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Emphasizing

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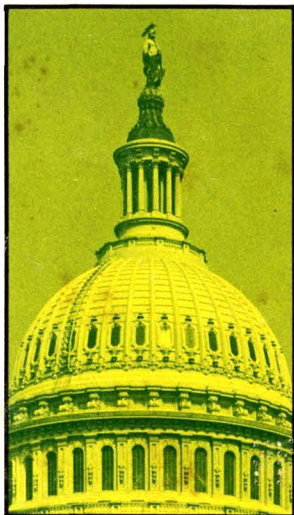
Air, &

Waste

Chemistry

MARCH 1968

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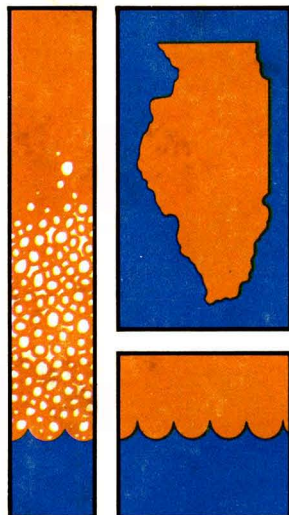


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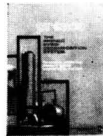
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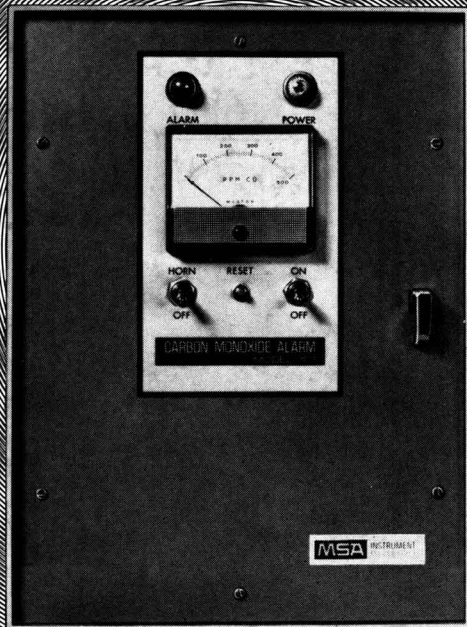
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March 1968

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Ronald Long and B. B. Chakraborty

According to the original authors of the paper (ES&T, October 1967, page 833), the unknown hydrocarbon peak is a mixture of hydrocarbons including an unidentified pyrene derivative having a higher molecular weight than the methylpyrenes. An earlier peak corresponds to a mixture of the methylpyrenes and is explained as a mixture of 1-methylpyrene and 4-methylpyrene.

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EDITORIAL

Air, water, land—elements of beauty that shape our lives

President Johnson proposes broadened program for solving the no longer quiet crisis of conservation

This month President Johnson spelled out for Congress how he feels the legislature should go about implementing the expanded environmental program that he outlined at the end of January in his budget request for fiscal 1969 (see page 172). Specifically, the President has asked that federal expenditures for conservation in the coming fiscal year be raised to \$1.2 billion, compared with \$565 million to be spent in the current fiscal year.

In his January budget message, President Johnson had requested selective increases in several programs designed to enhance the quality of our environment, such requests including special funds to bolster the nation's fight against air and water pollution and solid waste problems. Some of these requests offer interesting examples of how less can mean more. For example, the National Center for Air Pollution Control was required to reduce the budget for its controllable programs by \$1.9 million. However, the Air Quality Act of 1967 established a program that even within the current fiscal year has led to an NCAPC request for a supplemental appropriation of \$16 million. And for fiscal 1969, NCAPC is seeking an increase of \$26.5 million, bringing its total 1969 fiscal year requests for its air pollution program to \$107 million. Also, the NCAPC budget for research dollars will more than double if plans for fiscal 1969 are carried through.

In his special message to Congress this month, President Johnson also spelled out what he considers to be the urgent conservation needs for the country (see page 168). Wide-ranging, the message discussed conservation needs in air, water, land, and oceans—"the elements of beauty."

Among the many features of the President's message, two stand out: • A proposal that Congress permit federal aid in the form of annual installments rather than lump sum grants. • A proposal that new financing be restricted to only those cities that have a system of user charges.

Under these proposed financing programs, \$500 million granted to cities for construction would generate, in turn, \$2 to \$3 billion of construction. Thus, the President argues, communities would get their urgently needed plants quickly and the fight against pollution could proceed in earnest.

What may be one of the most controversial aspects of the President's proposal is the suggestion that municipalities impose a system of user charges on those who benefit from the existence of the new treatment plants. Through adoption of the user-charge system, the President says, industry would be encouraged by incentive to curb pollution through improved manufacturing techniques. But at the same time these industrial efforts would relieve pressure on an overloaded local government tax base.

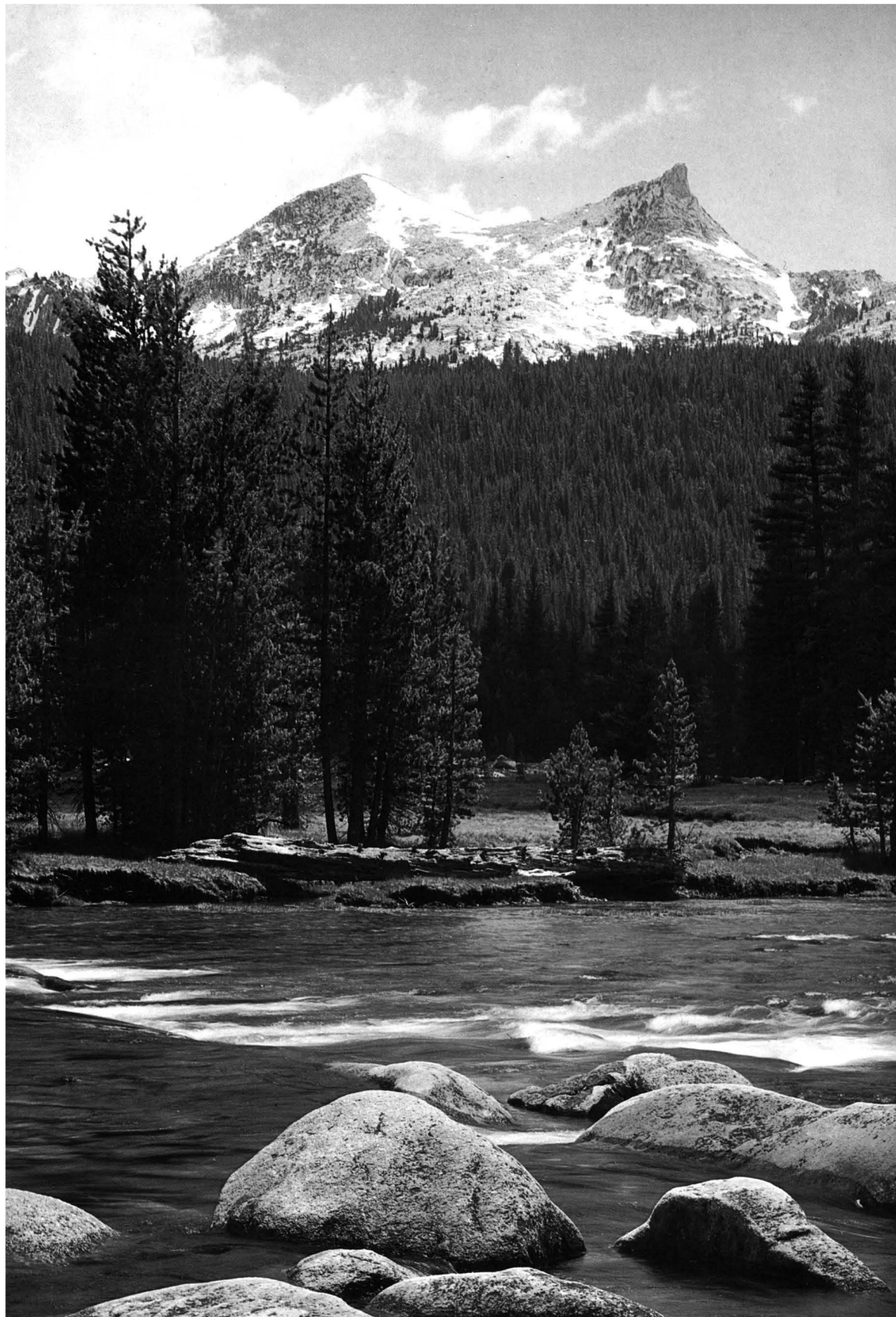
The President's message is a comprehensive one. It brings together and considers all the major aspects of our environment. It deals with how we must act in regard to these aspects of our environment and how we must coordinate our efforts if we are to preserve the natural heritage of the American people.

It may be quite true that technology useful in correcting an environmental problem in one sector cannot be transferred easily—or transferred at all, in some instances—to another. It is equally true that cleaning up an environmental problem in one sector can easily create a problem in another. Therefore, the environment must be considered as a whole, and approached as an integrated unit.

The President, aware of the need to improve the environment in all its major aspects notes: "To succeed in meeting their [environmental dangers] challenge requires a wide-ranging response, with special emphasis on the items of highest priority."

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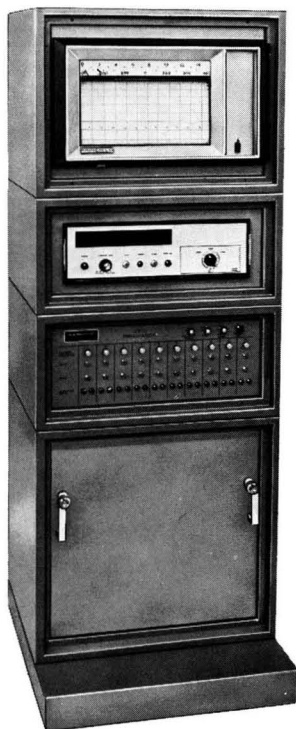


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Legislation Proposed for Environmental Quality

An Environmental Quality Preservation Act of 1968 has been introduced by Sen. Gaylord Nelson (D.-Wis.). His bill would serve to coordinate and expand the state, local, and Federal Government's role in meeting our environmental crises. S. 3031 includes provisions for the following: • A council on environmental quality in the executive office of the President. • Authority for Department of the Interior to conduct studies of natural environmental systems in the U.S., to document and define changes in these systems, and to maintain an inventory of natural resource development projects and other related projects. • A comprehensive research program for waste management in the Department of Health, Education, and Welfare. • A national inventory of needs, problems, and technology of waste management, to be conducted by HEW. • A Clearinghouse for information on all aspects of air, water, and soil pollution, and waste disposal.

Nuclear Industry Plans to Control Its Thermal Pollution

The Vermont Yankee Nuclear Power Corp. (Vernon, Vt.) has agreed to construct cooling towers—at a cost of \$6.5 million—to control its thermal output to the Connecticut River, according to its president, Mr. Albert A. Cree, at recent hearings (Montpelier) of the Senate Public Works Subcommittee of Air and Water Pollution. By using giant, fan-forced air radiators in a closed circuit cooling system, Vermont Yankee will discharge effluent water so that no increase in the temperature of the river occurs during the summer months and no more than a 4° F. increase occurs during the winter months. Without this new equipment, the medium sized (540-megawatt) nuclear steam electric station, for which foundation construction has already started, would use two thirds of the total flow of the Connecticut River and discharge effluent water having a temperature more than 20° F. higher than the intake water. Operation and maintenance of these towers will cost \$900,000 annually, resulting in an estimated increase of one quarter cent per kilowatt hour, approximating a 1% increase in the cost of electricity, according to Vermont Yankee.

Drilling a Window into the Earth's Past

Scientists have drilled through 7100 feet of ice, from snow surface to the bottom of the West Antarctic ice cap at Byrd Station. The bottom ice may be as old as a few hundreds of thousands of years. Analysis of the cores will provide a vertical profile of polar history, according to the National Science Foundation, which administers the U.S. Antarctic Research Program. Among the things core analysis may provide information on: rate of snow accumulation; climatic history; rate of deposition of meteoritic particles; properties of ice and underlying material; and composition of the earth's atmosphere from ancient times, as recorded in air trapped in the ice. Preliminary tests have already turned up what appears to be volcanic ash at levels 10,000 and 14,000 years old. Further tests will determine if the material is indeed volcanic ash and its origin.

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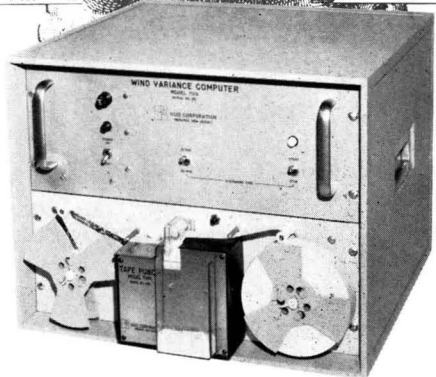
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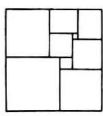
The basic system, comprising a Model 7000 Computer and Model 7005 Tape Punch Unit, eliminates the need for manual data extraction from strip chart recorders. It was originally designed for use in NUS meteorological diffusion studies, and is currently installed at a number of power plant sites for pre-operational data collection. Ultimately, the system will be used for real-time diffusion estimates at operating stations. In addition to the variance computer and associated data reduction and analysis, NUS also provides the full spectrum of professional consulting services in environmental pollution and programming.

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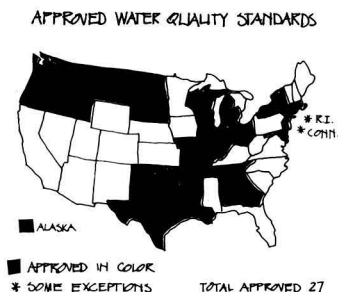


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More States Receive Approval of Water Quality Standards

As of March 12, approval for their water quality standards has been granted to 27 states by the Department of Interior. In letters to the governors of each of the additional eleven states—Alabama, Alaska, Connecticut, Delaware, Louisiana, Missouri, Montana, New Jersey, Ohio, Oklahoma, and Tennessee—Secretary Udall emphasized Interior's position on the need for protection of high quality waters and noted that most approvals were made with some exceptions.



