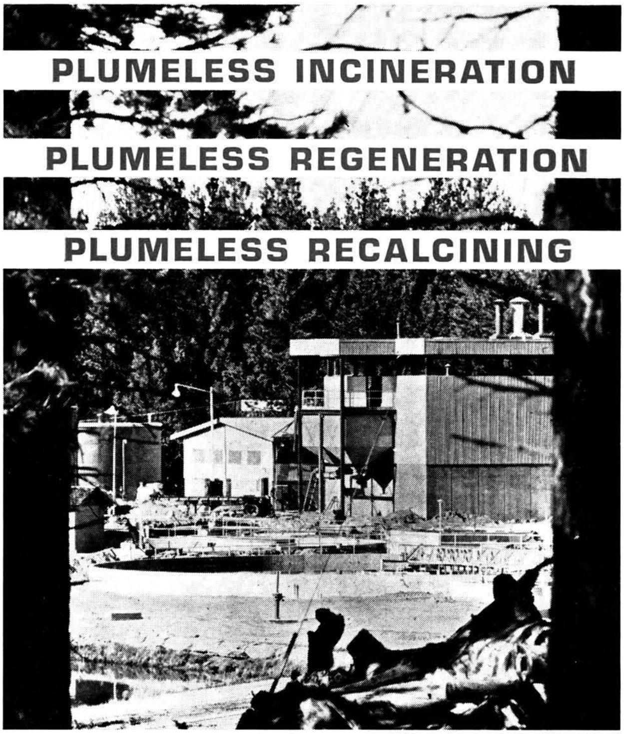
Cost for Pollution Abatement by Industry Spelled Out

The economic impact of pollution abatement is spelled out in two recent reports which were prepared by a federal committee, created by Presidential mandate and chaired by Dr. Jack W. Carlson of the President's Council of Economic Advisers. The two reports, "Cost Sharing with Industry?" and "The Secondary Impact of Air Pollution Abatement," include the following findings: • Cost of water pollution abatement to industry will be approximately $250 million annually or 0.125% of value added by manufacturing companies each year. • Cost to abate air pollution by 60–75% will be $750 million annually. The cost to industry will be approximately $350 million or 0.166% of value added by manufacturing companies each year. • Financial assistance should be made only in hardship cases. • Use of tax credits or accelerated depreciation allowance, above those already provided, should not be allowed. • Cost of abatement can double or quadruple if abatement of all wasteloads, both air and water, is pursued instead of just abatement of harmful wastes.

Clean-up Program Approved for Lake Michigan

Secretary of Interior Stewart L. Udall has approved a Lake Michigan clean-up program that draws heavily on suggestions of enforcement conferences of representatives of Michigan, Indiana, Illinois, Wisconsin, and the Federal Government earlier this year (ES&T, February 1968, page 88). The program contains timetables for some government and industry actions, and encourages the formation of technical committees to cope with other problems. Among other things, the program recommends: • *By the end of 1972,* that all cities in the Lake Michigan Basin remove at least 80% of the phosphorus from their wastes, and that cities and industries comply with water quality standards for Lake Michigan approved by Secretary Udall. • *By no later than May 1969,* that the same cities provide continuous disinfection throughout the year for all municipal wastes. • *Within six months,* that the U.S. Department of Agriculture submit to the conferees a report on agricultural programs to prevent pollution from silting, and that each state water pollution control agency list cities and industries discharging wastes into the lake basin. The Department of Interior will prepare a similar list for federal installations. • *Within sixty days,* that representatives of the conferees agree on uniform rules and regulations for controlling wastes from boats. • *As soon as possible,* that dumping of polluted dredging material into the lake be stopped, and that the Army Corps of Engineers and the states report within six months what they are doing to solve this problem. • *Effective immediately,* that combined sewers be prohibited in all new developments and be separated in coordination with all urban reconstruction projects, except where other techniques can be applied to control such pollution. Pollution from combined sewers is to be controlled by 1977.

Also recommended are the following programs: control of pollution from dead alewives; the discharge of treatable industrial wastes into municipal sewers; maximum use of area-wide sewage facilities; and technical committees to study pesticide pollution, interstate coordinated water quality analyses, and the problems of nuclear power plant wastes.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Sites for Nuclear Power Plants Hard to Find

Sites for the location of large thermal and nuclear electric generating plants are fast becoming impossible to find in large enough parcels. For this reason, Sen. Robert F. Kennedy (D.-N.Y.) introduced a bill, S. 3330, the Electric Power Plant Siting Act of 1968, calling for a national inventory of such sites, to be prepared by the Federal Power Commission, the agency most experienced and knowledgeable in power matters. Site considerations for nuclear fueled plants are considerably more restrictive than those currently associated with fossil fueled plants. Unless special steps are taken (ES&T, March 1968, page 165), nuclear electric generating plants require as much as 40% more cooling water than conventional fossil fueled electric generating plants. By 1980, the power industry estimates that approximately 20% of all the fresh water runoff in the U.S. will be used for cooling purposes.

Land requirements for nuclear electric generating plants

Capacity of plant (kilowatts)	Land area required (acres)
1.0 million	350
1.5 million	600
2.0 million	900

Source: Battelle-Northwest

Noise Effect on Health Subject of New Study

Noise is certainly a nuisance but does it affect the health and welfare of our people? Current thinking on this subject will occupy center stage at the forthcoming first meeting on the subject, scheduled for June 13–14 in the Nation's Capital. Sponsored by the Bureau of Disease Prevention and Environmental Control of HEW's PHS, the meeting will assess current thinking on noise as a health hazard. "Most people are not aware that noise is a health hazard," says Dr. George E. Urban, Jr., of the Bureau's National Center for Chronic Disease Control. He continued, "The organic and psychological effects of noise have not been clearly defined in many areas. This is why we're calling the conference." He and Dr. Alexander Cohen of the Bureau's National Center for Urban and Industrial Health are co-project-officers for the conference. Based on a survey of attendees to last month's 56th annual meeting of the Chamber of Commerce of the U.S. (Washington, D.C.), only 36% of the attendees felt that their community had a noise pollution problem, 60% felt that their community did not have this problem, and only 4% did not know. On May 17, the House Subcommittee on Transportation and Aeronautics ordered H.R. 3400 reported with several clarifying amendments. H.R. 3400, as amended, for the abatement of aircraft noises (ES&T, December 1967, page 976), places the responsibility for prescribing aircraft noise abatement and control measures, including sonic booms, with the Federal Aviation Authority. Also, H.R. 3400, as amended, requires that FAA place decibel limits on aircraft.

Interior's New Symbol Expresses Its Environmental Mission

Department of Interior's new official seal, its sixth since establishment of the Department in 1849, expresses Interior's growing environmental mission. Stylized symbols of the dynamic forces that have shaped the earth—the sun, mountains, and water—are framed by a stylized pair of hands. The new seal replaces the old bison symbol.

Cost of City Sewage Treatment Plants Report Ready

FWPCA's last input for this year's report on the "Cost of Clean Water," Volume IV, describes the five-year cost of constructing municipal sewage treatment plants and sanitary sewers. Entitled "State and Major River Basin Municipal Tables," Volume IV of the report contains a tabular breakdown of costs for each of the 50 states, the District of Columbia, and the major river basins of the U.S.

Cost of muncipal sewage treatment plant construction 1969–73

(All figures in billions of dollars)

Upgrading existing treatment facilities	$1.2
Construction of facilities for urban populations discharging untreated wastes	2.7
Replacement of depreciated plants and equipment	1.2
Operation and maintenance of treatment works	1.4
Construction of sanitary sewers	6.2
Construction of facilities for increases in urban population	2.2
Total	**$14.9**

Most Serious Oil Pollution Threat Not Covered by Law

Used and uncollected motor oil presents the most serious domestic problem regarding oil pollution, according to Secretary of Interior Udall. Some 350 million gallons of used motor oil must be disposed of annually by more than 210,000 gasoline filling stations in this country. Changes in labeling requirements and in the tax laws have put more than half of the re-refiners of used motor oil out of business. The petroleum industry has no means for collecting the used oil, and the oil often finds its way into city sewers, simply because it is the easiest way to dispose of the material. At the concluding hearings on some 20 bills dealing with the various pollution threats to this nation, Rep. George H. Fallon (D.-Md.) pointed out that the administration backed Oil Pollution and Hazardous Substances Control Act of 1968 (H.R. 15906) does not even cover this aspect of the oil pollution threat. Fallon indicated that provisions for the control of used and uncollected motor oil will be introduced as an amendment to proposed legislation.

Advisory Group for NCAPC Appointed

A fifteen-member National Air Quality Criteria Advisory Committee has been formed by HEW Secretary Wilbur J. Cohen to act as an advisory group to the National Center for Air Pollution Control. The Air Quality Act of 1967, which appropriated $125 million for air pollution control research over the next two years, called for the establishment of such an advisory committee to provide assistance in administration of the research programs. The committee expects to meet this summer to review two major classes of air pollutants, particulates and oxides of sulfur.

Members of NCAPC

- Dr. Herman R. Amberg, Crown Zellerbach
- Dr. Nyle C. Brady, Cornell
- Dr. Seymour Calvert, Statewide Air Pollution Research Center, Riverside, California
- Dr. Adrian R. Chamberlain, Colorado State University
- Dr. Raymond F. Dasmann, The Conservation Foundation
- Mr. James R. Garvey, Bituminous Coal Research, Inc.
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- Mr. Ian L. McHarg, University of Pennsylvania
- Dr. Frederick Sargent II, University of Wisconsin
- Mr. William J. Stanley, Chicago Dept. of Air Pollution Control

DOT-FAA Join in Plan to Protect Our Environment

The quality of our environment will be maintained in face of aircraft operations and airport construction, according to the Department of Transportation's proposed change in a Federal Aviation Administration rule. The proposed change, applying to several types of airport assistance programs administered by FAA, contains eight considerations for the protection of parks, wildlife refuges, recreation areas, and historic sites. These considerations would have to be met before assistance is made available. According to Secretary of Transportation, Alan S. Boyd, the proposed change is one of a series of steps taken by DOT to implement President Johnson's message, "To Renew A Nation." Last month, DOT-FAA initiated a program to combat air pollution caused by jet engines (ES&T, May 1968, page 327).

ENVIRONMENTAL

CURRENTS

Defense Funds for Pollution Abatement Are Reduced

Reductions in the Department of Defense's air and water pollution abatement programs may set a precedent for nonmilitary planners, both governmental and private, to follow. The military construction authorization bill for fiscal year 1969 calls for a 49% reduction of DOD's request for fiscal 1969. Slicing it another way, the bill calls for a 68.6% reduction of the program from its actual spending in fiscal 1968. Earlier DOD estimated that the total cost for its 5 year programs, one each for air and water, would total 270 million. In fiscal 1968, DOD initiated and spent $45.2 million for its water pollution program. DOD had planned to launch its air pollution program in fiscal 1969.

DOD's pollution abatement programs

	Fiscal 1968	Fiscal 1969		
(Millions of dollars)	Funded	Requested	Reduction	Recommended
Water pollution abatement:				
Army	$12.0	$ 4.7	$ 1.6	$ 3,1
Navy	21.3	10.3	5.7	4.7
Air Force	11.9	3.6	1.4	2.7
Air pollution abatement:				
Army	1.4	3.3	1.7	1.5
Navy		7.8	4.2	3.6
Air Force	0.7			
Total	**$47.3**	**$29.7**	**$14.7**	**$15.6**

Nation's Capital Will Be a Model for Clean Air

The National Capital metropolitan area will serve as a model in the nation's struggle for clean air, according to Secretary of Health, Education, and Welfare, Wilbur J. Cohen, whose confirmation to that post was recently approved by the Senate on May 9, 1968. Twelve recommendations aimed at the control of sulfur oxides, odors, dusts, and smoke, based on the federal abatement conference held last December in that area, were recently issued by Cohen. The Secretary's recommendations have been forwarded to the governors of the two states and the mayor of the District of Columbia along with his endorsement that the Metropolitan Washington Council of Governments should continue its services to Council members in the region. The abatement conference remains in continuing session, subject to the call of the presiding officer, until the proposed regional air pollution control mechanism is established, staffed, and in operation, according to Cohen.

National Capital metropolitan area

District of Columbia

State of Maryland
  Counties: Montgomery
    Prince Georges

State of Virginia
  Counties: Arlington, Fairfax,
    Loudon, Prince William
  Cities: Alexandria,
    Falls Church, Fairfax

An Abandoned Strip Mine Is to Fill

Using abandoned strip mines for sanitary landfills may help solve the serious problems of solid waste disposal and rid America's countryside of some eyesores

More than 2300 abandoned strip mines break the surface of a two-county area in northwestern Maryland. Long considered a blight, the strip mines offer promising sites for disposal of solid wastes, or so the Maryland Health Department decided a couple of years ago. Also, such landfills could mean reclamation of the stripped out areas and reduction of the problems of acid mine water drainage.

As solid waste disposal sites, the mines have the following advantages:

- They are out of the normal range of neighborhood objections. (But the "normal" range is often extended by emotional response to news of a coming sanitary landfill.)
- They are easily accessible, since routes had to be constructed to haul out the coal.
- They have plenty of cover material in the spoil from the original stripping operations.
- They are economic to lease or purchase because they have practically no other use.

With the help of a $126,000 Public Health Service grant, the Maryland Health Department is now operating a model landfill in a mine near Frostburg, in Allegany County. Halfway through the three-year demonstration project, the department finds its optimism being borne out; it has had some success in seeking a way to dispose of solid waste while reclaiming land.

According to Wilfred H. Shields, Jr., acting chief of the Maryland division of solid wastes: "The mine sites have so far posed no technical problems and public acceptance has been good. We're just getting underway on the acid mine drainage aspects of the project. Our work to date indicates these mines do, indeed, offer real promise for disposal of solid wastes."

While a small landfill for disposing of local wastes has been accepted, some citizens seem to want to draw the line there. Despite the apparently successful operation of the small-scale strip mine landfill at Frostburg, the first proposal for a large-scale commercial operation in the area aroused vigorous vocal opposition. However, Allegany County officials granted the required zoning and the Maryland Health Department is now considering granting a health permit. But local citizens have retained attorneys to appeal the decision. So, the role of Maryland's abandoned strip mines in solving a serious environmental pollution problem is still somewhat in doubt.

Winning public acceptance

Selling local citizens on the Frostburg demonstration was not all that easy. When word got around, various organizations and news media objected. The state had authority to go ahead with the project, but it wanted local support and money. The PHS grant requires $65,000 in nonfederal matching funds. The state was putting up some of the money and wanted contributions from Frostburg and Allegany County, whose solid wastes were to be handled by the project.

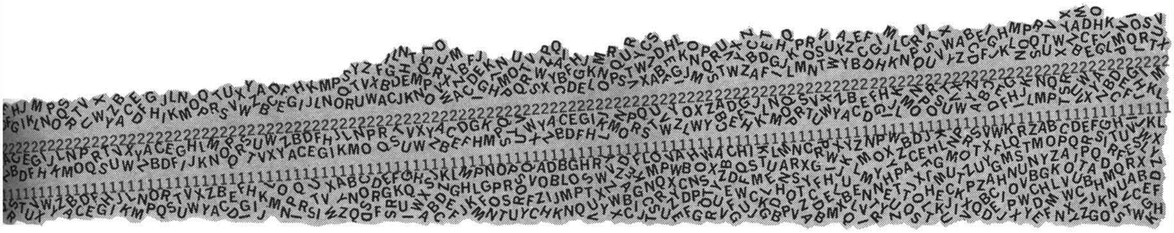
At the time, Frostburg was spending $7200 annually to maintain an open dump on the Frostburg State College campus—and the college was trying to put a stop to it. The county was spending nothing on solid wastes, and the countryside was pocked with uncontrolled, illegal, unsightly, and unsanitary roadside dumps.

After the issue was aired for several months, the citizenry became convinced this strip mine facility could be an advantage and that it would not be just another open dump. The Frostburg city council decided to appropriate $7200 per year to the project and the county commissioners $6000.

Acquiring a site

The next problem was to acquire a site. The Maryland Coal and Realty Co., which owns a great deal of

Scenic Maryland. *Open burning and roadside dumps need no longer blight the picturesque landscape of western Maryland. Abandoned strip mines—another blight on the landscape—can be filled with refuse and the land reclaimed.*



stripped out land in the area, hesitated. According to Shields, the feeling seemed to be "The fill *could* be operated well, but *would* it be?" Having the State Health Department as the responsible authority, however, assured the company, and it finally leased a 21-acre site to the state for $50 an acre annually—"a very modest price," in Shields' words. The abandoned mine, which is 1900 feet long, 50 feet wide at the bottom and 110 at the top, and 35 to 50 feet deep, was selected in the summer of 1966.

When Shields, who is project director, G. Ward Barstow, also of the State Health Department, Edgar A. Woods, of the Allegany County Health Department, and other members of the demonstration team returned to the site early the next spring, they found 5 feet of water in the strip mine. They dynamited to construct a 300-foot ditch to drain the water from the pit. After draining the pit, they used spoil to stabilize the base of the mine and to slope it so that water getting into the pit would drain into the ditch. They also constructed a simple diversion ditch along the top edge of the mine to eliminate runoff from surrounding areas.

These preparations, which took until late April, were a cause of considerable concern because the agreement with Allegany County and Frostburg required that the project begin accepting refuse as of April 1, 1967. In this interim period, the project was fortunate in being able to use a smaller pit adjacent to the main pit. This initial, small landfill was completed, covered with 2 feet of compacted earth, blended into the surrounding landscape, and seeded. Being able to see what the final result would look like was an important factor in winning a skeptical public over to the idea of a neighborhood sanitary landfill, Shields says.

Solving early problems

When the project got under way, its main assets were a bulldozer and an operator with no experience in landfill operation. And the first few weeks were hectic. The site was beset by extremely heavy winds, which, coupled with the bulldozer operator's inexperience, could very well have turned the landfill into just another blowing dump.

But it couldn't be—it had to be a model. Snow fences were put up to catch blowing paper. "You wouldn't believe how much paper we all picked up on those windy days," Shields points out. Extreme care was taken to see that trash was covered quickly—usually within an hour and a half and always by the end of the day.

The staff had a lot of company those days—and still does. "Many visitors came with their rifles to shoot bottles and rats," Shields says. "We were a big disappointment to them, I'm afraid. But we bought a mechanical rat—the only rat in evidence at the landfill—just so we'd have something to show them."

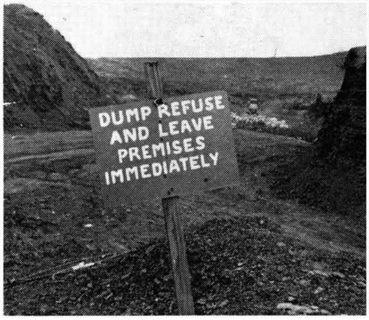
But most of the visitors to the landfill were opponents come to prove to themselves how right they'd been. "We had to disappoint them, too," Shields points out. "But it's interesting that our biggest detractors have come to be our biggest admirers. We had a lot of complaints over what they thought we'd do, but practically none over what we have done."

Administering the project

Another task during that early period was to develop administration facilities and procedures. An office trailer was purchased to serve as headquarters on the site. Water and sewage systems were installed in the trailer as were other items. Because this Frostburg landfill is a demonstration project, considerable data must also be collected for supportive studies.

A Thurman portable truck scale,

Inspecting. *Maryland health officials keep close tabs on the demonstration landfill. Charles M. Kenneally (left), Edgar A. Woods, and Wilfred H. Shields, Jr., walk over a small pit that has been filled and the land reclaimed*



Socializing. *Officials have had to discourage lingering and socializing at the Allegany County sanitary landfill site.*

Welcome. *Anyone can use the Allegany County sanitary landfill. At any time, private individuals can deposit their refuse in the dump truck (center), located just outside the*

along with a time and date sampling device, was installed so that the weight of refuse can be correlated with the time it is brought in.

In addition, Shields wanted to assemble data that would help develop a system usable by all major refuse treatment, transfer, and disposal facilities in Maryland. Therefore, Shields arranged to collect the following information: vehicle number, vehicle type, type of refuse, area from which the refuse came, and weather conditions.

The information is coded and printed directly onto cards which can be processed through a key punch machine. The data collection system costs $6758 ($6271 for the scales alone) but Shields feels it will provide valuable information for developing a comprehensive state plan.

Because many rural areas around Frostburg do not have organized refuse collections, the project must provide for private individuals to deliver their own refuse to the site. Initial experience indicated the landfill could not operate efficiently with a large number of private automobiles driving directly into the fill area. There was also the problem of recording every load brought in. And, finally, if there was to be any hope of reducing the indiscriminate dumping that long plagued the area, persons had to be able to dump at their convenience.

So, the staff set up a dump truck in a trench outside the entrance to the site. Individuals driving their cars to the landfill can dump their trash into the truck at any time. The truck, which is emptied twice a day, collects an average of 5 tons of trash a week. For more than a year, the landfill has been open to and used by commercial vehicles six days a week from 8:30 a.m. to 4:30 p.m.

Reducing haphazard dumping

Not only has the new landfill been working as planned, but according to the Allegany County Department of Health, haphazard dumping throughout the county has been reduced. However, even this development was conditioned by the example and action of the site operators. When the landfill started, the county started a campaign to clean up these dumps. During the first summer, it eliminated 24 of the 87 dumps located within a 6-mile radius of the landfill. And people get used to the nonlittered area.

The landfill is receiving a total of about 250 tons of refuse weekly from the 16,000–18,000 inhabitants of Frostburg and Allegany County. (Automobiles are not accepted because the bulldozer is not big enough to compact them. Fly ash, which gets blown around too much, is not generally accepted either, except in winter when the overburden is too frozen to use and the fly ash can be used as cover.) This tonnage is brought in by about 300 commercial vehicles dumping in the fill itself, plus 100 private vehicles dumping in the truck. The cost comes out to about $1.40 per person served per year. This cost could be reduced to less than $1 if the landfill served more people.

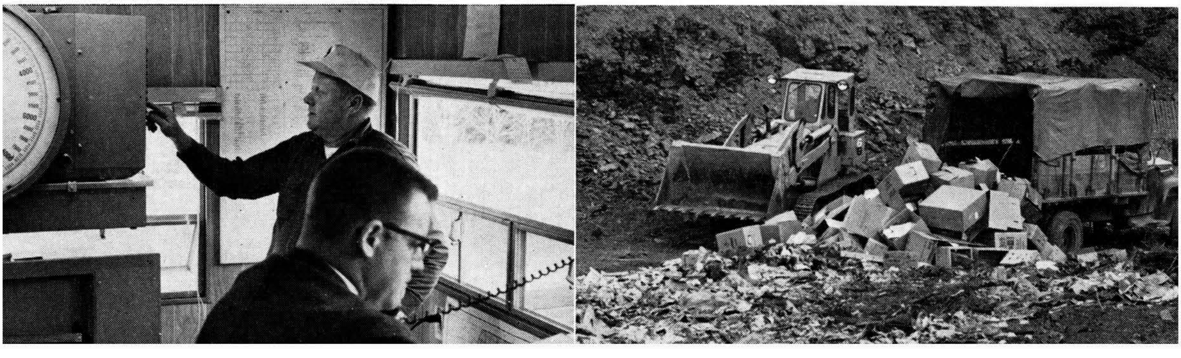
To this end, the State Health Department has been negotiating with the nearby city of Cumberland (population 33,000) about hauling its refuse to the landfill instead of to the open burning dump it currently uses. To date, Cumberland has balked because the longer haul—9.5 instead of 3.4 miles—would increase costs.

However, as of May 28 Maryland's Air Pollution Control Act bans open burning. Cumberland will then have to do something with its refuse other than the open, burning dump. Shields believes, and is trying to convince Cumberland, that it would be cheaper for the city to dispose of its refuse at the landfill than to construct and operate a landfill of its own.

Additional refuse would offer another advantage: it would reduce the rate at which the mine is being filled. Unlike most landfill operations, the strip mine landfill has available a vast amount of cover material—the overburden removed to gain access to the coal. Indeed, in Frostburg, the mine operators stripped at least 30 feet of overburden to reach a two-foot-thick seam of coal.

Because so much cover material is available, the bulldozer operators tend to mix in unnecessarily large quantities of soil with the refuse. More refuse would probably lessen this tendency. The use of excessive quantities of soil in relation to the amount of solid waste means that while covering and compaction are good, land is used up more rapidly than necessary—9.3

Processing. *As a demonstration project, the landfill must assemble various kinds of data. Robert M. Turner (rear) and Edgar A. Woods process a vehicle, recording weight, vehicle number and type, refuse type and source, and weather conditions. Paper poses special problems when the site is windy—as it frequently is. Loads are covered quickly,*



entrance to the site. The truck is weighed then dumped in the fill site twice daily. Commercial haulers are restricted to certain hours. They check through headquarters (right), where weight and other pertinent data are recorded, then drive into the site. About 100 private and 300 commercial vehicles dump their refuse at the site weekly

acre feet per year per 10,000 persons served, *vs.* the 6 acre feet the staff believes adequate.

Serving its present population, the landfill should last 10 to 15 years. "We'd like to see it filled up faster. When people see the light at the end of the tunnel, it helps our efforts to sell the concept of sanitary landfill," Shields points out.

Acid mine drainage study

With the first phase of the project well in hand, the staff is now working on the second phase, which is designed to determine if using abandoned strip mines for solid waste can cut down on acid mine drainage. The staff looked for a mine that could meet the following conditions:

- It had to have acid water flowing through.
- It had to be small enough to fill completely in 1½ years.
- It had to be located within reasonably short haul distances from the locality it was to serve.

However, the staff could find no such mine. After considering several alternatives, the staff then decided on this plan: They will fill a small strip mine downstream from mines higher on the mountain. Then they will divert part of a local stream through the fill and compare properties of the entering stream with properties of the leaving stream.

generally within an hour and a half, always by the end of the day. Overburden supplies cover material

The staff located such a stripped out area near Westernport, Md., in the southern part of Allegany County. Negotiations are now under way with the communities that would be served by the landfill: the Maryland communities of Westernport and Luke, and the West Virginia communities of Keyser and Piedmont. All four towns dispose of solid wastes in open dumps.

Maryland Health Department would operate the facility if the communities contributed the applicant's share. In effect, the communities would pay one third of the costs, and the Federal Government, two thirds. Each community would pay on a per capita basis. The communities, in turn, would get a well-operated facility. And they would get it cheaper on a regional basis than if each tried to go it alone, Shields points out. With four towns and two states involved, the other factor in pollution control—politics—comes into play. How this new venture will fare is really anybody's guess at this stage.

Commercial proposal opposed

The need to sell the concept of sanitary landfills was readily apparent when the first commercial proposal to fill area strip mines was announced. The American Land Reclamation and Resort Corp. (Cleveland, Ohio) wants to haul trash to fill in three large strip mines on a 1000-acre site it has leased in the Savage Mountain area of Allegany County. The company is negotiating with the City of Baltimore to bring in the city's general refuse on an existing siding of the Western Maryland Railroad. American Land plans to bring in 2000 tons of refuse daily.

When the land is filled in—which would take 3 to 4 years—it would be developed as a ski resort. The area is within a 3–4-hour drive of Washington, D.C., and Baltimore, making it potentially one of the closest ski resorts to both these densely populated metropolitan areas.

Considerable opposition was stirred up late last summer when the proposal went to the Maryland Health Department. One local resident told ES&T that if the Mount Savage landfill begins operation "the whole bunch of us will have to get shotguns and water pails to keep the rats down."

Two public zoning hearings were held in Mount Savage in early 1968. Allegany County zoning officials granted the zoning, contingent on approval from the Maryland Health Department. Despite the zoning hearings, a local legislator felt the public was not informed and got a bill through the state legislature requiring that the Maryland Health Department hold public hearings on landfill proposals. Although the bill does not take effect until July 1, this year, the department chose to hold a hearing anyway. At the hearing, held on April 15, the Health Department made it clear that it would issue the permit if it is satisfied that the project is well designed and poses no potential hazards from rodents, insects, and water pollution. The department is now waiting for the reports of two State Departments (Water Resources and Geology). Whatever happens, at least a year would elapse after the permit is issued before the engineering aspects could be worked out and landfill started.

Water pollution seems to be a major concern of some local citizens. Yet, Shields points out, if a landfill is well designed, water does not get in. Furthermore, he notes, "We could revoke a permit any time we felt the fill wasn't being operated satisfactorily. In addition, American Land Reclamation and Resort Corp. has posted a performance bond of $20,000, which we could use to straighten things out if the company reneged on its promises."

Deep Well Injection Is Effective for Waste Disposal

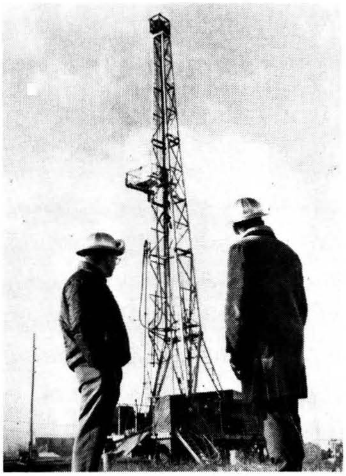
Liquid wastes can be safely discharged into deep wells in many parts of the U. S. But much more information is needed before deep well waste disposal becomes commonplace

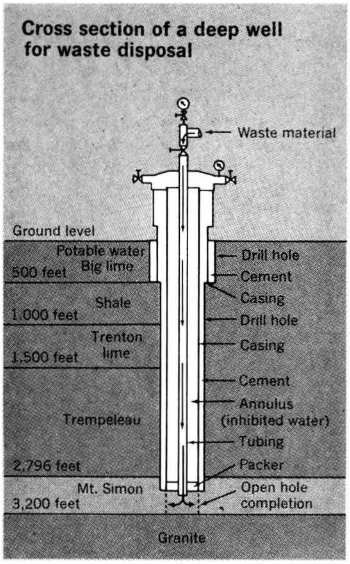
Deep well injection is steadily gaining in popularity as a liquid waste disposal method among the chemical processing and allied industries. Such wells have been long used by petroleum companies for disposing of oil field brines brought to the surface as a byproduct of crude oil production.

Only since about 1960 has there been a significant increase in use of the technique for disposing of industrial wastes. In fact, in the past four years, the number of waste injection wells drilled in the U. S. has more than doubled—to about 110. More than one half of this total number were drilled by chemical, petrochemical, or pharmaceutical companies for the disposal of organic and inorganic wastes.

The technology of injection well site evaluation, drilling, and installation is already highly developed. The number of brine injection wells drilled in the U. S. in the last 40 years is not known definitely, but some estimates run as high as 40,000. Texas alone is believed to have about 20,000. Thus, with this backlog of injection well technology, it is only natural that the technique would eventually be applied to the disposal of industrial wastes.

This recent surge of interest in deep well waste disposal stems from the geographic concentration of manufacturing activity which has been overloading the capacity of surface streams to disperse industrial waste effluents. Surface dispersal methods are becoming severely restricted, and deep well injection is perhaps the cheapest alternate disposal method for liquid wastes. In some instances, as with highly toxic materials, it is the only disposal technique feasible.





Cross section of a deep well for waste disposal

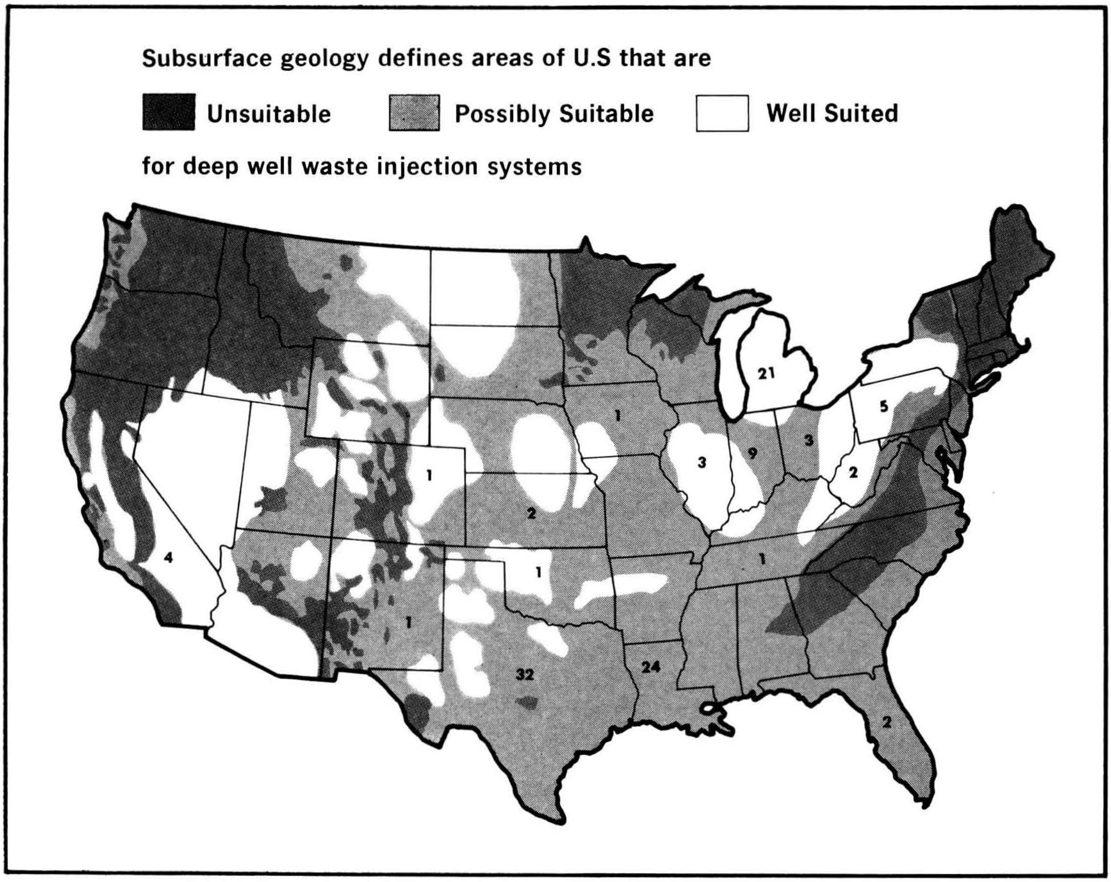
FWPCA survey

A recent survey by the Dept. of Interior's Federal Water Pollution Control Administration shows that waste injection wells have been drilled in 16 states. Texas and Louisiana lead in the total number of wells drilled, with 32 and 24, respectively; Michigan has 21, and Indiana 9. The remaining wells are scattered through the remaining dozen states, each of which has five or fewer wells.

Policies and regulations governing the drilling and operation of disposal wells vary from state to state. A few states do not allow their construction, others allow only oilfield brine injection wells, and some do not discourage the use of waste injection wells but have no specific requirements for them. About two thirds of the states do allow the construction of waste injection wells subject to certain requirements. Of these, only two—Texas and Ohio—have legislation referring specifically to industrial waste injection. The requirements of the remaining states allowing disposal wells are the same as those pertaining to brine injection wells or to waste disposal systems in general.

Limitations

To be sure, deep well injection as a disposal technique has its limitations. For one thing, not all areas of the U. S. are suitable for injection well construction. The geological features required for disposal wells are porous, sedimentary rock strata, usually sandstone, limestone, or dolomite, permeable enough to readily accept large amounts of liquid. These porous reservoirs must be suitably capped above and below by impermeable strata. In addition, the



Site selection. *Porous and permeable rock strata favorable for injection wells exist in many parts of the U. S. For example, the synclinical basins shown in* **white** *contain relatively thick sequences of salt-water bearing sedimentary rock, although in a few instances, such factors as the danger of seismic activity, the presence of oil and gas deposits, or the cost of obtaining adequate geological data make these areas unfavorable. Areas shaded in* **grey,** *though not underlaid by major basins or prominent geological features, may be suitable if underlaid by a sufficient thickness of strata that contain saline water and if injection horizons are sealed from fresh-water bearing strata by impermeable confining beds. Injection wells are usually not feasible in areas with little or no sedimentary rock cover. The* **color** *shading indicates where metamorphic or volcanic rock sequences are exposed at the surface. The* **figure** *in the state indicates the number of deep waste injection wells—and the associated well systems—that have been drilled in the state.*

porous strata must lie below ground water tables, and contain no commercial brine or mineral deposits.

Such geological conditions are found in roughly one half of the land area of the U. S., predominately in the central plains states and the coastal areas of the southeast. Thus, present injection systems in this country are heavily concentrated in the northcentral and Gulf coast areas. This distribution is a result of a combination of factors: favorable geology, heavy industrial concentration, and the attitudes of the states in those areas regarding subsurface disposal systems.

Another limitation of the use of injection well disposal is that not all wastes are suitable for disposal by this means. For one thing, the solids content of the liquid stream must be low enough to prevent clogging of the porous rock deposit and subsequent reduction of permeability. These factors can cause a rapid buildup in injection pressure and reduce the operating life of the well. Clogging can also be caused by the precipitation of alkaline earth and heavy metals as insoluble salts within the well, or by *in situ* polymerization of resinous wastes within the aquifer. Heat generation, for example in radioactive wastes, can also present problems that preclude injection well disposal.

Even within these limitations, deep waste wells are already being used by a wide variety of processing plants. Perhaps most common among them are manufacturers of basic chemicals and petrochemicals, and steel mills, which use them for disposing of spent pickling acids. Other types of plants using deep wells include plastics plants, pulp mills, photoprocessing facilities, catalyst plants, coking plants, and a uranium mill. The types of wastes being pumped also cover a broad spectrum, including alkalies and acids, radioactive wastes, chromates, nitrates, phosphates, chlorides, and sulfites and organic materials such as alcohols, ketones, acetic acid, phenols, cyanides, chlorinated hydrocarbons, and waste process waters as well.

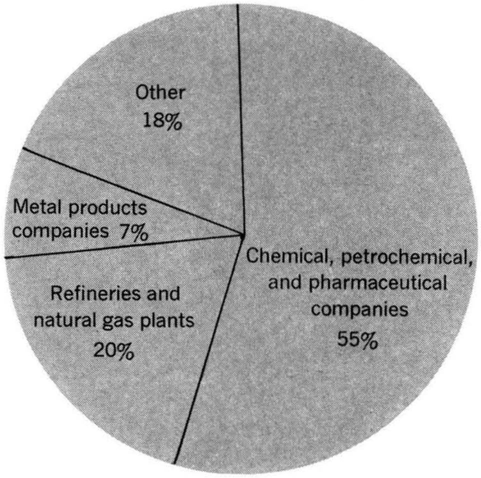
An efficient method

When geological considerations and regulatory legislation permit, deep well injection can prove to be an efficient, effective, and economic disposal method. This is amply demonstrated by a well soon to be put into operation by Standard Oil Co. (Ohio) at its Vistron division plant in Lima, Ohio. Vistron is the first chemical plant to seek and get approval for a waste disposal well under Ohio waste injection legislation enacted last year. Vistron had been incinerating a waste stream from its Lima acrylonitrile plant, at an operating cost of $600,000 per year. Of the half dozen alternative disposal methods for the waste, only deep well disposal represented any significant cost advantage. But prior to last year, the state did not permit subsurface injection of any waste other than oil field brines.