Development of Control Techniques for SO₂ Emissions

Thirteen research and development contracts for control of sulfur dioxide emissions have been awarded to industry by the National Center for Air Pollution Control. The award of these contracts represents NCAPC's accelerated research on low-cost, control techniques for combustion by-products of fuels, as authorized by the Air Quality Act of 1967 (ES & T, November 1967, page 884). Totaling \$1,437,000, these contracts, with one exception, are for the development of techniques for control of SO₂ from fuel combustion. The one exception is a contract for SO₂ control from smelter industries involved in smelting copper, zinc, or lead.

Protecting Parks from People

The national parks have been too successful for their own good, says a Conservation Foundation report. More people, with more leisure and more mobility have already brought signs of "ecological deterioration" to many parks. "If the national parks are to continue to be a retreat from urban civilization for increasing numbers of people, much of what was permissible in the less crowded past will need to be more carefully controlled or eliminated," warns the report "Man and Nature in the National Parks—Reflections on Policy." Among its recommendations: removal or establishment of hotels and campgrounds, wherever possible, to areas outside the parks; proper zoning control of areas adjoining the parks; re-examination of policies for constructing highways and buildings within parks; a biologically informed policy for park management; and a decision to conserve wilderness areas in the parks.

Problem: How Do Thermal Inputs Affect Aquatic Life?

The biological effects of thermal inputs to the Columbia River is the subject of a two-year study by the Department of Interior. The \$600,000 project will probe all aspects of thermal effect on aquatic environment and resolve certain inconsistencies in the water quality standards of Washington and Oregon on allowable changes in temperature in the Columbia River. The study will draw heavily on current work involving the development of a mathematical model for predicting heat inputs. One of the first objectives will be to check recent evidence, from the Bureau of Commercial Fisheries, which indicates that the combination of excessive amounts of nitrogen gas and temperature changes can cause fish kills, in a manner similar to the well-known diver's bends.

President Johnson Spells Out Urgent Conservation Needs

Conservation needs

President's proposal for federal expenditure and legislative action for fiscal year 1969

Air ● Spend \$128 million for air pollution control.

Water ● Authorize \$225 million in grants to states for construction of waste treatment plants.
● Authorize Central Arizona Project.
● Establish National Water Commission for water resources management.
● Develop and enforce federal standards for drinking water and study of hazardous ingredients.
● Outlaw discharge of oil from shore installations and ships within 12 miles of land.

Solid Waste ● Review current solid waste disposal technology.
● Extend the Solid Waste Disposal Act and authorize research in disposal methods.

Land ● Funds to states to regulate strip mining, forcing mining companies to reclaim land after use.
● Spend \$130 million for Land and Water Conservation Fund.
● Develop a network of scenic trails and roadside parks.
● Complete House action on Senate approved National Parks and Lakeshores.

Noise ● Give more power to Secretary of Transportation to curb aircraft noise.
● Direct all federal agencies to take into account the noise factor in site selections involving federal funds.

Oceans ● Spend \$5 million for floating electronic buoys to transmit ocean data.
● Spend \$6 million for training oceanographers and marine scientists.
● Ask other nations to join U.S. in an International Decade of Ocean Exploration for the 1970's.

Legislation ● New financing plan for the construction of water treatment plants.
(pending or proposed) ● Surface Mining Reclamation Act of 1968.
● Safe Drinking Water Act of 1968.
● Oil Pollution and Hazardous Substances Control Act of 1968.
● One year extension of Solid Waste Disposal Act.
● Highway Beautification Act.

President Johnson asked Congress to double federal expenditures for conservation in fiscal year 1969, by spending \$1.2 billion compared with \$565 million spent last fiscal year. "Conservation's concern now is not only for man's enjoyment—but for man's survival," the President said in his message to Congress. The message outlines steps that this country must take this year to preserve the natural heritage of its people, including not only the wilderness of the unbroken forest, but a safe environment for the crowded city.

Under a proposed new financing plan for the construction of waste treatment plants, the Secretary of Interior could make annual installment payments for the construction of these plants—in addition to the current practice of making lump sum grants. The proposed legislation would permit the Federal Government to make construction commitments in fiscal 1969 to a total of \$475 million. These grants, in turn, would generate a total of \$1–\$1.4 billion in funds for this purpose. As one criterion for federal assistance, the municipalities must impose a system of user charges on those who use the treatment plants. According to the proposal, the system of user charges would provide not only an equitable way of sharing costs but would also do the following: ● Provide an incentive for industries to curb pollution through improved manufacturing techniques.
● Relieve the pressure on the overloaded tax bases of local governments.

Charged with setting a good example for the nation, federal installations across the U.S.—involving 13 separate federal agencies and 360 abatement projects—will spend \$53 million to control their air and water pollution.

Law Requires Approval of Industrial Process Equipment

Permits to construct, install, and alter, and certificates to operate control apparatus and industrial process equipment are now required by law in New Jersey. Under the provisions of Chapter IX of the state's Air Pollution Control Code, the Department of Health will issue permits and certificates for any equipment capable of causing emission of any air contaminant into the open air and for any apparatus for the control of such emissions including the following types of equipment: • All incinerators except those in private dwellings and small apartments. • Liquid storage containers for certain acids, solvents, and the like with more than 10,000 gallon capacity. • Manufacturing processes involving surface coating.

"The main import of the code and the law on permits is that much air pollution—mostly industrial—may be prevented before it even becomes a problem in the atmosphere," said Richard J. Sullivan, Director of New Jersey's Division of Clean Air and Water. According to Sullivan, operating certificates shall be valid for five years, unless revoked, and can be renewed. The certificates cannot be transferred.

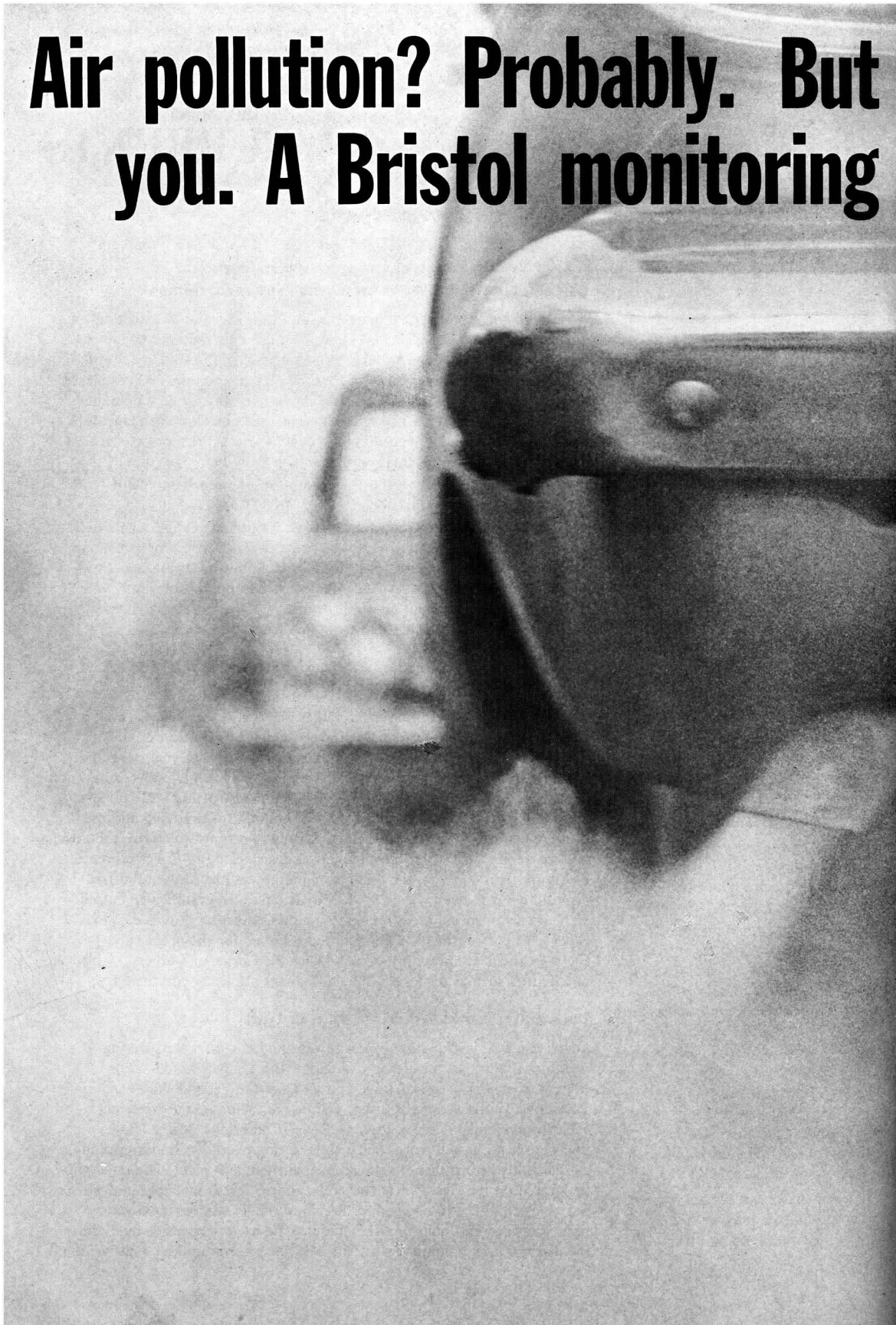
Corps of Engineers Studies Alternative Dredging Waste Disposal

Diked disposal areas offer possibilities for the disposal of polluted harbor dredgings, according to Brigadier General Robert M. Tarbox, Corps of Engineers. At the recent Lake Michigan Water Pollution Enforcement Conference, Gen. Tarbox stated that a four-year program for the construction of such areas at the 15 most critically polluted harbors of the Great Lakes would cost \$95,566,000 in construction costs for the dikes plus an additional annual cost of \$3 million for dredging and use of dumping areas. The increase in cost would be from two to five times the present annual cost of harbor maintenance, according to Corps estimate. For more than 40 years, the dredged material was placed in authorized disposal areas in deep waters of the Great Lakes. In accord with current U. S. policy, disposal areas for retaining dikes must be provided at local expense as part of the local cooperation required for the projects. Eight localities are presently working with the Corps, and other possibilities such as disposal in pits and mines are being considered.

Underwater Tanks Will Store Run-off Water

Underwater tanks can store excess sewage and run-off waters during overflow conditions, according to Melpar, Inc. (Falls Church, Va.). Melpar, recipient of a \$410,000 contract from the Federal Water Pollution Control Administration, will design, operate, and construct such storage tanks in the Choptank River (Cambridge, Md.). These underwater tanks will store such waters during overflow conditions and subsequently return them to the municipal treatment plant. The tank will be located on the river bottom several hundred feet from shore and will not be a hindrance to navigation. Previously, land storage tanks have been proposed and built, but they require the use of expensive land and the disruption of community activities during excavation and construction.

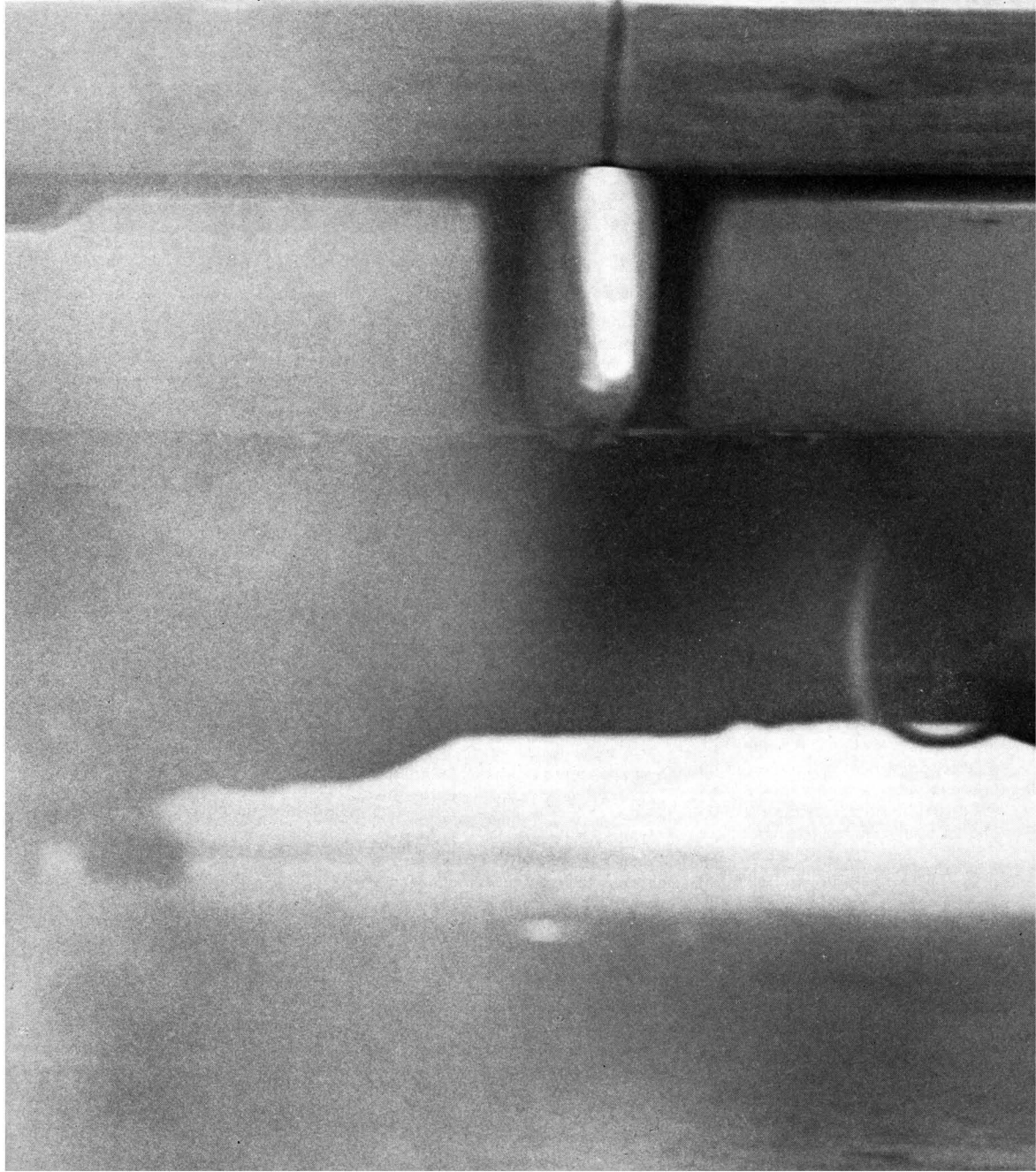
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President Calls for Increases in Environmental Programs

In his budget request for fiscal 1969, the President calls for increased fundings for on-going environmental programs which will bolster this nation's fight against air, water, and solid waste pollution

Delivered on January 29, the President's budget request for fiscal year 1969 calls for selective increases for several urgent domestic programs including the program for the enhancement of the quality of our environment. The President's request includes adequate provisions for the nation to continue its fight against air, water, and solid waste pollution.