When Ohio enacted its new legislation, the company promptly filed for and obtained a permit to conduct exploratory drilling. Core sampling confirmed that the 200-ft. thick Mt. Simon sandstone layer, which lies about 3000 feet below the Lima area, is one of the most favorable deposits in the state for injection well construction. Its 20% porosity indicated substantial storage capacity, and the permeability of the deposit was well above the minimum required for efficient lateral dispersion. Furthermore, the sandstone strata, located well below the ground water

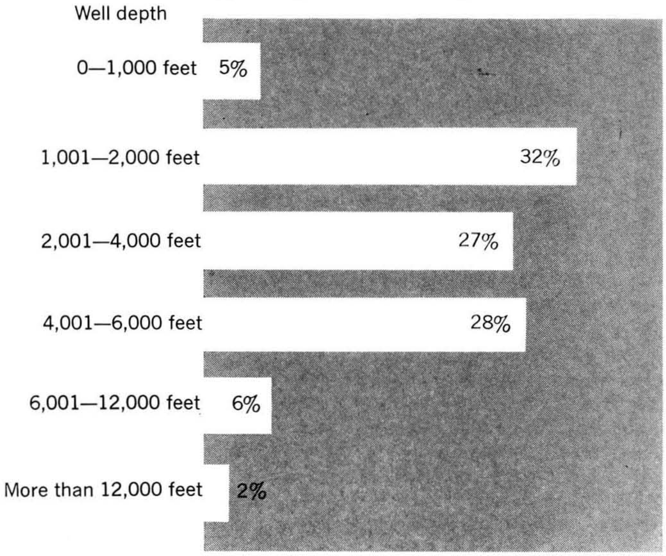
Distribution of injection wells by industry type

Figures in per cent of existing wells



Depth of injection wells

Figures in per cent of existing wells



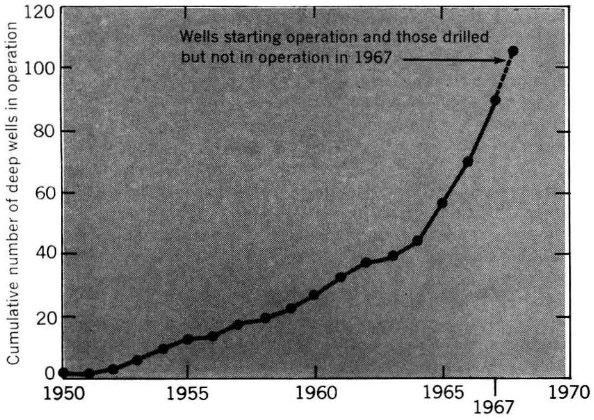
table, was sealed above by shady dolomite and below by solid granite, and contained only noncommercial brines.

The disposal system which evolved from these tests, and which Vistron hopes to put into operation this summer, will be more than adequate to handle the acrylo plant effluent, column bottoms which contain typical organic acrylo byproducts such as acetonitrile and HCN, as well as catalyst solids and up to 10% ammonium sulfate. The permanent installation will include settling pits to remove up to 90% of the solids content, a sand filtration step, holding tanks, and the main pumping equipment. Also included as part of the installation will be suitably placed test wells to monitor the ground water table, which is only 400 to 500 feet below the surface.

Vistron's Bill Warnement, project engineer for the injection well, estimates that total investment costs for the injection system will run about $270,000. Drilling and casing the well has cost $60,000, and the above ground test facilities another $110,000. An estimated additional $100,000 will be required for the permanent installation. Although operating costs are not yet firm, the company estimates this at $100,000 per year.

Of course, these costs are not typical. Some areas require wells as deep as 10,000 feet or more, and drilling costs and the need for more extensive waste pretreatment can run the cost per well to as much as one million dollars. But the majority of wells that have been drilled so far are less than 6000 feet deep, and some systems have been built for under $50,000. In the light of such economics, and as more and more experience is gained in the operation of deep wells, more and more firms are sure to consider this method of waste disposal.

Almost 100 deep wells are in operation in the U.S.



Legislation

With the increased interest in waste injection wells, state regulatory agencies will undoubtedly be under pressure to overhaul existing legislation governing disposal well drilling and operation. At present, most state regulations covering the granting of drilling permits are aimed primarily at the protection of ground water supplies and commercial mineral and brine deposits. As more wells are put into operation, the problems of regulation become more complex.

For example, although the earth's capacity to absorb liquid waste in porous subsurface deposits is undoubtedly large, this capacity can be limited in some specific geographic areas. To some observers, this storage capacity should be considered a limited natural resource, to be reserved only for those wastes impractical or impossible to dispose of by other means. The point that then could arise is: Should a guarantee against potable water or mineral deposit contamination be the sole requirement for issuance of disposal privileges, or should a petitioner be required to demonstrate significant need for disposal well facilities?

Legal questions

Other observers cite some legal questions that could arise, that could bear some clarification by legislation. The matters of subsurface trespass and pollution of public waters, though at present highly developed by the courts, take on a new dimension in the light of injection wells. Do restrictions against subsurface trespass pollution of public water apply to subsurface deposits of brine that while saline, contain valuable minerals such as bromine, iodine, or magnesium? And to what extent is the well operator liable for damage to both public and private subsurface waters as a result of operation of a state approved injection well?

Tremors in Denver

In the background of the recent interest in disposal wells and their regulation is the controversy surrounding the deep disposal well at the U. S. Army's Rocky Mountain Arsenal in Denver, Colo. The 12,000 foot well, one of the deepest injection wells drilled, was put into operation in March 1962 for the disposal of wastes from the arsenal, including some that contained ammonia, nitrates, chlorides, phosphorus. The well was shut down chlorinated hydrocarbons, and organic in February 1966 when it was suggested that the well operation was responsible for the increased frequency of earth tremors in the Denver area. The question is still hotly debated between those who hold that no direct mechanism for a relationship has been demonstrated and those who claim that the statistical evidence alone is convincing. Whether or not the controversy is ever resolved, the issue is likely to weigh heavily on those responsible for injection well regulation.

Research requirements

The growing use of waste injection wells demonstrates their feasibility, but further research could broaden the reliability and applicability of the technique. Little is known about how to confine injected wastes laterally in a specific geological structure. Although not generally necessary or practical, it may be desirable under certain circumstances to store waste in a predetermined manner rather than to allow it to circulate randomly into the injection horizon. Such a technique could conceivably allow subsequent recovery of the injected liquid. In order to restrict the lateral spread, methods would have to be developed for predicting the rate of mixing of injected liquid with interstitial waters.

Another possible area for further study is a way of determining the maximum safe well injection pressure. As fluid is injected into a porous rock strata, the injection pressure gradually rises, and in some instances the increased pressure may be sufficient to cause hydraulic fracture. It is not certain that hydraulic fractures if they do occur are vertical, or that they damage the confining beds if they are vertical.

Although a wide variety of waste effluents is currently being disposed of in deep wells, further research and exchanges of data would be helpful in further generalizing on which types of wastes are suited for deep well disposal, and what types of pretreatment can make wastes more suitable. Such studies would aid pollution control agencies to accurately assess the feasibility of deep well disposal as a solution to specific pollution problems. In addition, such research would be a step toward a concept not yet investigated, but mentioned in the literature: regional injection well systems to serve an industrial system or geographical area.

Deep disposal well operators face many restrictions

Last year, Ohio became the second state (Texas was the first) to enact specific legislation covering the drilling and operating of liquid waste disposal wells. Since the law was enacted on June 26, 1967, three permits for disposal well systems in the state have been approved, and at least a half dozen more applications are expected this year. Here are some excerpts from the legislation:

"As used in [the following sections], 'Well' means any borehole, whether drilled or bored, within the state, for production, extraction, or injection of any gas or liquid mineral, excluding potable water to be used as such, but including natural or artificial brines and oil field waters, sewage, and any liquid used in or resulting from any process or industry, manufacture, trade, business, or agriculture."

"No person shall use a well for the injection of sewage or any liquid used in or resulting from any process of industry, manufacture, trade, business, or agriculture, without having a liquid disposal permit issued by the chief of the division of oil and gas . . ."

"An application for a permit to drill a new well, drill an existing well deeper, reopen a well, plug back a well to a different source of supply or use a well for injection of a liquid for which a permit is required . . . shall be filed with the chief of the division of oil and gas . . ."

"Upon receipt of an application for a permit to drill a new well, drill an existing well deeper, reopen a well, or use a well, for injection of a liquid for which a permit is required . . . the chief of the division of oil and gas shall determine whether the proposed injection would present an unreasonable risk that waste or contamination of oil and gas in the earth will occur . . . If he determines such risk not to exist, he shall transmit copies of the application . . . to the water pollution control board, the director of health, the chief of the division of geological survey, the chief of the division of water, and, if so required by [another section of this code], to the chief of the division of mines."

"The chief of the division of geological survey shall approve the application unless he determines that the proposed injection would present an unreasonable risk of loss or damage to valuable resources."

"The chief of the division of water shall make a report and recommendation to the director of natural resources."

"The water pollution control board shall approve the application if it determines that the proposed injection will not cause pollution . . ."

"Upon approval by the water pollution control board, the department of health . . ., and the chief of the division of geological survey and by the chief of the division of mines . . . the chief of the division of oil and gas shall issue a liquid disposal permit with such conditions as may be necessary to protect health, safety, or the conservation of natural resources, including all conditions appended by the water pollution control board and the department of health."

"The chief may order that a liquid disposal permit be suspended and that operations cease if he determines that the well is being operated in violation of law, regulation, order, or condition of the permit."

"The chief may order that a liquid disposal permit be suspended and that operations cease if he has reasonable cause to believe that the permit would not have been issued if information available at the time of suspension had been available at the time a determination was made by one of the agencies acting under authority of this section. . .. ."

"This act is hereby declared to be an emergency measure necessary for the immediate preservation of the public peace, health, and safety. The reason for this necessity is that its enactment into law at the earliest possible time will enable industries which have a present need to dispose of untreatable waste materials to dispose of them safely underground, and thus avoid pollution of the rivers and streams of the state."

IBP

The International Biological Program, already plagued by lack of funds, loose organizational structure, and manpower shortages, last month was subjected to extensive scrutiny by Congress

The International Biological Program, a cooperative effort on the part of the world's scientists to understand the environmental systems which support life on their planet, is experiencing many hardships. In spite of IBP's laudable goals, which optimistically will lead to an understanding of the biological basis of human welfare, IBP's hardships are associated with a lack of funds, loose organizational structure, manpower shortage, and lack of understanding and endorsement by Congress and the Executive branch.

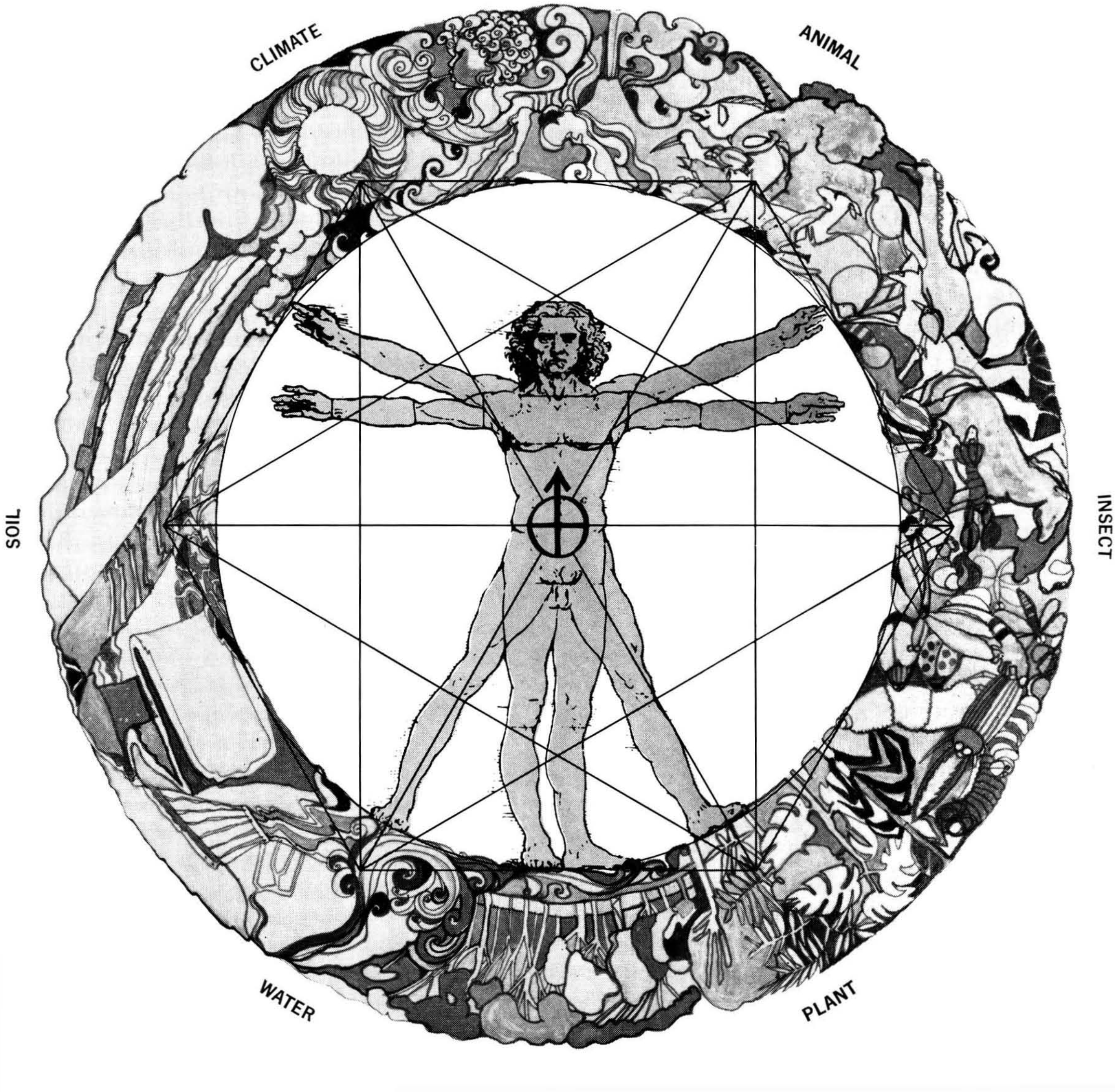
Last month, the House Subcommittee on Science, Research, and Development held hearings specifically to sound out the need for this nation's financial committment to IBP. Loss of momentum and loss of U. S. prestige in the scientific communities of the world would result if funding is not made available. This was the minority point of view held solely, but resoundingly, by Dr. W. Frank Blair, chairman of the U. S. National Committee for IBP.

The majority point of view, shared by representatives from the President's Office of Science and Technology and the National Science Foundation, was that a program memorandum should review IBP and delay funding until its completion, hopefully in August.

But can we wait until August? No consensus among biologists exists. If we wait, the argument goes, then some of the scientists who have already been committed will lose interest and do other things. After several years of planning and determining intents from scientists, it would be disastrous to delay in view of our increasing environmental problems, or so goes the discussion.

Mainly through new research, IBP scientists are seeking the relationship—and the meanings of such relationship

Desinged and executed by
Ben Heck
Geraldine Lucas



—from man to animal, animal to insect, insect to plant, plant to water, water to climate, climate to soil, and from each to all the others, according to the recent report, "The International Biological Program, Its Meaning and Needs."

"Until we understand through new research the environmental systems which support life on Earth, we cannot know exactly what we must do in order to maintain—or regain—an environment of reasonable quality," says Rep. Emilio Q. Daddario, chairman of the House Science and Astronautics Subcommittee on Science, Research, and Development, which prepared the report. "We are dealing here with the total ecosystem of our world," says Daddario.

Steps necessary

Steps involving both short-term and long-range plans for IBP must be taken today, the report points out. The first step involves finances. The program needs from $3–5 million for fiscal 1969 alone, according to the report. Blair informed the subcommittee that the U. S. National Committee for IBP has a list of programs which could and should be put into the operational phase at once, if the necessary funding is available. The list covers IBP research costing more than $7.5 million for fiscal 1969. Before the end of its five-year life-span, IBP may cost as much as $30–50 million, the report notes.

A second step involves legislation to commit the U. S. to its partial responsibility regarding the world's environment, says Rep. George P. Miller (D.-Calif.), chairman of the parent House Committee on Science and Astronautics. On April 24 the congressman from California introduced House Joint Resolution 1240 to meet this nation's responsibility to IBP. H. J. Res. 1240 calls for an appropriation of not more than $5 million for fiscal 1969, such sums as may be necessary for each of the following four years, and administration of the program by the National Science Foundation.

Large scope for IBP

Involving more than 50 nations, IBP is not just another international cooperative agreement or program. On the contrary, IBP deals with one of the most crucial situations to face this or any other civilization. As the report continues, this situation involves the immediate—or potential—ability of man to damage, beyond repair, the ecological system of his planet on which all life, as we know it, depends.

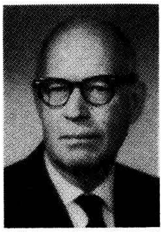
Nonetheless, ecological understand-

Timeliness of IBP

"IBP is developing at a time when virtually for the first time in U.S. history, the thinking in both the executive and the legislative branches of the government is being directed to the quality of the environment and to what we must do to preserve and improve it. A number of bills, both in the House and the Senate, call for a national panel of ecological, or environmental, advisors to the President. Also a number of bills call for solutions to the problems of pollution of air, of our fresh waters, of our lands, and of our estuaries. IBP can furnish an important input into whatever panel may be established by the Administration in the next few months or by future legislation . . .

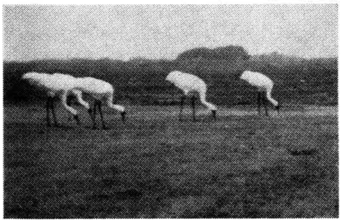
". . . Another related phenomenon at the national level is the developing sentiment for a National Institute of Ecology. Such an institution seems inevitable in the very near future. The institute would continue much of the research started in and related to the various IBP programs. For example, the entire ecosystems program, with its potential for providing the environmental base lines called for in currently proposed legislation, would fall logically under the administration of such an institute . . .

". . . The Ecological Society of America has made a feasibility study of such an institute through a subcommittee of its Ecology Study Committee, and a recommendation has been made for an organization patterned after the National Center for Atmospheric Research (NCAR). Ecologists feel that a semi-autonomous agency comparable to NCAR is more preferable than an in-house agency under, for example, the Department of the Interior, as has been proposed in some of the bills introduced into Congress . . ."



W. Frank Blair (Univ. of Texas, Austin), Chairman, U.S. National Committee for IBP ing is both an international and national problem, the report points out. It goes on to say that the Federal Government has a definite responsibility to support IBP and that the government's responsibility cannot and should not be left to lesser government units nor to private institutions and foundations.

However, the report is quick to recognize that the problems are everyone's problems. Local and state governments, the industrial complex of the nation, the academic community, the private foundation, and philanthropies—all have a strong stake in the outcome. They, too, should help support the U. S. effort in relation to IBP. Perhaps, they could contribute funds amounting to one third of the amount needed to carry out a successful American program, the report goes on.



WHOOPING CRANES *saved*

Defense of U. S. IBP

At the recent hearings, Blair responded to the four major IBP problem areas noted in the recent report. Item by item, he assured the subcommittee that U. S. IBP is ready to move into its operational phase.

First, the *organizational* setup has been completely restructured. Eliminated are the nine subcommittees with from nine to 10 members each. In their places are the following:

- A prime executive unit of five to six persons who report to the Division of Biology and Agriculture of the National Academy of Sciences–National Research Council.
- A coordinating unit, a nine to 10 man effort which will devote its full attention to international cooperation.
- A unit of 8 research managers whose most recent endeavor is the list of research.

On *funding,* Blair feels strongly that large amounts of money are necessary for fiscal 1969 and concedes that U. S. involvement in IBP should proceed as a line item in the NSF budget.

U. S. IBP management

Old management structure	
Total	94 persons 14 elements
NAS full-time scientist	4
Nine subcommittee with from nine to ten persons each	90
New management structure	
Total	24 persons 3 elements
Executive committee	5
International coordinating committee	9
Research managers	8

On *manpower,* Blair said that we have enough of the right kind of manpower to launch the show today. But he cautions that this team was put together in the past several years, when IBP was still in the planning phase. If adequate financing is not made available now to move into the operational phase, the team will become splintered and a loss of momentum will result, Blair continued.

On *lack of understanding* by Congress and the Executive branch, Blair commented, "In view of this concern in both legislative bodies, it is difficult to see how the U. S. effort could fail of enthusiastic support in both houses."

One example of a program which might suffer from a delay of timing and finances is the program to explore development of a world-wide monitoring system to establish base lines for pesticides, heavy metals, carbon dioxide, and the like. At the recent meeting (Varna, Bulgaria) of the Third General Assembly of IBP, to which 37 countries sent delegates, a three-member committee agreed to launch this program. The chairman of the committee, Dr. Bengt Lundholm (Sweden), is joined in his efforts by Dr. Winberg (U.S.S.R.) and Dr. Blair (U.S.A.).

Cons

On the other side of the IBP argument is Dr. Ivan L. Bennett, Office of Science and Technology, who noted that U. S. leadership in the IBP program has resulted in many foreign scientists being attracted to the IBP program in the U. S. The real reason for the attraction may be that the analysis of ecosystems (biomes) and the studies of human adaptability are really precursors of the big biology in the future, he noted.

Lack of a management superstructure for these programs does not justify the funding levels specified in H. J. Res. 1240, Bennett noted. Management arrangements must be devised at all levels of involvement to assure orderly execution of studies.

But, they simply do not exist at this time. Thus, he favors a program of intermediate scope at this time and, concurrently, development of a program memorandum which would review and assess the U. S. IBP. The U. S. IBP is simply not sufficiently developed to warrant large-scale special funding for fiscal year 1969, particularly in the prevailing fiscal situation.

Already the President's budget request for fiscal 1969 contains a specific line item of $700,000 for NSF to support the U. S. IBP effort. No assessment has been made of the requirement for fiscal year 1970 at this time. And for this additional reason, Bennett feels, that NSF should develop the program memorandum on the IBP.

The recent hearings did not question the merits or desirability of U. S. IBP. These questions had already been answered—a resounding yes. The hearings were solely concerned with implementation of this nation's contribution to the IBP—how and when to put U. S. IBP into its operational phase.

Without reservation, Dr. Leland J. Haworth, Director of NSF, told the subcommittee that NSF endorses IBP and the intent of H. J. Res. 1240 to provide adequate financial support. But with the express provisions on funding, Haworth said that NSF sides with OST and the Bureau of the Budget. Already the Bureau of the Budget has asked NSF to prepare the program memorandum which would look ahead toward appropriate funding levels for U. S. IBP in fiscal 1970.

Organization

A Special Committee for the International Biological Program (SCIBP) is responsible to the International Council of Scientific Unions (ICSU) for the IBP program. The international program consists mainly of national

U. S. IBP program funding[a]

(thousands of dollars)

Problems of environmental management	
Analysis of ecosystems[b]	$1,500
Convergent and divergent evolution[b]	500
Phenology	185
Physiology of colonizing species[d]	560
Aerobiology	485
Hawaiian program	500
Biogeography of the sea[d]	583
Nitrogen balance	380
Crop production under stress	500[c]
Biological control	1,661
Marine mammals	46
Problems of human adaptability	
Ecology of migrant populations[b]	291
Eskimo program[b]	200
Genetics of the South American Indian	500[c]
Biology of high altitudes	850
Nutrition	1,580[c]
NEW MONEY TOTAL	$7,741

[a] Arranged by Blair in decreasing order of importance
[b] High priority and ready-to-go
[c] Already funded for fiscal year 1969, and not included in the total
[d] Ready-to-go

programs which are the responsibility of national IBP committees.

The U. S. IBP is sponsored by the National Academy of Sciences–National Research Council, which adheres to ICSU, and which organized a U. S. National Committee and the nine, now defunct, subcommittees that helped plan the U. S. IBP.

Inaugurated in 1964–65, U. S. IBP will be managed in a fashion similar to other international scientific programs that have been sponsored by NAS-NRC. Similar to the International Geophysical Year in some aspects, IBP differs in others. First of all, at present, IBP is not formally funded by the Federal Government, as was IGY. Pending legislation may, however, provide funding. Also, IBP spans five years, whereas IGY was limited to 18 months.

Manpower

Dr. David Gates, an ecologist, pointed out in earlier testimony before Daddario's subcommittee that "Our budgetary support in National Science Foundation for biological facilities is shockingly small and grossly inadequate. The lack of training programs for modern ecologists is, or will be, an international disaster. We will go down in history as a elegant technological society struck down by biological disintegration for lack of ecological understanding."

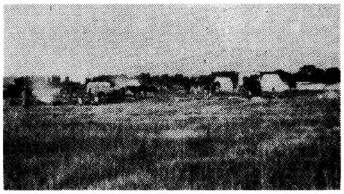
According to the National Register only 1354 (about 2.5%) of its 55,000 biologists are identified as ecologists. Only 20 of the major training institutions in the U. S. have programs in ecology and, on the average, produce 56 Ph.D.'s per year. In other terms, graduate enrollment in all sciences in 1963–64 was 36,941. Of this total only 111 graduate students were enrolled in ecology.

Research programs

Two major areas of research—problems of human adaptability and problems of environmental management—comprise the list of programs for U. S. IBP. These areas result from last month's successful, organizational meeting (Washington, D. C.) of U. S. IBP.

Analysis of ecosystems, the central core of the U. S. IBP effort, is headed by Dr. Frederick E. Smith (Univ. of Mich.). This research program is aimed at the ultimate understanding of environment and how man-made changes will affect it. One of the special goals is to look at a large area like the grasslands or a city as a whole interacting system, not just as a series of separate operations and events, the subcommittee report points out.

To get the broadest view of how a large environmental system operates and to perform a modern systems analysis approach to this complex function, some 80 senior scientists from 20 universities and government laboratories in the western U. S. plan a study of one specific biome, namely grasslands. Under the chairmanship of Dr. George van Dyne (Colorado State University), this biome study has top U. S. IBP priority and will concentrate on grasslands, including the 15,000-acre site in northeastern Colorado called Pawnee. Other grasslands in Canada and Mexico will also be included in the study of this biome if funding is made available for this nation's first attempt at big biology.



GRASSLANDS *Priority*
(*Wagon train, Wyoming, 1870*)

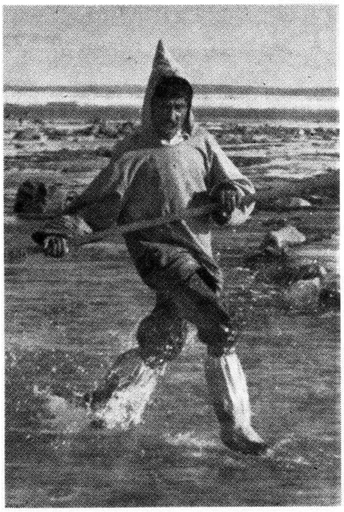
Already private industry plans to cooperate in the development of this particular research program on ecosystems. Traveler's Research, a private research organization, is providing the full time services of a professional systems analyst and two assistants who will aid substantially in the analysis of research data.

Five other biomes—tundra, desert, coniferous forest, eastern forest, and tropical rainforest—will also be investigated by IBP scientists. These biomes are still in the process of final site selection, but should be completed by late summer. Although Smith will head the entire ecosystems program, a director for each specific biome study will be appointed.

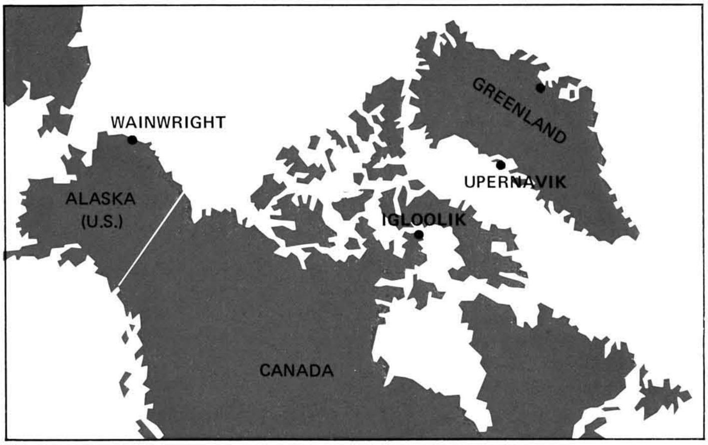
Migrant populations

Ecology of migrant populations, a second major research program in the U. S. IBP effort, will concentrate on a comprehensive socio-economic and medical characterization of Negro residents of Holmes County, Miss. A portion of this program involves study of the migration of some of these residents to Chicago. The migration study hopes to pinpoint for predictive purposes those attributes that lead either to successful or unsuccessful adaptation of young Negro adults (15 to 35 years old) to their newly-found environment.

At this time the Migrant Population Study is seeking financial support from the Office of Economic Opportunity and the National Institutes of Health, according to Dr. Harve J. Carlson of the Interagency Coordinating Committee for IBP. This program, its sponsors believe, may provide some insights to the problems of ghettos.


D. David Slavenwhite

ESKIMO *Evolutionary*



ARCTIC POPULATIONS *Human adaptability*

Eskimo populations, a third program, is a study to understand how a race has adapted to the adverse and stressful environmental conditions of the Arctic. The adaptation of the Eskimo to his hostile environment is a magnification of the adaptive processes that all men undergo. By studying populations under stress, IBP scientists hope to understand human adaptability in general.

The Eskimo study involves a cooperative effort of scientists from four nations—U. S., Canada, Denmark, and France. U. S. scientists will study a community of 300 Eskimos at Wainwright, Alaska. The Canadians will perform similar studies at Igloolik in their Northwest Territories. The Danes and French will study the Eskimos of Upernavik, Greenland.

According to Dr. Frederick A. Milan (Univ. of Wis., Madison), chairman of the Eskimo population research, "We hope to gain insight into the general patterns of human adaptability and evolution, since Eskimos illustrate the way in which man the species spent 99% of his evolutionary history. Much of the genetic endowment of modern men has been shaped by the mechanisms of natural selection in other evolutionary processes that still seem to affect the Eskimo culture."

Financial support for initial stages of the Eskimo program has been obtained through the Department of Defense-Air Force, according to Dr. Harve J. Carlson of the ICC for IBP, so that this program will move into its operational phase on July 1 of this year. He noted that additional funds are being requested from the National Institutes of Health, who have had a program on arctic physiology for at least two years. Also, the Office of Naval Research has promised logistics support at its Point Barrow, Alaska, installation for this research program, according to Carlson.

Research on convergent and divergent evolution in the Americas, a co-

PRIMITIVE TREE *Almost extinct* (*Auricaria*) operative program of research involving South American, Latin American, and U. S. scientists, focuses on an understanding of ecosystem and man and his relation with the ecosystem of which he is a part. Some of the important goals of this research are:

- Inventory of the total biological resources of the Western Hemisphere.
- Study of the acceleration of man's evolutionary process by stressing the adapations of organisms with which he lives through such things as pesticides and general environmental pollution.

INSECTS *Adaptability*

- Establishment of a base line for future exploitation of tropical ecosystems. (Exploitation of the Amazon rainforest is accelerating in countries such as Peru.)
- Graduate and post graduate training in Latin America in the kind of biological sciences that provide a sound basis to the wise use of renewable resources.

The South American Indian is yet another group which may provide an understanding of human adaptability. These Indians, unmixed with Negro and Caucasian populations, are the only major population whose time and place of arrival into a largely unoccupied area can be dated with some accuracy. These Indians represent the norm of human existence until very recent time. They derive their sustenance by hunting, gathering, and simple agriculture. Also, they possess a very simple technology—essentially a pre-Columbian mode of existence. By studying the Indian at this level, IBP scientists hope to gain an insight into the population structure of man during his evolution.

Biogeography of the seas will assess the physiological responses of marine and estuarine species to environmental factors through comparison of populations from different geographical regions. The comparison will be made on both coasts of the Americas and from Canada to Tierra del Fuego.

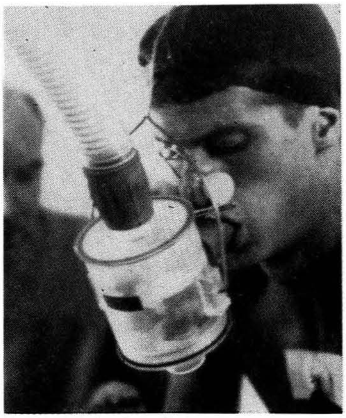
Human populations at high altitudes is the subject of another major research program of IBP. Populations in the Andes and Himalayan mountains, the Ethiopian highlands, and parts of Mexico and the Soviet Union will provide an understanding of how man adapts to his environment.

At heights greater than 10,000 feet, both lack of oxygen and the pressence of cold common in these environments have a variety of physiological effects on the inhabitants. These effects include enlargement of the heart and lungs, thickening of the blood, retardation of growth, and lowering of fertility.

One aspect of the effects of altitude will be noted at the 1968 summer Olympic games in Mexico City, whose altitude is 7500 feet above sea level. "Whether or not altitude affects athletic performance depends on the energy system the body must use to work at maximum efficiency," explained Drs. K. Lange Anderson (School of Therapy, Oslo) and Rodolfo Margaria (Institute of Human Physiology, Milan) at last November's Conference (Washington, D. C.) on Man at High Altitudes.

MEXICO68

Athletes who participate in events that require explosive bursts of energy for such events as the sprint, dash, shotput, or short races will probably not be affected by the altitude, according to Dr. Cutting B. Favour (St. Mary's Hospital, San Francisco). But individuals who participate in events lasting longer than one and a half minutes—distant runs, swimming, and the like—will certainly have to concern themselves with breathing. For example, Favour points out that swimmers are trained to go many strokes per breath. Swimmers who maintained this breathing discipline in trials at the Air Force Academy's pool (altitude is 7000 feet) became exhausted and turned in poor performances. In general their performance improved when the swimmers breathed after each stroke, according to Favour.

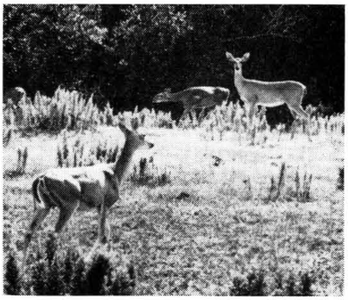


MAN *High altitudes*

Participation of other nations

The U.S.S.R. offers three contributions to the IBP studies. Their studies include:

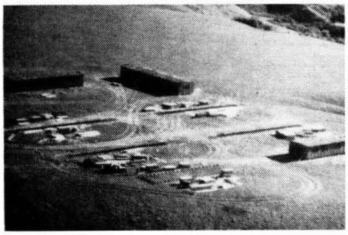
- Nitrogen fixation leading to increased soil productivity.
- Productivity of the sea.
- Range of national parks and a policy for managing them.



WILDLIFE *National refuge*

Lake Baikal (Siberia, U.S.S.R.), one of the great lakes of the world, is currently being considered as a site for a huge new U.S.S.R. national park. At the same time, this lake is the object of special studies on pollution.

Canada's largest national effort is a long-term study of biological productivity on grasslands near Matador, Saskatchewan. This area is the only remaining, uncultivated tract of first class wheat land on the prairies.



CANADA *Food production*

This wheat land accounts for 25% of Canada's contribution to IBP. The program will determine whether the use of the sun's energy in Western Canada is as efficient as it could be for the production of food and what level of food production can be maintained indefinitely, according to Dr. R. T. Coupland (University of Saskatchewan, Saskatoon), director of the program.

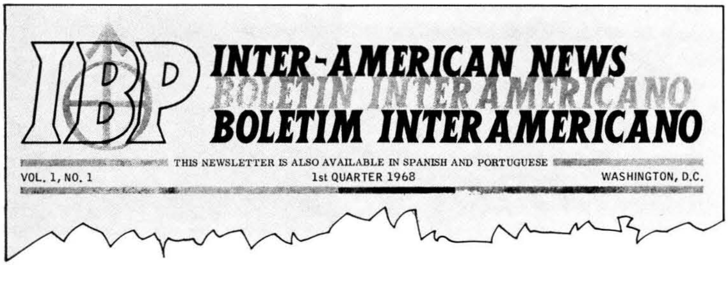
Australia's contribution includes the study of the changes in man's health and physique associated with the evolving human ecology of our time. Three populations—New Guinea natives, Australian aborigines, and European migrant groups in urban areas of the Commonwealth—are unique at least at this time, but are unlikely to continue in their present form for more than a few years.

India is planning a vigorous attack on her twin problems of exploding population and lagging food production. Central Brazil is the target for a field exposition in which IBP specialists will record all possible aspects of its unexplored area. Scientists believe that this unexplored area may have one of the most diverse flora in the world. Israel has been approved as a site of major population adaptation studies. These studies seek an understanding of the effect of climatic environment on man.

Financing

Thus far, U. S. financial support for IBP consisted primarily of unobligated money which had been solicited from various federal agencies that had an interest in IBP. Dr. Harve J. Carlson told the subcommittee that IBP support for fiscal 1968 reached a level of $385,200 from 11 components of eight federal agencies. Carlson explained that the reduced levels of funding for fiscal year 1969 are caused by the shift from planning phase to operational phase.

The amount of financing made available for IBP foreign research is largely unknown, according to the subcommittee's report, because foreign scientists obtain financial support from their own governments.



IBP INTER-AMERICAN NEWS
BOLETIN INTERAMERICANO
BOLETIM INTERAMERICANO

THIS NEWSLETTER IS ALSO AVAILABLE IN SPANISH AND PORTUGUESE

VOL. 1, NO. 1 1st QUARTER 1968 WASHINGTON, D.C.

Exchange of information

IBP Inter-American News, a quarterly newsletter, describes existing and developing projects in all of the countries of the Western Hemisphere, according to editor Dr. Clark Hubbs (University of Texas, Austin). The newly appointed editor says that the newsletter, which is published in the English, Portuguese, and Spanish languages, will be distributed extensively to biologists in North and South America. The newsletter will be particularly suited to the exchange of research information on convergent and divergent evolution in the Americas, Hubbs notes.

Eyewitness account

In his recent South American trip, Dr. W. Frank Blair, newly appointed chairman of U. S. National Committee for IBP, noted that western Colombia is as badly misused as any part of the U. S. His notes include the following observations:

- The U. S. Government sends advisors to high-ranking people in South American governments, but they never send people competent in ecology. "Ecological advice at high governmental levels would be of great help toward better conservation practices in South America," Blair says. Also, Blair suggests that Peace Corps workers receive ecological indoctrination before being sent into the field. Since they are indoctrinated in many other ways, they could serve as a force for the development of a concept of conservation in the countries in which they work.

- Streams in Colombia are badly polluted. The pulp industry and sugar cane mills are usually the sources of pollution. When effluents from paper mills are dumped, as they are at regular intervals, natives gather for many kilometers downstream to pick up the dead and dying fish.
- Certain species of *Eucalyptus* have been introduced in the Canea Valley to dry up its marshy areas so that they can be used for sugar cane production. This technique succeeded so well that the water table dropped to a point where "wells had been drilled for irrigation, and some of these have become dry."
- In some areas the native vegetation has been destroyed and replaced by pure stands of pine. Scarcely any of the native birds or other fauna enter the pine forest. This year there was a damaging outbreak of a beetle in the pine forest that was so bad that "workers were removing beetles by shovelfuls."
- Destruction of marshes has led to a decline of the native herons and egrets but has not affected the invading cattle egret, which is very abundant.
- Pesticides have been—and still are—being badly used by people who cannot understand the dangers of incorrect dosages. There have been deaths. Tomatoes, which are usually eaten without being washed, are often heavily dosed, with resultant illness. In one instance, aerial spraying was done without attention to wind direction with the result that "kilometers of river" were white with floating, dead fish. In another instance an insecticide was sprayed over an agricultural crop to kill mourning doves which were concentrating there. The affected doves were shot by hunters, who ate them and subsequently were hospitalized.
- Introduction of trout has done untold damage to native biotas and has resulted in extinction of endemic species in some areas. Trout were introduced in Lake Tota and the lake was closed to fishing. The trout destroyed an interesting endemic fish (*Rhizosomichenys totae*) and cannibalized each other. Since trout have been introduced into many places in the Andes, this kind or event could have happened often.
- Engineers built a hydroelectric dam in the Canea Valley, and because they were afraid that the dead leaves from the trees of the surrounding forest would clog the turbines, they cut down the forest. Now, the adjacent slopes are slumping into the lake.