Also, these provisions will reinforce the partnership between federal, state, and local governments to intensify our attack on air pollution, to clean up the Nation's water, to continue water resource development, and to make inroads in solving our solid waste disposal problems. Substantial total program levels appear to be available in fiscal 1969 to deal with the overall program for enhancement of environmental quality.

Precise programs of various federal agencies relating to air, water, and solid waste control activities make up the total air pollution program of the National Center for Air Pollution Control, in the Department of Health, Education, and Welfare; the water pollution program of the Federal Water Pollution Control Administration in the Department of the Interior, and the solid waste programs of both the Bureau of Mines in the Department of the Interior and of the Urban and Industrial Health Section of the Public Health Service in HEW.

Broad view of total budget

At the same time as the President's proposed selective increases, other steps have either already been taken or are being taken to hold the budget totals to the minimum consistent with national security and well being. These steps include:

- Cutbacks in controllable programs in 1968 which Congress enacted last December upon the President's recommendation.

- Reductions, deferrals, and program reforms which would reduce program levels in a variety of federal activities by \$2.9 billion in fiscal 1969.

- Determined efforts to slow the pace of federally financed construction programs as much as possible consistent with orderly government and sound practices.

- Careful review of all budget requests to ensure that increases are recommended only for high priority programs.

During the remainder of fiscal 1968, federal agencies will not be allowed to dispense their entire appropriation—amount of money that Congress approves for any agency to spend or lend.

Reducing expenditures

Enacted on December 18 of last year, Public Law 90-218 required all federal agencies to reduce their 1968 obligations and expenditures in con-

trollable programs. Thus, federal agencies were required to reduce their obligations by no less than \$9 billion and to reduce their expenditures by no less than \$4 billion below the President's budget request of fiscal 1968. In accordance with an overall general percentage formula, these reductions are equivalent to a 2% reduction of personnel compensation and benefits, and a 10% reduction in other objects of expenditures.

In many instances, the deferments of fiscal 1968 funds are those which will not be used and will revert to the U.S. Treasury at the end of the fiscal year unless Congress directs Treasury otherwise. However, for the most part, reductions in construction grants and loans are funds which will carry over to fiscal 1969. In many cases, these carryover funds, to the extent that they have been scheduled for obligations in fiscal 1969, have permitted reductions in budget requests without having caused a reduction in total program levels for fiscal 1969.

NCAPC

Under the cutback of controllable programs in fiscal 1968, the reduction for NCAPC amounts to \$1.9 million, for which NCAPC has not prepared a further breakdown. The funds, however, will not really be saved because they will be used for salary increases

Allocation of grant funds for waste treatment works construction

	1968 Allocations	1969 Estimate	Increase
TOTALS	\$203,000,000	\$225,000,000	\$22,000,000
Alabama	3,933,700	4,329,100	395,400
Alaska	867,300	894,700	27,400
Arizona	2,030,100	2,187,700	157,600
Arkansas	2,743,500	2,959,700	216,200
California	13,912,000	15,814,200	1,902,200
Colorado	2,293,300	2,505,600	212,300
Connecticut	2,786,400	3,093,200	306,800
Delaware	1,050,600	1,104,600	54,000
District of Columbia	1,248,600	1,341,000	92,400
Florida	5,093,900	5,693,200	599,300
Georgia	4,370,500	4,847,800	477,300
Hawaii	1,294,100	1,370,700	76,600
Idaho	1,539,000	1,619,800	80,800
Illinois	9,175,500	10,395,700	1,220,200
Indiana	4,728,500	5,292,800	564,300
Iowa	3,196,000	3,529,800	333,800
Kansas	2,667,200	2,930,900	263,700
Kentucky	3,654,200	4,022,000	367,800
Louisiana	3,827,500	4,221,600	394,100
Maine	1,825,300	1,942,600	117,300
Maryland	3,354,900	3,730,100	375,200
Massachusetts	5,068,600	5,691,700	623,100
Michigan	7,344,500	8,291,300	946,800
Minnesota	3,728,000	4,141,200	413,200
Mississippi	3,246,900	3,510,500	263,600
Missouri	4,490,500	5,013,400	522,900
Montana	1,478,900	1,560,600	81,700
Nebraska	2,067,900	2,238,700	170,800
Nevada	888,000	922,600	34,600
New Hampshire	1,371,900	1,445,300	73,400
New Jersey	5,790,000	6,524,300	734,300
New Mexico	1,797,000	1,912,100	115,100
New York	14,807,900	16,839,000	2,031,100
North Carolina	4,937,900	5,849,400	551,500
North Dakota	1,518,300	1,594,800	76,500
Ohio	8,966,500	10,141,300	1,174,800
Oklahoma	2,959,300	3,241,100	281,800
Oregon	2,294,200	2,508,200	214,000
Pennsylvania	10,348,600	11,718,600	1,370,000
Rhode Island	1,521,400	1,625,400	104,000
South Carolina	3,248,000	3,536,400	288,400
South Dakota	1,658,800	1,741,200	82,400
Tennessee	4,127,500	4,559,200	431,700
Texas	9,013,900	10,173,300	1,159,400
Utah	1,680,700	1,788,500	107,800
Vermont	1,301,700	1,348,900	47,200
Virginia	4,278,100	4,758,200	480,100
Washington	3,176,600	3,522,000	345,400
West Virginia	2,684,500	2,909,600	225,100
Wisconsin	4,166,700	4,645,000	478,300
Wyoming	1,143,300	1,183,300	40,000
Guam	1,470,000	1,478,100	8,100
Puerto Rico	3,391,200	3,675,500	284,300
Virgin Islands	1,440,600	1,444,500	3,900

granted under the recent federal pay increase action, according to an NCAPC spokesman.

With the enactment of the Air Quality Act of 1967, the nation is committed to an expanded effort to restore the nation's air to an acceptable quality and to prevent its future contamination. NCAPC has already (still in fiscal 1968) requested a supplemental appropriation of \$16 million to begin implementation of this act. The supplemental appropriation will be used to implement section 104 of the act calling for an accelerated research to find practical solutions to air pollution problems associated with motor vehicles and fuel combustion for the production of heat and electric power.

In its fiscal 1969 budget request, NCAPC calls for an appropriation of nearly \$107 million for its air pollution program. This sum is \$26.5 million greater than fiscal 1968 appropriations. Funds allocated to the R&D effort alone will reach the level of \$60.5 million, more than doubling those R&D funds that were available in fiscal 1968. Special emphasis will be given to support research into methods that have industrywide applications for the prevention and control of pollution resulting from combustion of fuels. Such programs will include laboratory and pilot plant testing to determine new or improved processes and plant designs that can lead to a reduction of emissions of oxides of sulfur and nitrogen.

NCAPC budget request for fiscal 1969

All figures in thousands of dollars

	Fiscal 1969	Increase from fiscal 1968
Grants		
Control program to state and local agencies	\$24,255	\$ 3,996
Research	8,000	569
Training to universities	2,859	168
Survey and demonstration	2,000	
Fellowship	468	
Grants subtotal	\$37,582	4,733
Direct operations		
Research	\$52,500	
Abatement and control	12,910	
Training courses for state and local officials	2,167	
Motor vehicle control	1,574	
Direct operations subtotal	\$69,151	\$35,689
NCAPC overall total	\$106,733	

PHS-HEW's budget request for fiscal 1969

All figures in thousands of dollars

	Fiscal 1969	Increase from fiscal 1968
Solid waste program		
Grants		
Survey and demonstration	\$ 5,546	\$ 546
Research	\$ 2,515	No change
Planning grants to state agencies	2,000	No change
Training	490	No change
Direct operations	\$ 6,983	\$1,386
Total	\$17,534	\$1,932

FWPCA budget request for fiscal 1969

All figures in thousands of dollars

	Fiscal 1969	Increase from fiscal 1968
Construction sewage treatment works	\$225,000	\$22,000
Research and development	56,002	4,424
Planning, management, assistance, and training	34,022	3,291
Administration	5,246	549
Regulation and enforcement	3,498	105
Administration of construction programs	2,667	484
Total	\$326,435	\$30,853

FWPCA research fund deferments for fiscal 1968

Water pollution control laboratory (location unspecified)	\$2,582,829
Great Lakes regional laboratory (Michigan)	2,543,242
National marine water quality research laboratory (Rhode Island)	1,733,000
Acid mine drainage field demonstration activity (Appalachian area)	1,274,000
Planning of water pollution control laboratory (Mississippi)	160,000
Total	\$8,293,071

These initial programs will be followed by large-scale demonstration of the newly developed processes and designs.

A related increase of \$4 million for effective control programs for state and local agencies brings the total program for such control activity to \$24.3 million. This money will support 286 grants to state, regional, and local agencies for planning, establishing, and maintaining their control programs.

That the program is important NCAPC has no doubt. Each year 125 million tons of pollutants are dumped into the atmosphere. Factories, furnaces, automobiles, burning dumps, and power generating stations, all add to our air pollution problem. This pollution costs billions of dollars per year, and totals \$65 per capita, NCAPC says.

FWPCA

Hard hit in the deferment of controllable programs for fiscal 1968, FWPCA has to defer funds to the tune of \$31.7 million—\$23.4 million for the construction of sanitary waste treatment plants and \$8.3 million for research and research facilities.

Bureau of Mines' deferments for fiscal 1968

All figures in thousands of dollars

Construction of solid waste demonstration plant	\$1,800
Research training and technical services	334
Disposal of culmbanks (Pa.)	150
Research grants	125
Solid waste subtotal	\$2,409
Drainage of anthracite mines	696
Health and safety	200
Conservation developments	100
Overall total	\$3,405

Allocation of funds for air, water, and solid waste

		Deferments fiscal 1968	Appropriations fiscal 1968	President's budget request fiscal 1969	Change from fiscal 1968	Total program level—fiscal 1969
Air	NCAPC (HEW-PHS)	\$ 1,914,000	\$64,185,000 \$16,000,000 ^a	\$106,733,000	(+) \$26,548,000	\$106,733,000
	Total		\$80,185,000			
Water	FWPCA (Interior)	\$23,400,000 ^b \$ 8,293,061 ^c	\$203,000,000 ^b \$ 92,581,695	\$225,000,000 \$101,435,000	(+) \$22,000,000 (+) \$ 8,853,305	\$242,000,000 \$101,595,000
	Total	\$31,693,061	\$295,581,695	\$326,435,000	(+) \$30,853,305	\$343,595,000
Solid waste	BuMines (Interior)	\$ 2,409,000	\$ 3,367,000	\$ 2,167,000	(-) \$ 1,200,000	\$ 4,576,000
	Urban and Industrial Health (HEW-PHS)		\$ 15,602,000	\$ 17,534,000	(+) \$ 1,932,000	\$ 17,534,000

^a Supplemental appropriations
^b Construction grants for sanitary waste treatment plants
^c Research and research facilities

By deferring \$23.4 million in obligations for fiscal 1968 to fiscal 1969, FWPCA will have a larger program for construction in fiscal 1969 without having to receive as large an additional appropriation. For example, a \$64 million carryover from fiscal 1967 put more money into the construction fund for fiscal 1968. As a consequence of the recently announced deferments, almost \$73 million will carry over into fiscal 1969.

As individual states have 18 months in which to apply for these construction grants, FWPCA predicts that the states will not apply for all funds nor will FWPCA commit all its available money. Therefore, FWPCA will carry over \$55 million into fiscal 1970.

FWPCA's carryover in construction grants

Fiscal year	Millions of dollars
1968	\$64
1969	\$73
1970	\$55

The difference between fiscal 1969 and 1970 carryover funds is \$18 million, which, when added to the budget request for fiscal 1969, makes available

a total of \$242 million. This \$242 million is FWPCA's total program level for construction grants in fiscal 1969.

For fiscal 1969 the FWPCA budget request amounts to \$326.4 million, \$30.8 million greater than 1968 appropriations. The major reason for the increase is the continued effort by the agencies involved in federal water pollution control programs to stimulate and support state and local governments to help in solving many of the nation's water pollution problems.

The construction of sewage treatment works will aid in reducing if not eliminating the discharge of raw sewage into the nation's streams. A wide variety of R&D studies is included in the program. The total funds for fiscal 1969 are directed toward expanding the participation of the scientific and technical community in seeking solutions through additional contractual effort and increased federal activity to the many critical water pollution problems facing the U.S.

Bureau of Mines

BuMines deferred close to \$2.4 million in funds for controllable programs for fiscal 1968, in accordance with the

provisions of PL 90-218. This cutback affected construction of its solid waste disposal demonstration plant (Hibbing, Minn.), which is less than 50% complete, and its anthracite mine drainage programs.

In fiscal 1969, program decreases will probably occur in several portions of the budget pertaining to various aspects of pollution. Completion of the demonstration plant to be used in a BuMines process that uses auto scrap to improve low-grade iron ore, will be postponed, allowing for a reduction of \$1.2 million. In addition, a series of air pollution research projects funded at \$400,000 during fiscal year 1968 will be discontinued.

HEW-PHS

The solid waste program in HEW places emphasis on solid waste management and environmental sanitation. Grants will be made to state and local agencies for demonstration of new methods and systems for improved solid waste management techniques. Research will take a look at the problem of reuse and disposal of solid wastes and the application of systems analysis to solid waste management.

A Preliminary Assessment of Herbicides and Defoliation

Each year the U.S. produces almost 300 million pounds of herbicides—the fastest growing segment of the pesticides industry. What are the ecological consequences of discharging these tonnages of herbicides into the environment? Particularly, what are the consequences in Vietnam, where enormous amounts are being applied repeatedly to large areas?

Some short-term answers can be found in a 369-page report prepared by the Midwest Research Institute, under contract with the Defense Department's Advanced Research Projects Agency. The report also points to areas in which it feels there is not enough information to draw reliable conclusions.

The report has gone to the American Association for the Advancement of Science, at whose request it was prepared. Late in 1966, some members expressed concern over the long-term consequences of widespread use of defoliants in Vietnam (ES&T, December 1967, page 971). The result is the report "Assessment of Ecological Effects of Extensive or Repeated Use of Herbicides." It is based on examination of over 1500 pieces of scientific literature, supplemented by discussions with more than 140 "knowledgeable people."

Before release the report was reviewed by the National Academy of Sciences. According to NAS president Frederick Seitz, it was agreed in advance that "the review would constitute an assessment of the thoroughness and accuracy with which the scientific literature relating to herbicides and their ecological effects had been examined and evaluated by the Institute." In forwarding the review to DOD, Dr. Seitz also said that he considers the report "only a first step in investigating further the ecological effects of intensive use of herbicides."

The NAS reviewers concluded that MRI had done a creditable job, particularly in the time allowed, but that "there is little quantitative data concerning their [herbicides'] truly long-term effects on various ecosystems."

The report is now due for additional review by the AAAS's Committee on Environmental Alteration. Such review has been delayed, however, by resignation of two members of the committee. Those who resigned are committee chairman David R. Goddard, provost

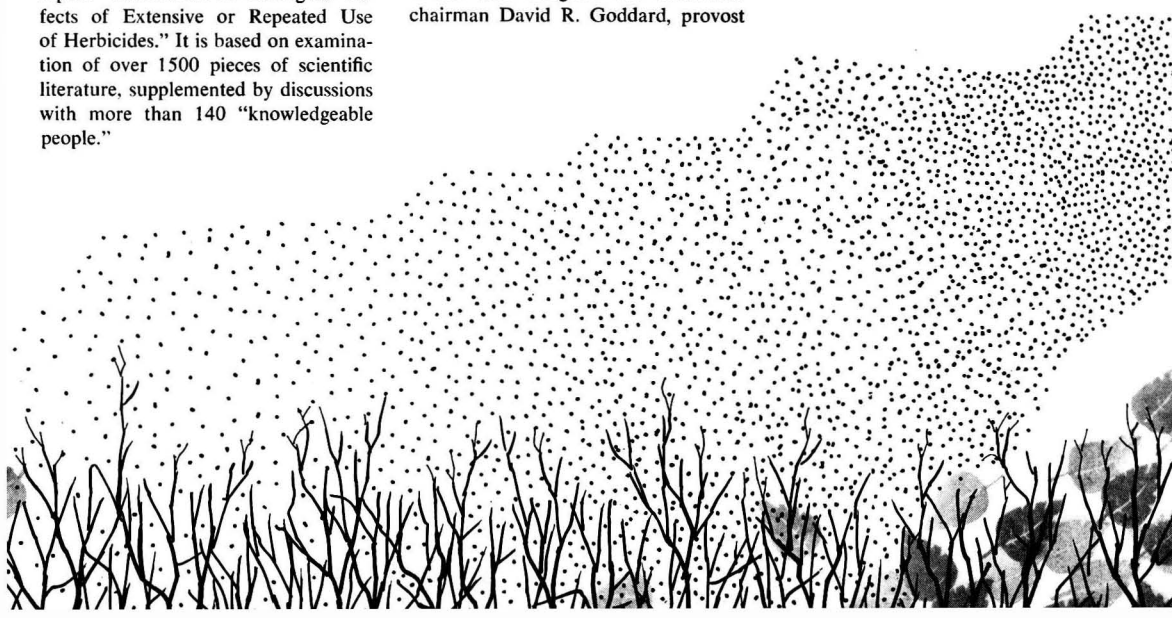
of the University of Pennsylvania, and Athelstan F. Spilhaus, president of the Franklin Institute.

According to the Feb. 23 issue of *Science*, both cited extensive professional commitments as the reason. However, *Science* quotes Goddard as saying in a telephone interview: "No sooner was my appointment announced than I started getting pressures from all directions. The emotional overtones were terrific."

Remaining on the committee are Barry Commoner, of Washington University, St. Louis, and René Dubos, of Rockefeller University. At its quarterly meeting in March, the AAAS board is scheduled to take up the appointment of additional members.

Noncrop uses stressed

The MRI report, authored by Dr. William B. House, Dr. Louis H. Goodson, Mr. Howard M. Gadberry, and Mr. Kenneth W. Dockter, concentrates on noncrop uses of herbicides. In ad-



dition to military uses, these include applications in forest management, brush control on range and grazing land, maintenance of rights-of-way, and aquatic weed control.

By far, crop uses are the most important application of herbicides, currently accounting for half of all consumption. However, the ecological consequences are minimal, the report says. Good cropland in continuous production is an artificially stabilized ecology. Most long-term effects are wiped out after the crop has been

harvested and the land prepared to grow next season's crop. Thus, assessment of herbicide use on crops must be based chiefly on economic and social grounds, not ecological.

Predicting the long-term ecological effects is difficult, the report says. Herbicides differ from other types of vegetation-control agents in that they enter into biological systems, are selective in their effects, and have some measure of persistence. They have an advantage over other types of vegetation control agents from an economic

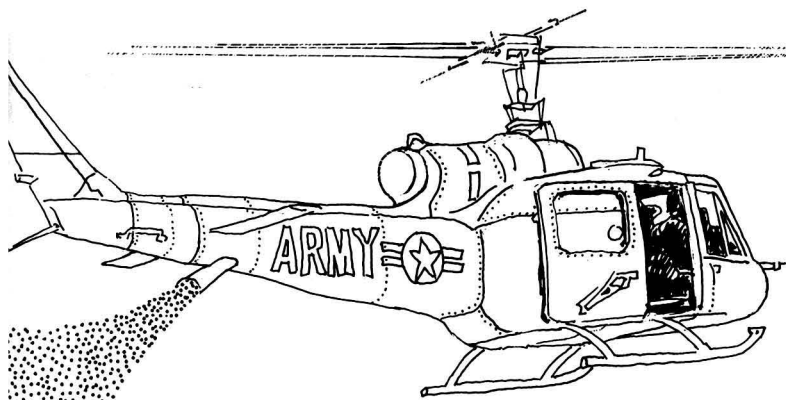
standpoint because they can be used to treat large areas selectively at low cost.

The possibility of ecological repercussions from herbicide use depends more on simply how these chemicals are used rather than on how much of these chemicals is used. Avoiding side effects depends ultimately on the degree of ecological knowledge, management skill, and social responsibility of those who employ the herbicides. In any particular application, the long-term consequences also depend on:

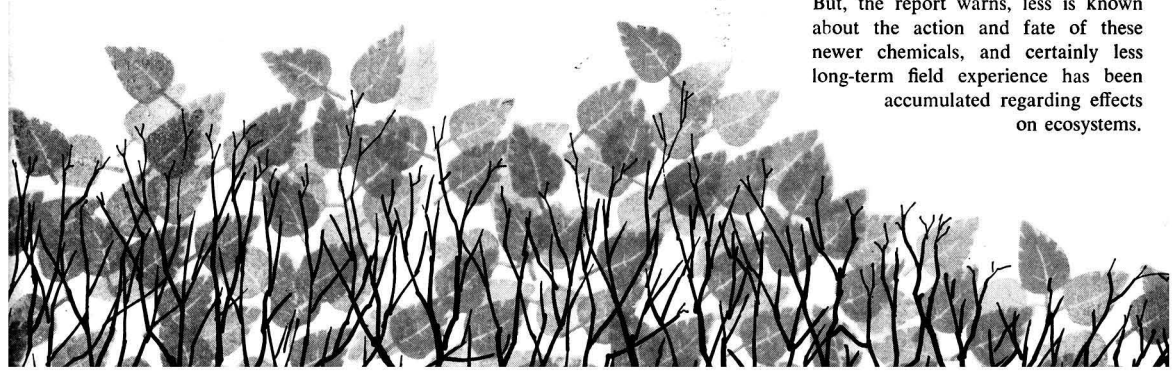
- Purpose of the use.
- The environment to which they are applied.
- The specific herbicide used.
- Dosage rate or frequency of treatment.
- Means of application and control of placement.

The pattern of herbicide use is shifting, the report notes. The older, inorganic herbicides and defoliants are losing ground as more effective and less hazardous agents are becoming available. The earliest organic herbicides, like 2,4-D and 2,4,5-T, are also losing ground to the newer organics such as picloram, bromacil, cacodylic acid, fenuron, and paraquat—each tailored to perform specific kinds of vegetation control.

In 1966, the U.S. produced about half as much 2,4,-D and 2,4,5-T as of other organic herbicides. And these newer organics will probably become even more important in the future. But, the report warns, less is known about the action and fate of these newer chemicals, and certainly less long-term field experience has been accumulated regarding effects on ecosystems.



Midwest Research Institute provides some short-term answers to problems associated with intensive use of herbicides. However, only more experience and more research can provide answers to problems of long-term ecological effects



Use in Vietnam

Herbicides were first tested for defoliation in Vietnam in 1961. Operational spray flights started in late 1962 and have increased steadily since then, totaling more than 3000 sorties by 1966. In 1967, about 40 million pounds of herbicides, mostly 2,4-D and 2,4,5-T, were used in Vietnam, causing shortages throughout the southern and midwestern markets in the U.S. The most critical shortages are for 2,4-D and 2,4,5-T. Indeed, all production of 2,4,5-T has been preempted by the Government until further notice.

Most of the herbicides used in Vietnam are for defoliation, with smaller amounts going for crop destruction. Three formulations are being used. Their names (derived from the color-coded stripes girdling shipping drums) are:

- *Orange*, a 50-50 mixture of normal butyl esters of 2,4,-D and 2,4,5-T. It is a general purpose herbicide designed to kill foliage: leaves fall in three to six weeks and control lasts seven to 12 months.

- *White*, a combination of picloram with 2,4,-D in a low volatility amine salt formulation. The combination provides relatively longer lasting control of a wide spectrum of woody plants, and permits accurate spray placement where volatility might create problems. This agent closely resembles compositions used for aerial spraying of power line rights-of-way in the U.S.

- *Blue*, cacodylic acid (dimethylarsenic acid) is a contact desiccant used for rapid defoliation. It does not kill many woody species but is an effective grass control agent.

More than 90% of the herbicides sprayed are the Orange and White formulations, which act systemically to kill plants and prevent root sprouting in most trees.

The problem in assessing military applications, MRI found, is that little has been published in the scientific literature—despite the fact that many military investigations have been unclassified.

“Aerial spraying of herbicides for defoliation or crop destruction cannot be directly compared with any of the civilian uses of herbicides,” the report points out. “Even forestry spraying to suppress deciduous trees, thereby releasing conifers, represents a poor anal-



ogy. Military use of herbicides differs from other applications in several important respects—in objectives, herbicide formulations, dosage rates, and application methods; and the effects are influenced by the climate, vegetation, and soils found throughout Southeast Asia.”

Biggest use—pastures

Vietnam has experienced the most widespread and concentrated application of herbicides that has ever been undertaken in a brief time span. But in terms of total acres sprayed, U.S. rangelands and pasturelands are much larger. A survey for 1965 shows that for agricultural uses only noncultivated land areas in the U.S. received herbicide treatment to the following extent:

Land use	Treated acres
Permanent pasture	6.7 million
Rangeland	3.2 million
Lawns and turf	1.1 million
Forestland	117,000
Aquatic sites	84,000
Other noncroplands	3.3 million

About half the total land in the U.S. is used for pasture and grazing; weeds and brush are a problem on nearly all this area. They can be controlled, changed, or prevented by many methods—chemical, mechanical, biological, burning, manual, and selective grazing. Combinations are frequently used, depending on such things as terrain, soil conditions, types of weeds, purpose of land use, and, above all, cost.

Herbicides have achieved good, and in many instances, outstanding control of noxious weed grasses and brush. However, the best chemical and conditions of application for most effective weed control must be determined for each species to be controlled.

Rights-of-way traverse ecosystems

The rights-of-way along power lines, communication lines, roads, railroads, and pipelines cover close to 26 million acres in the U.S. Vegetation control along these rights-of-way, which traverse many ecosystems, is important to many people—utility companies, road officials, and the general public.



C
Four months post-treatment. Foliage in the area sprayed with Orange begins to recover within four months

D
Seven months post-treatment. After seven months, the lianas (vines) and trees have grown new leaves

In recent times, two factors have become paramount in determining which of the various control methods are used: the high cost and the scarcity of qualified manual labor.

Utility rights-of-way are usually cleared initially by mechanical means, then maintained largely by herbicides sprayed from helicopters, fixed wing aircraft, and mobile road units. Herbicides have also been taking over as the principal means of controlling vegetation along roadways and railroad rights-of-way.

Forestry applications

Herbicides are being used in every stage of forest management, mostly in the areas maintained by commercial forest industries and in national forests. Herbicides are used in forest nurseries, where they can reduce weeding costs by more than 50%. They are used to prepare sites for reforestation. And they are becoming standard tools for minimizing competition from undesirable plants and promoting growth of desired species. (Aerial spraying is

widely used for the last two purposes.) But the biggest use is in thinning forests, where chemical control is markedly cheaper than conventional felling methods.

Controlling aquatic vegetation

Aquatic weeds are a serious problem in southern U.S. and in tropical areas. They can choke irrigation canals and block ship channels. They are the nat-

ural breeding places for disease-carrying insects and they shut out light necessary for oxygenation (photosynthesis) of water and they can have a marked and deleterious effect on the survival of fish.