Desalting Plant Down Time Predicted by Formula

Although nuclear electric power plant down time can be extrapolated from nuclear power plant experiences, predictions of nuclear electric power–desalting plant down time must be based on analyses of the many factors that can prevent operation at maximum capacity

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During 1966, two engineering feasibility studies to determine the cost of desalted water from dual-purpose nuclear power–water desalting plants were completed—one for a proposed sea water conversion plant of 150 million g.p.d. (gallons per day) capacity for the Metropolitan Water District of Southern California (Bechtel Corp., 1966), and the other for a proposed 100 million g.p.d. sea water conversion plant for the Government of Israel (Kaiser Engineers and Catalytic Construction Co., 1966). The U.S. Department of the Interior's Office of Saline Water and the U.S. Atomic Energy Commission were partners with the prospective owners in sponsoring both studies. (See page 428.)

In these studies, the unit cost of water was determined by dividing the annual cost allocated to water by the annual salable water production. Predictions of the annual salable water production require predicting desalting plant outage. Unlike predictions of electric power plant outages, which can be based on experience of other nuclear power plants, predictions of desalting plant outages (for lack of experience with large desalting plants) must be based on an analysis of the factors which may prevent operating the desalting plant at maximum capacity.

This article presents an analysis of the factors which may prevent operating the desalting plant at maximum capacity, based on the study of the Israel plant.

Definitions

Two terms used in this analysis are *availability,* defined as the time the equipment or component is capable of operating at design output divided by the total elapsed time in the same period, and *desalting plant operating factor,* defined as actual annual water production divided by the annual water production that would result from continuous operation at design output.

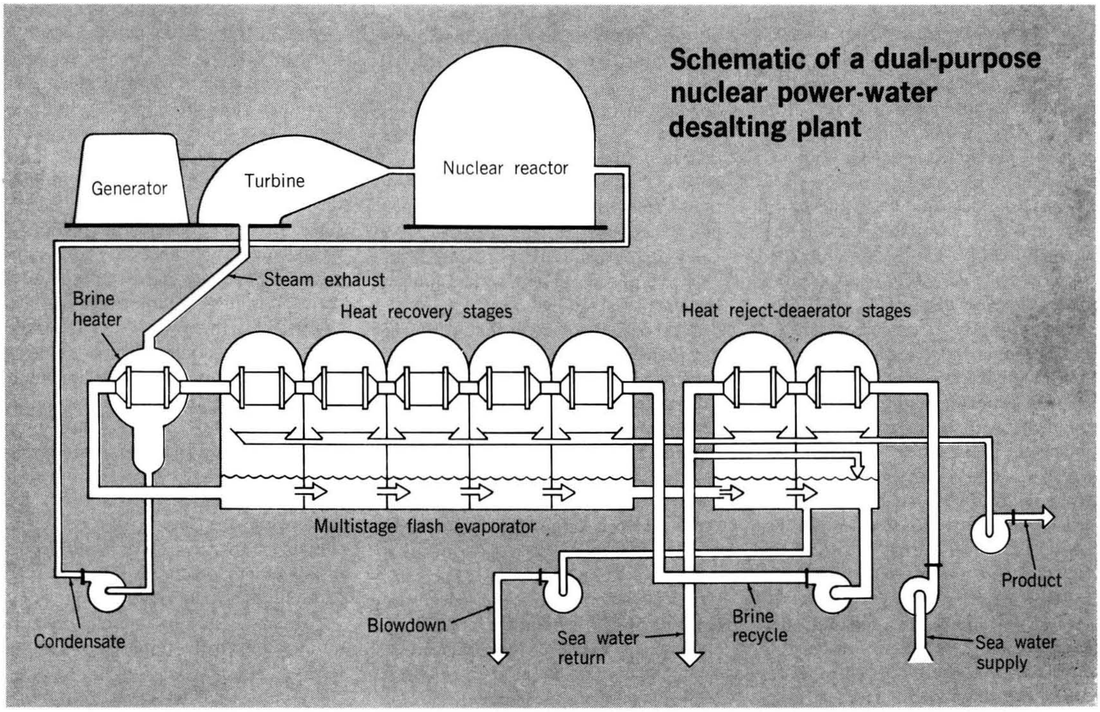
Method of approach

The dual-purpose electric power and water desalting plant complex consists of commercially proved nuclear power plant components such as a water-cooled reactor, steam generator, turbine generator and auxiliaries, and the multistage flash evaporator and its auxiliaries. The nuclear power plant, including nuclear reactor, steam generator, turbine generator, and auxiliaries, is similar in construction and reliability to nuclear power plant components presently in operation, and the availability of nuclear steam plants is anticipated to be 92% by 1972 (Wofford, 1966). Assuming that the nuclear power plant will operate in a narrow-capacity range above and below its design capacity when it is available, the nuclear steam plant operating factor can be conservatively assumed to be 90%.

Multistage flash distillation plants of modern design have been in existence for only a few years, and proposed plants are many times larger than those which are in service. Consequently, there is little directly applicable experience upon which to base assumptions of the desalting plant operating factor. To predict this operating factor, therefore, the desalting plant must be examined and analyzed component by component—the following being the most important: tubing in the heat reject stages, in the heat recovery stages, and in the brine heater; pumps and their drives for the brine recycle, product, blowdown, reject, and feedwater makeup; vacuum and venting equipment; evaporator structures (flash chambers); and auxiliary equipment and piping including instrumentation and controls.

In preparing the analysis, we assume that:

- The evaluation is based on a de-



salting plant consisting of four trains—each capable of independent operation.

- When operating, the evaporator train will be producing its design water capacity.
- The availability of the desalting plant steam supply from the adjacent power plant is 90%.
- Scheduled outage of the desalting plant for maintenance will be performed during the scheduled outages of the adjacent steam power plant.
- Outages due to marine fouling in the intake facilities are included in determining the power plant availability and will not be charged against the desalting plant.
- Salinity level in the plant product water is not to exceed 125 parts per million (p.p.m.) total dissolved solids (TDS). Based on a salinity level of 25 p.p.m. (TDS) with no leaks, this permits a rise of 100 p.p.m. (TDS) due to leaks before the plant must be shut down for repairs.
- The desalting plant has gone through all the procedures of "debugging," and all the failures due to faulty materials, fabrication, or assembly have been corrected.
- Failures of any one component that would force the plant to shut down will not occur simultaneously with failures occurring in other components and causing the same effect. Thus, the combined availability of the two components is the product of the availabilities of each.

Heat exchanger tubing

The first component analyzed was the tubing in the heat reject and heat recovery stages and in the brine heater. The tubing materials used in these components (stainless steel/90:10 Cu-Ni bimetallic in areas exposed to high concentrations of noncondensables, and 90:10 Cu-Ni elsewhere) were selected as reasonable compromises in first cost and expected performance. Other materials considered were aluminum brass and 70:30 Cu-Ni. There is considerable information on failure experience with aluminum brass in power plant and marine condensers and this material can give long service. However, the use of the more noble Cu-Ni will result in a lower failure rate.

An alloy of 70:30 Cu-Ni composition has been available for about 30 years. After the first few years of experience with this material, it was found that addition of approximately 1% iron to the alloy greatly enhanced its resistance to erosion. The 70:30 Cu-Ni alloy containing approximately 1% iron has performed with very few failures in land-based power plant condensers (Todhunter, 1967), and is regarded as the standard heat-exchanger tubing for the U.S. Naval and Coast Guard vessels. These government agencies have accumulated experience records indicating that, with vessels in reasonably continuous service, total failure may be less than 0.1% in 20 years.

While 70:30 Cu-Ni will give outstanding service, its cost led to a search for an intermediate-cost alloy which might give almost as good service at a substantially lower initial cost. An alloy of 90:10 Cu-Ni with 1 to 1.75% iron was developed about 15 years ago on a commercial basis.

A substantial amount of technical information is available on the behavior of 90:10 Cu-Ni, iron-modified alloy, under a variety of exposure conditions in sea water service. The information is derived from laboratory experimentation, power stations service, marine applications, and refinery service. The behavior of the Cu-Ni alloys, modified with iron for erosion impingement resistance, closely approaches, and is often superior to, Monel alloy. There has been only limited opportunity to observe the behavior of 90:10 Cu-Ni in sea water heated much above normal temperatures.

The indications are, however, that this alloy will retain good resistance to corrosion by sea water at temperatures well above those encountered in a desalting plant (Stewart and LaQue, 1952). One indication is that test spools of 90:10 Cu-Ni inserted in the brine stream in Point Loma showed corrosion rates to be independent of temperature. Similar results were obtained from test spools inserted in the vapor space. Earlier tests in a laboratory-size three-stage flash evaporator, conducted by International Nickel Co. at the Kure–Beach Harbor Island, N. C., Testing Station, produced similar results (1959).

While temperature does not appear to influence 90:10 Cu-Ni corrosion, experience has shown that other conditions such as brine velocity, pH, and noncondensables do influence corrosion. Steam condensate is seldom found to be corrosive to copper alloys unless the condensate contains a relatively high concentration of noncondensable gases (CO_2, NH_3, O_2, and H_2S). Corrosion rates of 0.0001 to 0.001 inch per year are considered normal for 90:10 Cu-Ni, provided that the condensate is relatively free of any contamination by noncondensables.

In general, the following conclusions may be drawn with respect to 90:10 Cu-Ni with 1 to 1.75% iron in salt water service:

- Corrosion rates in salt water exposure appear to be independent of temperature over the range studied (80–250° F.). Typically, corrosion appears to be evenly distributed over the entire surface rather than in localized pitting as with aluminum brass. Where the salt water is fully aerated, long-term corrosion rates of 0.001 inch per year appear to be reasonable as a basis for design. Lower rates may be expected for deaerated water, though few data are available.
- Tube-side velocities should not be less than 5 f.p.s. (to prevent settling of suspended matter with resultant localized corrosion) and not more than 12 f.p.s. (to prevent erosion attack, especially near the upstream end of the tube).
- Galvanic attack on 90:10 Cu-Ni is rare, since it is cathodic to virtually all of the other metals likely to be used in combination with it. Likewise, nickel depletion is not experienced under salt water evaporator conditions, although it has been experienced in some refinery condenser applications at shell-side temperatures about 450° F.
- Steam condensate per se is not corrosive to 90:10 Cu-Ni. Carbon dioxide, oxygen, ammonia, and hydrogen sulfide, which may occur along with the steam condensate, can cause serious corrosion, and great care should be taken to minimize the concentration of those substances. Improved tube life can be obtained in spite of high concentrations of these gases by using bimetallic tubes (Cu-Ni on water side, stainless steel on steam side).

On the basis of the foregoing, tubing throughout the salt water distillation plant could be expected to have an average corrosion rate of 0.001 inch per year on the salt water side and zero on the condensate side. Thus, at the end of the 30-year life an initial tube-wall thickness of 0.049 inch (18 BWG) would, on the average, have been reduced to approximately 0.015 inch of wall. Where corrosion rates can be held below the nominal 0.001 inch per year, as is expected to be the case in the heat-recovery stages where the salt water is essentially oxygen free, an initial tube-wall thickness of 0.035 inch (20 BWG) should last equally well.

Failure rate

An analysis of the tube failure rate based on the assumption that corrosion actually will be uniform (at the average rate) is completely unrealistic, since it assumes that the plant will be sound until the day of collapse. A statistical approach for predicting tube failures is much more realistic since there are in the order of a million tubes in the larger desalting plant designs. In order to perform this analysis, however, it is necessary to assume a tube failure rate and to assume what forms of failures will occur.

Inevitably there will be variations in corrosion rate, point to point, due to exposure, treatment during manufacturing and installation, and variation within the alloy itself. Thus, even though a general thinning of tube walls should be expected over the life of a plant, some tubes will certainly develop leaks while the "average" tube is still sound. Furthermore, there are mechanisms other than corrosion that can cause tubes to fail. These are:

- Breakout due to internal pressure of an abnormally thinned portion of tube wall.
- Pinhole leaks caused by pitting corrosion (localized rapid attack).
- Breaks or cracks caused by vibration, by improper metallurgical control or heat treatment, or by ammonia attack in the presence of tensile stresses.
- Improper fastening of tube into tube sheet.

The third- and fourth-type failures cited above are likely to develop quite rapidly after a plant is placed in operation, but after the first year of continual operation virtually all of these failures will have been discovered and corrective action taken.

The first two failures cited above appear initially as tiny pinhole leaks, and grow as the thinned edges of the hole are worn away by high velocity flow through the hole itself. This type of failure is likely to develop slowly over many years. Experience indicates that incidence of this type of failure can be treated statistically. Experience with one of the sea water distilling plants at Guantanamo Bay (originally located at Point Loma, San Diego, Calif.) indicates that a corrosion leak once started, will develop into a ⅛-inch diameter hole within about 10 days. The

Flow of tubeside brine into distillate steam

Rise in distillate salinity due to leaks is not to exceed 100 p.p.m. (TDS). The maximum permissible flow of tubeside brine or sea water into the distillate is represented as q, and

$$q = \left[\frac{\text{permissible salinity in product}}{\text{brine salinity in tube}}\right] \times \text{g.p.m. product}$$

In the reject section:

$$q = \frac{100 \text{ p.p.m.} \times 100 \times 10^6 \text{ g.p.d.}}{38{,}600 \text{ p.p.m.} \times 24 \text{ (hr./day)} \times 60 \text{ (min./hr.)}} = 180 \text{ g.p.m.}$$

where q = flow of seawater into distillate (g.p.m.)
In the recovery section:

$$q = \frac{100 \text{ p.p.m.} \times 100 \times 10^6 \text{ g.p.d.}}{68{,}000 \text{ p.p.m.} \times 24 \text{ (hr./day)} \times 60 \text{ (min./hr.)}} = 102 \text{ g.p.m.}$$

Assume an average permissible flow of 140 g.p.m.

Calculation for yearly tube failure[a]

In the extreme value statistical analysis correlation,[b] F represents the probability of failure of a tube in t years in the equation below, where k and A are constants—k being a constant which relates the distribution function to the corrosion phenomena (k is concerned only with purely statistical factors) and A being a constant which relates the distribution function to the failure rate.

$$F(t) = 1 - e^{-\left(\frac{t}{A}\right)^k}$$

Therefore, for the case where 0.1% of the tubes have failed in 10 years:

$$F = 0.1\%$$

$$t = 10$$

$$0.001 = 1 - e^{-\left(\frac{10}{A}\right)^{2.5}}; \text{ let } \left(\frac{(10)}{A}\right)^{2.5} = B$$

Where B is small, $e^{-B} = 1 - B$

$$0.001 = 1 - e^{-B} = 1 - 1 + B = B; B = 0.001$$

$$A = 159$$

$$F = 1 - e^{-\left(\frac{t}{159}\right)^{2.5}}$$

f, the probability of failure of a tube in year t, can be expressed as follows:

$$f = \frac{dF}{dt} = \frac{k}{A}\left(\frac{t}{A}\right)^{k-1} e^{-\left(\frac{t}{A}\right)^k}$$

$$= \frac{2.5}{159}\left(\frac{t}{159}\right)^{1.5} e^{-\left(\frac{t}{159}\right)^{2.5}}$$

[a] Where the total number of failures in a given number of years is known.

[b] Given by the Phelps Dodge Copper Products Corp. in "Resistance of Copper and Copper-Base Alloys in Ammoniacal Solution." The value of k cited in this work is about 2.5.

Probable tube failure per year[d]

t (year of operation)	f[c]	Total	Per train
1	0.00000784	7	2
2	0.00002215	21	5
3	0.0000416	39	10
4	0.0000627	59	15
5	0.0000880	83	21
6	0.0001152	108	27
7	0.0001450	136	34
8	0.0001772	167	42
9	0.0002115	199	50
10	0.0002495	235	59
15	0.000455	429	107
20	0.000697	656	164
30	0.001273	1200	300

[c] Where f is the probability of a tube failing during the year.

[d] Based on 940,000 tubes in the water plant.

weighted average leakage rate into the distillate trough from ⅛-inch diameter holes scattered through the plant was estimated to be 4 gallons per minute per hole. To avoid exceeding the 100 p.p.m. (TDS) salinity increase, the leakage flow should not exceed 140 g.p.m. for a 100 million g.p.d. plant.

Based on limited experience, it was assumed that 0.1% of the tubes in the heat-reject stages, heat-recovery stages, and brine heater would fail during the first 10 years. This is consistent with the experience of the Los Angeles Department of Water and Power—one of their power plant condensers has operated for 53,000 hours and none of the 800 90:10 Cu-Ni tubes has failed, although some tube-side corrosion pits have been observed. This observation gives greater confidence in the failure rate assumption of 0.1% in 10 years. Since experience is limited and not always applicable, other values of tube failure rates may be assumed according to the judgment of the designer. The resulting plant operating factor and, therefore, the unit cost of water, are heavily influenced by this choice.

The probable number of annual failures have been predicted by this distribution function (Tuthill, 1965):

$$F(t) = 1 - e^{-\frac{(t)k}{A}}$$

where *F* is the probability of failure of a tube in *t* years, and *k* and *A* are constants—*k* (equal to 2.5) being a constant which relates the distribution function to the corrosion phenomena, and *A* being a constant which relates the distribution function to the failure rate.

Pump and drive

Experience with existing plants indicates that great care must be exercised in the selection of materials for all sea water applications. Of the three pumps discussed in this section, by far the most problematic is the recycle pump, which is required to deliver large quantities of liquid under very unfavorable suction conditions. The approach to pump design, manufacture, erection, maintenance, and control should be such as to permit failure-free operation during the total time that the equipment is required to be in service.

Pump failures can be categorized into those which require a complete dismantling and parts replacement and

Frequency of outage for plugging

Rate of hole growth

Operating experience in Guantanamo Bay (Todhunter, 1956) reveals that a tube leak, once developed, will grow to $^1/_8$-inch diameter in about 10 days. It will be assumed here that the hole diameter will grow linearly with time.

Pressure differentials and leakage flow

- Deaerator (31st) stage

Tube-side pressure = 27.0 feet (absolute)
Shell-side pressure = 0.7 foot (absolute)
Δh = 26.3 feet = 11.4 p.s.i.
From hydraulic tables:
flow through $^1/_8$-inch diameter nozzle = 1.6 g.p.m.

- First stage

Tube-side pressure = 30.7 p.s.i.a.
Shell-side pressure = 14.9 p.s.i.a.
Δp = 15.8 p.s.i.a.
From hydraulic tables:
flow through $^1/_8$-inch diameter nozzle = 1.85 g.p.m.

- 28th stage

Tube-side pressure = 91.7 p.s.i.a.
Shell-side pressure = 0.3 p.s.i.a.
Δp = 91.4 p.s.i.a.
From hydraulic tables:
flow through $^1/_8$-inch diameter nozzle = 4.5 g.p.m.

Since rate of hole growth at higher pressure differential may be higher than that at low pressure differential, it will be assumed that the average flow through any $^1/_8$-inch diameter hole will be 4.0 g.p.m.

Frequency of plugging

For any given hole, the rate of leakage is proportioned to the second power of elapsed time.

$$f = At^2$$

where
f = flow, g.p.m.
A = constant
t = elapsed time (days)

Distillate salinity, due to leakage from n holes, has the following expression:

$$f_t = A \sum_{0}^{n} t^2_n$$

where
f_t = leakage flow at time t
n = number of leaking tubes
t_n = time since nth tube started to leak

$$A = \frac{f_1}{t_1{}^2} = \frac{4}{100} = 0.04$$

$$f_t = 140 = 0.04 \sum_{0}^{n} t^2_n$$

0.1% total tube failures in 10-year case

- 10th year forced shutdown requirements

In the 10th year a total of 235 tubes will fail (one tube every 1.55 days).

For this case:

t = 24 days (15 shutdowns required for plugging)
f_t = 140 g.p.m.
n = 16 tubes (4 tubes per train)

0.1% total tube failures in 10-year case

- 15th year forced shutdown requirements.

In the 15th year a total of 429 tubes will fail (one tube every 0.85 day).

For this case:

t = 20 days (18 shutdowns required for plugging)
f_t = 140 g.p.m.
n = 24 tubes (6 tubes per train)

0.1% total tube failures in 10-year case

- 20th year forced shutdown requirements

In the 20th year a total of 656 tubes will fail (one tube every 0.556 day).

For this case:

t = 17 days (21 shutdowns required for plugging)
f_t = 140 g.p.m.
n = 31 tubes (8 tubes per train)

- 30th year forced shutdown requirements

In the 30th year a total of 1200 tubes will fail (one tube every 0.305 day).

For this case:

t = 14 days (26 shutdowns required for plugging)
f_t = 140 g.p.m.
n = 46 tubes (12 tubes per train)

Tabulation of plugging frequency (not to exceed 140 g.p.m. brine or sea water flow into distillate)

t (year)	Probable tube failures	Frequency of plugging (days)	No. of outages	Tubes plugged each outage	
				Total	Per train
1	7	120	3	2	0 to 1
2	21	73	5	4	1
3	39				
4	59				
5	83	35	10	8	2
6	108				
7	136				
8	167				
9	199				
10	235	24	15	16	4
15	429	20	18	24	6
20	656	17	21	31	8
30	1,200	14	26	46	12

those which can be corrected without dismantling. Extended usage of pumping equipment causes some of the components to wear, but the rate of such wear is rather slow. Failures requiring pump dismantling should be completely eliminated by a combination of proper design, manufacturers' testing, erection, and balancing; otherwise, pump availability will drop very rapidly, as it may take as long as two weeks to dismantle and reassemble one of the pumps, particularly the recycle pump.

During the planned annual shutdown (required for reactor refueling), each pump should be overhauled. During this period, all smaller maintenance work items (such as stuffing-box packing) should be carried out, clearance taken, worn parts replaced, and motor-pump balancing checked. It will pay to invest in careful design, testing, erection, and maintenance if even one pump failure can be eliminated. Three 50% capacity recycle pumps have been provided for each train, thereby providing an installed spare.

The heat reject and makeup pumps, for each service, are grouped in paral-

Estimate of outage time for tube plugging

Shutdown

- Shut off steam and reduce load to zero.
- Cool the brine circuit by circulating cold water.
- Drain the tube bundles.

4 hours

Repairs

- Remove water box covers on both sides of bundles to be repaired.
- Cover tube sheets with plastic sheet for leak detection.
- Pull slight vacuum in entire train.
- Plug both ends of tube.
- Remove plastic sheet and replace water box covers.

12 hours for up to 8 tubes
18 hours for 9 to 12 tubes
24 hours for 13 to 16 tubes

Startup

Time required to reach steady-state operation at full load
4 hours

Contingency

Time to finish other repairs
Inspection
4 hours

Total: 24 hours for up to 8 tubes
30 hours for 9 to 12 tubes
36 hours for 13 to 16 tubes

Four crews of two men each plus superintendent

Availability values for tubing[a]

t (Year of opera-tion)	No. of out-ages in each train	Tubes plugged each outage		Dur-ation of each out-age (Days)	Equiva-lent days pro-duc-tion lost	Avail-ability
		Total	Per train			
1	3	2	0 to 1	1	2	0.992
2	5	4	1	1	5	0.986
5	10	8	2	1	10	0.973
10	15	16	4	1	15	0.959
15	18	24	6	1	18	0.951
20	21	31	8	1	21	0.942
30	26	46	12	1.25	32.5	0.911

[a] This table is based on data from the accompanying tables, including calculations for:

- Probable tube failure in any year, based on the assumption that 0.1% of the tubes will fail in 10 years of service.
- Frequency of plugging required to prevent the leakage flow of brine or sea water into the distillate stream from exceeding the permitted 140 g.p.m.
- Outage time for tube plugging.

lel, discharging into a common header. Failure in one heat-reject pump will slightly reduce the heat rejection capacity of the water plant, causing a slight reduction in the heat input to the brine heaters. Under these conditions, the train will continue to operate at slightly reduced capacity. A more serious reduction will be produced if one of the makeup pumps fails. Lowering the brine heater outlet temperature, and possibly some throttling in the recycle stream, will permit continuous operation at reduced capacity. A heat-reject or makeup pump failure will have some effect on the desalting plant operating factor and, therefore, one installed spare heat-reject pump has been provided. This pump is to be installed with the necessary piping, valves, and controls to allow it to be also used as a spare for the makeup pump in case one such pump fails.

Squirrel cage induction motors as well as synchronous motors of sizes and speeds required for the pump drives are well within the realm of current technology. During the planned shutdown period, the motors should undergo a complete maintenance checkup to prepare them for continuous operation. Under these conditions, failure-free operation of the motors may be assumed.

Spare pump system permits continuous full-capacity operation

Recycle pump	One installed spare on each train
Blowdown pump	Piping, valves, and controls provided on recycle pumps to permit their use as blowdown pumps
Reject pumps	One installed spare
Makeup pumps	Piping, valves, and controls provided on reject pump discharge permit reject pumps to serve as makeup pumps
Distillate pumps	One installed spare on each train

Under the conditions discussed above, the pumps and their drives can be expected to yield high availability values, yet it is hardly probable that all 20 pumps in service will operate failure-free for a continuous period of 11 months. Spare pumps should permit continuous full-capacity operation of the desalting plant in the event there is a pump failure. It can therefore be assumed that the combined availability of all pumps will be 100%.

Vacuum and venting equipment

The poor condition in which the air-ejector system of Point Loma was found indicates the need for a better selection of materials for this service. The corrosive noncondensables removed via the vacuum and venting system will require highly corrosion-resistant materials such as stainless steel for the nozzle, diffuser, and condenser shells; stainless steel copper-nickel bimetallic condenser tubes and tube sheets; and copper-nickel clad condenser water boxes. Since the investment in the vacuum and venting system components is rather small, a spare condenser and condensate pump with the appropriate piping was specified for each of the three systems on each train.

During the planned shutdown period, the vacuum and venting system should undergo a complete maintenance checkup, replacing all worn components and preparing the equipment for continuous operation. Except for the condensate pump, there are no moving parts in the system. Proper selection of materials, careful maintenance of the components, and some reliance upon spares will produce a very high system availability, presumably 1.0.

Evaporator structure

The evaporator body should be so designed that no failures will occur. Otherwise, the availability and the resulting desalting plant operating factor will drop very rapidly, since a failure would require an extended period of time for repair. Means will have to be developed for detecting leaks and, if the air inleakage exceeds the venting system capacity, remedial measures will be taken for temporary sealing while the train is in service. During the planned shutdown period, the evaporator structure will be checked for deterioration, and the appropriate repairs made. The availability of the evaporator structure was thus taken as 1.0.

Auxiliary equipment

All pieces of hardware that are not discussed in the preceding sections are grouped into a category called auxiliary equipment. Most of this equipment is composed of small units, the availability of which can be substantially increased by properly grouping the various components and installing spares in weak spots. During the planned shutdown period, the controls and the auxiliary equipment will be checked for malfunctioning, and components replaced where required. Failure-free operation of the multitude of components, systems, and subsystems that are associated with the controlled operation of the desalting plant seems unlikely, so some allowance should be made for possible forced shutdown due to malfunctioning or failure of the equipment involved. The availability of this equipment is thus taken as 0.99.

Desalting plant operating factor

From the previous analyses, the combined availability of all components involved and the resulting desalting plant operating factor can now be tabulated.

Availability summary

Year of operation	Tubes	Pumps	Ejectors	Structures	Auxiliary equipment	Heat source	Desalting plant operating factor
1	0.992	1.0	1.0	1.0	0.99	0.90	0.884
2	0.986						0.879
3							0.875[a]
4							0.870[a]
5	0.973						0.867
6							0.864[a]
7							0.862[a]
8							0.860[a]
9							0.858[a]
10	0.959						0.856
15	0.951						0.847
20	0.942						0.839
30	0.911						0.812
arithmetic mean	0.952						0.846
(arithmetic mean)[b]	(0.952)					(1.0)	(0.942)

[a] Interpolated
[b] If heat source availability is 100%

Only normal operating conditions were considered in this analysis and no attempt was made to account for abnormal conditions, such as major structural or equipment failures or corrosion pitting caused by small seashells settling in the tubes.

The foregoing statistical method of determining the plant operating factor identifies tube availability as the most important variable, which in turn is dependent on:

- Tube failure rate.
- Hole growth pattern.
- Outage time to plug tubes.

The assumptions used in this analysis are subject to considerable engineering judgement, which will gradually be improved by experience. However, the results obtained do indicate that the 94% mean desalting plant availability or, equivalently, the 85% dual-purpose mean plant operating factor assumed in some recent studies is not unreasonable. The analysis can be used to evaluate the economics of such design features as installed spare pumps and corrosion-resistant materials. It also indicates the frequency of forced outage for tube plugging and the importance of developing efficient repair techniques.

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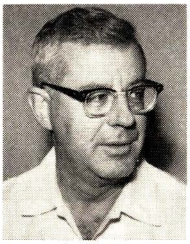


S. F. Mulford *is manager of the Office of Saline Water's San Diego Saline Water Test Facility where he is responsible for operation of the multistage, multieffect Clair Engle Plant, and for construction and operation of the new 17 m.g.d. test module. Earlier, Mr. Mulford was manager of the Saline Water Test Facility at Point Loma, Calif. Mr. Mulford began his work in desalting in the Department of Engineering of the University of California (Los Angeles), continuing it from 1955–60 while he worked for Griscom-Russell Co. He has been with OSW since 1960. Mr. Mulford received his B.S. (1940) from the University of California (Berkeley) and his M.S. (1964) from the University of California (Los Angeles).*

J. R. Wilson, *who is manager, Desalting Engineering Development, for Kaiser Engineers, is presently on leave of absence from the company while he works with the International Atomic Energy Commission. He has directed preparation of the* Manual on Water Desalination *for the Agency for International Development and the preliminary and detail design of a 250,000 g.p.d. multistage flash sea water desalting plant to be installed on Kwajalein in the Marshall Islands for the U.S. Army Corps of Engineers. Before joining Kaiser Engineers, Mr. Wilson was manager of Special Technology at the Westinghouse Research Laboratories, where his responsibilities included direction of desalting research activities. Prior to that assignment, he was Supervisor of Thermodynamics at the Westinghouse Aviation Gas Turbine Division. Earlier, Mr. Wilson was engaged in process plant equipment design at Stratford Engineering Corp. and in fossil fuel power plant design at Black & Veatch. Mr. Wilson received his B.S. (1947) and M.S. (1957) in mechanical engineering from the University of Kansas. He is a member of the American Society of Mechanical Engineers and the American Society of Naval Engineers, and is a Registered Professional Engineer in Missouri.*

Desalination–Power Plant Proves Economically Feasible

An evaluation of capital costs and potential cost variables reveals that the variables can affect the projected unit cost of water from dual-purpose plants by no more than 15%, from best to worst conditions

P. D. Bush, J. Finke, and J. R. Wilson, *Kaiser Engineers, Oakland, Calif. 94604*

Studies for large, dual-purpose, electric power–sea water desalting plants are based on a substantial scale-up of presently operating desalting plants and on processes which are in a state of development. In preparing these studies, certain assumptions regarding technical features of the plant, design variables, and construction and operating costs, must be made. Should the study be based on ultra-conservative assumptions, the plant economic feasibility decision may be unduly negative. Should the study be based on optimistic assumptions, the worriers on the project and among the potential owners may be overly concerned with whether the estimates of performance and cost are realistic.

In our engineering feasibility and economic study for Israel, we at Kaiser Engineers (and our subcontractor, Catalytic Construction Co.) employed technical and economic variables which we believe to be neither optimistic nor pessimistic. Upon completion of the preliminary designs and cost estimates, we evaluated the effects of changes in the values of these variables upon the capital and unit water cost. For example, we evaluated demisters, which are often used to prevent entrainment of brine droplets in the product. Should demisters prove unnecessary, unit water costs will be reduced one-half cent per thousand gallons.

Since the Israel study will be used to illustrate the effects of changes in variables, a short review of this project follows.

Israel study

In December 1964, Kaiser Engineers contracted to conduct an engineering feasibility and economic study of a dual-purpose power generation and desalting plant to be located in Israel. The study, completed in 1966, concluded that:

- A plant is technically feasible.
- It should be based on a light water nuclear reactor heat source, a back-pressure turbine-generator, and a multistage flash evaporator desalting plant.
- Capacities should be 200 Mw_e. (net salable) and 100 million gallons per day (m.g.d.) potable water.
- The plant could be in full commercial operation in 6½ years from initiation of preliminary design.
- The cost of desalted water produced would vary from 28.6 to 67.0 cents per 1000 gallons, depending upon the fixed charge rate (5–10%).

During the performance of the study a reference plant was selected as a basis for determining technical feasibility and cost. The reference plant consists of a nuclear power plant, a desalting plant containing four multistage flash evaporator trains, and auxiliary structures and equipment. The contemplated location for the plant is on the Mediterranean seashore, 9 kilometers south of Ashdod. The overall plant occupies approximately 40 acres and is approximately 3 kilometers from the main Tel Aviv–Ashkelon railroad and adjacent highway.

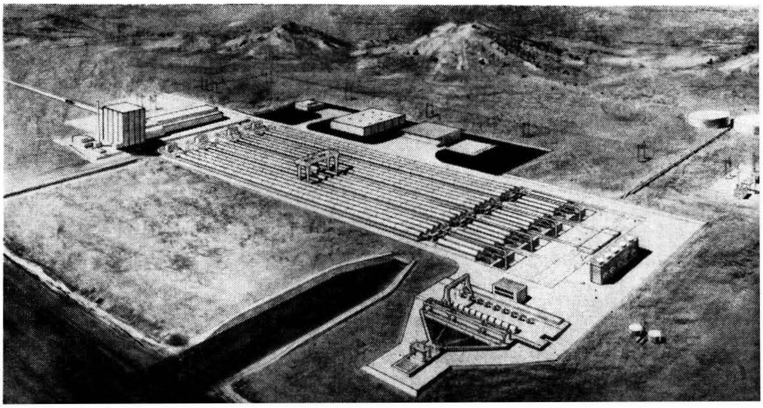
The power plant includes a nuclear steam generating facility using a conventional light water nuclear reactor (either a BWR or PWR), with a rating of 1250 Mw_t. Essentially all of the steam generated in the reactor passes through the 3000-r.p.m., 50-cycle noncondensing turbine-generator, rated at 250 Mw_e. (gross). The steam exhausted from the turbine at 25 p.s.i.a. is condensed in the shell side of the brine heaters of the desalting plant.

The conceptual design of the reference plant employs desalting plant process and component design criteria considered to be reasonable extrapolations from current proved technology.

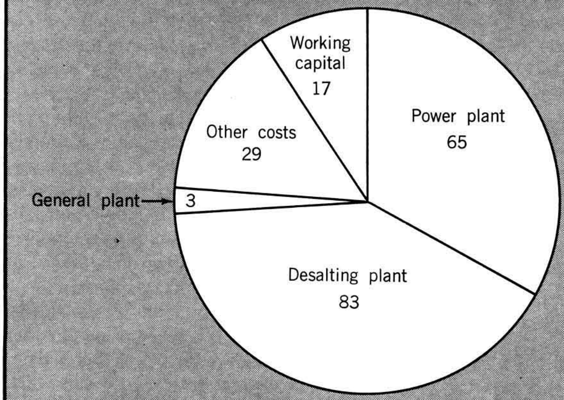
The major equipment of the desalting plant includes the evaporator structures, brine heaters, air ejectors, gantry crane, and the recycle, makeup, product, and blowdown pumps. The evaporator structures consist of the heat recovery stages, heat reject, and heat reject–deaerator stages. The structures are field erected, arch-shaped reinforced concrete or steel enclosures within which are located the removable tube bundles, product water trays, and flashing brine channel.

A multiple sea water intake structure would be located 450 meters offshore and 7 meters deep. An outfall facility would consist of a buried con-

Model. *The dual-purpose power–water desalting plant planned for Israel will probably resemble this mock-up*



Israel plans $197,000,000 for dual-purpose plant



Note: All figures are in millions of dollars, and based on a 7% fixed charge rate.

Characteristics of a 100 m.g.d. desalting plant

Capacity	100 m.g.d.
Tranis	4
Module streams/train	4
Number of stages	31
Maximum brine temperature	220° F.
Economy ratio	10.3 lb. water/1000 B.t.u. heat
Concentration ratio	2.0
Tube materials:	
Brine heater, heat recovery, and heat reject stages (except heat reject–deaerator stage, and air cooling sections of heat reject and heat recovery stages)	90–10 Cu-Ni alloy
Heat reject–deaerator stage and air cooling sections of heat reject and heat recovery stages	Stainless steel/90:10 Cu-Ni bimetallic
Chlorine consumption	140 metric tons/year
Sulfuric acid consumption	33,000 metric tons/year

Estimated total capital cost–1965 cost basis

	Nominal fixed charge rate		
	5%	7%	10%
Depreciable items			
Power plant	$ 52.850	$ 52.850	$ 52.850
Desalting plant	74.540	74.540	74.540
Intake and outfall	4.950	4.950	4.950
General plant facilities	2.440	2.440	2.440
Other construction costs	16.980	26.090	37.560
SUBTOTAL	$151.760	$160.870	$172.340
Contingency @ 12%	18.240	19.330	20.660
TOTAL DEPRECIABLE ITEMS	$170.000	$180.200	$193.000
Nondepreciable items			
Land cost	$	$	$ ....
Working capital	16.000	16.000	16.000
SUBTOTAL	$ 16.000	$ 16.000	$ 16.000
Contingency @ 6%	1.000	1.000	1.000
TOTAL NON-DEPRECIABLE ITEMS	$ 17.000	$ 17.000	$ 17.000
TOTAL DUAL-PURPOSE PLANTS	$187.000	$197.200	$210.000

Note: All figures are in millions of dollars. Additional investments for electrical transmission facilities are estimated at $5 million, and for water conveyance facilities, at $25 million.

crete box culvert with transition to an open channel beyond the desalting plant limits. Other on-site facilities include a warehouse and central repair shop.

Estimated unit water cost

The unit cost of water is defined as the net annual cost of water production divided by the quantity of water produced annually. The net annual cost of water production consists of:

Annual fixed charges
Annual operating and maintenance cost
Annual fuel cost
Total annual cost
Less power credit
Net annual cost of water production

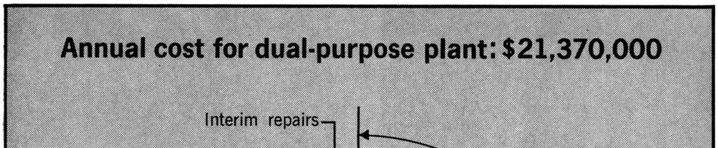
The power credit is based on 200 Mw_e. salable at 5.3 mills/kwh. and 85% power plant operating factor. This figure of 5.3 mills/kwh. has been estimated by Israel Electric Corp. as the cost, based on 1965 prices, of producing power in a single-purpose power plant of 200 Mw_e. capacity operating at 85% plant operating factor and consistent with the prevailing 10% fixed charges for electric power plants in Israel.

Annual water production is based upon a plant capacity of 100 m.g.d. and a desalting plant operating factor of 85%.

The reference plant used to prepare the capital cost, annual cost, and unit water cost estimates is based on the best information available to the engineer, on the results of many engineering calculations and optimizations, and on engineering judgment. There are many uncertainties, however, in the variables upon which the technical characteristics and cost estimates are based. The effect of the most important uncertainty—fixed charge rate (interest on investment)—is readily evident from accompanying tables. Should the 5% fixed charge rate (interest rate of 1.9%) be realized, the unit cost of water will be approximately 29 cents per 1000 gallons. On the other hand, should the fixed charge rate be as high as 10% (8% interest rate) the unit cost of water is more than doubled at approximately 67 cents per 1000 gallons. The actual interest rate and corresponding fixed charge rate cannot be determined until the loan commitments have become firm. One of the important conclusions of the study, however, is that the desalting plant design which is optimum for one fixed charge rate may be used for other fixed charge rates with essentially no economic penalty. Thus the desalting plant design can be commenced in advance of final commitments on the interest rate.

Other uncertainties whose effect is not so readily determined arise because of the scale-up of the reference plant capacity from the capacity of desalting plants presently operating. The largest single desalting plant module in operation today has a capacity of 2.5 m.g.d., and the largest unit on order has a design capacity just under 4 m.g.d. The Israel reference plant has a capacity of 100 m.g.d. Even though the reference plant design utilizes four trains of 25 m.g.d. and each train is partially subdivided even further, there is still a substantial scale-up in capacity over existing plants, with resulting uncertainty in cost and performance.