With 2,4,-D and its various formulations, as well as some of the newer herbicides, man can control more weeds with less manpower than any other method currently available. Biological methods of control are being studied, but at least for a while, herbicides will continue to be the method of choice for most aquatic weed control.

Making judgments

After examining the literature, the MRI investigators declare in the report that "our studies have led us to certain judgments which we feel can be made with confidence." They are:

- The greatest short-term and long-term *direct* ecological consequence of using herbicides in Vietnam or anywhere else is the destruction of vegetation.
- Food chains for animals, birds, and lower forms of animal life and heterotrophic plants will be altered. The long-term effects on wildlife may be beneficial or detrimental.
- The herbicides now being used in Vietnam will not persist at a phytotoxic level in the soil for a long period of time.
- The possibility of lethal toxicity to humans, domestic animals, or wildlife is highly unlikely.
- Herbicides seldom persist in animal or insect tissues.
- When aquatic weeds are controlled with herbicides, the direct toxic effects on fish and bottom organisms

Areas in Vietnam treated with herbicides (estimated)			
Acres sprayed per year			
Year	Defoliation	Crop destruction	Total
1962	17,119	717	17,836
1963	34,517	297	34,814
1964	53,873	10,136	64,009
1965	94,726	49,637	144,363
1966	775,894	112,678	888,572
1967 (Jan.-Sept.)	843,606	121,400	965,006

Notes: Areas not actually measured, but estimated from number of sorties flown, calibrated spray rates, and average width of spray swath covered.

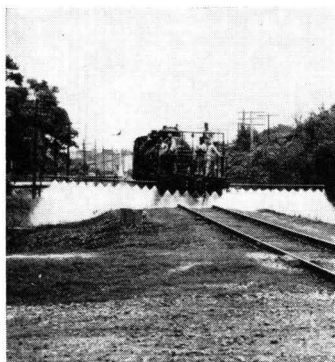
Areas include respraying. Some areas were sprayed annually, or more often if needed. No estimates available on respraying.

can be relatively minor if the herbicides have been properly used. However, the indirect effects resulting from destruction of vegetation may produce more important changes on the biota of the aquatic environment. These changes may be beneficial or deleterious.

Avoiding making judgments

The MRI report also points to "areas of our inquiry that are so inconclusive that reliable judgments cannot be made:"

- It is impossible to draw any conclusions concerning the effects on water quality of spraying 2,4-D and 2,4,5-T esters.
- The destruction of vegetation may cause certain geographical and climatic conditions that would bring about environmental change.
- Tropical forests in particular present a problem if the soil is principally lateritic. When the forest cover is removed, soil is exposed and may dry into hard red rock.



Caution. In populated areas or in sensitive agricultural areas, chemical treatment must be used cautiously to prevent wind spreading the material



Control. Herbicides are fast replacing such methods for the control of unwanted vegetation as burning, rotary mowing, and hand removal

Economical. Aircraft offer one of the most economical and fast ways of applying herbicides along rights-of-way

NAS Review of Herbicide Report

The primary function of the NAS reviewers was to determine the accuracy and the completeness of the report, based upon their own knowledge of the field. **Dr. A. G. Norman**, chairman of the NAS division of biology and agriculture, was in charge of the review. Other reviewers:

Dr. A. S. Crafts (review chairman), University of California at Davis.

Dr. Keith C. Barrons, director, plant science research and development, Dow Chemical Company.

Dr. Richard Behrens, department of agronomy and plant genetics, University of Minnesota.

Dr. William S. Benninghoff, department of botany, University of Michigan.

Dr. William R. Furtick, department of farm crops, Oregon State University.

Dr. Warren C. Shaw, crops research division, Agricultural Research Service, U.S. Department of Agriculture. Excerpts from NAS reviewers' comments:

The title of the report is more comprehensive than the contents. The report represents an attempt to summarize what is known about the use of herbicides and to indicate, to the degree possible, the nature and the extent of actual and potential ecological effects.

However, as the new organic herbicides have been known only since World War II and have been used intensively only in the past several years, there is little quantitative data concerning their truly long-term effects on various ecosystems.

The report is essentially a literature survey of several aspects of the use and effectiveness of various herbicides, with particular attention being paid to those now employed extensively in South Vietnam. The consensus of the reviewers can be expressed as follows:

(1) Midwest Research Institute has done a creditable job of collecting, correctly abstracting, and citing much of the relevant published information although, under the circumstances, the report could not be expected to cover in a truly comprehensive way so vast a literature.

(2) Of necessity, the preponderance of the material deals with herbicides as they are used in vegetation management in a diversity of situations and environments. On this general topic, abundant data are available. However, the scientific literature provides markedly less factual information on the ecological consequences of herbicide use and particularly of repeated or heavy herbicide applications. The Midwest Research Institute report correctly reflects this disparity.

Distribution of sales of U.S. herbicide producers—1965

(Millions of pounds)

Exports	32.0
Farm use on croplands	78.4
Farm use on noncroplands	10.6
Nonfarm uses (including Vietnam)	61.9
Total	182.9

The MRI report draws some conclusions with confidence . . .

Our studies have led us to certain judgments which we feel can be made with confidence:

1. There is no question that the greatest short-term and long-term *direct* ecological consequence of using herbicides in Vietnam or anywhere else is the destruction of vegetation. As long as soil sterilization is not an objective, destruction of vegetation by herbicides is a selective process, and denuded earth does not occur especially in forest spraying (40 to 75% defoliated at the end of one month). Furthermore, the end result of the use of the herbicides from an ecological standpoint represents a process that is common after uncontrolled fires, or the wild regrowth of abandoned fields, that is, the ecosystem is set back to an earlier sere. The succession of plant life that follows the use of herbicides is similar in some respects to the pattern of revegetation which has been observed when vegetation has been removed by other means.

2. Food chains for animals, birds, and lower forms of animal life and heterotrophic plants will be altered.

The long-term effects on wildlife may be beneficial or detrimental. Studies in other countries have shown that herbicidal treatment of forested areas improves wildlife habitat and is favorable to animal populations. The extent and pattern of herbicide treatment in Vietnam have no precedent; therefore it is difficult to predict the effects on wildlife with any accuracy.

In many instances where the disruption of food chains has occurred due to the use of herbicides, the animals or birds involved have a restricted habitat. Their dietary dependence is usually on a very narrow spectrum of foodstuffs (for example, the sage grouse and the black-footed ferret in the United States and the Douc Langur in Vietnam).

3. The herbicides now being used in Vietnam will not persist at a phytotoxic level in the soil for a long period of time. On the basis of the average temperatures and rainfalls in Vietnam, it would be reasonable to expect that the chlorophenoxy acid esters will be dissipated quickly. Picloram will leach into the soil perhaps even to depths of 24 to 36 inches. In areas that normally have low rainfalls (20 inches), with medium to heavy soil, the leaching of picloram will continue at a slower

rate. Cacodylic acid presents no persistent phytotoxicity problem from soil residues. This herbicide is tenaciously bound to soil particles and it resists leaching. Crops can be planted without risk in a matter of days after spraying with cacodylic acid. Application of 5 lb. per acre of cacodylic acid to alfalfa and rye grass did not result in residues in the cuttings.

4. The possibility of lethal toxicity to humans, domestic animals, or wildlife by use of the noncropland herbicides discussed in this report is highly unlikely and should not be a matter of deep concern.

5. A number of insecticides (chlorinated hydrocarbons) have a propensity to concentrate in some animals or insect populations. Herbicides, on the other hand, seldom persist in animal or insect tissues. Toxic transfer to the next higher animal in the food chain is minimal. In fact, biological concentration does not occur with most herbicides, since they are readily excreted from animals.

Acute toxicity data are presently available for all the non-cropland herbicides. For some, however, there is a lack of information on the effect of chronic exposure. For this reason it would be advisable to conduct feeding, teratogenic, and reproduction studies for several of the herbicides, particularly cacodylic acid, before their use in a single area is continued for a prolonged period of time.

6. When aquatic weeds are controlled with herbicides the direct toxic effects on fish and bottom organisms can be relatively minor if the herbicides have been properly used. However, the indirect effects of herbicides resulting from the destruction of the vegetation may produce more important changes on the biota of the aquatic environment. Whether these changes are beneficial or deleterious depends upon a number of factors; for example, a fish such as tilapia (indigenous to Southeast Asia) would be in trouble if the herbicide destroyed the specific plants upon which this fish feeds. On the other hand, serious oxygen depletion of an aquatic environment may occur when mats of floating weeds completely cover the surface of the water and shade the photosynthetic plants in the water. In this case an important benefit to fish and other aquatic biota can often be produced through the application of herbicides for the management of fish habitat.

. . . But does not draw others, which would be unreliable

Areas of our inquiry that are so inconclusive that reliable judgments cannot be made are as follows:

1. An area of difficult assessment is the effect of spraying 2,4-D and 2,4,5-T esters on water quality in streams, lakes, and waterways. It is impossible to draw any conclusions concerning water quality detriment without concrete data indicating the amount of sprayed chlorophenoxy acid esters that actually arrives at the surface of the water, and knowledge of water conditions.

2. There are a number of mammals and Aves in southeastern Asia area that are recognized to be in danger of extinction. Whether the application of herbicides will be the critical point in the survival of these endangered species is not known.

3. The destruction of vegetation may cause certain geographical and climatic conditions that would bring about environmental change. For instance, the average temperature of a deforested area is elevated. There is a possibility that the rainfall in that area may decrease if it is denuded of vegetation. By far, the most drastic condition necessary to bring about decrease of rainfall would be a bare earth situation. As far as we are able to judge (from the limited amount of literature in this area available to us) even if there is a recession in the amount of rainfall, it is not a drastic reduction.

In fact, in at least one major study of a large denuded area, there were so many variable factors concerning the measurement of the rainfall that the differences between that area and the surrounding forest were not definitive.

4. Tropical forests in particular present a problem if the soil is principally lateritic. The removal of forest cover may result in accelerating the conversion of latosols into laterite rock, which would greatly and irreversibly lower the biotic potential and productive capacity of the treated ecosystem. We have discussed the types of soils that prevail in the tropics, including specifically the soils of Vietnam (Chapter IX). As indicated there are at least two well known lateritic swamps in the Mekong Delta and various latosols are the most common soil predominating throughout the rest of South Vietnam. We are not aware of any instances where this final and irreversible stage of the laterization process has occurred because of its acceleration by herbicidal destruction of vegetation. Observers in Vietnam have said that plant succession which occurs following defoliation of a tropical rain forest is one where the grasses cover the ground in dense stands first, and then weeds and vines become very rank in a matter of several months. Although no related evidence for irreversible changes of the abiotic factors in Vietnam exists, it is a point that deserves further consideration.

Phosphate Removal Processes Prove Practical

As much as 90–95% removal of phosphates can be achieved in municipal waste waters with present technology, and the cost is moderate—less than 5 cents per 1000 gallons

With present technology, phosphorus can be removed from municipal waste waters, according to ample demonstrations by the Federal Water Pollution Control Administration (FWPCA). Water treatment facilities, being designed and built on technically and economically sound bases, can remove at least 80% of the phosphorus found in municipal waters. The available evidence shows that higher percentages—approaching 90–95%—are actually being achieved in some systems.

The treatment process that has been operated with the greatest confidence for phosphorus removal employs chemical treatment, according to Dr. Leon F. Weinberger, Assistant Commissioner of Research and Development, FWPCA. The chemical treatment may be employed as a tertiary treatment or independently as a separate treatment for various waste waters. It can also be used to eliminate or reduce the recycle of phosphorus from digester supernatants or from thicker liquids.

Chemical treatment

The two most common types of chemical treatment are alkaline removal with lime and adsorption or precipitation with metallic hydroxides such as alum. Data derived from operational experience in the U.S. show that chemical (tertiary) treatment reliably removes 90 to 95% of the total phosphate present in municipal waste water at a cost of less than 5 cents per 1000 gallons.

Total cost of phosphate removal

(Cents per 1000 gallons)

	Size of plant			
	1 m.g.d.	10 m.g.d.	100 m.g.d.	1000 m.g.d.
Capital amortization	.97	.79	.65	.53
Land amortization	.09	.09	.09	.09
Operating and maintenance	.41	.14	.08	.07
Cost of chemicals				
Lime	1.75	1.75	1.75	1.75
Iron salt	.87	.87	.87	.87
Cost of sludge disposal by hauling to land fill (25-mile one-way trip)	.67	.67	.67	.67
TOTAL	4.76	4.31	4.11	3.98
Savings if sludge can be recalcined	— .96	— .96	— .96	— .96
TOTAL (with recalcining)	3.80	3.35	3.15	3.02

Source: FWPCA, Lake Michigan Water Pollution Enforcement Conference

The advantages of such chemical treatment include:

- Close control can be maintained in actual plant operation.
- Lab data can be used to predict dosage levels for various phosphate residuals and to determine settling rates for clarifier design.

Also, chemical treatment results in reductions in turbidity, biological oxygen demand, chemical oxygen demand, and bacterial counts. Even though there may be fluctuations in the treatment steps preceding tertiary treatment, chemical treatment yields a more uniform effluent quality than any other phosphorus removal process.

Chemical-biological treatment

The chemical-biological treatment, offering at least 80% removal of phosphorus, can be accomplished by adding the chemical in either the primary sedimentation stage or the activated sludge stage.

When chemical treatment occurs at the primary sedimentation stage, a precipitant is added. This precipitant removes most of the phosphorus in the primary tank, the remainder being removed in the biological phase.

Improved clarification and better BOD removal are additional advantages of the chemical-biological approach. In addition, lime can be recovered so that further reductions in cost are possible. Several new plants have been designed to use this chemical-biological treatment, for example, a new plant already in operation at Rochester, N. Y.

When chemical treatment occurs at the activated sludge stage, minerals are

added directly into the aeration tank. This addition results in the formation and precipitation of slightly soluble phosphorus compounds. Additives such as salts or aluminum or iron do not interfere in the biological activity, and the mixing and residence times in the aerator allow sufficient time for the formation of precipitates.

Significant reductions in cost appear reasonably attainable, leading to an approximate cost of 3 cents per 1000 gallons. Operational data for a full-scale plant should be available within a year.