Annual cost for dual-purpose plant: $21,370,000



Note: All figures are in millions of dollars, and based on a 7% fixed charge rate.

Estimated unit water cost at plant boundary—1965 cost basis

	Nominal fixed charge rate		
	5%	7%	10%
Capital cost (millions of dollars)[1]			
Depreciable capital	$170.000	**$180.200**	$193.000
Nondepreciable capital	17.000	**17.000**	17.000
TOTAL	$187.000	**$197.200**	$210.000
Annual cost (millions of dollars)			
Fixed charges (depreciable capital)	$ 8.500	**$ 12.610**	$ 19.300
Fixed charges (nondepreciable capital)	.370	**.880**	1.540
Operating and maintenance expenses	3.470	**3.470**	3.470
Fuel expense	4.430	**4.410**	4.390
TOTAL	$ 16.770	**$ 21.370**	$ 28.700
Power credit	(7.900)	**(7.900)**	(7.900)
NET ANNUAL WATER COST	$ 8.870	**$ 13.470**	$ 20.800
Water production			
Million gallons per day	100	**100**	100
Million gallons per year	31,050	**31,050**	31,050
Million cubic meters per year	117.5	**117.5**	117.5
Unit water cost			
Cents per thousand gallons	28.6	**43.4**	67.0
Cents per cubic meter	7.6	**11.5**	17.7
Agorot per cubic meter	22.6	**34.4**	53.1
Dollars per acre-foot	93.1	**141.0**	218.0

[1] Excluding electrical transmission and water conveyance facilities

There are also site-related uncertainties, such as the scaling characteristics of the sea water, the oceanographic characteristics of the site which will influence the design of the intake structures, and subsoil characteristics which may affect foundations and other construction costs.

At the conclusion of the Israel dual-purpose plant feasibility study, certain variants (variables not directly under the control of the plant designer, but which are susceptible to change before the plant achieves commercial operation) were identified. A study was conducted to determine the range of uncertainty in each variant and the influence of each of these variants on the capital cost and the unit cost of water. The most important variant, fixed charge rate, was evaluated by preparing all estimates for 5%, 7%, and 10% fixed charge rates.

Capital cost variants

The important capital cost variants and their range of uncertainty follow.

General construction cost. The total capital cost of the dual-purpose plant is based on preliminary vendor quotations on major components and on unit construction costs obtained from contractors experienced in construction in Israel. Several factors may increase the total capital cost—increases in general construction costs, increases in heat exchanger material cost, increase in world copper price, and longer construction schedule. Several factors may result in a decrease in the total capital cost from that presently estimated. Examples of possible process and equipment improvements which may reduce costs are improved disengaging hardware, lower cost evaporator shells, and lower cost tube-bundle fabrication techniques.

Construction period. At the time the Engineering Feasibility and Economic Study was issued, it was possible to achieve commercial operation of the dual-purpose plant within 6½ years (by December 1972) providing detail design was started immediately. However, the starting date of the detail design has been delayed and, during the past year, delivery schedules of major components have increased substantially. A 7½-year schedule is now more realistic. A stretch-out of the construction schedule will result in increased interest during construction and in additional escalation with corresponding increase in capital cost and unit water cost. The effect of interest during construction on capital cost and unit cost of water for each year delay during the construction period (assuming this year occurs approximately at mid-construction) was calculated.

Heat exchanger. The cost of the heat exchanger tube bundles is based on information and preliminary quotations obtained from vendors based on 1965 material prices. The range of variation in heat exchanger cost was assumed to be ±10%.

Evaporator enclosures. The reference plant is based on the use of steel for the evaporator enclosures, although concrete was considered as an alternative. If concrete could be used for evaporator enclosures, a significant cost saving could be realized.

The use of concrete for the evaporator enclosures is contingent upon demonstrating that concrete is suitable for this service. Such a demonstration requires determining the capability of concrete to withstand the leaching action of product water, to withstand the attack of hot concentrated brine, to withstand thermal stresses, and to be vacuum tight. Development programs being conducted by the Office of Saline Water and the Bureau of Reclamation are directed toward resolving these problems.

Evaporator mass flow. The reference plant mass flow design value is 1

How capital cost variants affect unit cost of water[a]

Variant	Range of variation	Capital cost	Unit water cost (per 1000 gal.)
Reference plant		$197,200,000	43.4¢
General construction cost	May increase with increased construction costs, higher materials costs, rise in world copper price. slower construction schedule, and the like (for example, an increase of $10,000,000)...	$197,200,000 +10,000,000 $207,200,000	45.6¢
	...Or decrease due to such factors as conservatism in the reference plant estimate or use of concrete for the evaporator enclosures rather than steel (for example, a decrease of $5,000,000)	$197,200,000 −5,000,000 $192,200,000	42.3¢
Design value of evaporator mass flow (1,000,000 lb./hr.-ft. of weir width, requiring an evaporator stage enclosure width of 17 ft.)	May have to be decreased to 750,000 lb./hr.-ft. of weir width mass flow, calling for an evaporator stage enclosure width of possibly 23 ft....	$197,200,000 +5,000,000 $202,200,000	44.6¢
	...Or may be increased to 1,250,000 lb./hr.-ft. of weir width mass flow, calling for an evaporator stage enclosure width of possibly 14 ft.	$197,200,000 −2,700,000 $194,500,000	42.8¢
Design value of tube-bundle heat transfer coefficient (600 B.t.u./hr.-sq. ft.-° F., with a fouling factor of 0.0003)	A fouling factor of 0.0007 would require the heat transfer coefficient to be lowered to 500 B.t.u./hr.-sq. ft.-° F....	$197,200,000 +7,600,000 $204,800,000	45.1¢
	...Or a fouling factor of 0.0001 would permit the heat transfer coefficient to be raised to 700 B.t.u./hr.-sq. ft.-°F.	$197,200,000 −5,400,000 $191,800,000	42.2¢
Construction period	Assume an increase of one year at approximately mid-construction (excluding effect of escalation)	$197,200,000 +6,600,000 $203,800,000	44.9¢
Heat exchanger cost	Should the cost of the heat transfer surface increase by approximately 10%	$197,200,000 +3,800,000 $201,000,000	44.3¢
	Should the cost of the heat transfer surface decrease by approximately 10%	$197,200,000 −3,800,000 $193,400,000	42.6¢
Demisters	Should the development program confirm that product water of 25 p.p.m. (without tube leaks) is obtainable without demisters	$197,200,000 −2,500,000 $194,700,000	42.9¢
Evaporator enclosure (use of concrete)	May result in reducing the capital cost of the plant by about $3,600,000	$197,200,000 −3,600,000 $193,600,000	42.6¢

[a] 7% fixed charge rate

million pounds per hour-foot of weir width, with a 0.7° F. nonequilibrium allowance. While this value is considered reasonable, the highest demonstrated value (at Point Loma) is only 500,000 lb./hr.-ft. of weir width.

If the design mass flow is not confirmed in the development program, and it becomes necessary to design the desalting plant for 750,000 lb./hr.-ft. weir width mass flow value, it will be necessary to increase the evaporator stage enclosure width from the present 17 ft. to a width of possibly 23 ft.

If the development program were to demonstrate that the design mass flow can be increased from the design value of 1 million lb./hr.-ft. of weir width to a value of 1,250,000 lb./hr.-ft. of weir width, the stage width could then be decreased from the present 17 ft. to possibly 14 ft.

Tube-bundle heat transfer coefficient. The reference plant design is based on heat transfer data supplied by the Office of Saline Water. Our experience with desalting plants operating with brine temperature above 200° F. is limited and, therefore, there is some uncertainty about the appropriate fouling factor to use in the design. The design overall heat transfer coefficient has an average value of about 600 B.t.u./hr.-sq.-ft.-°F., which includes a fouling factor with an average value of 0.0003.

Should it be necessary to design the desalting plant using a lower overall heat transfer coefficient such as 500 B.t.u./hr.-sq. ft.-°F. (by changing the average fouling factor from 0.0003 to 0.0007), the heat transfer surface would be increased by 20%, with a corresponding increase in cost.

Should it be possible to design the desalting plant using a higher overall heat transfer coefficient such as 700 B.t.u./hr.-sq. ft.-°F. (by changing the average fouling factor from 0.0003 to 0.0001), the heat transfer surface could be decreased by 16%, with a corresponding decrease in cost.

Demisters. The reference plant estimate includes the cost of demisters and an allowance for the pressure drop through the demisters. Improvements in disengaging hardware within the flash evaporator may reduce or eliminate the need for demisters.

Should the development program confirm that product water of 25 p.p.m. (without tube leaks) is obtainable without demisters, the demisters could be eliminated, reducing the capital cost directly and also reducing the pressure drop between flashing brine and condensing steam.

Annual cost variants

The important annual cost variants follow.

Plant life. We have assumed that the life of the dual-purpose plant will be 30 years, a life consistent with conventional power plant and utility practice. While the life of water plants and water utilities is usually higher than 30 years, the similarity of the equipment in a desalting plant to that

How annual cost variants affect unit cost of water[a]

Variant	Range of variation	Annual cost	Unit water cost (per 1000 gal.)
Reference plant		$13,470,000	43.4¢
Plant life (now 30 years)	May decrease to 25 years, thus increasing fixed charge rate to 7.6%...	$13,470,000 +1,090,000 $14,560,000	46.9¢
	...Or may increase to 35 years, reducing the fixed charge rate to 6.6%	$13,470,000 −720,000 $12,750,000	41.1¢
Desalting plant capability (now 100 m.g.d.)	If increased to 110 m.g.d.	$13,470,000 +350,000 $13,820,000	40.5¢
Desalting plant operating factor (now 85%)	May increase to 89%, yielding 104 m.g.d. of water...	$13,470,000 +270,000 $13,740,000	42.2¢
	...Or may decrease to 80%, yielding only 94 m.g.d.	$13,470,000 −140,000 $13,330,000	45.6¢
Tube failure rate (0.1% at the end of the first 10-year period)	If doubled to 0.2% in first 10-year period, reduces plant operating factor to 82%	$13,470,000 −130,000 $13,340,000	44.5¢
Interim tube replacement (expected life of tube bundles now 30 years)	If full retubing becomes necessary in 15 years	$13,470,000 +640,000 $14,110,000	45.5¢
Top brine temperature (220° F. design value)	If possible to increase to 235° F. without scaling	$13,470,000 −420,000 $13,050,000	42.0¢
Power output (now 200 Mw. net salable electric power)	Should a net power output of 210 Mw. be realized (at 85% plant operating factor)	$13,470,000 +190,000 $13,660,000 −400,000 $13,260,000	42.7¢
Fuel cost	Should lower fuel cycle costs be realized, as predicted by a leading reactor manufacturer	$13,470,000 −1,220,000 $12,250,000	39.4¢

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[a] 7% fixed charge rate

found in steam power plants appears to justify a 30-year life for each.

Should it appear necessary to change the design life of the dual-purpose plant from 30 years to 25 years, it will be necessary to increase the fixed charge rate from 7.0% to, say, 7.6% because of the increased amortization rate associated with the shorter amortization period.

Should it prove possible to increase the design life of the plant to 35 years, there will be a reduction in the fixed charge rate (from 7.0% to 6.6%, for example).

Desalting plant capability. The desalting plant design capacity is 100 m.g.d. Should the plant produce more than the design value, there will be a small increase in the annual cost due to an increased usage of fuel and chemicals. However, the increase in the annual water production will result in lower unit water costs.

Because of the lack of experience in the construction of large desalting plants, it is possible that the present design could result in a desalting plant capacity as high as 110 m.g.d. with companion reduction in the unit cost of water.

Desalting plant operating factor. The plant operating factor for the reference desalting plant is estimated at 85%, although the availability of the nuclear heat source is estimated at 90%. Should the availability of plant components, particularly evaporator tube bundles, be higher or lower than those assumed in the plant operating factor analysis, a higher or lower annual water production will be realized.

Should it become possible to increase the desalting plant operating factor to 89% (based on 90% reactor availability), annual water production would be increased by 5%.

Should it develop that the desalting plant operating factor is only 80%, water production would be decreased by 6%.

Tube failure rate. The experience with 90:10 copper-nickel tubing materials in sea water service is limited to about seven years. It has been estimated that for the reference plant design, 0.1% of the tubes will have failed at the end of the first 10-year period. The plant operating factor of 85% includes consideration of the time required to plug tubes failing at the design rate, along with considerations of other plant component availabilities.

Should the tube failure rate of the 90:10 copper-nickel tubing be twice that assumed in the reference plant design, namely, 0.2% tube failures during the first 10 years, more frequent shutdowns for plugging tubes will be required and the plant operating factor over the 30-year life of the plant will average 82% instead of 85%, with a resulting increase in the unit cost of water.

Interim tube replacement. Tubing materials selected for the tube bundles include bimetallic tubing in critical areas. Because of the uncertainty of tube life, however, an allowance for occasional retubing has been included in the annual costs.

Future information may show it is necessary to provide for full retubing of the desalting plant after approximately 15 years' operation of the plant, with a corresponding increase in annual costs.

On the other hand, future information may show it is *not* necessary to provide for any retubing of the desalting plant during its operating life, with a resulting elimination of the interim replacement allowance and a corresponding decrease in annual costs.

Top brine temperature. The design value of the top brine temperature of the reference plant is 220° F.

Recent information indicates that the top brine temperature can be increased to 235° F. or higher without scaling or increasing the chemical treatment cost, and this increase would result in a decrease in the unit water costs.

Fuel cost. The nuclear fuel cycle costs include prices for fuel fabrication and spent fuel reprocessing quoted by U.S. manufacturers and fuel processors in late 1965 and on a uranium cost of $6 per lb. of U_3O_8. There have been several published predictions of lower fuel cycle costs for the period of the 1980's and 1990's. Should the reduced fuel cycle costs be realized, there will be a significant reduction in the unit cost of water.

Power credit. The net annual water cost was determined by applying the annual power credit to the total annual costs of the dual-purpose plant. The annual power credit is determined by multiplying the annual quantity of salable electric power (kilowatt hours per year) by the power credit (mills per kilowatt hour). The power credit was determined in a separate study and fixed at the value which would be charged by a power-only plant with the same salable power capacity as the dual-purpose plant. The value used in the study was 5.3 mills per kilowatt hour.

The turbine generator capacity of the reference plant is sufficient to generate 250 Mw. (gross), with in-plant power requirements estimated at 50 Mw. The credit for salable power has been based on 200 Mw. (net salable) and an 85% plant operating factor.

Should the overdesign and stretch characteristics of the plant permit operation of the turbine-generator at a higher capacity, or should the in-plant power requirements be less than estimated, and should it develop that the Israel Electric Corp. can efficiently absorb this power, the increase in annual power credit will result in a decrease in annual water costs.

Variant effect

After we identified the important variants and reasonable variant changes, the effects of these changes on capital cost, annual cost, and unit cost of water were calculated.

When one assumes the worst condition for all of the above variants, the capital cost of the plant increases by 15%. If the change of the variants is in the optimistic direction, however, the capital cost of the plant would decrease by almost as much. It is unlikely that all the variant changes will be in one direction. But confidence in the cost estimates improves as awareness grows that should this occur, the change in capital costs of the facility is surprisingly small and is the same order of magnitude as the contingency included in the estimates.

The uncertainties identified above and the range of variation which may be expected in each represents the best information available at the completion of the feasibility study. Some of the uncertainties will be resolved in the data and experience gained in several very important programs currently being conducted. The first of these programs is the test module now being constructed at the San Diego Saline Water Test Facility. This test module is designed to have performance characteristics similar to a 50-m.g.d. desalting plant train being designed for the Metropolitan Water District in San Diego, and should provide data on the mass, flow characteristics, plant hydraulics, plant dynamics, and general performance achievable in this size module. These data may validate several of the above mentioned design variables (such as design value of tube-bundle heat transfer coefficient, evaporator mass flow, necessity for providing demisters, and the desalting plant capacity). And the data may permit a reduction in the conservatism of the reference plant design, which will result in lower initial capital costs.

The above list of variants indicates that a significant saving in capital cost is possible by the use of concrete enclosures instead of steel enclosures for the evaporator. At the conclusion of the feasibility study, however, there were insufficient data available to indicate that concrete enclosures were suitable. Programs now being conducted by the Bureau of Reclamation in Denver for the Office of Saline Water may resolve this uncertainty.

Long-range experience with large desalting plants is very limited. During the next several years, however, a number of new plants will begin operation and this experience may reduce the uncertainties associated with the tube failure rate, plant operating factor, interim replacement requirements, and overall plant performance.

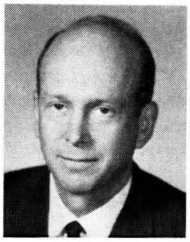
The table of variants has proved valuable to the prospective owners of the Israel dual-purpose plant in allaying concern that specific variables which may change will have a major effect upon the capital cost or the unit water costs. The straightforward approach of having the engineer identify the uncertainties in his design, the range of variation in these uncertainties, and the effect of possible variation has already proved of value in increasing confidence in the cost estimates.

ADDITIONAL READING

Engineering and Economic Feasibility Study for a Combination Nuclear Power–Desalting Plant, TID 22330, Vols. I, II, and III, Bechtel Corp., January 1966

Engineering Feasibility and Economic Study for Dual-Purpose Electric Power–Water Desalting Plant for Israel, prepared for U.S.-Israel Joint Board, Kaiser Engineers and Catalytic Construction Co., January 1966

"Multistage Flash Evaporator Plant Operating Factor," presented at the 153rd National Meeting of the American Chemical Society, Symposium on Desalination Plants, Miami Beach, Fla., April 9–14, 1967.



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J. R. Wilson *(For biographical sketch, see page 427).*

CURRENT RESEARCH

Film Actinometer for Measurement of Solar Ultraviolet Radiation Intensities in Urban Atmospheres

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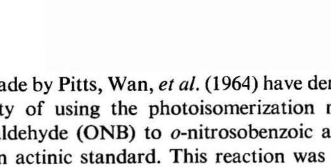
■ A versatile chemical actinometer, suitable for field as well as laboratory studies, has been developed for the measurement of radiation intensities in the near-ultraviolet region. The actinometer is a thin film of poly(methyl methacrylate) in which the actinic material, *o*-nitrobenzaldehyde, is dispersed. On absorption of light in the 2800- to 4100-A. region *o*-nitrobenzaldehyde photoisomerizes to *o*-nitrobenzoic acid with a quantum efficiency of 0.50. The extent of this reaction upon irradiation can be related to the intensity of the radiation source. This actinometer is suitable for measuring solar radiation intensities within the region 3000 to 4100 A., the photochemically reactive wavelength region for the production of photochemical smog.

Under the influence of near-ultraviolet solar radiation, many air pollutants undergo reactions to produce photochemical or "Los Angeles type" smog (Leighton, 1961). Thus absolute and relative measurements of near-ultraviolet solar radiation intensities in the lower atmosphere are an essential part of investigations of photochemical air pollution.

To obtain a complete picture of the nature of the photochemical reactions occurring in the lower atmosphere above an area as large as the Los Angeles Basin (1250 square miles) data must be obtained concurrently at several different points within the basin. While many data have been obtained on a day-to-day basis for many years for concentrations of pollutants, visibility, wind direction, etc., no such data exist for near-ultraviolet solar radiation intensities. Some short-term studies have been made (Gordon and Bonamassa, 1967; Nader, 1967; Stair, 1955).

Several instruments for such measurements (Hewson, 1956; Huschke, 1959) have been available for a number of years. However, the complexity of the instrumentation with subsequent economic overtones and their physical size have apparently precluded their use on all but a limited basis. The necessity for a more adaptable actinic instrument was apparent.

Studies made by Pitts, Wan, *et al.* (1964) have demonstrated the feasibility of using the photoisomerization reaction of *o*-nitrobenzaldehyde (ONB) to *o*-nitrosobenzoic acid (Equation 1) as an actinic standard. This reaction was discovered by Ciamician and Silber (1900) and subsequent work (Bowen, Harley, *et al.*, 1924; Leighton and Lucy, 1934) showed that the photoisomerization had a quantum efficiency of 0.50 in liquid, solid, or vapor phase and the quantum efficiency was independent of the exciting wavelength over the range 3000 to 4100 A. The studies of Pitts, Wan, *et al.* (1964), in which the ONB was dispersed in a potassium bromide pellet, further confirmed these conclusions.



Thus, the ONB actinometer has certain characteristics which warrant its application to photochemical air pollution studies. The ONB actinometer can be used in a variety of experimental setups—i.e., liquid, solid, vapor, or dispersion systems. The absorption spectrum of ONB has an absorption onset at about 4100 A. (Figure 1), which coincides with the wavelength threshold for the photodissociation of NO_2 into NO and atomic oxygen (Blacet, Hall, *et al.*, 1962; Pitts, Sharp, *et al.*, 1964; Schuck and Stephens, 1968). Since the ozone in the upper atmosphere cuts off all wavelengths below 3000 A. at the earth's surface, the solar radiation which causes photodissociative reactions involving NO_2 is in the region 3000 to 4100 A. This onset at 4100 A. also coincides with the beginning of the spectrally active region for the production of synthetic photochemical smog in laboratory studies with irradiated auto exhaust (Altshuller and Bufalini, 1965). Thus, the effective spectral region for photochemical smog formation in urban atmospheres is in the same 3000- to 4100-A. region over which the authors' ONB film actinometer is effective (Altshuller and Bufalini, 1965; Schuck and Stephens, 1968).

In its application to air pollution studies thus far, the ONB system has been used successfully as a liquid system (Gordon and Bonamassa, 1967) and as a solid-state system (Nader,

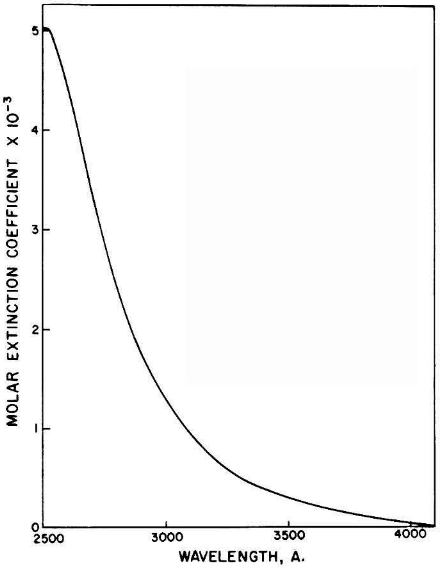


Figure 1. Absorption spectrum of *o*-nitrobenzaldehyde in poly(methyl methacrylate)

1967; McCormick, Vernon, *et al.*, 1967). In the continuous recording liquid system used by Gordon and Bonamassa, the data obtained are in good agreement with those obtained with an apparatus utilizing photoelectric cells under identical experimental conditions.

The authors report data obtained for studies in which ONB is dispersed in a thin film of poly(methyl methacrylate). In such a form the actinometer possesses certain advantages over the liquid or solid actinometer systems previously employed.

Experimental

Preparation of Poly(methyl Methacrylate). Methyl methacrylate monomer was supplied by Matheson, Coleman and Bell, Norwood, Ohio. Purification was by the method of Shultz (1961), and the monomer was polymerized for 72 hours at 60° in a constant temperature bath using 0.1% (by weight) azobisisobutyronitrile initiator. The polymer was purified by dissolving in benzene, precipitating three times in petroleum ether to remove monomer and low molecular weight polymer, and then freeze-drying to remove solvent. The molecular weight of the polymer was determined viscometrically to be 20,000 ± 3000.

Preparation of Actinometer Film. The requisite weight of polymer is dissolved in the minimum volume of benzene and the solution is stirred for 12 hours. ONB is added and the solution is stirred for an additional 2 hours in the dark. The resulting solution is poured into a Petri dish with an optically flat base. The benzene is allowed to evaporate at a controlled rate, by inverting a vessel over the Petri dish in the dark, over a period of 24 hours to leave a perfectly transparent film at the bottom of the dish. Most residual solvent can then be removed by subjecting the film to high vacuum for several days. The average film thickness was $2.20 \pm 0.05 \times 10^{-3}$ cm.; all film was handled in red light.

Quantum Yield Determination. All photochemical reactions were carried out at room temperature with the film suspended in the light path of a high pressure mercury arc (PEK 100-watt) equipped with one of two interference filter systems (Jenaer Glaswerk Schott und Gen., Mainz, West Germany), one having a maximum transmittance of 41% at 3290 A. and a half width of 80 A. and the other 30% at 3560 A. and a half width of 75 A.

ONB dispersed in poly(methyl methacrylate) obeyed Beer's law over the entire concentration range studied (0.90 to 2.82×10^{-6} gram mole cm.$^{-2}$). The photochemical isomerization to *o*-nitrosobenzoic acid was followed by monitoring, as a function of irradiation time, the nitro peak at 1530 cm.$^{-1}$ (asymmetrical stretching band) using a Perkin-Elmer 621 infrared spectrophotometer. Assuming a value for the quantum yield of isomerization to be 0.50 as obtained by careful studies in other environments, the absolute light intensity was calculated for various irradiation times and extrapolated back to zero irradiation time. The latter extrapolation corrects for absorption due to internal filtering of the ultraviolet light by the nitroso product. This intensity value could then be compared to that obtained using standard liquid phase potassium ferrioxalate actinometry (Parker and Hatchard, 1953) or the photoisomerization of ONB dispersed in a potassium bromide pellet (Pitts, Wan, *et al.*, 1964).

Solar Radiation Intensity. These determinations were made using a semicontinuous exposure device in which a shutter (0.9 cm. wide) was moved stepwise one shutter width across a large piece of film (40 cm.) at 4-minute intervals (at the same time maintaining the film perpendicular to the incident solar radiation). No significant obscuring of the sky by the film holder-shutter device occurred. In this manner it was possible to monitor the solar radiation for about 2 hours. Intensities were determined as for the laboratory determinations.

Results and Discussion

The absolute incident intensities of the mercury light source at 3340 and 3660 A. as measured, and assuming the quantum yield of isomerization to be 0.50, are shown in Table I. The source intensity was deliberately varied. The agreement, within experimental error, is good, thus validating the authors' assumption that the quantum yield for photoisomerization of ONB dispersed in poly(methyl methacrylate) is 0.50 and

Table I. Absolute Incident Light Intensity Values of Mercury Source at 3340 and 3660 A.

Wave-length, A.	*o*-Nitro-benzaldehyde, Gram Moles Cm.$^{-2}$ × 10^{6}	Absolute Incident Intensity,[a] Einstein Sec.$^{-1}$Cm.$^{-2}$ × 10^{9}	Ferrioxalate Intensity, Einstein Sec.$^{-1}$Cm.$^{-2}$ × 10^{9}
3340	0.90	1.85 ± 0.16	1.69 ± 0.05
	1.77	1.80 ± 0.16	1.99 ± 0.05
	2.77	1.57 ± 0.15	1.76 ± 0.05
3660	0.90	3.98 ± 0.25	3.73 ± 0.10
	1.80	4.73 ± 0.25	4.64 ± 0.10
	2.82	3.37 ± 0.25	3.50 ± 0.10

[a] Incident light intensity, per square centimeter of film, based on assuming quantum yield of isomerization of *o*-nitrobenzaldehyde = 0.50.

independent of wavelength. This system is therefore capable of being used as an actinometer.

Preliminary experiments using solar radiation showed that exposure periods as short as 2 minutes were all that were required to compute a value of the intensity. This time period may be considered small compared to the time usually necessary for a significant change in the solar radiation intensity to occur.

Using the semicontinuous exposure device, data were obtained on clear days and when significant amounts of smog were present at the campus in Riverside, Calif. A typical plot is shown in Figure 2. Each point represents one individual reading for a particular piece of film before the shutter was advanced to the next piece of film. Thus, the continuous line represents the variation of the absorbed solar radiation intensity with time of day. The depression around 12.25 hours indicates a reduction of intensity during this period. The expected intensity in the absence of any significant absorbing or scattering material in the lower atmosphere is indicated by the dashed line. On analyzing data obtained at the University of California Air Pollution Research Center at Riverside for concurrent monitoring of oxides of nitrogen, oxidants, and particulate matter, using standard air pollution monitoring techniques, it appeared that the reduction of absorbed solar intensity observed in this particular experiment was brought about primarily by the presence of particulate matter in the atmosphere, although some absorption by pollutants also must have been involved.

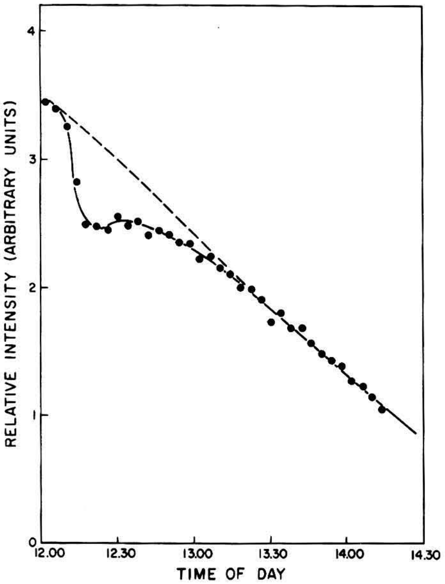


Figure 2. Variation of absorbed solar radiation intensity with time of day (Pacific standard time) in presence of air pollutants

— Actual intensity recorded

– – – Expected intensity in absence of significant concentrations of air pollutants

Conclusions

The utility of the ONB film actinometer as a convenient and reliable device for measuring relative solar radiation intensities in the region 3000 to 4100 A. has been demonstrated and the authors foresee the development of a truly continuous recording device for the entire 3000- to 4100-A. region or at any particular wavelength or group of wavelengths in this region using this film. The device could be a conventional camera equipped with a constant-speed motor to drive the film, in roll form, past an aperture where it would be exposed to the solar radiation, suitably filtered to give the desired spectral band or bands. The roll of film after exposure could be removed from the device and intensities recorded by running the film through an infrared machine operating at the fixed frequency of 1530 cm.$^{-1}$ The device would be a little larger than a conventional camera, inexpensive, and truly portable. One laboratory infrared spectrophotometer would suffice to analyze the data from several such devices instead of having to set up analyzing equipment for each instrument as is now needed with the continuous recording liquid actinometer or photoelectric devices.

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Estimation of Radiation Doses to the Respiratory Tract from Inhalation of Airborne Radioactivity

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■ A "graded filtration" sampler developed to estimate the respiratory deposition of airborne fallout provides information which when used with a suitable lung model permits estimation of the radiation dose to the nasopharyngeal, trachecbronchial, and pulmonary regions of the adult respiratory tract. Estimated doses to adults from airborne fallout collected in November 1966 and January 1967 were 85 and 130 microrem per 70 years to the nasopharyngeal and pulmonary regions of the respiratory tract, respectively. Estimated radiation dose to the tracheobronchial region was less than 0.01 microrem per 70 years. A dose of 225 microrem per 70 years to the thyroid gland was estimated due to inhalation. The greatest single dose commitment from fresh fission products was to the respiratory lymphatic nodes due to inhaled ^{144}Ce and ^{144}Pr. This was approximately 40 times the pulmonary region dose. Among long-lived radionuclides, ^{239}Pu delivered the greatest dose to the respiratory lymph nodes. Doses to the respiratory tract from the levels of airborne fresh fission products encountered in this study are low when compared with nonoccupational radiation doses due to inhaled radon and its short-lived daughters. This approach to estimation of respiratory doses is applicable to monitoring of nuclear facilities for airborne particulate hazards evaluation.

The assessment of public health hazards resulting from exposure to radioactive materials of the general population is an objective of the National Center for Radiological Health. As part of this work, the Northeastern Radiological Health Laboratory developed a field method to collect airborne particulates classified by size so that an estimate of their deposition in the nasopharyngeal, tracheobronchial, and pulmonary regions of the respiratory tract can be made (Shleien, Friend, *et al.*, 1967). A logical extension of this work is to use the results of these deposition studies with recent information on respiratory physiology to assess radiation doses to the regions of the respiratory tract. This paper describes the information and calculations required to make the above assessment, using fallout data as an example. Although regional respiratory doses from these events proved to be small, the approach employed in their calculation has general applicability for hazards evaluation of airborne nuclear releases.

Results of analyses of airborne nuclear debris from foreign nuclear tests which were reported to have occurred on October 27, 1966, and December 28, 1966, are the basic data used in this paper. Debris from each test reached Winchester, Mass., approximately 8 days after the detonations. The U. S. Atomic Energy Commission has reported (1966, 1967) that the first detonation was of low to low intermediate yield (20 to 200 kilotons TNT equivalent), and the second had a yield of a few hundred kilotons and both detonations employed enriched uranium. Samples of airborne fallout were collected 1 meter above the ground at a rate of approximately 40 cubic feet per minute with a "graded filtration sampler." This apparatus has been described in detail in previous publications (Shleien *et al.*, 1965).

Briefly, a "graded filtration sampler" is a particle size classifying device consisting of a series of three or five filters nested in order of increasing retentivity. The distribution of materials collected on the filters in the nest can be determined by suitable physical or radiochemical analysis. Two mathematical models serve to estimate deposition in the respiratory tract. The first model is based on laboratory calibration of the filters with homogeneous aerosols and relates aerosol size to filter collection efficiency (Shleien, Cochran, *et al.*, 1966). The second model (Task Group on Lung Dynamics, ICRP, 1966) relates deposition in the nasopharyngeal, tracheobronchial, and pulmonary regions of the respiratory tract to particle size. Linear programming techniques, using the above models, then relate the collection of airborne fallout on the graded filters to its deposition in the three regions of the respiratory tract.

Biological and Mathematical Considerations

The lung model (Task Group on Lung Dynamics, ICRP, 1966) provides information on clearance mechanisms required for calculation of doses to the various regions of the adult respiratory tract, as well as size *vs.* deposition data. Radionuclides are classified into three clearance groups: classes *D*, *W*, and *Y*. Classification is based on radionuclide residence time in a region, which in turn depends upon the chemical and physical characteristics of the material. Since in several instances removal by different physiological modes takes place with the same biological removal time, the clearance model can be simplified. Table I presents the abbreviated clearance model employed in this work. For example, class *D* materials are removed from the nasopharyngeal tract by two mechanisms—i.e., direct transfer to the blood stream and ciliary mucous transport to the gastrointestinal tract. Since the removal time is the same for both mechanisms, a single clearance half-time of 4 minutes can be employed. Only in the removal of class *W* and *Y* materials from the pulmonary region and the removal of class *Y* materials from the lymph nodes are two clearance times used. In pulmonary clearance, materials are cleared by a rapid as well as a slow removal mechanism, 60% being cleared by the slow mechanism and 40% by a rapid one. Lymphatic clearance proceeds by a biological mechanism for 10% of the deposited amount, while the remainder of the deposited material is subject only to radiological decay.

The dose delivered to a given region is the product of the microcurie-days of radionuclide residence in the region and the energy absorbed per disintegration, divided by the appropriate mass (Ford and Snyder, 1966):

$$\text{Dose} = \frac{51\,(\text{microcurie-days residence}) \times (\text{energy absorbed per disintegration})}{(\text{mass of region})}$$

where microcurie-days of radionuclide residence is a function of the microcurie intake, fraction of the material deposited, fraction of material cleared, and rate of radioactive decay. The numerical factor (51) is equal to the product of disintegrations per microcurie-day multiplied by gram-rads per million electron volts.

The masses of the adult nasopharyngeal and tracheobronchial regions used in this work are based on the mass of a surface layer of tissue 45 microns thick. These and other adult organ masses were obtained from the literature (Ford and Snyder, 1966; Committee II, ICRP, 1959). Use of smaller sensitive tissue volumes would yield higher dose estimates. However, since most of the radionuclides considered are β and γ emitters, and geometrical considerations indicate energy transfer to surrounding tissue, the tissue masses employed are appropriate.

The energy absorbed per disintegration takes into consideration the type of emission—i.e., x-ray, γ, α, β^-, β^+, e^-, and atomic recoil—the fraction of the disintegrations of the specific emission considered based on the decay scheme of the radionuclide, the energy of the emission, and the effective radius and density of the organ. Values published by Committee II, International Commission on Radiation Protection (1959), for energy absorbed per disintegration in the lungs and thyroid gland were used in calculating doses. As yet, estimates of energy absorption for specific radionuclides to the lymph nodes or tissue sheaths, such as the lining of the nasopharyngeal and tracheobronchial regions of the respiratory tract, are not available. Energy absorbed from α particles in a small tissue layer is efficient. However, only a small portion of the energy of a γ photon would be absorbed in a thin tissue layer. Energy absorption from β emitters lies somewhere between these extremes. No attempt was made to resolve these difficulties and published values of energy absorption in the lungs were used for all organ regions except the thyroid. Thus, doses to regions other than the lungs and thyroid may be somewhat overestimated.

A detailed explanation of the dose calculations to regions of the respiratory tract and thyroid are presented in the Appendix. The portions of the dose equation determined from analysis of field data include the microcurie intake and

Table I. Clearance Mechanisms

(Task Group on Lung Dynamics ICRP, 1966)

		Class *D*		Class *W*		Class *Y*	
Region	Clearance Pathway[a]	Clearance half-time	Cleared, %	Clearance half-time	Cleared, %	Clearance half-time	Cleared, %
Nasopharyngeal	Direct to systemic blood(a) and ciliary mucus transport to G. I. tract (b)	4 min.	100	4 min.	100	4 min.	100
Tracheobronchial	Direct to systemic blood(c) and ciliary mucus transport to G. I. tract(d)	10 min.	100	10 min.	100	10 min.	100
Pulmonary	Direct to systemic blood(e). Slow clearance via T-B to G. I. tract(g) via lymphatics(h).	30 min.	100	90 days	60	360 days	60
	Rapid clearance via T-B to G. I. tract(f)			1 day	40	1 day	40
Lymph	Biological(i)	30 min.	100	90 days	100	360 days	10
	Radiological					Radio-logical half-life	90

[a] Superior alphabetic designations in parentheses refer to physiological pathways described by the Task Group on Lung Dynamics, ICRP, 1966.

fraction of inhaled aerosol deposited in a region. Because of the complexity of transfer of material to, and elimination of material from the lymphatics, lymph node dose was estimated by a graphical method proposed by Ford and Snyder (1966). This method is limited to class Y materials with long radiological half-lives and effective pulmonary clearance half-time of 150 to 1500 days. When applying the graphical solution, appropriate corrections need to be made for differences in particle size, effective energy, and intake as compared with a standard particle size (1 micron), effective energy (1 million electron volts), and intake (1 microcurie).

Determination of Microcurie Intake and Fraction of Inhaled Material Deposited in a Region

The determination of the concentration and particle size characteristics of each radionuclide in the fission product debris collected would be extremely tedious. Differences in particle size distribution between radionuclides occur due to radionuclide fractionation—i.e., alteration of radionuclide composition occurring between detonation and analysis. It causes the debris sample to be nonrepresentative of the total detonation product (Freiling, 1961). However, radionuclides can be arbitrarily classified into refractory, intermediate, and volatile groups (I, II, and III), based on mode of formation at the time of detonation. During the fireball stage of a nuclear detonation, nuclides whose oxides have high vaporization temperatures are incorporated into relatively large particles. These refractory materials are classed as group I. Nuclides which have relatively long-lived volatile precursors do not condense until some time later when temperatures have decreased. They then condense primarily on smaller particles. These volatile materials are placed in group III. Other radionuclides behave in a manner intermediate between these two extremes and are placed in group II. Radionuclides were classified in these groups based on previous studies of nuclear detonations (Freiling and Kay, 1965; Mamuro *et al.*, 1966) which indicated that their mode of formation and degree of volatilization were similar. The authors assumed for the purpose of this study that radionuclides in any one group will tend to be associated with particulate materials of similar or comparable size because of similarities in mode of formation. Thus, it is possible to estimate the concentration, the particle size, and the deposition characteristics of radionuclides which contribute to the inhalation dose, but for which concentrations and deposition coefficients are not directly determined.

The particle size characteristics (in terms of distribution on each filter in the graded filter sampler) and activity concentrations of three "type elements"—namely, ^{95}Zr–^{95}Nb, ^{131}I, and ^{89}Sr—were empirically determined by γ spectroscopy or radiochemical analysis. The distribution of ^{95}Zr–^{95}Nb, ^{131}I, and ^{89}Sr on each filter in the "graded filter sampler" was used as input to the computer program and provided data on the maximum deposition of these materials in the nasopharyngeal, tracheobronchial, and pulmonary regions of the respiratory tract (Table II). The deposition coefficients for all radionuclides in a fractionation group are considered to be the same as the "type element" in the group.

Radioactivity concentrations determined on 3-day samples collected during November 1966 and January 1967 are presented in Table III. Activity concentration for specific radionuclides in a particular fractionation group were estimated from its fission yield relative to the "type element" in the group (Bolles and Ballou, 1956). The microcurie intake per sampling period is equivalent to the microcurie activity per

Table II. Deposition Factors

Date Sample Collected, Inclusive	Maximum Deposited, %								
	Nasopharyngeal			Tracheobronchial			Pulmonary		
	^{95}Zr–^{95}Nb	^{131}I	^{89}Sr	^{95}Zr–^{95}Nb	^{131}I	^{89}Sr	^{95}Zr–^{95}Nb	^{131}I	^{89}Sr
NOVEMBER 1966									
Nov. 3–Nov. 6	91	29	59	5	6	12	7	32	30
Nov. 6–Nov. 9	84	36	39	8	17	10	13	47	32
Nov. 9–Nov. 12	47	18	9	5	9	8	20	48	52
Nov. 12–Nov. 15	51	28	11	7	16	17	33	49	53
Nov. 15–Nov. 18	70	25	12	7	9	19	25	44	56
Nov. 18–Nov. 21[a]	54	19	21	6	13	11	21	43	50
Nov. 21–Nov. 24	69	30	12	3	6	3	12	26	25
Nov. 24–Nov. 27	53	14	9	7	17	7	24	52	50
JANUARY 1967									
Jan. 1–Jan. 4[a]	83	91	32	6	3	12	13	6	29
Jan. 4–Jan. 7[a]	95	67	37	3	11	6	4	23	10
Jan. 7–Jan. 10	56	15	25	9	22	16	29	60	50
Jan. 10–Jan. 13	83	46	39	8	15	14	13	40	44
Jan. 13–Jan. 16	93	79	56	4	8	13	5	16	33
Jan. 16–Jan. 19[a]	78	62	30	7	10	14	18	24	43
Jan. 19–Jan. 22[a]	84	56	33	8	11	15	13	28	30

[a] ^{89}Sr deposition estimated from average ratio to ^{95}Zr–^{95}Nb for both periods. N-P ratio (0.39), correlation coefficient (0.89); T-B ratio (1.89), correlation coefficient (0.65); P ratio (2.34), correlation coefficient (0.83).

Table III. Measured Activities of ^{95}Zr–^{95}Nb, ^{131}I, and ^{89}Sr

Date Sample Collected, Inclusive, Approx. 0800 to 0800	Activity, Microcuries $\times 10^{-3}$ per Cu. Meter		
	^{95}Zr–^{95}Nb[a]	^{131}I[b]	^{89}Sr[c]
	NOVEMBER 1966		
Nov. 3–Nov. 6	31	38	5
Nov. 6–Nov. 9	36	53	16
Nov. 9–Nov. 12	57	45	42
Nov. 12–Nov. 15	19	37	21
Nov. 15–Nov. 18	24	15	20
Nov. 18–Nov. 21	56	31	32
Nov. 21–Nov. 24	192	46	67
Nov. 24–Nov. 27	50	20	33
	JANUARY 1967		
Jan. 1–Jan. 4	27	73	2
Jan. 4–Jan. 7	328	1053	220[d]
Jan. 7–Jan. 10	7	113	5
Jan. 10–Jan. 13	16	83	7
Jan. 13–Jan. 16	109	192	19
Jan. 16–Jan. 19	80	119	17[e]
Jan. 19–Jan. 22	52	56	14[e]

[a] Counting error at 95% confidence level < 10% in all but one measurement.
[b] Counting error at 95% confidence level < 12% in all measurements.
[c] Counting error at 95% confidence level as high as 50% for samples of low activity.
[d] Filter (*A*) sample lost. Estimated from ratio activities ^{89}Sr:^{95}Zr–^{95}Nb.
[e] Filter (*E*) lost. Estimated as half the filter (*D*) activity which occurred in the three previous samples.

cubic meter of air multiplied by the quantity of air inhaled during the sampling period (60 cu. meters for a 3-day period). Radionuclides having activity concentrations of less than 0.5% for a period of 10 to 30 days after detonation were excluded from dosage calculations. The radionuclides for which doses were calculated together with other pertinent data are presented in Table IV.

Results and Comment

Doses in terms of microrem per 70 years for the nasopharyngeal and pulmonary regions of the respiratory tract are presented in Table V. The doses from individual radionuclides to the tracheobronchial region were less than 0.01 microrem per 70 years and were not included in the table.

Total dose to the nasopharyngeal region was 85 microrem per 70 years, ^{140}Ba–^{140}La contributing approximately 40% of this total. The largest portion (70%) of this dose was caused by debris collected in January 1967 because of the significantly larger particle size of the airborne debris from this event and, hence, greater nasopharyngeal deposition.

Pulmonary doses were approximately equivalent for each period of fallout, 70 and 60 microrem per 70 years, respectively. The major radionuclide contributing to this dose was ^{144}Ce and its daughter, ^{144}Pr, in equilibrium. The second major group of contributors to pulmonary radiation dose included ^{89}Sr, ^{91}Y, ^{103}Ru–^{103m}Rh, ^{95}Zr–^{95}Nb, and ^{140}Ba–^{140}La in decreasing order of dose contribution.

The limitations set by the graphical method of respiratory lymph node dose calculations—i.e., class *Y* materials having

Table IV. Factors for Radionuclide Dose Calculation

Fractionation Group	Radio-nuclide	Absorbed Energy per[a] Disintegration, Million Electron Volts	Clearance Class
I	^{91}Y	0.59[b]	*Y*
	^{95}Zr	0.52[c]	*W*
	^{95}Nb	0.26	*W*
	^{99}Mo	0.48[d]	*Y*
	^{140}Ba	1.4[c]	*W*
	^{140}La	1.1	*Y*
	^{141}Ce	0.18	*Y*
	^{143}Ce	0.83[c]	*Y*
	^{143}Pr	0.32	*Y*
	^{144}Ce	1.3[c]	*Y*
	^{147}Nd	0.30[e]	*Y*
II	^{131}I	0.3	*D*
		0.23 (thyroid)	*W*
	^{132}Te	1.1[c]	
	^{132}I	1.0	*D*
		0.65 (thyroid)	
	^{133}Xe	0.16	*D*
	^{103}Ru	0.27[c]	*W*
	^{103m}Rh	0.055	*W*
III	^{89}Sr	0.55	*W*

[a] Report of ICRP Committee II on Permissible Dose for Internal Radiation (1959). $\Sigma E(RBE)n$ for insoluble material, in the lung except where noted.
[b] Because of low abundance during period of consideration the $\Sigma E(RBE)n$ of parent radionuclide not considered.
[c] $\Sigma E(RBE)n$ for decay chain.
[d] Based on $\Sigma E(RBE)n$ (87% abundant chain) $\times$ 0.87 plus $\Sigma E(RBE)n$ (13% abundant chain) $\times$ 0.13.
[e] Total $\Sigma E(RBE)n$ for ^{147}Nd, ^{147}Pm, and ^{147}Sm decay chain employed. Because of low abundance during period under consideration and low $\Sigma E(RBE)n$, dose from ^{147}Pm and ^{147}Sm not considered.

Table V. Respiratory Tract Dose, Microrem per 70 Years

Radionuclide	Nasopharyngeal		Pulmonary	
	I[a]	II[b]	I[a]	II[b]
^{91}Y	1.07	2.26	8.25	5.82
^{95}Zr	1.05	2.20	5.98	4.20
^{95}Nb	0.18	0.22	0.74	0.33
^{99}Mo	0.71	3.67	0.26	0.50
^{140}Ba	5.10	15.62	8.57	7.79
^{140}La	4.00	12.24	1.19	1.08
^{141}Ce	0.46	1.10	1.45	0.98
^{143}Ce	0.21	1.43	0.02	0.10
^{143}Pr	1.21	3.24	2.24	4.90
^{144}Ce[c]	1.11	2.18	27.30	18.26
^{147}Nd	0.54	1.65	1.55	1.40
^{131}I	0.20	2.97	<0.01	0.07
^{132}Te	0.36	8.58	1.14	6.47
^{132}I	0.32	7.58	<0.01	0.05
^{133}Xe	0.17	2.56	<0.01	0.02
^{103}Ru	0.14	1.35	3.81	9.02
^{103m}Rh	0.03	0.26	<0.01	<0.01
^{89}Sr	0.18	0.53	9.65	4.44

[a] For samples collected during November 1966 (30-day period).
[b] For samples collected during January 1967 (30-day period).
[c] In equilibrium with its daughter, ^{144}Pr.

long radiological half-lives and effective pulmonary clearance half-times of 150 to 1500 days—permitted estimation of the dose from only one fresh fission product. The respiratory lymphatic dose from ^{144}Ce in equilibrium with ^{144}Pr was estimated to be 4800 and 1400 microrem per 70 years, respectively, for the first and second periods under study. This by far is the greatest single dose commitment from inhaled fresh fission products.

The dose to the thyroid gland from inhaled radioactivity totaled 225 microrem per 70 years. A majority of this dose, approximately 200 microrem per 70 years, was attributable to high ^{131}I activity present on large particles collected in January 1967. This material was trapped by the nasopharyngeal region of the respiratory tract and transferred directly to the blood stream or indirectly carried via ciliary transport to the gastrointestinal tract and, hence, to the blood stream. The radionuclide was then absorbed by the thyroid from the blood stream. During this period, ^{131}I concentrations in milk in the northeastern United States were not detectable ($<10 \times 10^{-6}$ microcurie per liter). The lack of ^{131}I in milk may be attributable to stored feed rather than pasture feeding of dairy animals during the winter season.

A comparison between doses from fresh fission products and long-lived naturally occurring and artificially produced radionuclides in the air collected over the same two 30-day periods, indicates that ^{210}Pb, a naturally present long-lived daughter in the radon decay chain, delivers a greater dose commitment over a 70-year period to the pulmonary region than did the fresh fission products studied above. The average activity concentrations for ^{90}Sr, ^{210}Pb, and ^{239}Pu were 1.9×10^{-9}, 16.9×10^{-9}, 0.02×10^{-9} microcurie per cu. meter, for the two 30-day periods during which fresh fission products were collected. Concentration and particle size distribution data for long-lived radionuclides were obtained from previous publications (Shleien *et al.*, 1967). Dose commitments to the pulmonary region from ^{90}Sr and ^{239}Pu inhaled during these two 30-day periods were small (less than 10 microrem per 70 years). Because of the higher concentration of ^{210}Pb, its

Table VI. Explanation of Symbols in Equations

Symbol	Designation	Remarks
I	Microcurie intake	Product of microcurie concentration per cu. meter of air and quantity of air inhaled during sampling period
51	Conversion factor to yield dose in terms of rem per unit time	Product of disintegrations per microcurie-day and gram-rad per million electron volts
E	Effective energy absorbed	Product of effective energy per disintegration, relative biological effectiveness and damage factor
m	Mass of tissues for adult organs Nasopharyngeal, 1.35 g. Tracheobronchial, 400 g. Pulmonary, 500 g. Lymph nodes, 15 g. (respiratory) Thyroid, 20 g.	Weight of T-B region based on the mass of a surface layer of tissue 45 microns thick (range of an α particle of energy about 5 million electron volts). If one assumes that the surface of the nasopharynx is about 300 sq. cm., its tissue weight is approximately 1.35 grams (Ford and Snyder, 1966)
$D_{N\text{-}P}$, $D_{T\text{-}B}$, D_P	Fraction of radionuclide inhaled which is deposited in various portions of the respiratory tract	
f_a, f_b, etc.	Fractions cleared by pathways *a*, *b*, etc., as described in Table I	Details of physiological pathways published elsewhere (Task Group on Lung Dynamics, ICRP, 1966)
λ_a, λ_b, etc.	Effective elimination constant for pathways *a*, *b*, etc.	Equals sum of $\frac{0.693}{\text{clearance half-time}}$ and $\frac{0.693}{\text{radiological half-time}}$. λ_a and λ_b are equal; λ_c and λ_d are equal; and for class *W* and *Y* radionuclides λ_e, λ_g, λ_h, and λ_i are equal
λ_f^b, λ_h^b	Biological elimination constants for pathways *f* and *h*	
T	Time in days after collection for which dose is calculated	Taken to be 70 years (25,550 days), although total dose may be delivered in a shorter time period
t	Time for passage of material through the T-B region from the P region to the G. I. tract	t is short (10 min.)
f_{th}	Fraction of radionuclide from region to blood stream and hence to thyroid.	For N-P and T-B equals 0.30 For P equals 0.12
λ_{th}	Effective elimination constant from thyroid	7.6 days^{-1}

greater deposition and a very high effective energy absorbed for the ^{210}Pb decay chain, a dose of approximately 2000 microrem per 70 years to the pulmonary region was calculated from inhalation of this radionuclide during the two 30-day periods.

Of the long-lived radionuclides considered above, only ^{239}Pu has an effective clearance half-time and insolubility which permit estimation of lymphatic dose by the graphical method. The respiratory lymphatic dose from inhalation during the two 30-day periods due to ^{239}Pu is estimated to be 4800 microrem per 70 years.

Apparently, the radiation doses estimated in this paper and the models for dose calculation at present employed show that the respiratory lymph nodes receive the greatest radiation dose from inhaled radioactive debris. Studies of the concentrations of ^{144}Ce and ^{239}Pu in this tissue, along with elucidation of the lymphatic levels of long-lived airborne radionuclides such as ^{238}Pu, ^{210}Pb, ^{210}Po, ^{90}Sr, and ^{238}U, appear to be required to understand more fully the effect of environmental radiation.

When one considers the nonoccupational exposure from inhaled radon and its short-lived daughters, which has been estimated to be between 15 and 1500 millirem per year (Havlovic, 1965), the calculated doses above do not appear to pose a significant hazard.

Although doses calculated from the examples used in this paper were low, the approach employed can serve as a model for future situations in which airborne radioactivity may be released. Monitoring of nuclear facilities such as fuel processing plants and power reactors by the above technique would yield data directly amenable to evaluation of inhalation hazards.

One factor in particular contributed to the low dose estimates. This factor is inherent in the approach itself. The above assessments were made on the basis of uniform distribution in an organ region. If smaller tissue volumes are considered to be affected by the inhaled radioactivity than those assumed in this paper, radiation doses would be correspondingly higher. Furthermore, it should be recognized that solid airborne debris are likely to be distributed in a nonuniform manner and therefore high localized dose may be expected. Assessment of inhaled particulate radioactivity on a local dose basis—i.e., to a sphere of tissue surrounding a particle—is more difficult to ascertain and for the most part has been avoided by investigators. Investigations of microdosimetry in cellular tissue layers, while laborious, appear to be required before the hazardous nature of airborne particulate radioactivity can be fully evaluated.

Appendix

The mathematical equation for calculating dose to the nasopharyngeal (N-P), tracheobronchial (T-B), and pulmonary (P) tracts are as follows (Ford and Snyder, 1966):

For the nasopharyngeal region, the dose is expressed:

$$\text{Dose}_{\text{N-P}}(\text{rems}) = \frac{51\ I\ E}{m}\ D_{\text{N-P}}\left(f_a \frac{1 - e^{-\lambda_a T}}{\lambda_a} + f_b \frac{1 - e^{-\lambda_b T}}{\lambda_b}\right) \quad (1)$$

An explanation of symbols used in these equations is presented in Table VI.

Two sources of deposited materials cause a dose to the tracheobronchial region. Dose to this region is attributable to material inhaled and deposited in the tracheobronchial region and from material cleared from the pulmonary region through the tracheobronchial region to the gastro-intestinal tract. This latter pathway is valid from class *W* and *Y* materials only. Dose to the tracheobronchial region is described in the following equations:

$$\text{Direct dose}_{\text{T-B}}(\text{rems}) = \frac{51\ I\ E}{m}\ D_{\text{T-B}}\left(f_{\text{c}} \frac{1 - e^{-\lambda_c T}}{\lambda_{\text{c}}} + f_d \frac{1 - e^{-\lambda_d T}}{\lambda_{\text{d}}}\right) \quad (2)$$

$$\text{Indirect dose}_{\text{T-B}}(\text{rems}) = \frac{51\ I\ E\ t}{m}\ D_{\text{P}}\left(f_f \lambda_f{}^b \frac{1 - e^{-\lambda_f T}}{\lambda_f} + f_g \lambda_g{}^b \frac{1 - e^{-\lambda_g T}}{\lambda_g}\right) \quad (3)$$

The dose to the pulmonary region is:

$$\text{Dose}_{\text{P}}(\text{rems}) = \frac{51\ I\ E}{m}\ D_{\text{P}}\left(f_e \frac{1 - e^{-\lambda_e T}}{\lambda_e} + f_f \frac{1 - e^{-\lambda_f T}}{\lambda_f} + f_g \frac{1 - e^{-\lambda_g T}}{\lambda_g} + f_h \frac{1 - e^{-\lambda_h T}}{\lambda_h}\right) \quad (4)$$

Thyroid dose must consider transfer from the region of deposition to the blood stream (direct and via G. I. tract) and, hence, from the blood stream to the thyroid gland. Dose is expressed as:

$$\text{Dose}_{\text{T}h}(\text{rems}) = \frac{51\ I\ E}{m}\ D_{\text{N-P, T-B, P}}\left(f_{\text{th}} \frac{1 - e^{-\lambda_{\text{th}} T}}{\lambda_{\text{th}}}\right) \quad (5)$$

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Effects of Acute Hydrogen Fluoride and Nitrogen Dioxide Exposures on Citrus and Ornamental Plants of Central Florida

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■ Six citrus varieties and six ornamental species of economic importance to central Florida were subjected to high concentration–short duration exposures of gaseous hydrogen fluoride (HF) or nitrogen dioxide (NO_2). Postfumigation observations showed that the effects of acute pollutant exposures differ markedly from those of chronic exposures. HF exposures of 0.5 to 10 p.p.m. for periods of from 0.5 to 8 hours induced tip, marginal, and intercostal chlorosis and necrosis, and abscission of leaves of most plants tested. Symptoms were most severe on, but not limited to, young leaves. The effect of duration of exposure had a greater influence on abscission of young citrus leaves than did HF concentration. However, the effect of HF concentration on foliar F accumulation could not be separated from exposure time. The NO_2 concentrations used ranged from 25 to 250 p.p.m. for periods of from 10 minutes to 8 hours. NO_2 damage was characterized by rapid tissue collapse, necrosis, and defoliation. Symptoms were sporadic in appearance, affecting leaves of all ages. The relative contributions of concentration and duration to NO_2-induced injury were about equal.

Atmospheric hydrogen fluoride (HF) is toxic to many plant species. Exposures as low as 1 to 9 p.p.b. for 6 or 7 days have been shown to induce appreciable visible symptoms of injury on several gladiolus varieties (Hitchcock, Zimmerman, *et al.*, 1962). Therefore, most experimental fumigations with HF have employed exposures in the parts per billion range to simulate conditions that might occur under ambient atmospheric contamination. Reports of acute HF exposures (high concentration, short duration) are limited in number. Daines, Leone, *et al.* (1952) induced severe foliar necrosis on peach trees with 12 p.p.m. of HF for 3 hours and on tomato plants with 1.5 p.p.m. for 2 hours. Rice and barley plants were killed by 2000 p.p.m. HF, and yields were significantly reduced by 25 p.p.m. for 1 hour (Yamazoe, 1962).

Nitrogen oxides are much less phytotoxic than equivalent concentrations of HF. Pinto bean plants were visibly damaged by exposure to 3 p.p.m. nitrogen dioxide (NO_2) for 4 to 8 hours (Middleton, Darley, *et al.*, 1958). Mustard and sunflower, the most sensitive of 10 weed species tested by Benedict and Breen (1955), required 50 p.p.m. NO_2 for 4 hours to induce damage. Growth suppression and foliar distortion, without concomitant necrosis, were observed by Taylor and Eaton (1966) on tomato and Pinto bean plants exposed to less than 0.5 p.p.m. for 10 to 22 days.

The limited probability of an accidental release of large quantities of HF or NO_2 to the atmosphere prompted the studies reported herein. Experimental fumigations using acute HF and NO_2 exposures were performed to catalog the symptoms of acute pollutant-induced plant damage, and to separate, if possible, the contributions of pollutant concentration and duration of exposure on citrus and ornamental plants of economic importance in central Florida.

Materials and Methods

Plant Materials. Uniform, container-grown plants of six citrus varieties (five *Citrus sinensis*, one *C. paradisi*) and 14 ornamental species, selected for their economic importance in central Florida, were obtained from a commercial nursery. Citrus trees were 3-year-old grafts on sour orange stock. Plants of each ornamental species were of similar size, age, and vigor. In all fumigations, plants were placed in the fumigation chambers according to a predetermined statistical design.

Hydrogen Fluoride. Gaseous HF was injected into portable fumigation chambers (Hitchcock, Zimmerman, *et al.*, 1963) modified to include an air recirculating system. The return line had provision for inserting a calcium hydroxide–impregnated polyethylene screen eight layers in thickness, to scrub fluoride from the recirculated air. Fluoride concentrations within the chamber were continuously monitored using the method described by MacLean, Weinstein, *et al.* (1967).

Nitrogen Dioxide. NO_2 concentrations were achieved by introducing gas from a cylinder containing liquid nitrogen tetroxide (N_2O_4) under pressure through two needle valves (in series) and 0.125-inch I.D. Teflon tubing into the air stream of the fumigation chamber blower. The cylinder was maintained at or above 25° C. by means of a flexible heating tape to vaporize N_2O_4 to NO_2. By manipulating the needle valves, the rate of NO_2 injection was manually increased or decreased as dictated by a continuous recording NO_2 monitor

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(BillionAire Analyzer, Mine Safety Apparatus, equipped with a Bausch and Lomb potentiometric chart recorder). The chamber used in NO_2 fumigations was equipped with a recirculating system without a scrubber.

Results

Preliminary Fumigations. Two plants each of Hamlin and Valencia orange, *Ixora coccinea*, and *Hibiscus rosa-sinensis* were used in preliminary fumigations with HF and NO_2 to determine the concentrations and durations of exposure necessary to induce visible plant responses ranging from no injury to severe damage.

Fumigations with HF included 18 exposures ranging from 0.5 p.p.m. hours (0.5 p.p.m. for 1 hour) to 40 p.p.m. hours (10 p.p.m. for 4 hours). The lowest exposure was not injurious to Valencia orange trees or to hibiscus or ixora plants, but slight tip and marginal chlorosis was induced on approximately 20% of the young leaves of Hamlin orange trees. The most acute exposure resulted in damage to all plants. This consisted of complete defoliation of young leaves, necrosis of succulent shoots, abscission of all young fruit, and moderate intercostal necrosis of the older foliage of both citrus varieties. All hibiscus leaves were severely necrotic, brown, and desiccated. Foliar necrosis of ixora plants was most pronounced at the terminal portions of stems and became generally less severe toward the base of the plants. Many of these symptoms were evident within 1 hour after fumigation. Exposure values between these extremes resulted in plant damage of intermediate severity.

The 13 preliminary NO_2 exposures ranged from 10 p.p.m. hours (40 p.p.m. for 0.25 hour) to 375 p.p.m. hours (150 p.p.m. for 2.5 hours). However, concentrations of 25 to 250 p.p.m. NO_2 and durations up to 8 hours, providing p.p.m. hours values between these extremes, were also included in these fumigations. No visible symptoms were evident on plants exposed to the lowest NO_2 exposure, but the highest exposure resulted in necrosis on 90 to 100% of the surface area of all leaves of hibiscus and ixora plants. On Valencia and Hamlin orange trees there was complete necrosis of young leaves and defoliation of 90 to 100% of older leaves. The remaining exposures resulted in injury between these extremes.

Screening of Ornamental Plants. Five replicate plants of each of 14 ornamental species commonly grown in central Florida were exposed to the seven HF and nine NO_2 fumigations listed in Table I to ascertain their relative sensitivities to the pollutants. The magnitude of pollutant-induced injury was assessed by subjective rankings of foliar chlorosis or necrosis, defoliation, and, where applicable, fruit or flower abscission. Plants were then placed in the three arbitrary categories listed in Table II based on their susceptibility. Two species from each of the categories were selected for intensive testing.

Effects of HF and NO_2 on Selected Citrus and Ornamental Plants. The final series of fumigations were designed to determine the nature and extent of plant reaction induced by acute pollutant exposures.

Three replicate plants of each of the six citrus varieties and six ornamental species, selected as described above (see Table II), were provided the 15 HF and 13 NO_2 fumigations described in Table III. In most cases, concentrations and durations were selected so that two or more different concentra-

Table I. Fumigations Used to Determine the Relative Sensitivity of Ornamental Plants

Pollutant	Concentration, P.P.M.	Duration, Hours	Exposure Value, P.P.M. Hours
HF	0.3	2	0.6
	0.5	2	1
	1.5	4	6
	4	2	8
	2	4	8
	6	1	6
	8	4	32
NO_2	10	8	80
	25	6	150
	30	4	120
	40	3	120
	50	1.7	85
	100	1	100
	150	0.7	105
	200	0.3	60
	250	0.2	50

Table II. Relative Sensitivity of 14 Ornamental Species to Hydrogen Fluoride and Nitrogen Dioxide

Very Sensitive	Moderately Sensitive	Relatively Resistant
	HYDROGEN FLUORIDE	
Azalea (*Rhododendron canescens*)[a]	Oleander (*Nerium oleander*)	Croton (*Codiaeum variegatum*)[a]
Bougainvillea (*B. spectabilis*)	Cape jasmine (*Gardenia radicans*)	Carissa (*C. carandas*)[a]
Melaleuca (*M. leucadendra*)[a]	Pittosporum (*P. tobira*)	
Pyracantha (*P. coccinea*)	Shore juniper (*Juniperus conferta*)	
Gardenia (*G. jasminoides*)	Hibiscus (*H. rosa-sinensis*)[a]	
	Ligustrum (*L. lucidum*)	
	Ixora (*I. coccinea*)[a]	
	NITROGEN DIOXIDE	
Azalea (*Rhododendron canescens*)[a]	Pittosporum (*P. tobira*)	Carissa (*C. carandas*)[a]
Oleander (*Nerium oleander*)	Melaleuca (*M. leucadendra*)[a]	Croton (*Codiaeum variegatum*)[a]
Bougainvillea (*B. spectabilis*)	Ligustrum (*L. lucidum*)	Shore juniper (*Juniperus conferta*)
Pyracantha (*P. coccinea*)	Ixora (*I. coccinea*)[a]	
Hibiscus (*H. rosa-sinensis*)[a]	Cape jasmine (*Gardenia radicans*)	
	Gardenia (*G. jasminoides*)	

[a] Species selected for further study.

Table III. Final Series of Plant Fumigations with Hydrogen Fluoride and Nitrogen Dioxide

Pollutant	Concentration, P.P.M.	Duration, Hours	Exposure Value, P.P.M. Hours
HF	0.5	2	1
	0.5	4	2
	0.5	8	4
	1	2	2
	1	4	4
	1	8	8
	2	1	2
	2	2	4
	2	4	8
	4	1	4
	4	4	16
	4	8	32
	8	0.5	4
	8	1	8
	8	4	32
NO_2	25	4	100
	25	8	200
	50	2	100
	50	4	200
	50	8	400
	100	0.5	50
	100	1	100
	100	2	200
	150	2	300
	150	4	600
	200	0.5	100
	200	1	200
	250	1	250

tions and times of exposure resulted in the same total exposure values when expressed as p.p.m. hours. In this way, the existence of reciprocity between these two parameters, as they affect plant injury, could be determined.

Postfumigation observations of all plants were made to assess the nature and extent of the pollutant-induced chlorosis, necrosis, defoliation, and flower and fruit abscission.

Hydrogen Fluoride

Citrus Varieties. The six citrus varieties tested were all susceptible to HF, and the general pattern and progression of visible symptoms of injury were similar for all varieties; however, varietal differences in the extent and severity of HF-induced damage were obvious. The varieties are listed below in order of decreasing sensitivity to HF: Marsh seedless grapefruit, Pineapple orange, Temple orange, Tangelo orange, Hamlin orange, and Valencia orange.

The physiological age of citrus leaves affected their sensitivity to HF. For the purposes of this discussion, citrus leaves are divided into three age groups: expanding young leaves—i.e., those arising from nodes at or near the terminal buds—expanded young leaves—i.e., leaves produced during the current growing season but having attained full size—and old leaves—i.e., leaves produced during previous growing seasons.

To facilitate the description of HF-induced injury to citrus trees, the damage observed on relatively mild, moderate, and severe exposures will be described in general terms.

General chlorosis of expanding young leaves, which was more pronounced toward the leaf tip, and chlorosis localized at the tip and along the margins of expanded leaves were the first obvious symptoms of relatively mild HF exposures (1 or 2 p.p.m. hours). When the HF concentration was increased or the exposure time extended, wilting, marginal tissue collapse, or saturation of intercellular spaces with water were apparent within a relatively short time after fumigations. These damaged areas usually became necrotic. Occasional damage of intercostal leaf tissues and defoliation of young leaves also were noticed.

Fumigations with relatively high exposures of HF (16 or 32 p.p.m. hours) resulted in extensive abscission of young leaves and developing fruits. When young leaves were damaged by abscission, separation usually occurred at the base of the leaf blade, leaving the petioles intact. Abscission of older leaves was in the normal manner, at the base of the petiole. Defoliation usually occurred after visible symptoms of injury were evident; however, in many cases young leaves that showed no symptoms of injury were readily damaged by abscission.

Leaves remaining on plants subjected to relatively high HF exposures often displayed symptoms of severe tip, marginal, and intercostal necrosis, as well as cupping and other distortions. Necrosis and wilting of succulent portions of elongating shoots were also observed.

Defoliation was the most obvious effect on citrus plants and the same response, differing only in magnitude, was observed on all varieties. The percentages of HF-induced abscission of young leaves of the six citrus varieties were pooled, and the average percentage of defoliation for each exposure is shown in Figure 1. Reciprocity between pollutant

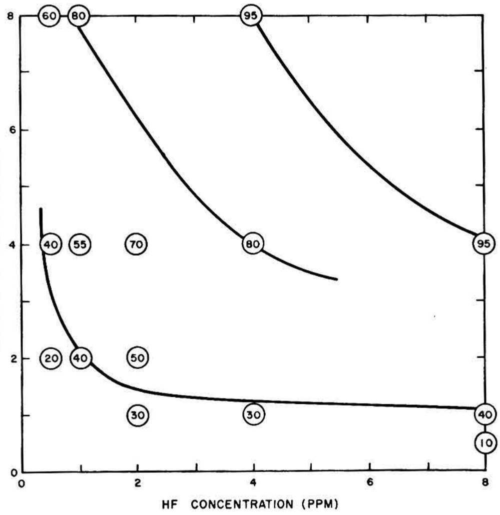

Figure 1. Percentage of defoliation of young citrus leaves induced by various acute HF exposures

○ Specific concentrations and durations of exposure provided
No. average per cent abscission of young leaves of six citrus varieties (to the nearest 5%)
—— Connection of 40, 80, and 95% defoliation values

concentration and duration of exposure for leaf abscission was not consistent over all concentrations and times. Defoliation of young leaves was essentially complete (95%) when exposed to 32 p.p.m. hours fumigations (8 p.p.m. for 4 hours and 4 p.p.m. for 8 hours). Reciprocal fumigations—i.e., those in which the same exposure value (p.p.m. hours) was provided by reversing the concentration and duration values—indicated that the duration of exposure exerted a greater effect in inducing leaf abscission than did concentration. For example, 1 p.p.m. for 8 hours and 1 p.p.m. for 4 hours were about two times more effective than 8 p.p.m. for 1 hour and 4 p.p.m. for 1 hour, respectively. The effect of duration on abscission was six times that of concentration when fumigations providing 8 p.p.m. for $^{1}/_{2}$ hour and 0.5 p.p.m. for 8 hours were compared. However, in fumigations of 2 p.p.m. for 1 hour and 1 p.p.m. for 2 hours, the contribution of concentration was only slightly greater than duration (Figure 1).

Thus, for citrus plants exposed to acute HF levels below those required for complete defoliation, the duration of exposure was more effective than concentration, and the greater the difference between the values for time and concentration, the greater the contribution of duration.

Ornamental Species. Azalea was the most HF-sensitive species tested. The lowest exposure (0.5 p.p.m. for 2 hours) resulted in necrotic areas covering 10 to 40% of the surface of all young expanding leaves. Occasional necrosis also was observed on older leaves. An HF exposure of 1 p.p.m. for 4 hours resulted in moderate to severe defoliation and severe tip and marginal necrosis of remaining leaves. Exposures providing 8 or more p.p.m. hours were extremely phytotoxic.

Carissa plants were relatively insensitive to HF. The two highest exposures (4 p.p.m. for 8 hours and 8 p.p.m. for 4 hours) were the only fumigations to induce visible symptoms. The observed injury was limited to slight tip necrosis and intercostal necrotic spotting on young expanding leaves. No defoliation occurred. None of the other exposures induced visible damage.

The variegated pigment pattern of croton foliage made evaluation of visible effects difficult. Critical inspection of these plants revealed some minor tip and marginal necrosis on expanding leaves of plants exposed to the highest dosages of HF (32 p.p.m. hours). Following exposure to 8 or 16 p.p.m. hours, no leaf markings were evident, but appreciable defoliation of older leaves was observed. Croton plants receiving lower levels of HF were not visibly affected.

The foliage of hibiscus plants was visibly affected at all concentrations and durations employed. Symptoms ranged from mild chlorosis induced by low dosages to severe necrosis of 80% of the leaves of all ages at the higher levels. Defoliation was not readily induced. Leaves that were killed often remained attached to the plant for more than 1 week. Postfumigation growth of severely marked plants appeared normal.

Exposures of 1, 2, and 4 p.p.m. hours did not materially affect ixora plants. When fumigated for 8 hours with HF at 1 p.p.m. severe marginal and tip necrosis was observed on 75% of the young and middle-aged leaves, which would defoliate readily when touched. Older foliage showed only slight necrotic spotting. The reverse exposure (8 p.p.m. for 1 hour) induced only slight marginal necrosis.

Complete necrosis of Melaleuca foliage occurred within 7 days after the mildest fumigation (0.5 p.p.m. HF for 2 hours). All other exposures were equally phytotoxic.

Tissue Analyses. Fluoride will be adsorbed on surface tissues of plants exposed to HF. This surface fluoride may be relatively nontoxic but serves as a source of internal (absorbed) fluoride. In chronic exposures (long duration, low concentration) of plants to HF, absorbed fluoride is readily transported to the terminal portion of the leaf via the transpirational stream where it accumulates (Thomas, 1961). Little is known of the foliar absorption of fluoride during acute HF exposures. Therefore, to determine absorption, each plant was sampled from eight sectors, representing the four upper and four lower quadrants of the branch structure. A total of 8 to 16 leaves from the eight sectors constituted a sample for fluorine (F) analysis. The number of sampled leaves was kept small purposely to minimize damage due to defoliation and to allow for continual observation of the experimental plants.

Two samples were taken from each plant; one sample was washed for 30 seconds in an aqueous Alconox/EDTA solution [0.05% Alconox, w./v.; 0.05% tetrasodium (ethylenedinitrilo)tetraacetate, w./v.] and rinsed three times in deionized water for 30 seconds each. The washed sample was used to estimate the absorbed (internal) F content, and the other, which was not washed, served as an estimate of the total F content (external plus internal). Fluorine was determined by the semiautomated method of analysis (Mandl, Weinstein, *et al.*, 1966; Weinstein, Mandl, *et al.*, 1963).

Mean values for total F and absorbed F in leaves of plants exposed to each of the fumigations are plotted in Figures 2 and 3. The correlation between the F content of washed and unwashed foliage samples was determined for the pooled data for the six citrus varieties and the six ornamental species and for each species and variety individually (Table IV). In every case, there was a significant positive correlation between total F content (unwashed leaves) and the internal F concentration (washed leaves).

Table IV. Linear Regressions for Mean Values of Fluoride Content of Unwashed and Washed Leaf Tissue of HF-Fumigated Plants

Tissue	Regression Equation[a]	Correlation Coefficient	Number of X, Y Pairs
Citrus varieties, pooled	$\hat{Y} = 46.01 + 1.44x$	0.924	88
Hamlin orange	$\hat{Y} = 52.80 + 1.38x$	0.943	15
Valencia orange	$\hat{Y} = 71.53 + 1.17x$	0.867	15
Temple orange	$\hat{Y} = 31.99 + 1.55x$	0.949	15
Pineapple orange	$\hat{Y} = 37.12 + 1.50x$	0.957	15
Tangelo orange	$\hat{Y} = 37.46 + 1.72x$	0.911	14
Marsh grapefruit	$\hat{Y} = 40.08 + 1.38x$	0.947	14
Ornamental species, pooled	$\hat{Y} = 34.80 + 1.35x$	0.956	90
Azalea	$\hat{Y} = 57.56 + 1.18x$	0.960	15
Carissa	$\hat{Y} = 23.90 + 1.36x$	0.897	15
Croton	$\hat{Y} = 40.25 + 1.44x$	0.943	15
Hibiscus	$\hat{Y} = 66.61 + 1.36x$	0.965	15
Ixora	$\hat{Y} = -4.01 + 1.61x$	0.885	15
Melaleuca	$\hat{Y} = 11.95 + 1.25x$	0.978	15

[a] $\hat{Y} = a + bx$ where x = fluorine content of washed leaves and $\hat{Y}$ = fluorine content of unwashed leaves.

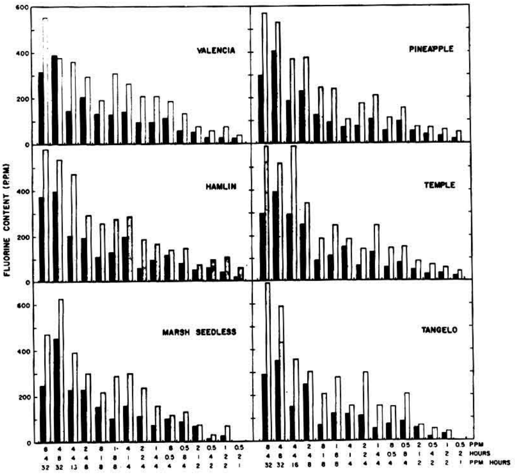

Figure 2. Fluorine content (p.p.m. dry weight) of washed (solid) and unwashed (shaded) leaves of six citrus varieties as affected by HF exposure

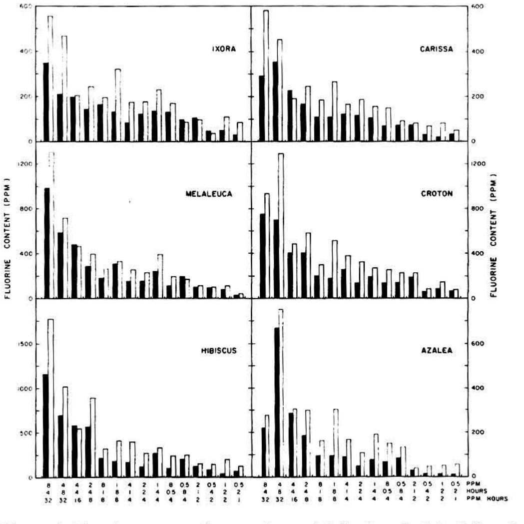

Figure 3. Fluorine content (p.p.m. dry weight) of washed (solid) and unwashed (shaded) leaves of six ornamental species as affected by HF exposure

When the six citrus varieties were compared without regard to exposure levels, 52 to 59% of the foliar F accumulated was absorbed—i.e., not removed by washing—suggesting that accumulation and absorption were similar for all varieties. When the various exposures were compared, disregarding variety, 41 to 76% of the total F was absorbed. However, there was no consistent effect of either HF concentration or duration of exposure on the per cent of accumulated F that was absorbed by citrus leaves. Similar results were obtained with the ornamental plants.