The mineral addition process is included in FWPCA's waste water treatment plant at Xenia, Ohio. Previously, the plant removed only 20% of the phosphorus. However, phosphorus removals of 85 to 92% were realized with the addition of sodium aluminate at a ratio of Al:P of 1.8:1. When the addition of aluminum was discontinued, the plant returned to its 20% phosphorus removal rate.

Costs for tertiary treatment

Local factors affect the operational costs for the various processes, such as sludge handling, disposal requirements, acid requirements for neutralizing the effluent, and filtration requirements to remove suspended solids in the effluent. The choice of either process—chemical addition at either the primary sedimentation stage or the activated sludge stage—is dictated by local considerations. Only a brief engineering study is required to develop the best method for a specific location.

For both the chemical and chemical-biological systems, the most important

operational item is the recovery and reuse of lime or alum.

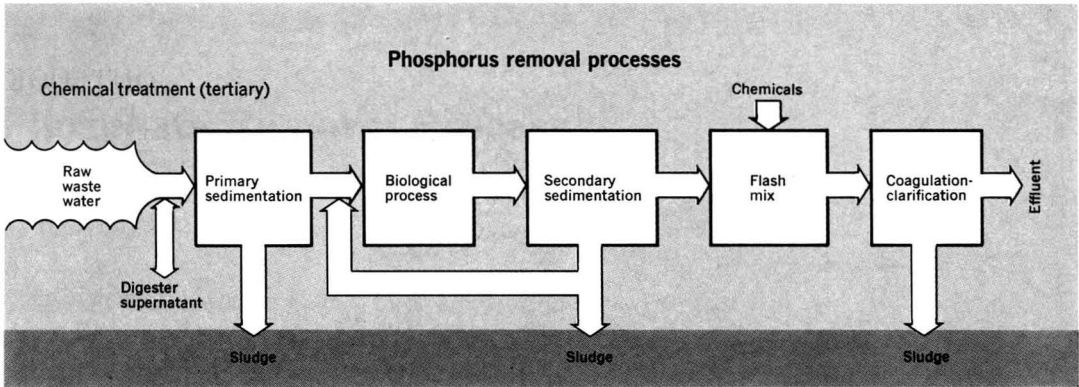
In the chemical process, for example, chemicals, alone, account for 50% of the cost. At present, lime has a greater potential than alum for economical advantage by recalcination of the sludge and recovery of the CO₂ byproduct for recarbonation.

A typical 10-million-gallon-per-day plant can provide 90–95% removal of phosphorus for either the chemical or chemical-biological systems at a cost of 5 cents per 1000 gallons. The economics of these kinds of systems will probably not improve much in the next few years.

Selected chemical treatment plants

In Lake Tahoe, Calif., a treatment plant with a capacity of 2.5 million gallons per day started operation in the summer of 1965. This new plant renovated secondary effluent from an activated sludge plant, adding alum at the rate of 200 p.p.m. just ahead of two mixed-media filter beds operated in series and followed by granular activated carbon contactors. In addition to reducing BOD, COD, and ABS (alkyl benzene sulfonate) levels to potable water standards, the system consistently achieved phosphate reduction from 25 p.p.m. to less than 1 p.p.m.

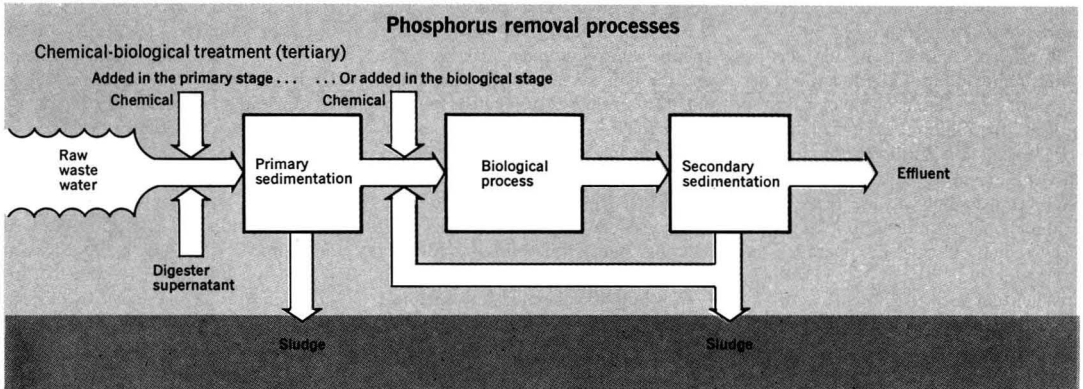
The plant was recently expanded to 7 m.g.d. capacity, and has started operation at the 4 m.g.d. level using the same alum tertiary process. However, the plant will soon convert to the cold lime process that uses a lime dose at the rate of 400 p.p.m. in both the primary and tertiary systems. In this operation, the tertiary precipitation step



Selected operational phosphate removal process experience in the U. S.

	Location	Status	Size in m.g.d.	Process	Actual or projected cost at 10-20 m.g.d. (cents per 1000 gal.)	Actual or projected phosphate removal efficiency
Chemical	Lake Tahoe, Calif.	Start up Feb. 1968	4 to 7.5	Lime tertiary with separation beds	< 9 cents	>95% (0.1-1.0-p.p.m. in effluent)
	Las Vegas, Nev.	Operational since 1961	4	Lime tertiary with single clarifier	< 4	>95 (0.5 p.p.m. in effluent)
	Lake Tahoe, Calif.	Operational (2 sites)	2.5-4	Alum tertiary with separation beds	< 9	>95 (0.1-1.0-p.p.m. in effluent)
	Nassau County, Long Island, N. Y.	Operational since 1965	0.6	Alum tertiary with separation beds	< 7	>60
	Lansdale, Pa.	Operational	0.3	Alum tertiary with separation beds	<10	>90
	Washington, D. C.	Operational	Pilot plant (0.1)	Lime tertiary with dual clarifiers and lime recovery	< 4	>95
Chemical-biological	Wayne, Mich.	Operational for short period	45	Alkaline waste calcium chloride to raw sewage	—	>80 (jar test)
Biological	Black River Plant, Baltimore, Md.	Operational (test)	20	Activated sludge phosphate uptake	< 1	>90
	South Central Region	Prior operations (5 sites)	Pilot plant	Activated sludge phosphate uptake	< 1	to 87
	Irvine, Calif.	Operational	Pilot plant	Activated sludge phosphate uptake acid elutriation chemical removal	< 5	~90

Source: Lake Michigan Enforcement Conference



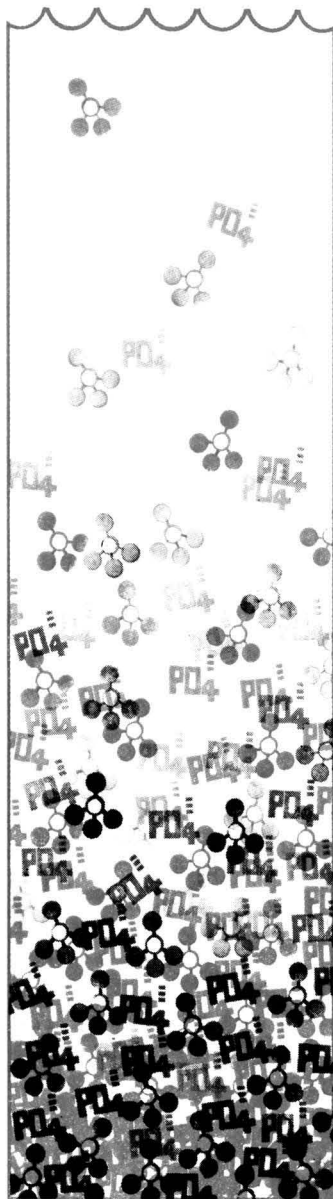
is followed by recarbonation and filtration through two mixed-media filter beds in series and activated carbon. The effluent phosphate content is reduced to levels ranging between 0.1 and 1 p.p.m. Also, most of the lime is recovered and reused.

The projected cost for the cold lime process, including filtration of the recarbonated effluent, is 10.46 cents per 1000 gallons at 7.5 m.g.d. and using lime at a dose rate of 400 p.p.m.

In the southwestern and western parts of the U.S., several industrial enterprises and public utilities are renovating secondary effluents from municipal sewage plants, just as current water conservation economics suggest. In Amarillo, Tex., the Southwest Public Service Co. uses the cold lime process as tertiary treatment for removing scale-forming phosphate from the effluents prior to using the effluent water for cooling purposes.

After the precipitation step, the pH is lowered by adding sulfuric acid in lieu of recarbonating as contemplated at Lake Tahoe. At the Amarillo plant more than 4 million gallons of effluent are processed daily to produce cooling water having a phosphate level of 1 p.p.m. This level of phosphate means that the system has an average phosphate removal efficiency of nearly 93%, and requires a lime dose rate of 300 p.p.m. to assure consistent removal.

Plans are under way to expand a newly constructed 5 m.g.d. activated sludge plant at Piscataway, Md., in the Potomac River Basin. The expansion will add a tertiary treatment process that includes lime precipitation, recarbonation with clarification, filtration, and activated carbon treatment. As in the Tahoe treatment plant, both spent lime and activated carbon are to be regenerated.



Although lime dosage of 400 p.p.m. is scheduled for use at Lake Tahoe, a rate of only 200 p.p.m. of lime is initially planned for the plant in Piscataway. The projected cost of the phosphate removal tertiary system, excluding the filtration operation, at Piscataway will lead to an overall processing cost of less than 5 cents per 1000 gallons.

Commercial process

A commercial process, available from Dow Chemical Co., promises 90% removal of the phosphates, up to 75% removal of the solids, and 60% reduction in BOD in the primary portion of a treatment plant. The process involves the addition of metal ions to the waste waters to convert the phosphate to an insoluble form. An organic flocculant (some of the specialty polymers recently made available, for example) is then added, causing the insoluble particles to settle out.

Using the Dow process, the primary treatment plant at Grayling, Mich., removes phosphates from raw wastes by plain sedimentation, for example, through the addition of ferrous chloride at the rate of 20 mg. per liter, sodium hydroxide at the same rate, and an anionic polymer at the rate of 0.5 mg. per liter. With temporary equipment and under overloaded conditions, phosphate removals averaged 72% at the Grayling plant.

Similar operations using the Dow process at the municipal facility at Lake Odessa, Mich., removed, on the average, 82% of the phosphate. In this location, the facilities included trickling filters and sludge digester facilities. In both the Grayling and Lake Odessa plants, the process had to be tailored to meet local conditions including the plant hydraulics and the chemistry of the water being treated.

MAN AND HIS CITY

With his unique skills, the technically trained person can find an exciting and rewarding career in helping to control the urban environment

About 130 million Americans live in urban areas, and slightly less than half of them in the central city. Living with them is a host of pressing problems—problems of pollution, health, housing, food, transportation, and education.

Urban problems are not new, but as never before all Americans are coming to feel the urgency of solving them. The Federal Government is deeply involved in the city with money and manpower. Industry is becoming more involved with capital investment and training programs. The education establishment is lending its considerable intellectual and physical resources to focus on the problems.

With his special training, the young chemist or chemical engineer can make a unique contribution to the city today, says *Chemical and Engineering News* in its annual special issue devoted to career opportunities. The special March 11 issue, "Man and His City," includes five articles on specific city problems, a guide to career information, and a directory of 750 organizations that hire chemists and chemical engineers. Most listed organizations have estimated the number of chemists, chemical engineers, and allied professionals now employed

and the number of openings they hope to fill in the next 12 to 18 months. Of special interest to readers of ENVIRONMENTAL SCIENCE AND TECHNOLOGY are the nearly 90 listed organizations that are active in the waste disposal and sanitary engineering field and are offering career opportunities.

Environmental profile of a city

"Environmental control in the city is indeed going to present the chemical community with problems it used to ignore or read about as fantasy," says C&EN's special issue's article on environment. And St. Louis, Mo., is a typical tale of urban America. Its new air pollution ordinance, which takes effect in October, prohibits burning coal containing more than 2% sulfur. One big source of airborne sulfur compounds in the St. Louis area is Union Electric Power Co., which burns coal having 3.5% sulfur. The company is installing sulfur-removal equipment that uses the dolomite process. However, the reliability of this process has not yet been tested on a large scale, C&EN says.

Other big companies—Monsanto, Anheuser Busch, and McDonnell Douglas

—can afford to install equipment to control their sulfur emissions. But it's a struggle for smaller companies, some of which will have to buy equipment that costs more than they earn in a year.

Controlling air pollution can't be geared to specific pollutants or health problems. Rather it requires the systematic approach toward managing the total environment. St. Louis is moving in this direction. The U.S.'s first thorough probing of regional air pollution was recently completed in a 3567 square mile area that includes two states, six counties, St. Louis City, and 125 small, independent towns. As a result of this study, control efforts in the St. Louis air shed in a few years should lead to:

- A continuing air quality monitoring network.
- A continuing emission inventory.
- Air quality goals and standards based on air quality minimums.
- Tools to help in gaining a better understanding of the conditions influencing the transport of air pollutants.
- Urban planning decisions based on air quality as well as other environmental factors.
- Air pollution control decisions and resulting ordinances based on air quality information and relationships between the quality of air and its effects.

Water problems, too

The water pollution picture is beset with the same complexities. "I think our water is going to get much worse before it gets better," says Conway Briscoe, head of the city's public works activities. Probably the most challenging problem is industrial pollutants—particularly trace organics, chlorinated hydrocarbons, and the residue from the many

QUOTE . . .

NO TIME-SPACE CUSHION FOR ERROR

The increasing power of technology to destroy and disrupt the natural environment and the ecological systems upon which life depends has reduced man's margin for error in the use of this power. We must act, therefore, to deter and prevent the occurrence of future ecological disasters such as that caused on the British and French coasts by the sunken oil tanker, the TORREY CANYON, the Clinch River fish kill which occurred when a dam broke and released coal ash from plant operation, or that which threatened on the Clark Fork River in Montana when a strike at the Anaconda Copper Company threatened to shut down pollution control activities, thereby endangering fish and plant life on the Clark Fork River with copper waste.