Although there was a general reduction in the tissue F content with decreasing exposure value (Figures 2 and 3), the contribution of HF concentration or duration of exposure within a given exposure value was not consistent for all species or varieties. Thus, in relation to the amounts of F accumulated or absorbed, reciprocity between exposure time and HF concentration did not exist.

Differences in the amounts of F absorbed or accumulated in foliage during these acute fumigations did not follow the general patterns observed in chronic exposures. Usually, resistant plant species are capable of accumulating large amounts of F without expressing symptoms of injury, whereas leaves of susceptible species often become chlorotic or necrotic when lower foliar F concentrations are attained. This relationship did not prevail in these tests. Hibiscus plants were very susceptible to HF but accumulated more F than the relatively resistant croton plants. Similarly, azalea, which was the most HF-sensitive species tested, accumulated more foliar F than carissa plants, the most resistant species (Figure 3).

Nitrogen Dioxide

The manner in which atmospheric NO_2 is absorbed and translocated by plants is not known because of the high endogenous nitrogen content and the diverse nature of nitrogen-containing compounds in plant tissues. However, the nonspecific marginal and intercostal necrosis induced by acute exposures to NO_2 suggested that it was not transported via the transpirational stream.

The effects of NO_2 in these experiments were often visible at the end of 1-hour exposures. Tissue collapse and a water-logged appearance were first evident on the upper leaf surfaces, suggesting initial damage to the palisade cells. In time, these areas extended through the leaf and became necrotic.

Citrus Varieties. Injury to citrus plants by NO_2 was characterized by wilting and defoliation of young leaves. Remaining young leaves and the older leaves developed areas of intercostal and marginal necrosis. Exposure to 200 p.p.m. for 4 to 8 hours or 250 p.p.m. for 1 hour resulted in necrotic areas along many succulent young shoots. The extent of defoliation and necrosis was dependent upon the variety. The varieties are listed below in order of decreasing sensitivity to NO_2: Marsh seedless grapefruit, Pineapple orange, Valencia orange, Tangelo orange, Hamlin orange, and Temple orange.

The severity of abscission varied with variety, but the general response of all varieties was similar. Therefore, the percentage of young leaves defoliated from each variety was averaged for each of the 13 NO_2 exposures (Figure 4). Abscission increased with time at all concentrations and increased with concentration at any given exposure period. Forty-five per cent abscission of young citrus leaves was induced by two fumigations providing 200 p.p.m. hours—i.e., 25 p.p.m. for 8

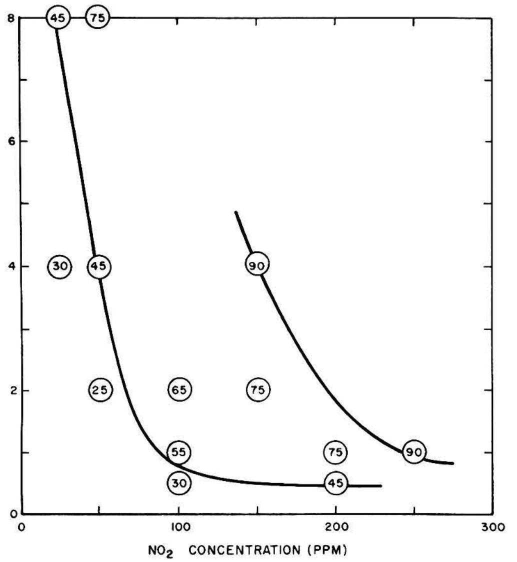

Figure 4. Percentage of defoliation of young citrus leaves induced by various acute NO$_2$ exposures

○ Specific concentrations and durations of exposure provided
No. Average per cent abscission of young leaves of six citrus varieties (to the nearest 5 %)
—— Connection of 45 and 90 % abscission values

hours and 50 p.p.m. for 4 hours. Forty-five per cent defoliation was also induced by an exposure of only 100 p.p.m. hours (200 p.p.m. for $^1/_2$ hour). Other fumigations providing 200 p.p.m. hours, as 100 p.p.m. for 2 hours and 200 p.p.m. for 1 hour, induced 65 and 75% abscission, respectively. The pattern of defoliation, therefore, indicated that the contributions of time and NO$_2$ concentration were approximately equal (Figure 4).

Ornamental Species. Azalea plants were extremely sensitive to NO$_2$ exposure. The progression of injury was characterized by rapid tissue collapse of leaves of all ages which rapidly became necrotic and desiccated. Severe defoliation was common.

Exposure of croton plants to 150 p.p.m. NO$_2$ for 4 hours and 50 p.p.m. for 8 hours induced slight intercostal necrosis on leaves of this relatively resistant species. All other fumigations were without effect.

Hibiscus plants were severely injured by all but the mildest NO$_2$ fumigations. The first apparent symptoms were intercostal areas of tissue collapse limited to the upper leaf surfaces. With time, these areas became necrotic and were visible on the lower leaf surfaces as well. Relatively high NO$_2$ exposure induced complete necrosis followed by desiccation and eventual abscission.

NO$_2$-induced damage in ixora was characterized by chocolate-brown marginal and intercostal necrosis of leaves of all ages. Damage was most severe on older foliage.

Melaleuca plants were severely damaged by NO$_2$. Injury was characterized by the rapid development of a general desiccation and necrosis of leaves of all ages.

Carissa plants were insensitive to NO$_2$ at the exposures provided.

Recovery. Although defoliation and/or necrosis was complete in several instances, all citrus and ornamental plants survived HF and NO$_2$ fumigation regardless of exposure. Normal postfumigation growth occurred from axillary buds and was evident within 2 to 6 weeks after fumigation. Long-term effects on subsequent plant growth, vigor, and yield were not assessed.

Discussion

Plant responses to acute pollutant exposures differ markedly from chronic exposure effects. For example, chronic NO$_2$-induced plant damage has been described (Benedict and Breen, 1955) as areas of tissue collapse, necrosis, and a general over-all waxy appearance on leaves. Acute NO$_2$ exposures induced similar responses; however, these appeared soon after fumigation and became rapidly accentuated. Defoliation was also induced readily. Young citrus leaves were most sensitive to acute NO$_2$ exposures, but leaves of all ages were affected. Tissue age was not necessarily a factor for NO$_2$-induced damage to most ornamental species. Chronic exposures to HF infrequently injure mature tissues, and damage to young foliage usually progresses from marginal and tip chlorosis to necrosis. Acute exposures, however, often induced defoliation and/or rapid necrosis without chlorosis. Although young foliage was most sensitive, chlorosis and necrosis of older tissues were readily induced by acute HF exposure.

Severe defoliation and/or foliar necrosis and chlorosis were observed on plants containing quantities of F that, if accumulated over longer periods, would induce little or no visible damage. Under chronic exposure conditions F is gradually absorbed by foliage and transported to the tips and margins of leaves. During this time much of the absorbed fluoride is probably complexed at cationic sites rendering it ineffective. However, in acute exposures active metabolic sites probably become "saturated" with F and injury ensues.

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Gas Chromatography of Pesticide Residues Containing Phosphorus or Sulfur with the Flame Photometric Detector

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■ The flame photometric detector of Brody and Chaney has been used to analyze residues of phosphorus- and sulfur-containing pesticides and their metabolites. Little or no cleanup was required, and compounds could be eluted quickly because extraneous material caused no appreciable interference. Conditions for the gas chromatography of the phosphorus compounds are given. Recoveries generally exceeded 90%, and sensitivities were 0.01 p.p.m. or less. The detector is easy to operate and maintain; it is not contaminated by column bleed or by unclean extracts; its response may be attenuated; the switch from sulfur to phosphorus sensing can be accomplished in less than a minute; relative response of phosphorus to nonphosphorus compounds is very high. Derivatives of carbamate residues containing phosphorus or sulfur have also been analyzed. The detector appears to have broad applicability to the analysis of multicomponent residues, identification of insecticides, and monitoring of environmental samples.

A concerted effort is being made within our agricultural and scientific community to replace chlorinated hydrocarbon insecticides with the less persistent carbamate and phosphorus-containing insecticides. As a consequence of these efforts, attention during the past few years has been focused on the need for analytical methodology to assure the safe usage of these materials.

Just a few years ago, quantitative analysis of phosphorus insecticides was accomplished mostly by colorimetric, spectrophotometric, or enzymatic (cholinesterase inhibition) means. These procedures often lacked specificity and sensitivity, and a rigorous cleanup was usually required to obtain valid results. Gas chromatographic procedures that were developed were limited to the thionophosphate (P═S) or halogen-containing insecticides to which electron-capture detectors respond with high sensitivity. Following the appearance of this analytical methodology, many reports detailing the amounts of these pesticides remaining in various crops appeared; but the fact is that these insecticides often change or metabolize in plants and animals to compounds more toxic than the parent insecticide, and these compounds may not be detected. Although this fact was recognized, many metabolites were not determined simply because the means of estimating their presence were not available.

Early in 1966, Brody and Chaney reported the development of a flame photometric detector that was highly sensitive to compounds containing phosphorus or sulfur. With an interference filter passing light of 526 mμ, the detector responded to phosphorus compounds; with a 394-mμ filter it detected sulfur compounds. The detector (MicroTek Instrument Corp., Baton Rouge, La.) may be attached readily to most gas chromatographs.

When this detector became available, the authors were interested in determining its suitability for analyzing residues of the oxygen analogs (P═O) of thionophosphate (P═S) insecticides since the oxygen analogs formed from the thionophosphates are more toxic than the parent insecticides. Also, the detector might be generally useful for determining phosphorus compounds not containing electron-capturing groups and for determining those containing sulfur.

The detector proved effective in the analysis of a wide variety of compounds. As little as 0.1 ng. of phosphorus compounds and 2 to 5 ng. of sulfur compounds could be detected (twice noise level). Response of the phosphorus compounds in terms of peak height was linear over at least three decades of concentration. The response of the sulfur detector was not linear; a calibration curve relating concentration to response was used for quantitation. The high specificity of the detector made it remarkably insensitive to the extraneous material present in crop extracts.

This paper reviews applications of the flame photometric detector to the analysis of pesticide residues, with particular emphasis being placed on the gas chromatography of the phosphate insecticides. At this writing the authors are not aware of reports on pesticide residue analyses with this detector except those from this division. Since the thermionic detector may also be used to determine phosphorus insecticides (Giuffrida, Ives, *et al.*, 1966), many of the procedures described here may also be useful with that detector or one of its modifications. The chemical names of pesticides mentioned are given in Table I. Other procedures for the analysis of these compounds are cited in the references given in Table II. Some early applications of the detector to pesticide residue analysis have been described by Brody and Chaney (1966) and by Getz (1967).

Conditions for Gas Chromatographing Phosphorus Insecticides

Early attempts in this laboratory to use gas chromatography for the analysis of residues of phosphorus insecticides with the flame photometric detector gave no difficulties with P═S insecticides, but resulted in much difficulty with P═O insecticides. This situation pointed out a serious defect in analytical capabilities because, as noted, the P═O insecticides

Table I. Chemicals Cited in Text

Insecticides	
Aldrin	1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene
Azinphosmethyl	*O*,*O*-Dimethyl phosphorodithioate *S*-ester with 3-(mercaptomethyl)-1,2,3-benzotriazin-4(3*H*)-one
Azodrin	3-Hydroxy-*N*-methyl-*cis*-crotonamide dimethyl phosphate
Banol	6-Chloro-3,4-xylyl methylcarbamate
Bay 30911	*O*,2,4-Dichlorophenyl *O*-methyl methylphosphonothioate
Bay 37344	4-(Methylthio)-3,5-xylyl methylcarbamate
Bay 39007	*o*-Isopropoxyphenyl methylcarbamate
Bidrin	3-Hydroxy-*N*,*N*-dimethyl-*cis*-crotonamide dimethyl phosphate
Carbaryl	1-Naphthyl methylcarbamate
Carbophenothion	*S*-{[(*p*-Chlorophenyl)thio]methyl} *O*,*O*-diethyl phosphorodithioate
Chevron RE-5353	*m*-(1-Methylbutyl)phenyl methylcarbamate
Ciba C-9491	*O*-(2,5-Dichloro-4-iodophenyl) *O*,*O*-dimethyl phosphorothioate
Ciba C-9491 (O-analog)	2,5-Dichloro-4-iodophenyl dimethyl phosphate
Compound 4072	2-Chloro-1-(2,4-dichlorophenyl)-vinyl diethyl phosphate
Coumaphos	3-Chloro-7-hydroxy-4-methylcoumarin *O*,*O*-diethyl phosphorothioate
Coumaphos (O-analog)	3-Chloro-7-hydroxy-4-methylcoumarin diethyl phosphate
Diazinon	*O*,*O*-Diethyl *O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate
Diazoxon	Diethyl 2-isopropyl-6-methyl-4-pyrimidinyl phosphate
Dursban	*O*,*O*-Diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate
Dursban (O-analog)	Diethyl 3,5,6-trichloro-2-pyridyl phosphate
EPN	*O*-Ethyl *O*-*p*-nitrophenyl phenylphosphonothioate
Ethion	*O*,*O*,*O*′,*O*′-Tetraethyl *S*,*S*′-methylene phosphorodithioate
Fenthion	*O*,*O*-Dimethyl *O*-[4-(methylthio)-*m*-tolyl]phosphorothioate
Hercules 5727	*m*-Cumenyl methylcarbamate
Hercules 9699	*o*-(2-Propynyloxy)phenyl methylcarbamate
Imidan	*O*,*O*-Dimethyl *S*-phthalimidomethyl phosphorodithioate
Imidoxon	*O*,*O*-Dimethyl *S*-phthalimidomethyl phosphorothioate
Lindane	1,2,3,4,5,6-Hexachlorocyclohexane, gamma isomer
Malathion	Diethylmercaptosuccinate *S*-ester with *O*,*O*-diethyl phosphorodithioate
Mala-oxon	Diethyl mercaptosuccinate *S*-ester with *O*,*O*-diethyl phosphorothioate
Methyl parathion	*O*,*O*-Dimethyl *O*-*p*-nitrophenyl phosphorothioate
Methyl Trithion	*S*-{[(*p*-Chlorophenyl)thio]methyl} *O*,*O*-dimethyl phosphorodithioate
Mobil MC-A-600	Benzo[*b*]thien-4-yl methylcarbamate
Niagara NIA-10242	2,3-Dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate
Parathion	*O*,*O*-Diethyl *O*-*p*-nitrophenyl phosphorothioate
Phorate	*O*,*O*-Diethyl *S*-[(ethylthio)methyl] phosphorodithioate
Ruelene	4-*tert*-Butyl-2-chlorophenyl methyl methylphosphoramidate
Shell SD-8447	2-Chloro-1-(2,4,5-trichlorophenyl)-vinyl dimethyl phosphate
Stauffer N-2788	*O*-Ethyl *S*-*p*-tolyl ethylphosphonodithioate
Union Carbide UC-21149 (Temik)	2-Methyl-2-(methylthio)propionaldehyde *O*-(methylcarbamoyl)-oxime
UC-21149 sulfoxide	2-Methyl-2-(methylsulfinyl)-propionaldehyde *O*-(methylcarbamoyl)oxime
UC-21149 sulfone	2-Methyl-2-(methylsulfonyl)-propionaldehyde *O*-(methylcarbamoyl)oxime
Zinophos	*O*,*O*-Diethyl *O*-2-pyrazinyl phosphorothioate
Chemosterilants	
Apholate	2,2,4,4,6,6-Hexakis(1-aziridinyl)-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorine
Hempa	Hexamethylphosphoric triamide
Metepa	Tris(2-methyl-1-aziridinyl)phosphine oxide
Methiotepa	Tris(2-methyl-1-aziridinyl)phosphine sulfide
Tepa	Tris(1-aziridinyl)phosphine oxide
Other	
1-Naphthol	1-Naphthol
NIA-10272	2,3-Dihydro-2,2-dimethyl-7-benzofuranol

Table II. Gas Chromatographic Analysis of Insecticid

Compounds	Extraction Solvent	Adsorbent and Eluents for Liquid Chromatography	Gas Chromatographic Conditions[b]			Retention Time, Min.	Products Analyzed[c]	Reference
			Liquid phase	Column length, cm.	Column temp., ° C.			
			Insecticides—Phosphorus Detector					
Azodrin, Bidrin	$CHCl_3$	None	1% Carb 20M	45	170, 150	2.0, 1.5	Sweet corn	Bowman and Beroza (1967a)
Ciba C-9491 and O-analog	Benzene	5 grams of SG, 5 grams of alum-benz, acet, MeOH	10% DC-200	50	160	4.4, 3.5	Corn (milk)	Bowman and Beroza (1968a)
Coumaphos and O-analog	$CHCl_3$	5 grams of SG-benz, acet and partition	10% DC-200	50	210	4.0, 3.3	Feces (milk)	Bowman, Beroza, *et al.* (1968)
Diazinon and diazoxon	CH_3CN	None (solvent partition used)	2% DEGS	61	165	2.4, 3.9	Corn	Corley and Beroza (1968)
Dursban and O-analog	Benzene	10 grams of SG–benz, acet	5% DC-200	45	150	1.95, 1.85	Corn, grass	Bowman and Beroza (1967b)
Fenthion and five metabolites	Benzene	4 grams of SG-1 and 10% acet-benz, acet	10% DC-200	90	210	1.75 ...	Corn, grass (milk)	Bowman and Beroza (1968b)
Imidan and Imidoxon	Benzene	10 grams of SG–10% acet-benz, acet	10% DC-200	45	200	2.8, 2.1	Sweet corn	Bowman and Beroza (1966b)
Malathion and mala-oxon	CH_3CN	None (solvent partition used)	2% DEGS	61	185	4.0, 5.0	Spinach, range grass, tomato, milk, fat	Corley and Beroza (1968)

[a] Abbreviations used: acet = acetone, alum = alumina, benz = benzene, Carb = Carbowax, $CHCl_3$ = chloroform, MeOH = methanol, O-analog = oxygen analog, SG = silica gel.

[b] Support was 80- to 100-mesh Gas-Chrom Q. Columns were 4-mm. I.D. glass except for malathion, diazinon, and their O-analogs (aluminum) and Compound 4072 and Shell SD-8447 (stainless steel). Flow rates were nitrogen (carrier) 160, oxygen 40, and hydrogen 200 ml. per minute.

are toxic (probably cholinesterase inhibitors). At first, nanogram amounts of the P=O compounds appeared to be irreversibly adsorbed. Only when microgram amounts were injected did a peak appear, and then the response was either erratic or weak. The gas chromatography of these compounds was finally accomplished, and excellent quantitative data were obtained by using a nonadsorptive support, performing the gas chromatography at as low a temperature as possible and as quickly as possible, and conditioning the column just before use with repeated injections of relatively large amounts of the P=O compound in crop extract.

Since P=O compounds are more polar than their P=S analogs, their greater polarity makes them susceptible to adsorption by the gas chromatographic support. Gas-Chrom Q (a silanized product of Applied Science Laboratories, State College, Pa.), 80- to 100-mesh, proved to be sufficiently nonadsorptive.

The P=O compounds are often not overly stable. Thus, rapid chromatography at as low a temperature as possible was desirable. Short columns (1.5 to 3 feet) were used for this purpose. With polar liquid phases, light loading (1 or 2% of weight of support) was required; with a nonpolar phase, a heavier loading (5 to 10%) could be tolerated because the polar phosphates were not detained excessively in passage.

In most of the procedures, glass columns were used, and the packings were conditioned in the usual manner 20° to 30° C. above the column temperature of the subsequent analysis. However, an additional column conditioning was invariably required for the P=O compounds. Repeated injections of 250-ng. amounts of the compound in the crop extract were made with the gas chromatograph operating under analytical conditions, and periodically 5-ng. amounts of the compound in crop extract were injected. The response of the 5 ng. of compound grew gradually. When the response from several successive injections of the 5-ng. amounts became constant, the column was ready for use. With the thionophosphates, a few injections sufficed to condition a column. With P=O compounds, repeated injections over as many as four to eight hours were necessary to achieve the desired conditioning of the column. This need for conditioning to

and Chemosterilants by Flame Photometry[a]

Compounds	Extraction Solvent	Adsorbent and Eluents for Liquid Chromatography	Gas Chromatographic Conditions[b]			Retention Time, Min.	Products Analyzed[c]	Reference
			Liquid phase	Column length, cm.	Column temp., °C.			
Compound 4072, Shell SD-8447	Benzene	None	5% silicone grease[d]	90	190	4.5, 5.1	Sweet corn	Beroza and Bowman (1966)
			Chemosterilants—Phosphorus Detector					
Apholate	MeOH	None	5% DC-200	45	200	2.00	Insect tissue	Bowman and Beroza (1966a)
Hempa	MeOH	None	1% Carb 20M	45	100	1.40	Insect tissue	Bowman and Beroza (1966a)
Metepa, methiotepa	MeOH	None	1% Carb 20M	45	110	2.70, 1.20	Insect tissue	Bowman and Beroza (1966a)
Tepa	MeOH	None	1% Carb 20M	45	125	1.90	Insect tissue	Bowman and Beroza (1966a)
			Insecticides—Sulfur Detector					
Mobil MC-A-600, hydrolysis product	$CHCl_3$	10 grams of alum–$CHCl_3$, MeOH	10% DC-200[e]	75	140	7.6, 2.0	Grass (milk)	Bowman and Beroza (1967e)
UC-21149, its sulfoxide and sulfone	$CHCl_3$	15 grams of Florisil + 1 gram of Nuchar-acet + pet. ether	1 to 1 5% Carb 20M and 10% DC-200	122[f]	115	0.8, 2.0, 4.3	Sugar beets, oranges, apples, potatoes	Maitlen, McDonough, *et al.* (1968)

[c] Products in parentheses were analyzed, but procedure given is different.
[d] On acid-washed Chromosorb W. Gas-Chrom Q would be better.
[e] To hydrolyze carbamate to phenol, plug of phosphoric acid is included at head of column.
[f] Column was stainless steel or aluminum. Support was 60- to 80-mesh.

obtain maximum and constant response appears to parallel the polarity of the compound being chromatographed. For the more polar phosphates, the conditioned state was lost if analyses were stopped for a prolonged period. However, the conditioned state of a previously conditioned column was readily regained by resuming the repeated injections of insecticide in extract. Frequently, between analyses, standards were injected to monitor the condition of the column. The conditioned state is probably needed to cover or sate adsorptive sites so the phosphates can pass without being adsorbed. The need to maintain the conditioned state indicates that the saturation of adsorptive sites is reversible and that conditioning sets up a steady-state situation with constant bleeding of the crop extract and pesticide; the bleed probably causes a slightly elevated base line that is not noticeable. Column conditioning of the type described has been recommended by Shuman and Collie (1963) in their analysis of pesticides.

Although the conditioned state may have to be regained at the start of each day for the polar phosphates, reproducibility of the optimum response from day to day remained within 10% of the norm value. Reproducibility of analyses were usually within 2 to 4%.

General Procedure for Analysis

Because of the high specificity of the detector for phosphorus and sulfur compounds, little or no cleanup of extracts was necessary. The crop was extracted with the appropriate organic solvent. (Tests should be made to check for complete extraction of compounds.) The parent insecticide was separated from its metabolites or interferences by liquid chromatography on a short column of adsorbent—e.g., silica gel—or by a solvent partition. After concentration of the eluate, an aliquot was injected into the gas chromatograph. With samples containing appreciable amounts of fat, which could alter column characteristics, a hexane-acetonitrile partitioning step was substituted for or added to the liquid chromatographic separation. Samples were usually injected in 5 µl. of solvent; injection of larger volumes was not necessary because sensitivity was adequate.

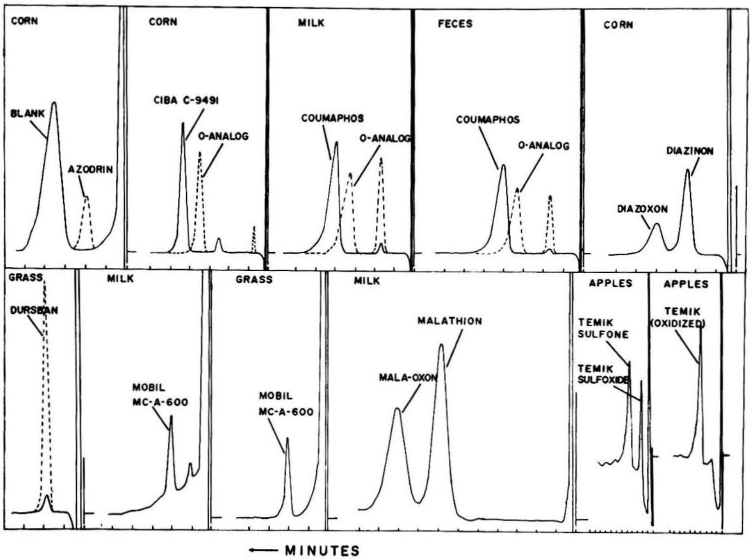

Figure 1. Typical chromatograms obtained with flame photometric detector

Each division under the chromatograms is 1 minute. When two chromatograms are given, dashed-line peaks of one are superimposed on the other which is given as a solid line

Results

Conditions used for analyzing a large variety of insecticides and chemosterilants are summarized in Table II. The original references given in the table should be consulted for details of the methods. Chromatograms from some of the analyses are given in Figure 1 to illustrate the type of data obtained.

Discussion

The most striking feature of the flame photometric detector in both the phosphorus- and sulfur-sensing modes is the freedom from background interference in the analysis of many crops. One of the phosphates analyzed (Compound 4072) possessed chlorine atoms and responded to both the electron capture and the flame photometric detector. A comparison of the response of the two detectors to a raw extract of corn containing 0.8 ng. of this compound is shown in Figure 2. The peak obtained from the compound in the electron capture chromatogram (3.8 minutes) sits on a large amount of interference. Interference in the flame photometric analyses was far less (peak at 4.5 minutes) even though 10 times as much corn extract was used. This result is, perhaps, not surprising since the electron capture detector is probably the least specific of the so-called specific detectors being used these days in pesticide residue analyses. Indeed, the successful use of the electron capture detector depends on an adequate cleanup, which often must be thorough and time consuming. Because of this need for cleanup, within the next few years new, sensitive, and highly specific detectors (some of which have already appeared) probably will supplant the electron capture detector in many and perhaps in most residue analyses.

Unlike the electron capture detector, the flame photometric detector is not contaminated by unclean extracts or desensitized by column bleed. It is relatively trouble-free and needs only an occasional cleaning; its response is not affected by carrier gases or samples containing small amounts of water; the response of the detector may be reliably attenuated, an operation that is not possible with many detectors used in pesticide residue analysis. In addition, maintenance of a very constant flow rate of the gases is not critical to its performance, and a steady baseline is easily obtained.

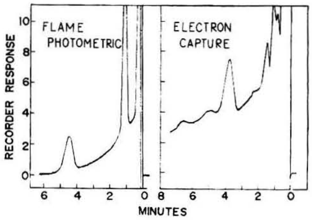

Figure 2. Chromatograms of Compound 4072 in corn extract

With electron capture detection: 0.833 ng. of Compound 4072 (peak at 3.8 minutes) in a raw benzene extract equivalent to 1.67 mg. of corn. With phosphorus flame photometric detection: 0.833 ng. of Compound 4072 (peak at 4.5 minutes) in a raw benzene extract equivalent to 16.7 mg. of corn

A comparison was made of the response of the flame photometric detector to pesticides with and without phosphorus or sulfur. A 50-cm. glass column containing 5% silicone grease on Gas-Chrom Q was operated isothermally with the detector in the phosphorus mode to determine the relative response (peak height) of parathion [retention time (t_R) 2.40 minutes], which contains phosphorus *vs.* two common pesticides, aldrin (t_R 2.31 minutes) and lindane (t_R 0.95 minute), which contain no phosphorus. The response of 100 ng. of parathion was 53 times greater than the response of 2500 times as much aldrin (250 μg.) and 19.5 times greater than the response of 2500 times as much lindane. The relative response, sometimes referred to as the selectivity ratio of the detector, was 132,500 to 1 (2500 × 53) for aldrin and 48,750 to 1 (2500 × 19.5) for lindane. The former ratio is the more appropriate measure of selectivity because the retention times of parathion and aldrin were about the same. The response ratio of almost 50,000 to 1 for the early-eluting lindane would have been much higher were the retention time of lindane adjusted (by lowering column temperature) to approximate that of parathion. The experiment was repeated with the detector in the sulfur-sensing mode and the response of the sulfur-containing parathion was 4.3 times that of aldrin which contains no sulfur; this response ratio was therefore 10,750 to 1 (2500 × 4.3). These unusually high selectivity ratios of the detector show why cleanup is usually unnecessary. For example, a detector with a selectivity ratio of 1000 for phosphorus compounds would give full scale deflection for compounds that would produce practically no observable deflection with the flame photometric detector.

These features of the detector help provide analyses that are rapid and reliable. Interference is low enough to allow peaks of interest to be eluted quickly, normally within one to six minutes. Quantitation is usually based on peak height which can be measured rapidly. Laborious and time-consuming cleanups are eliminated, thus saving solvents and glassware. Analyses are more accurate because losses in cleanup are avoided. Identifications are more certain because of the detector's highly specific response. Separations are more complete because the detector's high sensitivity allows very small amounts to be analyzed and lesser amounts of compound separate more completely than larger amounts.

In some of the analyses (see chromatograms of malathion and mala-oxon and diazinon and diazoxon in Figure 1), the parent and oxygen analog can be separated in a single determination. In an analysis to be described later, three metabolites were separated and determined by a single injection of sample.

As shown in Figure 1, interferences were sometimes encountered; presumably they were caused by the presence of phosphorus- or sulfur-containing compounds other than the pesticide in the extract. The analysis of 1 ng. of Azodrin in an extract equivalent to 16.7 mg. of sweet corn illustrates such a situation (upper left corner of Figure 1). The peak following the Azodrin peak did not interfere because it was allowed to emerge before the next sample was injected. In another instance, goat milk could not be analyzed for Imidan with the phosphorus detector because excessive interference was present, but no difficulty occurred when the sample was analyzed with the detector in the sulfur-sensing mode (Bowman and Beroza, 1967d).

The insect chemosterilants listed in Table II all contain phosphorus. Tepa, the most effective, was analyzed in insect tissue with no cleanup. The chromatogram in Figure 3, of tepa in fall armyworm moths, *Spodoptera frugiperda* (J. E. Smith), was obtained by blending the insect with methanol, filtering off the methanol solution, and injecting an aliquot of the filtrate into the gas chromatograph.

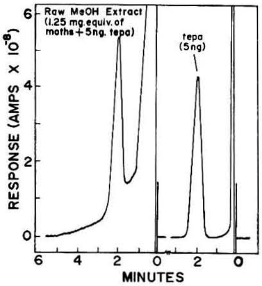

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Figure 3. Chromatograms of 5 ng. of tepa obtained with phosphorus flame photometric detector

Right, injected in 5 μl. of methanol. Left, injected in 5 μl. of a methanol extract of female fall armyworm without cleanup (Bowman and Beroza, 1966a)

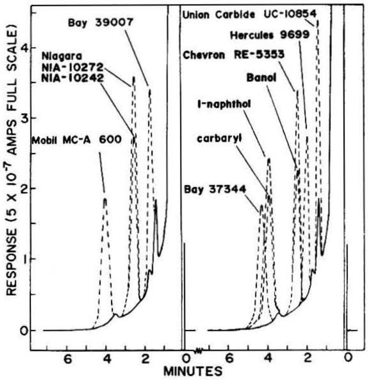

Figure 4. Chromatograms of dimethoxythiophosphoryl derivatives of nine carbamates and two phenols obtained with flame photometric detector

Solid lines are chromatograms of the reagent blank. Dotted lines show peaks obtained from indicated compounds

Since background interference with the phosphorus detector is extremely low, the possibility of making phosphorus derivatives of carbamates, which would respond with high sensitivity to the flame photometric detector, seemed appealing. [The approach parallels that of Gutenmann and Lisk (1963) who made electron-capturing derivatives of insecticides, which could then be analyzed at high sensitivity with the electron capture detector.] Thus, Niagara NIA-10242 was hydrolyzed to its phenol, and the phenol was steam distilled away from interference and reacted with dimethyl chlorothiophosphate (an acid chloride) in the presence of pyridine to form a thiophosphoryl derivative which gas chromatographed well (Bowman and Beroza, 1967c). Recoveries of residues from milk in the 0.5- to 2.0-p.p.m. range were 95 to 99%; from corn silage they were 88 to 98%. Derivatives of eight other carbamates prepared in the same manner gas chromatographed well too; but the application of the procedure to six others was not successful. Composite chromatograms of the carbamate derivatives are shown in Figure 4. The thiophosphoryl derivatives may also be detected with the sulfur flame photometric, electron capture, and thermionic detectors. The P=S derivative of the carbamates not only has the advantage of being sensed by all these detectors, but the P=S derivatives gas chromatograph far better than their P=O analogs.

Another carbamate that was successfully analyzed with the flame photometric detector is Mobil MC-A-600. This carbamate and other *N*-methylcarbamates break down during gas chromatography (Ebing, 1965). The carbamate, on hydrolysis, yielded a sulfur-containing phenol which gas chromatographed and responded well to the sulfur flame photometric detector (Figure 1). Recovery of the carbamate (as the phenol) at levels of 0.5 to 5.0 p.p.m. were 92 to 96% from Coastal Bermudagrass and 88 to 92% from milk. A unique feature in the grass analysis was the inclusion of a short plug of phosphoric acid on the gas chromatographic support at the head of the column; this plug instantaneously converted all of the carbamate to the phenol and gave a single peak for the compound, which facilitated the estimation of its quantity.

Union Carbide UC-21149 (Temik), its sulfoxide, and sulfone, all of which contain sulfur, may be analyzed with the sulfur flame photometric detector (Figure 1) after separating the compounds on a liquid chromatographic column. Because the retention time of UC-21149 was short, it was oxidized to its sulfone for analysis. After application UC-21149 changes rapidly to its more toxic sulfoxide (Maitlen, McDonough, *et al.*, 1968), a result that indicates the need to analyze for metabolites in addition to the parent compound.

Among the most difficult phosphates to analyze for residues are those containing a sulfide group. For example, fenthion (also Baytex) may form the five metabolites shown in Figure 5. An analysis of the insecticide and its five metabolites was accomplished by separating the crop extract into three fractions by liquid chromatography and then injecting aliquots of the individual fractions into the gas chromatograph (Bowman and Beroza, 1968b). The chromatograms are shown in Figure 6. Recoveries from corn, grass, and milk in the 0.05- to 0.1-p.p.m. range were 95 to 100% for all but one of the metabolites, and it was recovered in 75% yield. Sensitivity was better than 0.01 p.p.m. This analysis appears to be the first in which an insecticide of this type and the five metabolites have all been individually determined quantitatively. Other insecticides of this type are phorate, disulfoton, and methyl demeton. Perhaps they and their metabolites may be analyzed similarly in the future.

In several of the phosphorus insecticide residue analyses, hydrolysis products containing halogen atoms were determined by gas chromatography with electron capture detection because the phosphorus group was eliminated in the hydrolysis. Thus, the phenolic hydrolysis product of Ciba C-9491, present as a metabolite, was separated by liquid chromatography and determined by electron capture gas chromatography. The liquid chromatographic separation in this analysis was unusual because it involved chromatography on a silica gel and an alumina column operated first in tandem to bring the parent insecticide through both columns and then separately to elute the other two metabolites.

Finally, the flame photometric detector in the phosphorus- and sulfur-sensing modes was employed to analyze 20 phosphorus-containing insecticides by temperature programmed gas chromatography (Bowman and Beroza, 1967f). This technique made it possible to analyze multicomponent mixtures of insecticides of widely differing volatilities in a single run with good sensitivity and a large saving in time. From 12 to 28 minutes was required for each run. The four columns used were all programmed at the same rate, which made it possible to utilize two or more columns in the same oven at the same time. The change from phosphorus to sulfur detection can be made in less than a minute; thus the presence or absence of either element or the ratio of the responses to the two elements may readily be determined. The procedure is more than a screening method since quantitative data were obtained in trials on a DC-200 column. Late eluting peaks remain sharp, and therefore high sensitivity (based on peak height) is maintained, usually about 0.01 p.p.m. Relative retention times and conditions for the gas chromatography of the 20 insecticides on four column packings (DC-200, QF-1, DC-710, and stabilized DEGS) are given in Table III. Analyses of corn silage required virtually no cleanup; in analyses of milk, a single hexane-acetonitrile partitioning was included to avoid injecting the butterfat on the column. Recoveries generally exceeded 90%. Typical chromatograms on the DC-200 column are shown in Figure 7. The procedure is promising for identification or multicomponent analysis of compounds containing phosphorus or sulfur.

As part of the temperature programming study, the retention times of thionophosphate insecticides and their oxygen

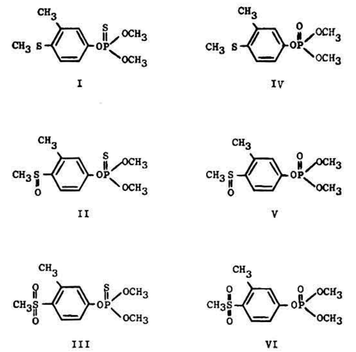

Figure 5. Fenthion (I) and five of its metabolites

Designations are I P=S, S; II P=S, SO; III P=S, SO$_2$; IV P=O, S; V P=O, SO; VI P=O, SO$_2$

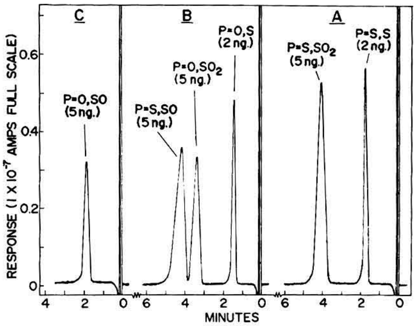

Figure 6. Chromatograms of fenthion and five metabolites with phosphorus detector

See Figure 5 for identification of peaks

Table III. Relative Retention Times of 20 Phosphorus-Containing Insecticides on Four Columns

Pesticide No.	Relative Retention Times (Parathion = 1.00) DC-200[a]	QF-1[a]	DC-710[a]	DEGS[b]
Zinophos, 1	0.48	0.40	0.55	0.52
Bidrin, 2	0.59	0.90	0.76	[c]
Phorate, 3	0.59	0.42	0.62	0.44
Bay 30911, 4	0.65	0.46	0.68	0.60
Diazinon, 5	0.74	0.47	0.73	0.46
Stauffer N-2788, 6	0.85	0.63	0.87	0.65
Methyl parathion, 7	0.85	0.92	0.91	1.04
Malathion, 8	0.94	0.88	0.99	0.92
Dursban, 9	0.99	0.70	0.97	0.73
Parathion, 10	1.00[d]	1.00[d]	1.00[d]	1.00[d]
Ruelene, 11	1.04	1.12	1.08	[c]
Shell SD-8447, 12	1.18	1.07	1.18	[c]
Ciba C-9491, 13	1.21	0.87	1.38	1.03
Methyl trithion, 14	1.33	1.00	1.32	1.23
Ethion, 15	1.39	1.12	1.34	1.09
Carbophenothion, 16	1.45	1.06	1.32	1.18
Imidan, 17	1.58	1.49	1.74	1.26
EPN, 18	1.61	1.47	1.62	1.63
Azinphosmethyl, 19	1.67	1.29	1.98	1.30
Coumaphos, 20	1.94	2.02	2.32	2.86

[a] 526 mμ filter (phosphorus detector) used.
[b] 394 mμ filter (sulfur detector) used.
[c] Contains no sulfur and is therefore not detected.
[d] With conditions described [Bowman and Beroza (1967f)] typical retention times of parathion on DC-200, QF-1, DC-710, and DEGS were 6.50, 7.30, 8.80, and 9.30 minutes, respectively.