In the past, pollution of the environment has tended to be slow. But now, the increased power of technology to damage nature, the loss of insulating space, and the compression of time—all reduce our margin for error and the cushion which space and time once provided for our mistakes.

That time and space cushion for our mistakes no longer exists. And the mining and metallurgical industry, among others, must realize this fact. We now have much less room for error and mistakes in the damage which we do to nature.

The mining and metallurgical industry has, to date, been one of the prime causes of the adverse effects on nature of our technological power.

This was not inevitable. It could have been partially avoided with some foresight and thought—with some attention to applying our technological power to preventing pollution, to cleaning it up when it occurred, and to restoring the environment which pollution destroyed.

We are only now starting to restore the balance in the use of our technological power by not only promoting economic growth, but also using our technology, our legal and institutional power to prevent pollution, to limit ecological damage when pollution occurs and to restore what pollution destroys.

We still have a long way to go before our power to prevent and control pollution is equal to our power to pollute—a power which is great, which is increasing, and which has taken many generations of neglect and growth of population, industry, of cities and technology to achieve.

Economic growth and environmental quality go together. In the long run, economic growth and life itself depend on environmental quality. And, in the short run, of what use is economic growth if, in promoting economic growth, we create an environment in which it is not a joy to live?

JACOB I. BREGMAN

Deputy Assistant Secretary of the Interior for Water Pollution Control, in a speech at the Annual Meeting of the American Institute of Mining Engineers, New York City, February 27, 1968

metal plating plants in the St. Louis area.

In about a year, the city will start operating two new primary sewage treatment plants, leaving New Orleans the only major city on the Mississippi that fails to treat its waste water. St. Louis voters are only now beginning to finance the \$95 million bond issue for construction of the plants. Primary treatment isn't enough. Though most St. Louisians don't yet realize it, the Federal Water Pollution Control Administration says the area must install secondary treatment by 1981 at the latest.

The citizens do realize, however, their mounting garbage problem. In metropolitan St. Louis, refuse is burned or used as land fill. Two ancient incinerators along the banks of the Mississippi burn all the city's trash, polluting the air in the process. New ones are required, but St. Louis faces the problem of what to do with the refuse while the new units are being built.

The counties, meanwhile, deposit their trash farther and farther away from subdivisions. Jefferson Countians, even its most educated residents, are currently protesting plans to develop a park out of a proposed sanitary landfill. "I don't care if it's going to end up as a park," C&EN quotes one resident as saying. "A dump is a dump and I don't want it in my back yard."

Bedeviling all of the St. Louis area is the problem of jurisdictions. St. Louis is not a city of 700,000. It's an urban area of 2.5 million people covering parts of two states. Coordination is a must. Thus, solving St. Louis' problems eventually means taking political action. St. Louis shares most of its problems with many other American cities. For this is a tale, not of one city, but of all cities.

A Nonmyopic Approach to the Problem of Excess Algal Growths

F. Alan Ferguson, *Stanford Research Institute, Menlo Park, Calif. 94025*

One of the more serious results of water pollution that prevails in the United States is excess algal growths. Even though some localities have struggled to control these growths for many years, the extent of the problem and the consequences if it is not controlled have only recently received nationwide attention.

The desirability of controlling algal growths is now generally acknowledged. Unfortunately, developing control programs is hampered by the problem's complexity and by the lack of adequate information on the effectiveness of possible control measures. Therefore, some authorities argue that a myopic approach is necessary and that any control measure with a chance of improving the situation should be imposed. Others insist that more research should be undertaken to provide some of the important information now lacking. Otherwise the enforced controls are apt to be unnecessarily costly, ineffective, or both. This article presents a case for the nonmyopic approach.

Character of the problem

Excess growths of algae occur in water wherever abundant quantities of food and nutrients are present and other conditions—such as adequate sunlight and proper temperatures—are favorable for growth. Reports indicate that more than 50% of the total municipal water suppliers are affected by the problem.

The near-term consequences of the excess growths are bodies of water

(particularly lakes and slowly moving rivers), so filled with algae that even they can't survive. Foul odors emanate from the decay of the dead algae, and the water tends to lose dissolved oxygen, causing extensive fish kills. The growths also create problems in raw water supplies for municipal and industrial use, since water containing excess algae costs more to clean up. Another serious result is lessened desirability of the water for recreational pursuits.

Eventually the body of water becomes so committed to the growth of algae that few forms of fish can survive and it gradually fills with dead organic matter.

The growth of algae is currently more serious a problem in lakes than in rivers and streams. Frequently, if algae grow in rivers or streams, the organisms are swept along and do not fill the river bottom. In many rivers, the silt load is so heavy that algae cannot grow abundantly, even though the water is polluted with growth-prompting materials. Unfortunately, as more dams and reservoirs are constructed along major rivers to improve navigation and flood control, large portions of rivers also will be subjected increasingly to periods of excess algal growth.

Studies into the causes of excess algal growths have tended to concentrate on the importance of nitrogen and phosphorus compounds with relatively little attention being given to the other substances known to promote the growths or to determining the un-

known causes of such growths. Technical journals of the past 20 years contain numerous technical articles on the role of phosphorus and nitrogen in excess growth of algae.

This concentrated attention has led the advocates of the myopic approach to propose that the quantities of nitrogen and phosphorus must be reduced to prevent excess growth of algae. Everyone agrees that if no phosphorus or nitrogen were available, algae would not grow. But equating a reduction in nitrogen and phosphorus concentrations to a proportional reduction in the growth of algae is not justified. Too many other factors contribute to the growth of algae. In order to control algal growth we need to know which are the major factors, how they contribute individually and collectively to algal growth, and how much control of each is necessary and possible. Few of these questions have been answered and I believe they should be answered before any extensive control measures are instituted.

Current state of knowledge

The rate and amount of algal growth depend on:

- The amounts of growth-promoting factors in the algae's environment.
- The relative importance of these factors to the growth.

The relative importance of temperature is known: The rate of algal growth roughly doubles with every 20° F. rise in water temperature between 32° F. and 90° F. Some data are available on effects of varying con-

Some authorities feel that something—anything—must be done at once to control excess algal growth in lakes and rivers. Yet, some additional study could prevent the adoption of unnecessarily costly or ineffective controls

concentrations of nitrogen and phosphorus. Studies of Wisconsin lakes show that excessive growths can be expected if the average concentration of inorganic nitrogen exceeds 0.3 p.p.m. and the inorganic (soluble) phosphorus content exceeds 0.01 p.p.m. during the seasons of algal growth. Other research shows that excessive growths can occur in waters containing less than 0.001 p.p.m. inorganic phosphorus. However, some waters containing as much as 0.05 p.p.m. soluble phosphorus do not support excess algal growths.

These wide ranges of phosphorus concentrations suggest that:

- In some cases drastic reduction in the availability of this element is necessary to prevent growth.

- Excess growth might be prevented in other instances, even though the phosphorus concentration might remain relatively high, by reducing the concentration of other materials that affect algal growth.

- Better means for inhibiting algal growth may exist than the reduction of the phosphorus concentration in algae infested water.

Among the materials that might be controlled to prevent excess growth in these waters are some trace elements: manganese, boron, cobalt, and vanadium, which are known to be required for optimum algal growth. Vitamins and hormones are also known to stimulate algal growth. As far as I have been able to determine, little has been done to establish how much of any of these materials can be present in sur-

face waters and still have them free of excess algal growth.

Once we get information on the relative effects of these other materials, we will then need to know their sources and how to regulate them and also the sources and mechanisms for regulation of phosphorus and nitrogen before excess algal growths can be controlled. Here again, the available information is sparse.

Sources of nutrients

Man and nature both supply nutrient materials that increase algal growth in surface waters. (Thermal energy added to surface waters from man-generated sources, such as waste cooling water from power plants, also increases algal growth, but the effect of such thermal energy is not examined here.)

The major natural sources of algal growth materials or AGM (see Table 1) identified to date are:

- **Air.** Provides carbon dioxide, as well as nitrogen, which some algae can fix or utilize.

- **Rain.** Contains not only carbon dioxide or carbonates, but also such nutrients as phosphorus and nitrogen. Nutrients are more prevalent in rainfall near urban areas, suggesting man contributes them to this source.

- **Water plants and animals.** Materials in the aquatic environment have the most direct impact on algal growth. Carbon dioxide is supplied as inorganic carbonates, from aerobic decomposition of natural organic matter, and by the breathing of water animals. Nutrients go through the biological cy-

cle, being stored, used, and discarded by all water plants and animals, including bacteria.

- **Muds under water bodies.** Muds receive dead and fecal matter from aquatic life, plus man-generated wastes heavy enough to settle. At least a portion is decomposed and returned to the water in soluble form. Muds, therefore, are potential sources of all the types of food and nutrients algae need.

- **Runoff from land.** Waters that run off natural or uncultivated land contain organic matter and at least some nutrients.

Man-generated sources include:

- **Sewage.** Domestic sewage from households contains decomposable organic matter, bacteria, and all known nutrients. They are present even after secondary treatment in a sewage plant. Industrial sewage may contain the same ingredients with, on occasion, just one or two nutrients in relatively high concentration.

- **Runoff from land.** The same materials will be in the runoff from the urban and agricultural land used by man as in the runoff from natural land.

Quantities of nutrients

Relatively few studies have been conducted in the U.S. to determine how much growth material is contributed by individual sources. The data from these studies have been used to estimate the total nationwide contribution from each source (as shown in Table 2).

Due to the paucity of data, some of the figures presented in Table 2 are

TABLE 1
Sources of algal growth materials

Source	Material contributed				
	Organic matter	Nitrogen	Phosphorus	Potassium	Other
NATURAL					
Air	a	X			
Rainfall	X ^a	X	X	X	
Aquatic plants	X	X	X	X	X
Waterfowl, fish, bottom fauna, and the like	X	X	X	X	X
Muds under water bodies	X	X	X		
Runoff from					
Forest land	X	X	X	X	
Other land	b	b	b	b	
MAN-GENERATED SEWAGE					
Domestic					
Human and food wastes	X	X	X	X	X
Washing wastes	X	X	X	X	
Industrial					
Food processing wastes	X	X	X	X	X
Other wastes		X	X	X	
RUNOFF FROM					
Urban land	X	X	X		
Cultivated land					
Fertilized	X	X	X	X	
Unfertilized	X	X	X	X	
Land on which animals are kept	X	X	X	X	

^a Source of carbon dioxide
^b Quantity undetermined

gross extrapolations of the available information. For example, the 200 million pounds of nitrogen expected from urban runoff is based on the assumption that the average runoff from the entire urban area in the country (close to 23 million acres) will be the same as that from a single 27-acre plot studied near Cincinnati, Ohio.

The AGM data are also subject to considerable uncertainty. In some instances, the reported values vary more than twentyfold. For example, nitrogen entering surface waters in the United States through rainfall might be anywhere from 30 to 590 million pounds a year.

The runoff from cultivated land is the only source that has been the subject of several studies. The data on phosphorus contribution from runoff from cultivated land show surprising consistency, considering the variations in rainfall, crops raised, amount of irrigation, and types of soils. Apparently the per-acre contribution of phosphorus to surface waters by small plots can vary widely. For example, phosphorus from runoff from cultivated land varied from 0.2 to more than 0.9 pound per acre per year from specific areas within 358 acres of cotton in the San Joaquin Valley in California. However, if the area studied is large enough, the variations seem to even out. Approximately a fourfold variation in runoff, from 0.35 to 1.33 pounds of phosphorus per acre, exists if averages are taken for each of the several areas studied (as shown in Table 3).

Data analysis

On the basis of available data (Table 2), U.S. surface waters receive 5.0-8.2 billion pounds of nitrogen and 0.9-1.7 billion pounds of phosphorus annually from natural and man-generated sources. While the total quantities of nitrogen and phosphorus would be higher if data on sources such as industrial wastes and bottom muds were available, the percentage contribution from natural and man-generated sources would probably remain the same (see Table 4). Not enough data on organic matter are available to make a meaningful comparison.

As much as 80% of the nitrogen and 75% of the phosphorus apparently come from man-generated sources.

These high levels indicate the tremendous impact man has on his environment. And, yet, they hold forth the hope that, by exercising proper control, man can restore balance to that environment.

Restoring that balance may not be easy. The largest identified man-generated source of nitrogen is runoff from cultivated land (see Table 5). While farming practices might be altered to reduce the amount of runoff, a sizable reduction is unlikely. Another possible approach might be to use slow release fertilizers that would not dissolve readily in the rain and irrigation water that constitute runoff.

Domestic sewage, which contributes about a third of the nitrogen known to enter surface waters, also presents a difficult control problem. Even though most of the sewage will be collected and treated in large plants, no economic means is currently available for removing nitrogen. Growing algae in sewage plant effluent should reduce the quantity of soluble nitrogen. However, removal of algae before effluent discharge has proved difficult and expensive. Anaerobic denitrification after secondary treatment can convert the nitrates to nitrogen, but this procedure requires addition of organic materials that do not themselves contain nitrogen, and, of course, adds to this treatment cost.

The distribution is somewhat different for the man-generated sources of phosphorus (compare Tables 5 and 6). Roughly half of this phosphorus comes from domestic sewage. In some situations, removal of phosphorus is simpler than removal of nitrogen, because, unlike compounds of nitrogen, many inorganic phosphates are insoluble in water.