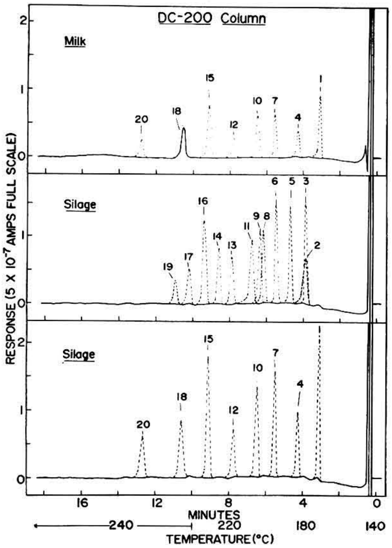

Figure 7. Temperature programmed gas chromatograms of 20 phosphorus-containing insecticides in extracts of milk and corn silage

Column: 5% w./w. DC-200 on 80- to 100-mesh Gas-Chrom Q. Detector: flame photometric for phosphorus. Insecticides indentified by number in Table III

analogs were compared on a nonpolar (DC-200) and a more polar (QF-1) column. The thionophosphates followed the oxygen analogs on the nonpolar DC-200 column; the order of elution was reversed on the more polar QF-1 column. In general, the response (peak height) of the oxygen analog was somewhat less than that of the parent thionophosphate. The reason for the lesser response has not been determined.

Important considerations relating to all residue analyses, which should be kept in mind even though they are outside the scope of the present study, include selection of a representative sample for analysis, stability of the pesticide and metabolites in cold storage (in the crop or as an extract awaiting analysis), completeness of extraction of both pesticides and metabolites from the crop, and confirmation of identity and purity of substances in gas chromatographic peaks.

On the basis of the methodology described, we conclude that gas chromatography with flame photometric detection is a versatile, sensitive, reliable, and efficient means of analyzing pesticides and their metabolites that contain phosphorus or sulfur; the detector has also proved useful for analyzing insecticides such as carbamates that were converted to derivatives containing phosphorus or sulfur.

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Gas Chromatographic Separation of HCN on Porapak Q

Analysis of Trace Aqueous Solutions

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■ A gas chromatographic procedure was developed for the determination of HCN in a cyanide solution without significantly shifting the HCN–CN^- equilibrium. Air is passed through the cyanide solution, the HCN vapor is trapped out of the air stream on a cold trap, and the contents of the cold trap are injected into a gas chromatograph equipped with a flame ionization detector. Excellent chromatograms were obtained on a polyaromatic polymer, Porapak Q. Concentrations as low as 1 μg. of HCN per liter of solution were analyzed in 5 minutes after a 30-minute collection period. Approximately 15 ng. of HCN gave a 1-sq. cm. peak at a sensitivity of 1.0×10^{-11} ampere per mv. The procedure is also adaptable for determining trace quantities of volatile organic compounds in water.

The toxicity of cyanide solutions to fish has long been known to scientists; however, Wuhrmann and Woker (1948) found undissociated HCN to be the toxic factor in acute toxicity studies of fish to alkali cyanide salt solutions, and not the cyanide ion as formerly believed. Milne (1950) found that complex cyanide ions of heavy metals were relatively nontoxic compared to the heavy metal cations. Recently, Doudoroff, Leduc, *et al.* (1966) established a direct relationship between the acute toxicity of fish and the HCN concentration in solutions containing metallocyanide complexes. Thus the need to determine undissociated HCN, rather than total cyanide ion concentration, is very important in the toxicological evaluation of cyanide waste disposal in natural streams.

In conjunction with the work cited (Doudoroff, Leduc, *et al.*, 1966), Schneider and Freund (1962) developed a gas chromatographic method for the determination of HCN in dilute aqueous solutions without appreciably shifting the $HCN \rightleftharpoons H^+ + CN^-$ equilibrium. Air was passed through a cyanide solution, the HCN vapor was removed from the effluent air by a cold trap, and the contents of the trap were injected into a gas chromatograph equipped with a thermal conductivity detector. A chopper-stabilizer d.c. amplifier with a gain of 20 was used to increase the detection sensitivity.

To study the effects of sublethal exposures of hydrocyanic acid on fish and the aquatic environment a more sensitive analytical method was needed. Previous work suggested that determination of 1 μg. of HCN per liter of solution would be required for subacute studies.

Experimental

Concentration Apparatus. The apparatus used in the concentration of HCN was similar to that described by Schneider and Freund (1962), with one important modification. A Hoskins Type FD-303A combustion furnace with a 30-mm. O.D. × 61-cm. quartz combustion tube filled with copper oxide and platinized asbestos was placed in the air stream in front of the cyanide solution and heated to red heat.

Gas Chromatographic System. The gas chromatographic system is shown in Figure 1. Two gas chromatographic air bath ovens 9.5 inches long, 6.5 inches wide, and 9.5 inches high were constructed from $^3/_8$-inch aluminum plate. The interior walls and upper lid were insulated with 0.5 inch of A. P. Green high temperature cement (A. P. Green Fire Brick Co., Mo.) and lined with asbestos sheet. The ovens were heated by hair dryers (Standard Products Corp., Whitman, Mass.) in which the voltages to the 80-ohm heating filaments were controlled by Variacs.

The nitrogen carrier gas flow was controlled by Nupro 2M needle valves (Nuclear Products Co., Cleveland, Ohio). A Perkin-Elmer gas-sampling valve was mounted on each oven. Provisions were made to backflush the second column. Valves 3 and 4 are closed, while the gas sampling valve and valve 2 are opened (Figure 1).

A Beckman flame ionization detector (Model 104000) was housed in a separate oven. The oven consists of an aluminum pipe 5 inches high and 5 inches in diameter, in which a 600-ml. copper beaker was inverted over the detector. A 32-ohm heating tape was wrapped around the copper beaker, and glass wool placed in the dead space between the beaker and the outside housing. At 110 volts a.c. the detector temperature was 115° C. The copper beaker, electrometer, and recorder were grounded to a common earth ground; and the anode lead was silver-soldered to the detector.

Columns. A 9-foot × $^3/_{16}$-inch O.D. aluminum column was packed with 15% 1,2,3-tris(2-cyanoethoxy)propane (TECP) on 60- to-80 mesh acid-washed DMCS-treated Chromosorb W and installed in the first oven. The aluminum tubing should be washed with concentrated HNO_3 to remove nickel in the aluminum alloy. A 6-foot × $^3/_{16}$-inch O.D. aluminum column was packed with 50- to-80 mesh Porapak Q and installed in the second oven. Both columns were conditioned at 90° C. (maximum oven temperature) for 72 hours.

Preparation of Standards. A 1-liter $0.1M$ KCN stock solution is prepared and standardized according to Kolthoff and

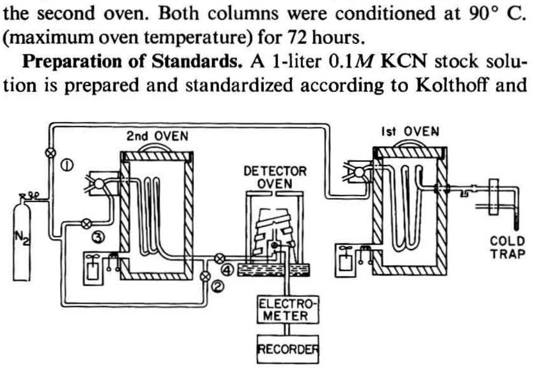

Figure 1. Gas chromatographic apparatus

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Sandell (1952). From the stock solution 0.02*M*, 0.001*M*, and 0.000125*M* solutions are prepared by quantitative dilution.

A phosphate buffer used to adjust the pH of the cyanide solution to 6.5 is prepared by diluting 4.26 grams of Na_2HPO_4 and 23.15 grams of KH_2PO_4 to 1 liter. Distilled water is passed through a strong cation exchange column in the acid form, and then boiled in 4-liter Erlenmeyer flasks to $^3/_4$ volume while the boiling water is swept with nitrogen gas to remove chlorine. The chlorine-free water is used in the preparation of all standard solutions.

An appropriate aliquot of KCN stock solution is added to 18 liters of water along with 100 ml. of the phosphate buffer. The solution is then diluted to 20.00 liters at 20° C., and stirred for 1 hour with a glass stirring propeller.

Procedure. The air combustion furnace is adjusted to a red heat temperature, and 1.5 grams of 20- to-30 mesh $CaCl_2$ is added to the drying tube. The temperature of the drying tube is adjusted to 70° C. The drying agent should be heated to 200° C. for 36 hours prior to use to remove volatile organic compounds. Air is swept through the apparatus while the HCN solution is being stirred.

After stirring, the air bubbler is placed in the cyanide solution and connected in series with the air stream. At the same time, a concentration column is cooled to −78° C. in a dry ice–acetone bath. After the air flow has been adjusted to approximately 50 ml. per minute, the concentration column is switched into the air stream. The air passing through the concentration column is measured by water displacement. Two-liter air samples are collected for the analysis of 0 to 20 μg. per liter HCN solutions and 1 liter for 20 to 2000 μg. per liter solutions.

The TECP and Porapak Q column temperatures are adjusted to approximately 37° and 51° C., respectively. The nitrogen carrier gas flow of each column is then adjusted to 75 ml. per minute. The flame detector hydrogen and air flow rates are adjusted to 35 and 400 ml. per minute, respectively, for optimum response.

Upon collection of a given volume of air, the concentration column is connected to the gas sampling valve of the second oven and warmed to 95° C. The contents are injected into the gas chromatographic column by switching the gas sampling valve for 40 seconds. The concentration column is removed from the gas sampling valve and connected to a vacuum line for 5 minutes at 95° C.; it is then ready to trap another sample. After HCN has eluted, the Porapak column is backflushed in preparation for the next sample.

Where interfering peaks are encountered on the Porapak Q column a second sample of HCN is first injected onto the column containing 1,2,3-tris(2-cyanoethoxy)propane (TECP) packing. The HCN solute is trapped as it elutes from this column and is reinjected onto the Parapak Q column for analysis. The trapping period should be approximately 5 to 9 minutes with a HCN retention time of 6 minutes.

Results and Discussion

Analysis of Aqueous Solutions. Figure 2 shows a typical chromatogram for the analysis of 2.5 and 40 p.p.b. HCN solutions. Symmetrical HCN peaks are obtained with complete separation from interfering compounds.

The calibration curve obtained from the analyses of 1 to 2000 μg. per liter standard solutions of HCN is shown in Figure 3. At higher concentrations the curve does not inter-

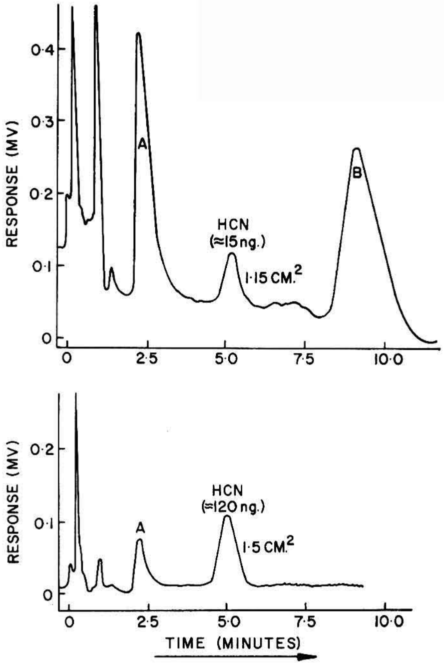

Figure 2. Chromatograms of HCN sample on Porapak Q column

Upper. Determination of 2.5 μg. of HCN per liter of solution, 2.0 liters of air, sensitivity = 1×10^{-11} ampere per mv.
Lower. Determination of 40 μg. of HCN per liter of solution, 1.00 liter of air, sensitivity = 5×10^{-11} ampere per mv.

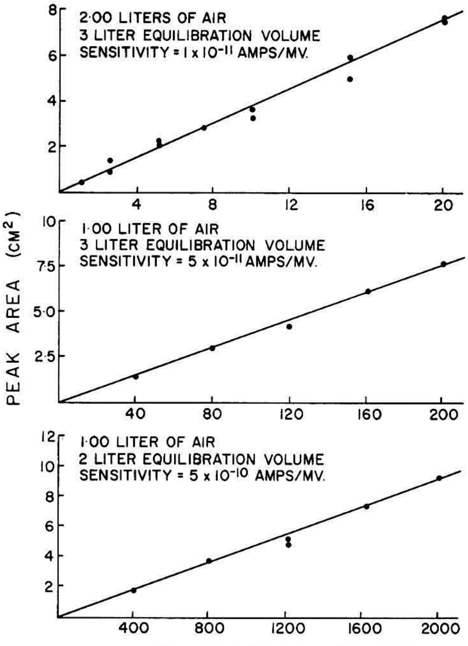

Figure 3. Calibration curves for determination of HCN

sect zero, indicating a slight loss of sample. Intersection of zero at the lower concentrations supports the absence of chromatographic interferences.

A preliminary chromatographic separation was not necessary for the analyses of natural streams in the local area. Samples were analyzed directly on the Porapak Q column. Most of the peaks shown in Figure 2 are observed in the analyses of distilled water blanks, indicating contamination in the concentration step.

The high sensitivity of the flame ionization detector requires the use of purified grade gases, especially where the impurities are concentrated in a cold trap. Thus the sweeping air and nitrogen carrier gas should be particularly free of organic compounds. A large combustion furnace was necessary for the purification of the sweep air.

The volume of air collected and the lower limit of sensitivity are limited by the efficiency of the drying agent. Of the many drying agents investigated, only $CaCl_2$ and $Mg(ClO_4)_2$ were chemically compatible with HCN, having sufficient capacity and efficiency. Since HCN will absorb on the drying agent, it is necessary to heat the drying tube. This, in turn, reduces the drying efficiency. Ten liters of air can be adequately dried by 1.5 grams of $CaCl_2$ at 70° C. and 20 liters by 1.5 grams of $Mg(ClO_4)_2$ at 95° C.

The volume of air necessary to reach equilibrium with the drying agent depends on the HCN concentration and the temperature and quantity of the drying agent. Equilibrium is established with 2 and 4 liters of air, respectively, for 1.5 grams of $CaCl_2$ at 70° C. or 1.5 grams of $Mg(ClO_4)_2$ at 95° C. with a HCN concentration of 1.8 mg. per liter. At a concentration of 0.01 mg. of HCN per liter of solution, 9 liters of air is required to establish equilibrium for 1.5 grams of $Mg(ClO_4)_2$ at 95° C. Reproducible results can be obtained with either $CaCl_2$ or $Mg(ClO_4)_2$ if collection is begun after 2 liters of air has passed through the apparatus, and new drying agent is used for each analysis. The calibration curve shown in Figure 3 is obtained using 1.5 grams of $Mg(ClO_4)_2$ at 95° C. after 3 liters of air has passed through the drying agent. The first sample of HCN trapped before equilibrium conditions are established is used to test the gas chromatographic system. The substitution of Teflon tubing for glass may reduce the equilibration period.

The $0.1M$ KCN stock solution decays at a rate of $0.0005M$ per day at 20° C., but the dilute standard solution was stable for at least 7 days. New stock solutions were prepared every 2 weeks.

The air sweep rate is not critical. Equilibrium between the air and water existed for all flow rates within the limitation of the apparatus (80 ml. per minute). A 2% error will occur for a 1° change in the solution temperature at 20° C. Thus rigid temperature control is not critical, but is desirable.

Chromatographic Columns. HCN adsorbs on the diatomaceous earth supports, making trace determinations of HCN particularly difficult. Even with a polar stationary phase on silanized Chromosorb W, HCN tailing was severe at nanogram levels. The fluorocarbon supports were investigated, and were too inefficient for trace analysis. With the polyaromatic polymer, Porapak Q, symmetrical HCN peaks are obtained with comparatively good column efficiency. This packing is useful for the chromatography of polar compounds (Hollis, 1966).

Table I. Relative Retention Times of Some Possible Interfering Compounds and Water Pollutants[a]

Compound	B.P., °C.	Relative Retention Time, Minutes
Ammonia	−33.4	. . .[b]
Ethane	−88.6	0.3[c]
Water	100	0.51[b]
Hydrogen sulfide	−61.8	0.54[b]
Trimethylamine	3.5	0.57
Methylamine	−6.5	0.58
Diethylamine	55	0.58
Propane	−42.1	0.97[c,d]
HCN	27	1.00
Methanol	64.7	1.35[d]
Carbon disulfide	46.3	6.0[b]
Cyanogen bromide	61.6	10[b,c]

[a] 1-meter × 1/8-inch O.D., 80- to 100-mesh Porapak Q at column temperature of 60° C. and nitrogen flow rate of 15 ml. per minute.
[b] Not detectable by flame ionization detector.
[c] Not a common water pollutant.
[d] Interferes with HCN.

Table I lists the relative retention times of some of the compounds which were examined as possible interfering compounds on Porapak Q. Methanol and propane are the only compounds tested which interfered with the determination of HCN. Cyanogen chloride may be found in chlorinated water containing cyanide ions, but this compound appears to be insensitive to flame ionization detection. Compound A in Figure 2 has a relative retention time of 0.46 and tails like the amines. This compound is not eluted as a plug from the concentration column and tails into the HCN peak if the gas sampling valve is not returned to its original position within 40 seconds after injection.

The procedure developed is also adaptable to determining other volatile organic compounds in water at trace levels. Using a Carbowax 1540 column in place of Porapak Q, 28 μg. of chloroform per liter of water was found in the chlorinated tap water. Small amounts of chloroform can be found in chlorine used to chlorinate municipal water supplies.

Because of the high sensitivity of a flame ionization detector, the concentration step has been considerably shortened. The flame ionization detector is also relatively insensitive to small fluctuations in temperature and flow rate. Its insensitivity to water is a distinct advantage in the analysis of aqueous solutions.

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Odorous Compounds in Natural Waters

An Earthy-Smelling Compound Associated with Blue-Green Algae and Actinomycetes

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■ Earthy-musty type odors caused by actinomycetes and, possibly, by blue-green algae have frequently been a problem in food and water supplies. Many actinomycetes and two species of blue-green algae produced the same earthy-smelling compound, geosmin, which has been obtained by preparative gas chromatography. Geosmin, $C_{12}H_{22}O$, has been shown to be a dimethyl substituted, saturated, two-ring *tert*-alcohol with the hydroxyl group very sterically hindered.

Persistent earthy or musty odors in water have been variously associated with the presence of large numbers of aquatic actinomycetes or algae in the raw water source (Aschner, Laventer, *et al.*, 1967; Cornelius and Bandt, 1933; Gaines and Collins, 1963; Lewis, 1966; Morris, Dougherty, *et al.*, 1963; Silvey and Roach, 1959). The literature reports that the major causative agent of such tastes and odors in waters may be a single compound. Gerber and Lechevalier (1965) isolated an earthy-smelling compound from several actinomycetes which they named geosmin and Safferman, Rosen, *et al.* (1967) presented evidence that suggested that an earthy-smelling compound produced by the blue-green alga *Symploca muscorum* was identical to Gerber and Lechevalier's geosmin.

Gerber (1967) has presented a partial structure for geosmin. However, work on the identical compound reported in this paper shows several discrepancies compared with Gerber's data.

Musty-earthy-smelling compounds other than geosmin have been isolated from waters. For example, Dougherty, Campbell, *et al.* (1966) have partially characterized a compound produced by actinomycetes having an empirical formula of $C_{12}H_{18}O_2$.

This paper describes work concerned with the isolation and characterization of geosmin from aquatic actinomycetes and from two blue-green algae, *S. muscorum* and *Oscillatoria tenuis*.

Materials and Methods

Actinomycete No. 18, a local isolate obtained in pure culture from J. K. G. Silvey, was maintained on M_1B_2 slants and grown on M_1B_2 medium [grams per liter: sodium citrate, 10.0; dextrose, 10.0; $CaCl_2$, 0.1; $MgSO_4$, 0.05; $FeSO_4$, 0.01; NH_4NO_3, 6.0; Na_2HPO_4, 2.0; K_2HPO_4, 2.0. For slants, add 25 grams of agar per liter of medium (Silvey, 1967)]. Three liters of M_1B_2 medium were introduced into a 20-liter borosilicate glass bottle which was laid on its side to provide a larger surface area for the growth of the aerial mycelia. The medium was inoculated with 300 ml. of M_1B_2 broth containing the organism. Air filtered through a carbon column and a 0.22-micron Millipore filter was passed over the culture surface at the rate of 500 ml. per minute. After eight to 12 days of growth at room temperature (22° to 26° C.), the earthy-smelling compound was usually present at concentrations of approximately 200 μg. per liter.

Symploca muscorum was obtained from R. S. Safferman, Cincinnati Water Laboratory, Federal Water Pollution Control Administration. The organism was unialgal but bacterially contaminated, primarily with a gram-negative rod. Medium 11 (Hughes, 1958) was used for maintaining the stock cultures and for growing the organism for odor production. A sterile 20-liter borosilicate glass bottle containing several lengths of glass tubing and 16 liters of Medium 11 was inoculated with about 1 liter of *S. muscorum* stock culture. Filtered air was bubbled through the medium at the rate of 500 to 1000 ml. per minute. The temperature was maintained at about 26° to 28° C. and illumination at about 200 to 300 foot-candles at the culture surface. After four to six weeks of growth, the yield of the earthy-smelling compound was approximately 1 mg. per vessel.

Although no actinomycete contaminants could be detected by microscopic examination, the possibility was suggested (Silvey, 1967) that actinomycete filaments may grow within, or closely associated with, the *S. muscorum*. To determine whether this was so, experiments designed to rupture the algal cells and release their contents were performed. A control culture of *S. muscorum* deliberately contaminated with *Actinomycete No. 18* was carried through all the experiments.

The *S. muscorum* culture in M_1B_2 medium was sonicated for a maximum period of 5 minutes in a Raytheon Sonic Oscillator, Model DF-101, at 0.8 ampere. Test portions were removed every 30 seconds. Microscopic examination revealed that the majority of the algal cells were ruptured by this treatment. The sonicated culture was serially diluted in M_1B_2 broth and incubated first for 48 hours at 37° C. and then for 2 weeks at 25° C. After both periods of incubation, aliquots of the diluted sonicate were plated out on Difco Actinomycete Isolation Agar and incubated at 37° and 25° C. for 1 week. No actinomycetes developed from the test culture, but they grew well from the intentionally contaminated control culture.

Further verification of the absence of actinomycete contamination in the *S. muscorum* was obtained by a freeze-thaw experiment. Fifteen-milliliter test tubes containing 3 ml. of algae in Modified Synthetic Sewage Medium [milligrams per liter of medium: $Ca(NO_3)_2$, 60; KNO_3, 70; NH_4Cl, 57; KH_2PO_4, 20; $Na_2SiO_3 \cdot 5H_2O$, 20; NaCl, 70; $MgSO_4$, 20; $NaHCO_3$, 125; $Na_3C_6H_5O_7 \cdot 2H_2O$, 250. Add 1 ml. of Hutner's trace elements and make up to a liter with tap water. Hutner's trace elements, grams per liter of solution: EDTA, 5.0;

$ZnSO_4 \cdot 7H_2O$, 2.0; H_3BO_3, 1.0; $CaCl_2 \cdot 2H_2O$, 0.66; $MnCl_2 \cdot 4H_2O$, 0.50; $FeSO_4 \cdot 7H_2O$, 0.50; $CoCl_2 \cdot 6H_2O$, 0.15; $CuSO_4 \cdot 5H_2O$, 0.15; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 0.10. Adjust pH of medium to 5.7 with HCl and autoclave. The final pH should then be in the desired range of 7.5 to 7.7 (Silvey, 1967)] were frozen for 48 hours at −10° C., then placed in a beaker of water at 70° C. for 7 minutes. After cooling to room temperature, the cultures were streaked out on nutrient agar and on Difco Actinomycete Isolation Agar and incubated for 48 hours at 38° C. Again no actinomycetes developed from the test cultures of algae but grew well in the controls.

Oscillatoria tenuis was obtained from J. K. G. Silvey, North Texas State University. The organism was bacterially contaminated, mainly with a gram-negative motile rod, but experiments similar to those described for *S. muscorum* failed to show the presence of actinomycete contamination. This organism was grown under conditions identical to *S. muscorum*.

Bacteria isolated from both of these blue-green algae were cultured in nutrient broth and did not produce the earthy odor associated with the algal cultures from which they were isolated.

Analytical gas chromatography was carried out with a Varian Aerograph Model 1520-B gas chromatograph with an auxiliary oven. A Varian Aerograph Model 700 Autoprep was used for preparative gas chromatography.

Instrumental analyses were carried out with a Varian Model HA-100 nuclear magnetic resonance spectrometer, a Consolidated Electrodynamics Corp. Model 110 mass spectrometer, a Cary-White Model 90 infrared spectrometer, and a Perkin-Elmer Model LR-1 Raman spectrometer with a Spectra-physics 80-milliwatt laser.

Sample material from *Actinomycete No. 18* was collected both by dry ice–methanol freeze-out traps on the aeration stream and by steam distillation of the culture medium containing mycelium. Sample material from the blue-green algae was obtained by homogenizing the cellular mass in a Waring Blendor followed by steam distillation. The distillates and freeze-out solutions were salted with about 20% NaCl and extracted twice with 5% (v./v.) methylene chloride and slowly evaporated to about 0.3 to 0.5 ml. at 30° C. and atmospheric pressure. Purification was accomplished by preparative gas chromatography using a 3 meter × 3 mm. I.D. stainless steel column packed with 2% SF-96 (50) + 0.005% IGEPAL on 100- to 120-mesh Chromosorb G, AW. The geosmin peak eluted in approximately 40 minutes when using a 30 ml. per minute helium carrier gas flow and a column temperature of 115° C. The geosmin peak was trapped in a 30 cm. × 1 mm. I.D. glass capillary tube fitted against the exit port of the instrument at the time of peak elution.

The purity of the collected sample material was checked by chromatography on an open-tubular gas chromatographic column with about 45,000 theoretical plates (Figure 1).

Results, Discussion, and Conclusions

A sample of geosmin had a mass spectral pattern identical to the major earthy-smelling compound produced by *Actinomycete No. 18*. Further, the two substances eluted together from a very efficient open-tubular gas chromatographic column. In addition, these compounds behaved in the gas chromatograph and the mass spectrometer in a manner identical to the earthy-smelling compounds obtained from *S. muscorum* and *O. tenuis*. It was therefore concluded that these compounds were identical and that instrumental analyses and other tests could be carried out on material derived from any of the three organisms. However, since *Actinomycete No. 18* produced the most geosmin in the shortest time, it was used largely for production purposes.

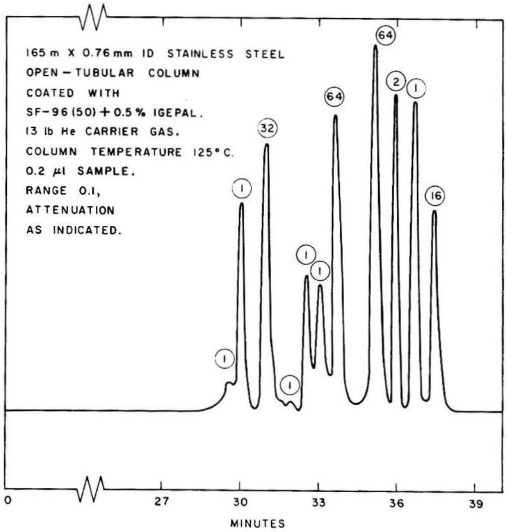

Figure 1. Dehydration peaks resulting from treatment of geosmin with concentrated HCl

Chromatographic odor profiles of the extracted and concentrated cultures of *Actinomycete No. 18* showed that while geosmin was the major odorous component, there were other odorous peaks—for example, peaks with woody, rubbery, floral, and putrid odors were detected. Odor profiles of the *S. muscorum* and *O. tenuis* showed that geosmin was the only significantly odorous component produced by these organisms.

Geosmin was a colorless, viscous liquid. When pure, or present in highly concentrated solution, it possessed a strong, camphorish odor which became earthy on dilution. A threshold odor of 0.05 μg. per liter was obtained.

Using the open-tubular gas chromatographic column and conditions described in Figure 1, geosmin had a retention volume index of 1391 (Kovats, 1958).

The Lucas test gave a strong, instantaneous positive reaction indicating the presence of a tertiary hydroxyl group.

When an 0.01% solution of geosmin in 2 ml. of CH_2Cl_2 was treated with one drop of concentrated HCl for 30 minutes or longer, and the resultant mixture gas chromatographed on the open-tubular column, the geosmin peak with a retention volume index of 1391 disappeared and was replaced by at least nine new peaks with retention volume indices between 1211 and 1261 and a single peak with a retention volume index of 1463. This behavior of geosmin in strong acid solution suggests acid catalyzed dehydration to form a series of isomeric hydrocarbons accompanied by some substitution of Cl^- at the hydroxyl group.

Confirming the work of Gerber and Lechevalier (1965), acid treatment of geosmin destroyed its odor since none of the nine gas chromatographic peaks showed any odor.

If the acidified solution was, in turn, treated with a drop of 1% bromine in methylene chloride and again chromatographed, a new set of at least seven peaks with retention volume indices between 1271 and 1348 was observed to have replaced the set of nine peaks obtained by acid treatment. When geosmin was treated with concentrated HCl in *n*-hexane and the reaction mixture hydrogenated with 30 cm. of positive H_2 pressure over Adam's catalyst, the nine peaks were replaced by a single new peak with an identical retention volume and a similar odor to geosmin. This new compound produced by hydrogenation, unlike geosmin, gave a negative Lucas test, eliminating the possibility that residual or regenerated geosmin caused the peak.

High-resolution mass (MS) spectra, infrared (IR), and proton magnetic resonance (PMR) spectra are shown in Figures 2, 3, and 4, respectively. The MS shows a parent peak at 182 which by exact mass measurement was confirmed to be $C_{12}H_{22}O$ (Gerber, 1967). When geosmin was deuterated, the mass spectrum showed a new parent peak at 183 and an empirical formula of $C_{12}H_{21}OD$. Additionally the MS shows a M-18 peak (loss of H_2O) further indicating the presence of a hydroxyl group. The presence of two methyl groups, one tertiary and one secondary, is indicated by PMR (Figure 4); also, a small M-15 peak (loss of CH_3) appears in the mass spectrum of geosmin (Figure 2). The presence of a sterically-hindered hydroxyl group is confirmed from the sharp IR absorption band at 3630 cm.$^{-1}$

Infrared absorption at 2800 to 3000 cm.$^{-1}$ is suggestive of saturated rings. No double bonds or aromaticity are indicated by IR or PMR. Even the possibility of a tetra-substituted double bond is unlikely in view of the high field position of the first PMR absorption. This is substantiated by ultraviolet (UV) data obtained by Gerber (1967). The two degrees of unsaturation required by the empirical formula are thus best accommodated by a saturated, two-ring skeleton.

The PMR peak at 9.1 to 9.2 τ results partially from the hydroxyl proton since deuteration followed by PMR analysis indicated the loss of one third of the peak area. Two methylene or methine protons (or, possibly, one of each) also contribute to this peak. These methylene or methine protons are at an extremely high-field position and could be the result of a highly and symmetrically shielded structural position or the presence of a three-membered ring.

Little positive can be said about the nature of the ring system. However, a number of the 20 possible, saturated, two-ring C_{10} skeletons can be tentatively eliminated on the basis of the given MS and PMR data. Further, a Raman spectrum of geosmin showed no similarity to spectra of Decalin, cyclopentylcyclopentane, spiro(4.5)decane-6-one or norbornane; there was, however, some resemblance to that of α-pinene.

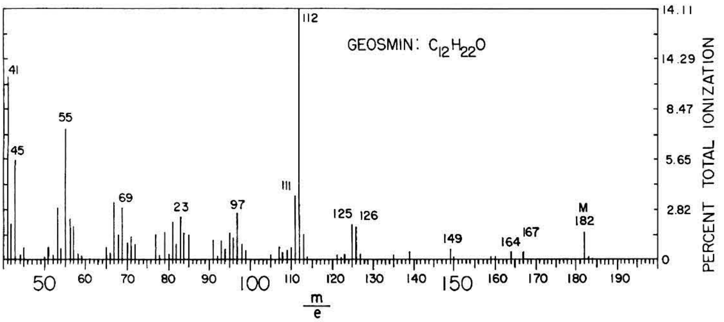

Figure 2. Mass spectrum of geosmin

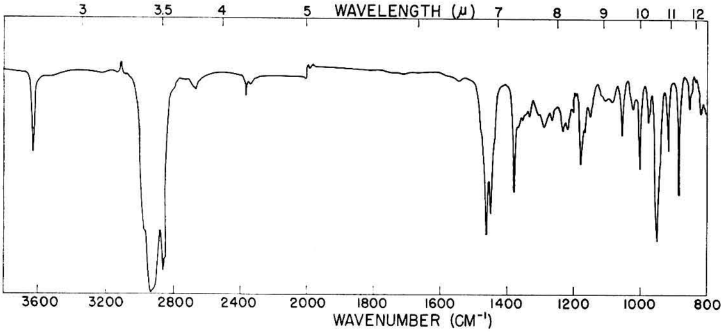

Figure 3. Infrared spectrum of geosmin, 10% in CCl_4

The Decalin structure also appears unlikely on comparison of the PMR spectrum of geosmin with the spectra of several monomethyl Decalins (Bhacca, 1966).

While this work tends to confirm the recent work of Gerber (1967) there are some significant discrepancies between the present data and those of Gerber (1967). While Gerber (1967) deduced the presence of a hydroxyl group she was unable to demonstrate its presence spectroscopically. Moreover, she reports three, rather than two, methyl groups, does not mention the major MS peak at $m/e = 112$, and implies that the product of acid treatment is a single compound.

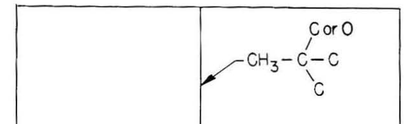

Figure 4. Proton magnetic resonance spectrum of geosmin in CCl_4

Acknowledgment

The authors express their thanks to Brnd Simoneit, Space Sciences Laboratory, University of California, Berkeley, and to Roy Teranishi, R. E. Lundin, and James Sherer of the U. S. Department of Agriculture, Albany, Calif., for their assistance with instrumental analysis and interpretation and to N. N. Gerber for supplying a sample of geosmin. The technical assistance of Susan Scorso, Cecil Pickett, Joseph Eliason, and David Yoon is acknowledged.

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COMMUNICATION

Estimation of Some Atmospheric Trace Gases in Antarctica

W. H. Fischer, James P. Lodge, Jr., Arthur F. Wartburg, and John B. Pate
Laboratory of Atmospheric Sciences, National Center for Atmospheric Research, Boulder, Colo. 80302

■ A series of rough measurements of nitrogen dioxide, sulfur dioxide, and aldehydes comprised one phase of a pilot study of the trace chemistry of the antarctic atmosphere. Compared with similar data obtained by more refined methods in the tropics (Panama), concentrations of nitrogen dioxide and sulfur dioxide were near the estimation limit of roughly 0.5 p.p.b., and clearly less than the tropical values. The aldehyde method, in practice, proved insufficiently sensitive to show a difference if one exists.

Studies of trace substances in the air of remote tropical locations (Lodge and Pate, 1966) have revealed a wide variety of organic and inorganic compounds. Since Antarctica represents conditions of temperature and biotic activity opposite to those of the tropics, the short-lived trace gases contained in the air could be equally dissimilar. On the other hand, gases whose lifetimes exceed the average tropospheric mixing times should be present in comparable amounts in tropical, temperate, or polar regions. This is true for ozone and carbon dioxide, each of which occurs in comparable amounts throughout the world (Junge, 1963).

A visit to Antarctica (November 1966) afforded an opportunity for some rough measurements of several of the principal trace gases which had been detected in tropical air. The results of other experiments performed during this visit have been reported Cadle, Fischer, *et al.*, 1968; (Fischer, 1967).

Apparatus and Methods

The basic gas sampling and analysis apparatus is shown in Figure 1. A Cenco field test kit (Central Scientific Co., Cat. No. 20770-1) was modified to accommodate three larger bubblers, to increase pump capacity, to permit using hypodermic needles for air flow control (Lodge, Pate, *et al.*, 1966), and to substitute a Cenco photoelectric colorimeter (Cat. No. 29290) for the arrangements for visual color estimation. Chemicals supplied with the kit were replaced by preweighed packages of reagents.

Samples were collected by passing air through the bubblers at 2 liters per minute for 60 minutes. Reagents were protected from freezing by keeping the assembly inside a tent and by drawing the sample through a heated stainless steel intake tube. This consisted of about 6 meters of 6-mm. ($^1/_4$-inch) tubing, the bulk of which was coiled into a cylinder of about 25-cm. diameter which was wrapped with electric heating tape. The coil was maintained at about 35° C. Electric power for heating and pumps came from a portable 1.5-k.v.a. generator carefully placed away from the sampling site, about 250 meters downwind. Teflon tubing led from the tent opening to the heated coil, and from the coil to a glass manifold connected to the three bubblers. Waste heat from the pump motors was used to warm the stock reagent solutions kept in a cardboard box on top of the kit.

Nitrogen dioxide was measured by the technique of Saltzman (1954). A modification of the West-Gaeke method was used for sulfur dioxide (Pate, Ammons, *et al.*, 1965). Aldehydes were estimated as formaldehyde with 3-methylbenzothiazolone hydrazone (MBTH) (Hauser and Cummins, 1964). Calibration curves for all determinations were constructed in the laboratory; because of the wide bandpass of the filters in the photometer, Beer's law was not obeyed, but this was unimportant since the values were derived from the curves, not from molar absorbance values.

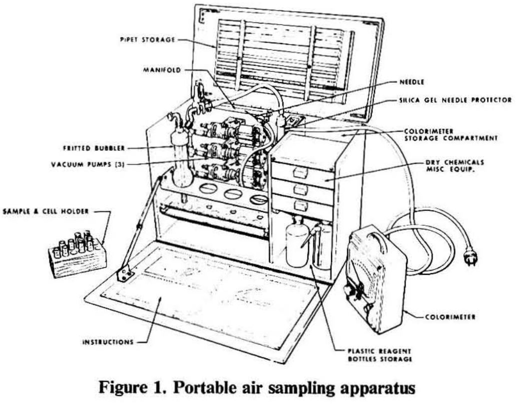

Figure 1. Portable air sampling apparatus

Results and Discussion

Table I displays the data from all samples. Sampling stations are shown in Figure 2. In the table, samples which appeared to have zero absorbance are denoted by 0; those in which the absorbance was detectable but too small to read with any accuracy are labeled trace. The footnotes show the corresponding concentrations. Laboratory studies with the equipment suggest that the numerical values given have an uncertainty of about 20%. All computations assume 100% collection efficiency in all bubblers. Field experience suggests this is not greatly in error, but the point is difficult to prove at these concentrations.

Table I. Estimated Antarctic Trace Gas Concentrations

Date 1966	Station	Concentration, P.P.B.		
		Aldehyde[a]	No$_2$[b]	SO$_2$[c]
Nov. 11	1	10	4.3	0
		4	2.0	0
	2	26	Trace	Trace
		7	Trace	0.6
Nov. 15	2	Trace	Trace	0
		Trace	Trace	Trace
		0	Trace	Trace
	1	4	1.6	0
		3	2.3	0
Nov. 17	3	0	Trace	0
		Trace	Trace	0
Nov. 20	4	Trace	Trace	1.1
		Trace	Trace	0
		Trace	Trace	0
Nov. 26	5	6	0	2.0
		6	Trace	1.0
		3	0	1.1
Dec. 6	6	Trace	1.6	1.4
		Trace	Trace	0.8
		Trace	0	0.8
Dec. 11	7	Trace	Trace	0.6
		Trace	Trace	0
		Trace	Trace	. . .
Dec. 13	8	Trace	0	0
		. . .	Trace	0
		Trace	Trace	. . .
Dec. 15	9	3	0	0.6
		Trace	0	0
		3	0	0
Dec. 17	10	3	0	0
		Trace	0	0
		Trace	0	0
Dec. 19	7	Trace	0	0.7
		. . .	0	0
		3	0	0
Dec. 20	1	4	Trace	0
		3	Trace	0
		Trace	0.7	0.6

[a] 0 means < 0.5 p.p.b.; trace means < 2.5 p.p.b.
[b] 0 means < 0.2 p.p.b.; trace means < 0.6 p.p.b.
[c] 0 means < 0.3 p.p.b.; trace means < 0.5 p.p.b.

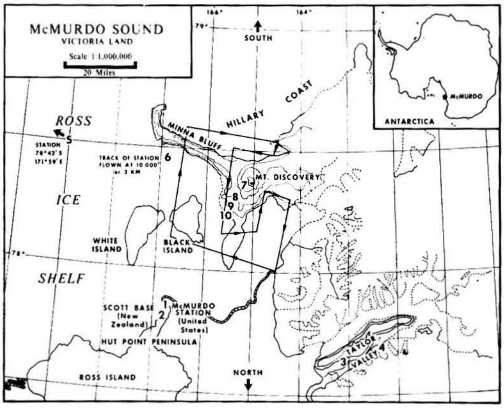

Figure 2. Location of antarctic sampling stations

1. McMurdo Station
2. Hut Point Peninsula Saddle
3. Lower Taylor Valley
4. Upper Taylor Valley
5. Ross Ice Shelf
6. Aircraft flown at 10,000 feet altitude

7 to 10. Mt. Discovery, 5000 to 140 feet elevation

Not surprisingly, samples at McMurdo Station (1) contained aldehydes and nitrogen oxides from local traffic. Sulfur dioxide was found there only once, and then only slightly above the limit of estimation, presumably indicating the use of high quality, sulfur-free fuels at that station.

Otherwise these gases were found only irregularly on the antarctic mainland. Aldehydes were present in measurable amounts at the Saddle (2) one day, but not the next, and appeared in a few samples on Mt. Discovery (7,8,9,10). Nitrogen dioxide appeared in a single aircraft sample (6), and may have derived from the exhaust of the airplane, since the craft retraced its path repeatedly during this period but not during the other two sampling periods. Sulfur dioxide was very similar to the aldehydes, although measurable amounts of both species did not always occur in the same samples.

It is tempting to dismiss these positive findings as contamination, since they are so inconsistent. Analysis at these concentrations is difficult, even in a well-equipped laboratory. Furthermore, some difficulty was encountered with gas bubbles (presumably nitrogen) forming in the cuvette in the aldehyde test; these proved very difficult to dislodge. Nevertheless, the colors appropriate to the tests were visible when the whole depth of solution in the cuvette was viewed by eye, even in samples marked trace. Fairly consistent contamination of all three tests, with species giving the proper colors, and in remote field locations, seems to involve a fairly high order of coincidence. Thus, the three gases probably were in fact present, at least intermittently, and a more complete study with more sensitive techniques is warranted.

Samples taken on the Ross Ice Shelf (5) show highly significant amounts of aldehyde and sulfur dioxide. Their presence in concentrations well above those found, on the average, on the mainland, strongly suggests a different source for them or their chemical precursors. Immediate marine sources appear to be ruled out, since the station was some 150-km. upwind from open water. No explanation can be offered on the basis of these data. Since only one sample showed even a trace of nitrogen dioxide, it apparently has a source different from that of the other two gases. This conclusion seems to be supported by data from the mainland as well.

Since the gases analyzed may be photochemical reaction products (or intermediates), weather records were examined to see whether the chemical values were related to sunlight. There was, of course, no night during the entire period of sampling. Comparison of cloudiness records at McMurdo with the chemical data gave a faint suggestion that high concentrations were in fact associated with cloudy rather than sunny days. If this association is real, one of two conclusions is possible: The substances are primary products of some rather local process, and cloudiness retards their dispersal and/or photochemical destruction; or under cloud there is enough light for their formation from precursors, but not enough for their destruction. The very low sun angle connotes a relative lack of ultraviolet energy, which makes the former the more plausible alternative.

For comparison, Lodge and Pate (1966) found the following typical levels in the Panamanian tropics, depending on location: aldehydes, 1 to 10 p.p.b.; nitrogen dioxide, 0.5 to 2 p.p.b.; and sulfur dioxide, about 2 p.p.b. Thus the antarctic values of the last two gases seem clearly lower than the tropical values. The aldehyde determination used in Antarctica proved insufficiently sensitive to show any difference between values there and in Panama.

Conclusions

Traces of nitrogen dioxide, sulfur dioxide, and aldehydes appear to occur at some times and places in Antarctica despite a nearly total absence of the biotic conditions which might be expected to constitute a major source of these gases. Concentrations of the last two substances seem clearly higher on the Ross Ice Shelf than on the antarctic mainland. If more sensitive methods can be developed, preferably coordinated through a base chemistry laboratory for more accurate final analysis, further study of these and related chemical species may unravel the source-and-sink relationships involved.

Acknowledgment

Allen Price assisted with the entire field operation. The United States Antarctic Research Program, National Science Foundation, and the United States and New Zealand Navies provided assistance, transportation, and shelter.

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BOOKSHELF

Unbalanced look at pest control techniques

Pest Control: Biological, Physical, and Selected Chemical Methods. Edited by Wendell W. Kilgore and Richard L. Doutt. xii + 476 pages. Academic Press, Inc., New York, N.Y. 10003. 1967. $19.50, hard cover. *Frank E. Guthrie is with the Department of Entomology, North Carolina State University, Raleigh, N.C. 27607*

By Frank E. Guthrie

The purpose of this book is to set forth the advances made in developing novel, alternative, or functional combinations of pest control techniques over the past decade. In a book devoted to the development of pest control techniques, one would have expected an in-depth treatment of the components of the methods, including all facets of the problems, ultimately outlining principles for theoretical field situations. The chapter on integrated control does this admirably, but there are vacuums in one context or another in other chapters making it difficult to readily segregate and comprehend the utilization of the suggested control methods.

The serious student of alternative pest control procedures will question the omission of extraphysiochemical means of genetic control (*Bull. World Health Organ.* **29,** 1963, for example) and the exclusion of chapters on plant resistance and environmental manipulations while including such narrowly restrictive, or questionably applicable, chapters as electromagnetic energy, repellents, and antifeedants.

The first chapter, "Biological Control," places greater emphasis on historical events than on principles. In electing to make defense of the biological control method a main theme of his well-written account, the author of this first chapter creates the impression that the method has no deficiencies. His well-documented presentation is conclusive proof that it is a splendid control measure in those situations where it is applicable. The second chapter, "Microbial Pesticides," is an academic account well suited as a textbook chapter.

An introduction to area-wide control would have seemed appropriate at this juncture to orient the reader to the problems inherent in such an undertaking, for three important chapters seem committed to this concept. It would also have seemed advisable to have outlined the extensive ecological considerations necessary for a well-planned study prior to utilization of the eradication method.

The chapter on radiation-induced sterility places undue emphasis on the history of the already well-publicized account of screwworm eradication. The chapter would have been an outstanding one had the perspective been broadened to include those components of the control method which likely have emerged from an extensive accumulation of data over a wide range of activities.

The authors rightfully acknowledge the successful use of radiation-sterility in the *Diptera,* but minimize the less successful utilization of radiation illustrated by studies on *Hemiptera, Lepidoptera,* and *Coleoptera.* The interested scientific community, overwhelmed by the amount of publicity and governmental research devoted to this subject, would benefit greatly by a treatment which would delineate all the parameters of this control method, including information gained from such programs as the one designed to eradicate the boll weevil.

Chemical Review

The chapter on chemosterilants is an excellent review of the chemicals per se (including structure-activity relations, metabolism, and mechanism of action) and practical aspects of chemosterilization. Ten lines devoted to the effects of chemosterilants on mammals seems to both minimize the very real public health aspects of the method and ignore an extensive background literature. A rationale for utilization of the chemosterilization technique might have suggested the likelihood that practical use of the method seems uncertain until chemicals of the nonalkylating type are discovered. An extremely good account of pheromones describes the fundamental work and the potential of these insect-produced secretions.

Chapters on repellents and antifeedants add little to the book. Indeed, the chapter on antifeedants detracts considerably by its failure to cite reliable scientific evidence on antifeedant effects of the triazene group.

A lengthy chapter on the possible use of electromagnetic energy, described in a similar review by the same author in 1966, covers the technical aspects of the use of energy adequately. But the author's unwillingness to present a critical analysis of the applied aspects of the method forces the reader to draw his own conclusions as to the practicality. For example, control of hornworms attacking tobacco is cited as one of the more successful uses of the light trap method of control. This finding is not reflected in the recommendations for control of these insects by any state agency in the tobacco-growing area. Thus, the reader who is perhaps not familiar with the details of previous work may question whether the author has tended to overemphasize the possibilities of the control method.

The most exceptional chapter deals with integrated control, of which a scholarly account is presented. The reader will find a readable account of intelligent use of insecticides.

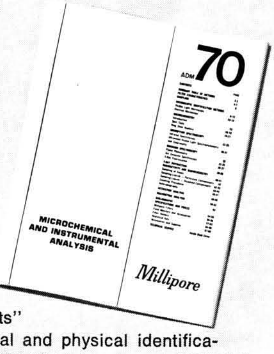
Control of vertebrates

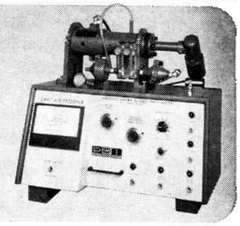
The final two chapters are devoted to control of vertebrates. The first, "Biocontrol and Chemosterilants," presents a comprehensive introduction to the problems of vertebrate control and places great emphasis on a knowledge of ecology and population dynamics. The unwise introduction of predators and normally ineffective increase of natural predators as control agents are emphasized in this review.

The use of chemosterilants, primarily (in this review) chemicals that affect sex hormones, is approached with a warning against the dangers of introducing broad spectrum sterilants into the ecosystem. The author concludes that nonbiocontrol methods are best suited for vertebrate control and should be integrated with natural control. This conclusion seems to directly oppose the concept of integrated control of invertebrates.

The final chapter reviews behavioral manipulations for vertebrate control, primarily birds. The most promising devices—recording and transmitting various distress signals—are discussed in the light of practical field experiments. The adaptation of birds to the recorded distress signals and the possibility that one transfers a pest problem from one area to another are adequately discussed.

Two or three chapters are excellent, but for the most part the book goes over the same ground thoroughly covered by recent reviews without offering anything particularly new to the subject. The audience for which it is intended eludes me. It is not applicable as a class text, or complete enough for a review, and there is little evidence that any attempt was made to coordinate the book into a balanced perspective of various pest control techniques. ■





Excellent source of atmospheric and astrogeologic data

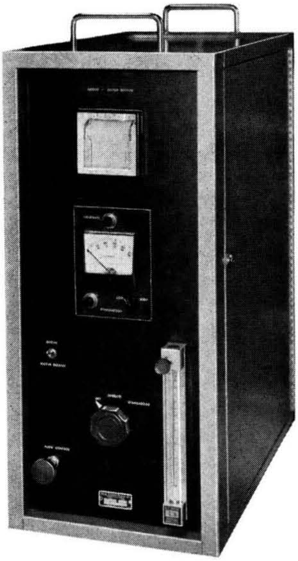
Encyclopedia of Atmospheric Sciences and Astrogeology. Edited by Rhodes W. Fairbridge. xv + 1200 pages. Reinhold Publishing Corp., New York, N.Y. 10022. 1967. $35, hard cover. *Frank A. Gifford is director, Atmospheric Turbulence and Diffusion Laboratory, ESSA, Oakridge, Tenn. 37830*

By Frank A. Gifford

"The Encyclopedia of Atmospheric Sciences and Astrogeology" is a single-volume work containing 400 articles in its subject area written by, according to my count, 150 experts. It is one of a projected series of eight volumes, intended to cover the entire field of earth sciences. The reviewer of such a substantial (1200 pages) book could approach it from various directions, but must necessarily end up with some version of the smorgasbord, or pot-luck supper approach, if only in order to finish the job in a reasonable amount of time. As this procedure could easily lead to a certain amount of literary indigestion, I am pleased to be able to report that the book is both readable and digestible.

Astrogeology is defined, according to the article appearing under this title, as "A discipline covering the overlap between geology and astronomy." Atmospheric sciences are defined as those "which are concerned primarily with the chemical and physical phenomena of the atmosphere of the earth, although . . . it may include the study of the gaseous envelopes of other planets." Thus, the scope of this book is extremely broad, and individual articles are, as a rule, necessarily somewhat restricted in the detail of their treatment. Bibliographies accompany each article, however, and these usually contain references to more extended discussions.

There are many excellent photographs and diagrams, for the most part reasonably well reproduced, and a good-sized subject index is included. The articles are extensively cross-referenced. Although the volume is not intended to serve as a handbook, it



contains a considerable amount of basic graphical and tabular information, including many useful nomograms, scales, and so on.

In trying to assimilate enough of the content and flavor of this book to formulate some general impressions and evaluations, I found myself considering groups of related articles on subjects I happen to be interested in. For instance there are excellent groups of articles on climate and climate change, planetary atmospheres, cosmology, and, of course, many other subjects. One interesting group of articles of a clearly pedagogical content, includes such titles as "Cycle analysis," "Units, numbers, constants and symbols," "Vector analysis," and even "'Iso' terms."

Uniform approach

The depth and style of treatment naturally varies somewhat, but, in general, the editor (who also is a major contributor, having authored more than 30 of the articles) has managed to get a reasonably balanced and uniform approach from his large stable of experts. Moreover, the quality of the contributions is certainly high. As I turned to articles on subjects with the details of which I am most familiar, I found myself being more critical of shortcomings, omissions, and limitations. On the other hand, when I turned to subjects like "Earth motion," or "Relativity," that were either very unfamiliar to me or which I never have really understood very well, I found the discussions to be enlightening and evidently expert contributions.

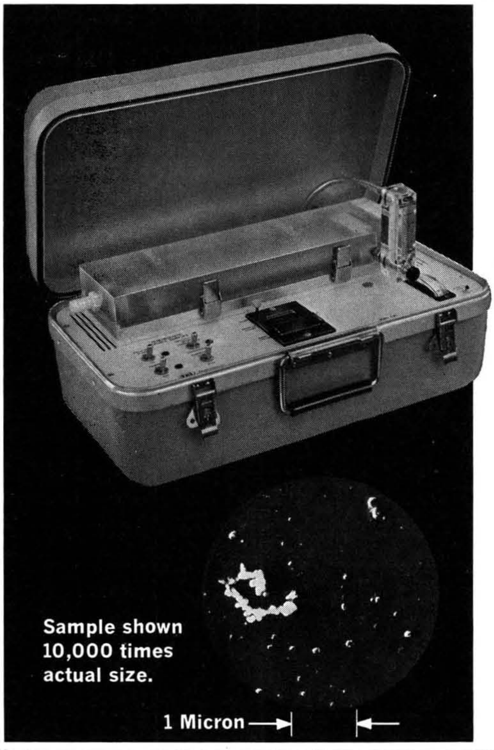
Approaches and styles naturally differ somewhat, but the editor has obviously maintained a very high and balanced standard. I suspect that other readers will have similar experiences and conclude that the volume serves its fundamental purpose, that of providing basic and authoritative, but not necessarily exhaustive treatments of a wide variety of subjects. The book does this very well, indeed.

I feel that I can recommend this book as an excellent, up-to-date, and readable source of information that broadly covers a rather vast field of science. Since much of this science has been developed only recently to any extent, no doubt the volume will be useful to a wide variety of readers.

No real purpose would be served by itemizing the handful of minor errors, mostly typographical, noticed by this reviewer, who begs to be excused from this traditional chore. In general, the standards of writing, editing, and production are obviously high. So, too, unfortunately, is the price, although, because of its size, scope, and other merits, "The Encyclopedia of Atmospheric Sciences and Astrogeology" must still be counted a good value on today's market. ■

New Developments in Air Pollution Control. Edited by Robert A. Fox. A symposium. 145 pages. Robert A. Fox, P.O. Box 607, Grand Central Post Office, New York, N.Y. 10017. 1967. $5, paper.

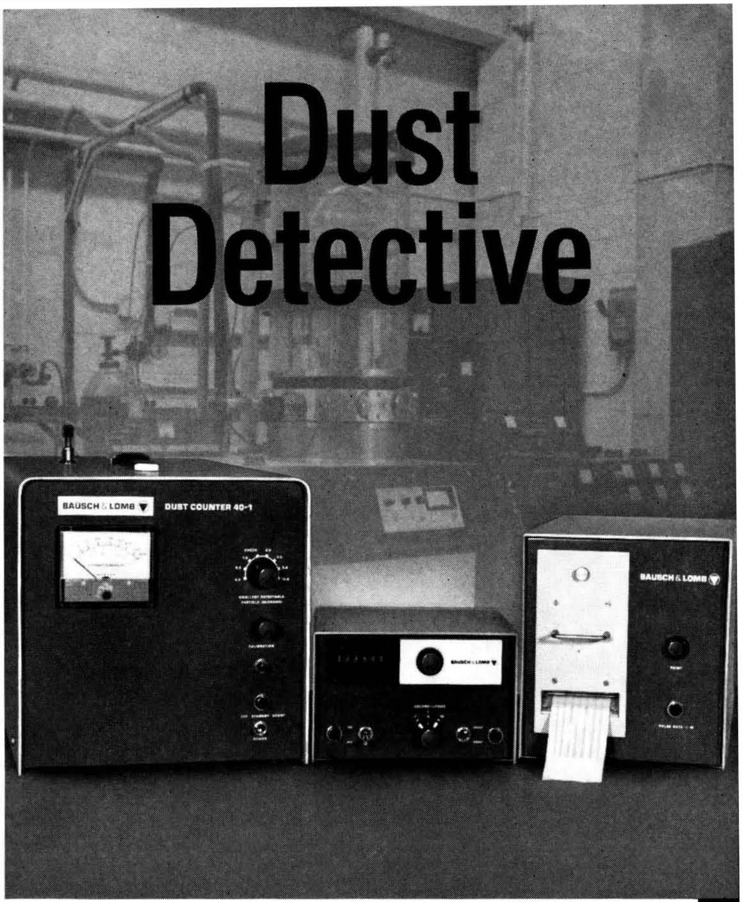
The volume contains the proceedings of the MECAR Symposium held Oct.

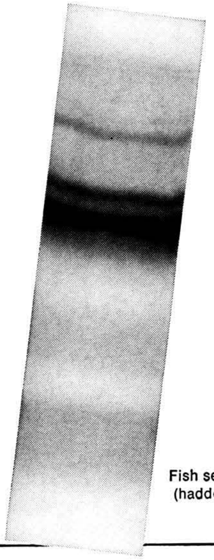


23, 1967, in New York City. Papers presented at the symposium touched on such subjects as control of particulate emissions, noxious gas emissions, solvent emissions, and recovery or removal of sulfur oxides from stack gases. Other papers dealt with the current work at Bureau of Mines and the federal program of engineering R&D. A special report on European installations described municipal incinerators at Paris, Munich, Dusseldorf, and Birmingham, noting that all are equipped with Lurgi electrostatic precipitators and, in the case of the installation at Birmingham, an evaporation cooling tower. ■

Biological Associated Problems in Freshwater Environments: Their Identification, Investigation, and Control. Kenneth M. Mackenthun and William M. Ingram. x + 287 pages. U.S. Government Printing Office, Washington, D. C. 20402. 1967. For free copy, write to Kenneth M. Mackenthun, acting chief, Biological and Chemical Section, Technical Advisory and Investigations Branch, Division of Technical Services, Federal Water Pollution Control Administration, Department of the Interior, 5555 Ridge Ave., Cincinnati, Ohio 45213

This handbook on the identification, investigation, and control of problems associated with the biota in flowing streams, lakes, reservoirs, and ponds is based on "Limnological Aspects of Recreational Lakes," a PHS publication now out of print. The book discusses the effects of temperature, dissolved oxygen, and light on the aquatic environment, and the effects of streams on reservoirs and reservoirs on streams. The responses of algae, vascular plants, benthos, and fish to the aquatic environment under various influencing factors are itemized. Methods of stream data collection and reporting are also delineated. Nutrients that stimulate and conditions that depress aquatic vegetation growths are detailed. Four chapters deal with water-associated pests and the multitude of problems they cause. Taxonomic keys are presented for some of the nuisance algae and common vascular plants. Finally, information is given on how to control or alleviate excessive production of biological nuisances. ■





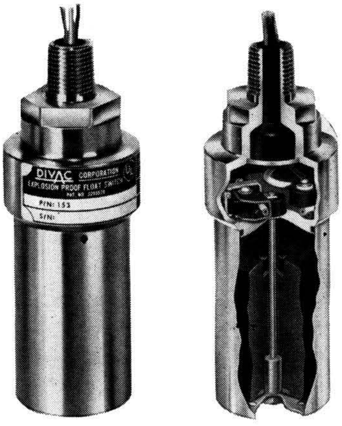
NEW PRODUCTS DIGEST

Fluorometer

A filter fluorometer designed for compatibility with automated analysis systems features a dual-beam reference system, a high-pressure mercury arc source lamp, selected photo-multipliers, and an advanced microflowcell design for rapid rates of analysis. Technicon Corp. **61**

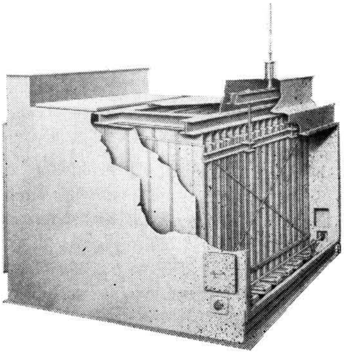
Oxygen Controller

Model PO 160C oxygen controller regulates oxygen content—either greater than or less than atmospheric levels—in closed containers that are used for shipping perishable goods or storing flowers. The device controls oxygen levels in incubators, oxygen tents, and other similar systems. The solid state device regulates oxygen partial pressure from 10 to 320 mm. Hg with a nominal sensitivity 1% of set point. Technology/Versatronics, Inc. **62**



Float Control Switch

High and low level float control switches for accurate level control of liquids such as chemicals, petroleum products, foodstuffs, and water for industrial and institutional uses, are available. The switches are explosion proof, and can be used to actuate alarms, pumps, solenoids, magnetic controls, and other electrical and pneumatic equipment, according to the manufacturer. Divac Corp. **63**



Electrostatic Precipitator

A compact, portable electrostatic precipitator recommended by the maker for foundries, steel plants, fertilizer plants, chemical plants, and like facilities, is completely fabricated at the factory and requires only hookup, supports, and ducting at the installation site. The manufacturer calls the unit the Minitrell, and says it is 99% efficient. Joy Manufacturing Co. **64**

Screw Pump

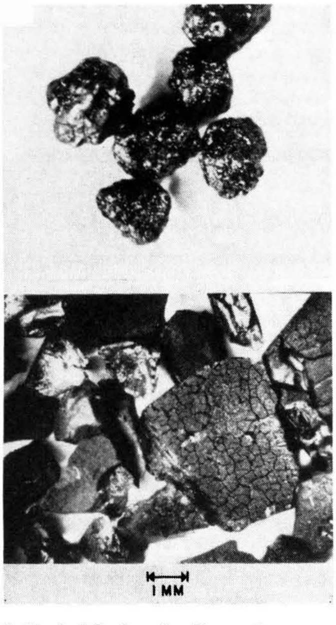
Screw pumps for transporting raw sewage, activated sludge, storm water, slurries, industrial wastes, and other liquids, operate at a constant speed to lift a continuous stream of liquid to a height 20–25 feet above the feed stream. Available in screw diameters 12 inches or larger (in 6-inch increments), the pump consists of a motor-driven screw conveyor in a concrete or steel trough. Capacities range from 50 g.p.m. upward, with almost unlimited maximum capacity obtainable from multiple units. FMC Corp. **65**

Gas Analyzer

Model GA-5b gas analyzer for evaluation of aircraft fire-extinguisher systems can record, from a remote location, the concentration of gas present in as many as 12 different fire zones aboard an aircraft. The system can detect and analyze any gas present in a monitored area. The manufacturer of the device anticipates its use in smog analysis and control. Statham Instruments, Inc. **66**

Bacterial Colony Counter

A bacterial colony counter that combines an electronic count register and a variable-illumination viewer in one compact unit, is available. The unit is designed to expedite the accurate counting of surface and subsurface colonies and plaques on any type of agar medium in standard 100-mm. Petri dishes. An adjustable electrode is inserted into the agar at one side, and a circuit is completed when the operator touches each colony with a second electrode. Fisher Scientific Co. **67**



Activated Carbon for Processing

An activated carbon has been developed for use in purification of liquid process streams. Grade 17 is characterized by high purity and granule abrasion resistance and, according to the company, has low ash content (<1%). Available in standard mesh sizes (12 × 30 and 20 × 40 U.S. sieves), the carbon does not require pretreatment acid to remove extractables. Witco Chemical Co., Inc. **68**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New basic package gives you an accurate picture—and records it—FOR ONLY $1268. Here's what the basic package includes:

◀ **Model F-1 AISI Automatic Sampler** provides detailed record of particles or gas concentration over extended periods. Also provides data for determining source and distribution of pollutants. Can be adapted to sample gases such as hydrogen sulfide. Included with sampler is model 363-A spot evaluator (not shown) for direct reading and measurement of filter tapes.

Model PV Sequential Sampler—fully automatic—can be programmed to provide 12 samples timed from ½ to 23¾ hours per sample, and with intervals of from ½ to 23¾ hours between samples. Ideal for gases such as SO_2, H_2S, NO, NO_2, NH_3, CO and many others. ▼

Dust-fall and SO_2 Stanchion includes stanchion, dust fall jar holder unit, and complete SO_2 lead peroxide candle station.

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Clean Room

Laminar flow clean rooms feature filters that occupy an entire ceiling or wall, sweeping clean air vertically or horizontally through the room. Particles are thus swept out of the room continuously, providing a suitable work place for projects concerned with electronic reliability, precise mechanical devices, biological materials, and coating applications. Battelle Memorial Institute. **69**

Extraction System

An extraction system for controlling fumes at all stages of the melting cycle in high-alloy steel manufacture processes, is available. The technique provides for direct evacuation of fumes from electric arc furnaces used in the processing. A pressure differential controller in the furnace holds the atmosphere at a point of equilibrium where it is impossible, according to the manufacturer, to obtain a black slag condition. United Sheet Metal Co., Inc. **70**

Glass-Reinforced Plastic Pipe

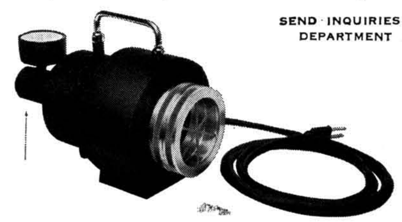
Good chemical resistance, low electrical and thermal conductivity, corrosion resistance, and a 40% reduction in installation costs, are the chief properties of the lightweight, glass-reinforced plastic pipe used as a replacement for chemical lead pipe. The polyester pipe is available in large diameter and in standard lengths, and in several wall thicknesses to match pressure requirements. Koppers Co., Inc. **71**

Quadrupole Mass Spectrometer

Model 1015 quadrupole laboratory mass spectrometer features a mass range from 1–750 amu., linear mass display, and compatibility with commercial gas chromatographs and recording systems. The basic system comprises an electronics console and a vacuum console. Finnigan Instruments Corp. **72**

Double-Port Valves

A line of valves designed for accurate throttling control of liquids, gases, or steam, has extra-heavy body wall thickness for resistance to corrosive and erosive fluids. Available in cast iron, carbon steel, and 316 stainless steel, the valves have actuators with two-stage positioners for fast response and positioning accuracy. Conoflow Corp. **73**



NEW LITERATURE DIGEST

Stream gages. Bulletin 18 describes eight accessories for gaging streams. Three instruments are designed for making current measurements: a tag line, a gaging reel, and a sounding reel. A cable hanger connecter is offered for use with the sounding reel. Staff gages for direct visual reading of water levels are porcelain enameled to resist rust and discoloration. Hook and point gages use vernier action to measure liquid surfaces within 0.001 foot. A float gage and an electric contact gage are also offered. Leupold & Stevens Instruments, Inc. **91**

Trickling filters. Bulletin N-960 presents a trickling filter for use in secondary treatment plants. Included, also, is a description of a rotary distributor accessory for the device. General American Transportation Corp. **92**

Noncontact thermometers. An 8-page illustrated booklet discusses applications of the Opti-therm infrared thermometer. Such uses include measuring thermal characteristics of streams, correlating cloud temperatures with ground temperature and elevation, and noting the relationship between plant and ground temperatures. A 4-page, two-color brochure also available describes a second device: a precision, noncontact radiation thermometer for remote sensing of earth environment. Barnes Engineering Co. **93**

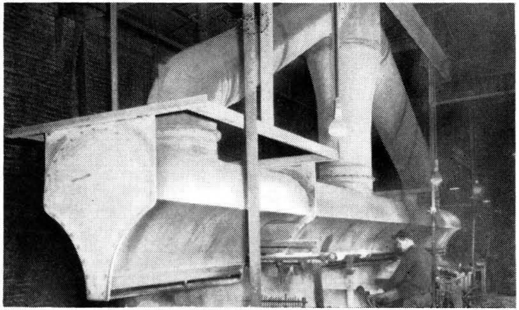
Labware. Catalog 101 describes a line of standard porcelain labware and two new lines of high-alumina ware. Coors Porcelain Co. **94**

Industrial pollution control systems. Bulletin 67-1 describes liquid and fume destruction systems for control of industrial wastes. The units feature special air-inlet tiles that admit air into the furnace chamber to cool the refractory lining. Heat recovery units are included in several of the systems. Bigelow-Liptak Corp. **95**

Gas chromatography journal. The first issue of the new publication, *The De-Tektor*, highlights the electrolytic conductivity detector for gas chromatography, especially for use in the detection of nitrogen, halides, and sulfur. Flame photometry and Coulson units are also featured. Tracor Analytical Instruments, Inc. **96**

Surfactants. A 31-page technical bulletin discusses properties, applications, physiological considerations, surface-active measuring procedures, and analytical methods for the use of an anionic sulfonate surfactant. The surfactant is useful in metal cleaning, phenolic resin solubilizing, and chemical specialty formulating, textiles, detergent disinfectants, shampoos, cosmetics, and emulsion polymerization. It also has pulp and paper industry applications, food processing applications. Dow Chemical Co. **97**

Filter paper. A 24-page brochure lists more than 100 grades of filter papers, extraction thimbles, and related products, in an assortment of sizes and shapes for special uses. Included is a table that suggests special papers for specific applications—phenylketonuria detection, isotope work, Kjeldahl determinations, and brewery operations, for example. Gallard-Schlesinger Chemical Manufacturing Corp. **98**



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PROFESSIONAL CONSULTING SERVICES

(*Continued from page 478*)

MEETING GUIDE

June 2–7
American Water Works Association
88th Annual Meeting
Cleveland, Ohio

What Price Water, a six-day conference, will examine the long-term problems of water supply. On June 1, three separate one-day seminars are offered on a first-come basis to water utility managers and executives: Managements' Role in Controlling Hazards, Motivating Managers and Employees, and Theory and Control of Coagulation–Flocculation. To enroll, write Education Committee, American Water Works Association, 2 Park Avenue, New York, N.Y. 10016

June 3–5 and August 14–16
Federal Water Pollution Control Association and Vanderbilt University
National Symposiums on Thermal Pollution
Portland, Ore. (June) and Nashville, Tenn. (August)

Two national symposiums on thermal pollution will be sponsored by these groups in 1968. The first, emphasizing biological consequences, will be in Portland, Ore. on June 3–5, and the second, oriented toward the engineering and economic aspects of thermal pollution, will be in Nashville, Tenn. on August 14–16.

June 4–5
Air Pollution Control Association and Others
Symposium on Air Quality Criteria
Hotel Commodore, New York, N.Y.

The meeting will be cosponsored by five organizations: Air Pollution Control Association, American Industrial Hygiene Association, American Petroleum Institute, Industrial Medical Association, and the Occupational Health Institute. Major papers will be presented on carbon monoxide, oxidants, sulfur oxides, particulates, and lead. Prepared discussion will follow each paper, then general discussions. Effects on vegetation, as well as health effects, are considered.

June 16–20
American Institute of Biological Sciences
Ecosystems: Evolution and Revolution
University of Wisconsin, Madison, Wis.

Process and Ecological Change, the symposium scheduled for June 17, will examine short term processes which contribute to organism diversity and metabolism, as well as long term processes such as climatic change, ancient catastrophes, rates of recovery, recolonization, and speciation. Man and Nature, planned for June 18, will explore the population explosion and its effect on the balance of nature.

June 17–21
University of California (Berkeley)
Atmospheric Noise Pollution and Measures for Its Control
University of California, Berkeley, Calif.

Topics include sources of noise, measurement of noise and setting noise criteria, legislative approaches to noise control, psychological and physiological responses to noise, and results of international studies on noise pollution.

June 19–21
Iowa Water Pollution Control Association
50th Annual Meeting
Holiday Inn, Ames, Iowa

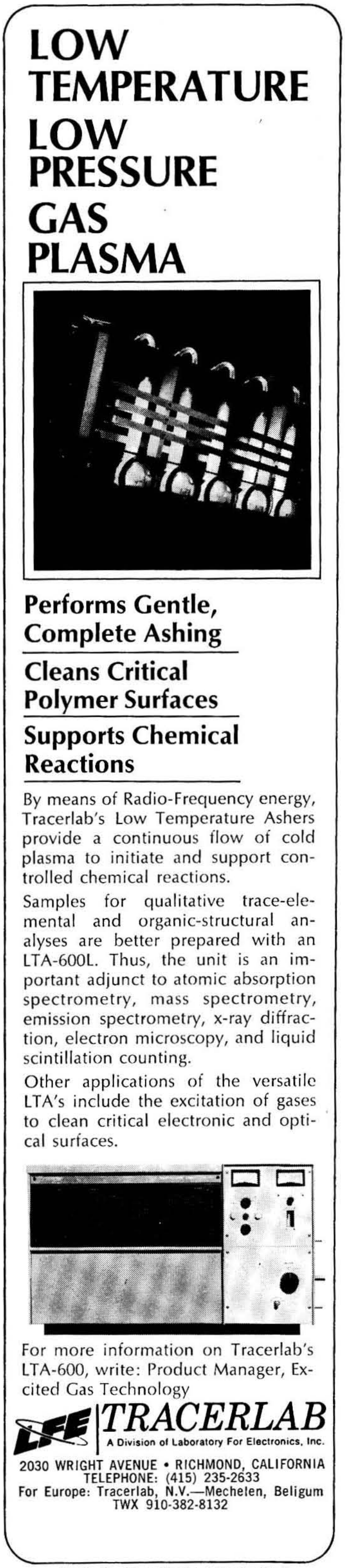
A program to honor the past, and an attempt to predict the future, will mark the meeting of this charter member of the WPCF. A strong technical program is planned for meeting today's problems.

June 23–27
Air Pollution Control Association
61st Annual Meeting
St. Paul Hilton Hotel, St. Paul, Minn.

Power, source analysis, ambient air standards, odor evaluation, control equipment, oxidants, aerosols, meteorology, ambient air analysis, air chemistry studies, agricultural effects, vehicular exhausts, control equipment, and other topics are scheduled for the technical sessions, and the latest in control and analytical equipment will be exhibited.

June 24–26
American Society of Civil Engineers and Engineering Institute of Canada
Great Lakes Water Resources Conference
Royal York Hotel, Toronto, Canada

The conference will consider problems relevant to the Great Lakes region. Contact Mr. Denis Temple, chairman, Public Information, P.O. Box 520, Clarkson, Ontario, Canada.



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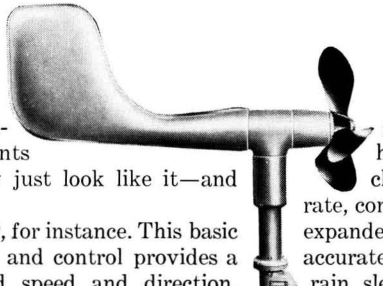

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Before settling on a final design, UOP engineers built a 1/16 scale model to study gas distribution in the unit and draft loss in the flue gas system from air heater to stack. Extensive testing showed that the design used would best minimize draft loss and, therefore, reduce operating costs.

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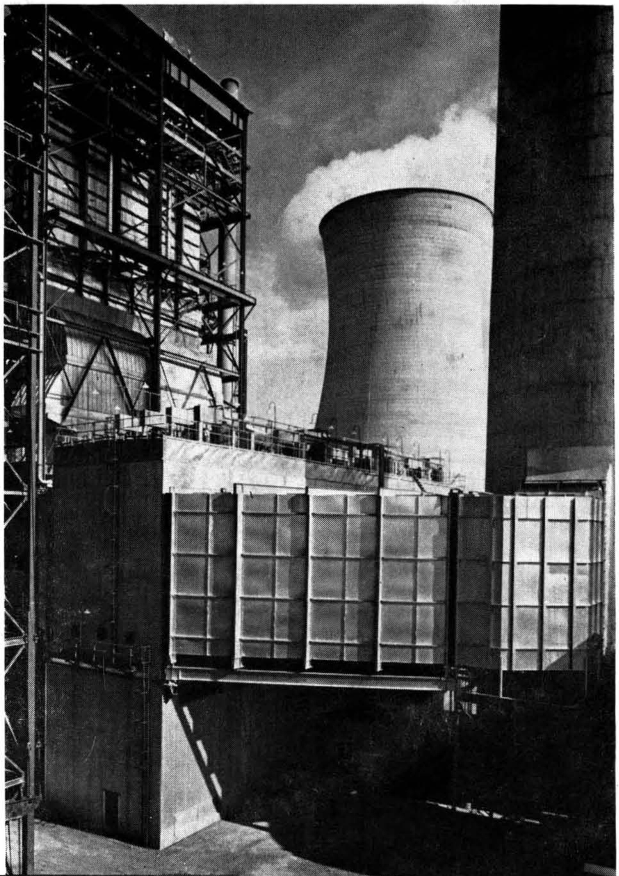

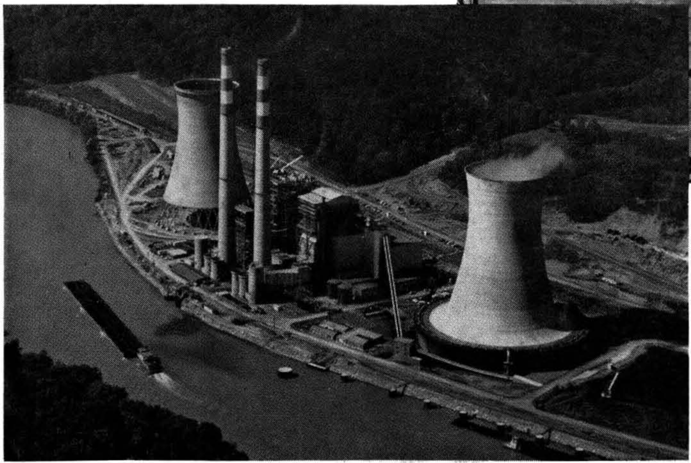

One of the largest precipitators ever built, this UOP unit collects ash from the boilers of Unit No. 1 at Fort Martin (owned jointly by Allegheny Power System and Duquesne Light Company). A second UOP precipitator is under construction for Unit No. 2 (owned by Allegheny Power System).

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