For example, more than three quarters of the phosphates entering one Chicago treatment plant are removed by the plant. The raw sewage to this plant comes from both residences and industry. The nature of the industrial portion of the sewage is such that it contains a greater than normal proportion of metal ions. These ions react with the phosphates to form precipitates that are removed as part of the sludge. Few treatment plants have such a fortunate combination of sewage sources. On the other hand, deliberately adding metal ions to sewage plant

TABLE 2
Approximate quantities of algal growth materials
(from sources either in or entering U.S. surface waters)

Source	Quantities available (millions of pounds per year)		
	Organic matter	Nitrogen	Phosphorus
NATURAL			
Air		15-300 ^a	
Rainfall (direct into surface water)	4,200-7,400 (COD)	30-590	2-17
Aquatic plants	n.a.	0-1,070	0-107
Waterfowl, fish, bottom fauna, and the like	n.a.	n.a.	n.a.
Muds under water bodies	n.a.	n.a.	n.a.
Runoff from			
Forest land (including commercial forests)	n.a.	990-2,250	243-587
Other land	n.a.	n.a.	n.a.
MAN-GENERATED SEWAGE			
Domestic			
Human and food wastes } Washing wastes }	5,200 (COD) ^b	1,330 ^b	137-166 ^b 250-280 ^b
Industrial			
Food processing wastes	n.a.	n.a.	n.a.
Other wastes	n.a.	n.a.	n.a.
RUNOFF FROM			
Urban land	5,500 (COD)	200	19
Cultivated land			
Fertilized	17,900 (COD) ^c	2,040 ^c	110-380
Unfertilized	n.a.	n.a.	n.a.
Land on which animals are kept	n.a.	420	170

n.a. Not available

^a Approximately half the quantity entering from rainwater

^b Data based on the assumption of 70% removal of COD and 30% removal of nutrients in treatment plant

^c Estimated

TABLE 3
**Phosphorus entering surface waters with runoff^a
from cultivated land**

	Size of site (acres)	Phosphorus entering surface water (pounds per acre per year)	
		Range	Average
Kaskaskia River, Ill.	3,320,000	0.02-0.76	0.35
Madison, Wis.	140,000	n.a.	0.40
San Joaquin Valley, Calif.	358	0.20-0.90	0.55
Yakima Valley, Wash.	265,000	0.9-8.9	1.33
Coshocton, Ohio	1.45	n.a.	1.2

^a Includes runoff through drain tile under the crop land

streams has not always been so successful in removal of phosphates.

Control of phosphorus in runoff from cultivated land could be affected by the same measures used to control nitrogen from this source—that is, better irrigation practices and use of slow release fertilizers.

Control of runoff from areas where animals are kept also appears necessary, since about 20% of the man-generated phosphorus (as this kind of phosphorus is categorized) may come from such areas. The tendency in animal husbandry is to grow animals in greater numbers in more controlled environments—feed lots and commercial broiler plants, for example. Thus, the time may soon come when the waste from these operations will have to be treated much as domestic sewage is treated.

Elimination of detergent phosphate

Many solutions have been proposed to alleviate local problems of excess algal growth, but the only proposal that would have a nationwide effect is to prohibit use of phosphates in household detergents.

The effectiveness of this proposal would depend on how much the phosphorus concentration could be reduced in receiving waters. If the available data are correct, about 280 million pounds of phosphorus would be kept from the surface waters annually if no phosphates were put in detergents. At the very least, 680 million pounds would still enter these waters from other sources. The total annual streamflow in the continental U.S. is nearly 450 trillion gallons. If phosphorus from sources whose contribution to surface waters has been estimated were distributed equally in this streamflow, the average concentrations based on the minimum quantities would be as shown in Table 7.

Reduction in average concentration from 0.26 to 0.18 p.p.m. is significant, but the 0.18 p.p.m. figure is still more than 10 times the concentration believed to induce excessive algal growth. If the maximum, rather than the minimum, quantities of phosphorus were distributed in the streamflow, average concentrations would be 0.46 p.p.m. from all such sources and 0.38 p.p.m. from all such sources except detergents.

TABLE 4

Natural and man-generated sources of phosphorus and nitrogen

	Nitrogen		Phosphorus	
	Quantities (million pounds per year)	Per cent	Quantities (million pounds per year)	Per cent
Natural	1,035-4,210	21-51	245-711	26-41
Man-generated	3,990	79-46	686-1,015	74-57
TOTAL ^a	5,025-8,200	100%	931-1,726	100%

TABLE 5

Man-generated sources of nitrogen

Source	Quantities (millions of pounds per year)	Per cent
Domestic sewage	1,330	33%
Runoff from Urban land	200	5
Cultivated fertilized land	2,040	51
Land on which animals are kept	420	11
TOTAL ^a	3,990	100%

TABLE 6

Man-generated sources of phosphorus

Source	Quantities (millions of pounds per year)	Per cent
Domestic sewage	387-446	56-44%
Runoff from Urban land	19	3-2
Cultivated land	110-380	16-37
Land on which animals are kept	170	25-17
TOTAL ^a	686-1,015	100%

TABLE 7

Phosphorus concentration (hypothetical) in surface waters

	Total phosphorus (million pounds per year)	Average concentration (p.p.m.)
All estimated sources	980	0.26
All estimated sources except detergents	680	0.18
If 90% of phosphate in sewage is removed	560	0.15

^a These totals do not include what may be substantial amounts of phosphorus and nitrogen from as yet unknown and unmeasured sources. Such additional phosphorus and nitrogen may have an effect on methods of controlling algal growth

Furthermore, since sizable quantities of phosphorus unquestionably enter the surface waters from sources such as industrial wastes and bottom muds (whose contribution is not included), the entering concentrations could be even higher. Thus, the benefits of prohibiting use of phosphates in household detergents seem marginal at best. If algal growth promoted by the presence of phosphorus is to be reduced significantly, means must be found to remove virtually all phosphorus arising from man-generated sources.

Those data also suggest another somewhat surprising possibility. A minimum of about 250 million pounds of phosphorus a year would still enter surface waters from natural sources even if all phosphorus from man-generated sources were excluded. The resulting average concentration in the total U.S. streamflow would be close to 0.07 p.p.m.—more than four times the concentration needed to induce excessive algae growth. Several explanations are possible:

- Excess algal growth from natural causes is more prevalent than generally believed.

- Estimates of phosphorus and nitrogen in runoff from natural or uncultivated land need to be revised downward.

- The frequently quoted concentration limit for phosphate (0.015 p.p.m. or less) is unduly low because the concentration of phosphate may not determine the extent of algal growth in many surface waters.

A course of action

This brief review of the present state of knowledge indicates that, before adequate solutions to the problem of excess algal growth can be found, we need to know more about the conditions leading to such growth and more information on the source of AGM.

For example, we need research to determine the effect of various forms of organic matter on excess algal growth. Can algal blooms occur when air and rain are the only source of carbon dioxide? If so, does the concentration of nutrients have to be higher than in water containing bacteria populations supported by biodegradable organics? Also, why is it that excess algal growths occur in some waters containing 0.001 p.p.m. soluble phos-

phorus but do not occur in waters where the concentration is 15 or even 50 times greater? The effect of the so-called micronutrients on algae growth should also be determined, as should the effect of other aquatic life.

Much of this work has already been done for phosphorus and nitrogen, although additional information is required on the quantities that come from sources for which no data exist—bottom muds, uncultivated land, and industrial sewage. Data on industrial sewage will be the most difficult to acquire because of the variety of materials in this type of sewage and the varying degrees of treatment it receives. Some additional work will also be required to establish how typical the nitrogen and phosphorus data are from a single area compared with those for the nation as a whole.

However, judging from the amount of effort expended to collect the information already available, completion of the tasks outlined above does not appear to be formidable. With this added knowledge, it should be possible to attack the problem of excess algal growth with a reasonable degree of assurance that the solutions proposed will have the desired effect.

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Mr. Ferguson received his B.S. (1947) and M.S. (1949) degrees in chemical engineering from the University of Washington. Before joining Stanford Research Institute, he worked with the research staff of Kaiser Aluminum and Chemical Corp. on liquids-solids separation, high-temperature systems, and corrosive atmospheres. Mr. Ferguson is a member of the American Institute of Chemical Engineers and the Western Chemical Market Research Group.

Major U.S. River Reflects Surfactant Changes

During 1959–66, when sales of detergents increased rapidly, surfactant levels in the Illinois River fell steadily as a result of the switch to biodegradable detergents

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Some possibly deleterious effects of commonly used surfactant compounds on receiving waters have caused wide-spread concern. The persistence of a certain percentage of these kinds of materials led to government-imposed minimums for biodegradability in some foreign countries. Voluntary limits for minimum biodegradability were established by a majority of the detergent manufacturers in the U.S., with a timetable for conversion.

The Illinois River serves as the major recipient of waste waters from many major industrial complexes and many communities, including Chicago. A chemical study of surfactant levels in the Illinois River from 1959–66 at Peoria was undertaken to provide better understanding of some of the effects of detergent compounds on water quality in a major river.

Following a change in surfactant formulation, surfactant concentration was reduced 61% (based upon mean value). These reductions occurred coincidentally with a marked increase in the use of synthetic detergents.

A global problem

The problem of elevated surfactant levels in major rivers has become worldwide. The concentration of detergent in the River Seine was between 1 and 2 milligrams per liter (Prat, 1962). The level of ABS (alkyl ben-

zene sulfonate) was increasing yearly in the Tama River on Honshu Island near Tokyo, causing concern (Osawa, 1965). And in Germany, the average detergent level at the outlet of 14 waste processing plants using biological treatment was 5.4 mg./l. for 1962–64 (Husmann, 1966).

The Ohio River below Cincinnati in 1965 was found to have had concentrations of ABS that ranged between 0.06 and 0.15 mg./l. Most rivers checked prior to 1960 had levels between 0.01 and 0.02 mg./l. ABS. The Illinois River in 1959 had a range of concentrations ranging from 0.5 to 1.3 mg./l. (Sayers, 1962). In 1964, the Illinois River was described as, "The largest river in the country that currently contains more than 0.5 p.p.m. ABS . . ." (Woodward, 1964).

Change to biodegradability

In the U.S., conversion from less biodegradable detergents to the more easily decomposed surfactant compounds occurred voluntarily on an industrywide basis in 1965. In Germany, a legally imposed minimum of 80% biodegradability reportedly went into effect in 1964. A similar standard was advised for Hungary in the same year (Horwath and Gulyas, 1964).

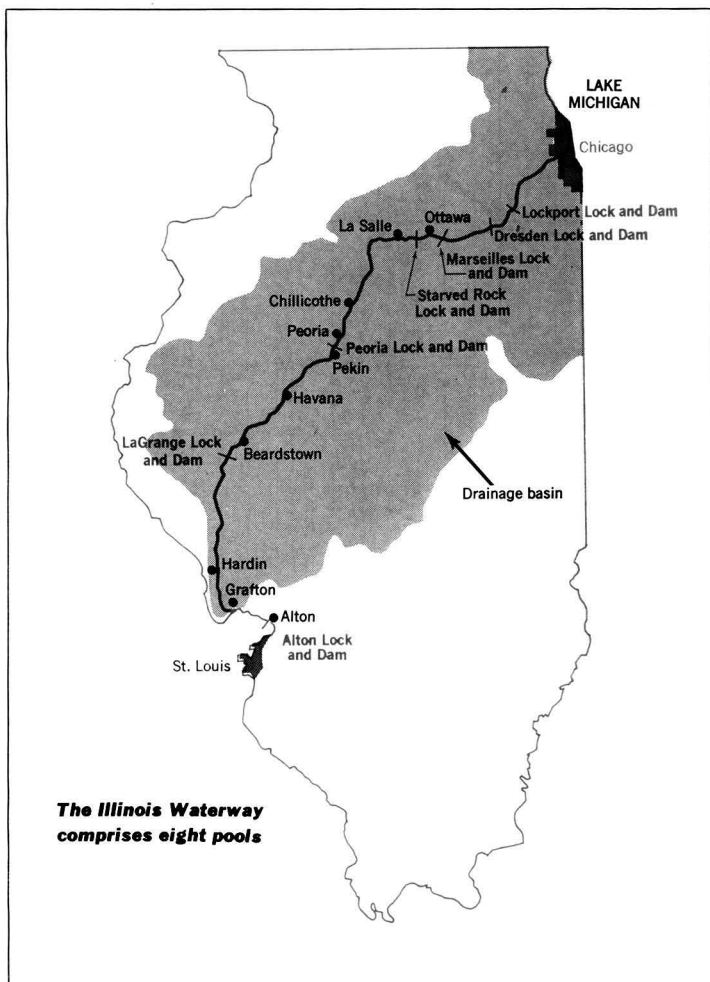
The Jephcott Committee in England in 1956 reported that 40% removal of ABS by conventional sewage treatment produced effluents containing as much as 10 mg./l. ABS. In drinking water drawn from these affected rivers, concentrations of 0.5 mg./l. were found (Eden and Truesdale, 1965). Replacement of hard (ABS) detergents by soft

linear alkylate sulfonate (LAS) compounds began in England on a national scale in 1962 with complete conversion accomplished by the early months of 1965. Detergent levels in England have subsequently diminished from 3.0 to 1.3 mg./l. at the sewage works' effluents (Ministry of Technology, 1966).

German experience has shown that present detergent levels in the Ruhr River are 70% lower than those found prior to the ban on hard detergents. This decrease is especially notable since there has been a reported 20% increase in detergent production in Germany since 1964. Also in Germany, an average outlet concentration for 1962–64 at 14 waste processing plants using biological treatment, decreased from 5.4 to 1.2 mg./l. in 1965.

A report by the University of California showed that in a standard-rate activated sludge plant the total detergent concentration had decreased from 5 mg./l. in March 1965 to 0.7 mg./l. in September 1965, reflecting an increase in efficiency of removal from 60 to 90%. An extended aeration activated sludge plant showed a drop from 3 to 0.3 mg./l. ABS for a similar period. At a high-rate trickling filter plant, levels from a tertiary pond effluent decreased from 8 to 1.3 mg./l. ABS. Other studies have shown the activated sludge process capable of 97–99% reduction of soft detergents. Even under overload conditions, degradation in excess of 95% was possible (*Water Works and Waste Engineering*, 1965).

This article is based on a paper presented at the 22nd Annual Purdue Industrial Waste Conference last spring.



with aesthetics than with toxicity, taste, and odor. The route taken by the ungraded detergent might also be used by other substances of waste water origin. Detergents of the ABS type are essentially nontoxic, odorless below concentrations of 1000 mg./l., and tasteless to 50% of the persons who sampled water with concentrations below 60 mg./l. However, frothing of drinking water was reported to occur at levels as low as 0.6 mg./l.

Possible dilemma

Some research workers feel that detergent foam might have deleterious effects during waste treatment, since the efficiency of aeration may thus be diminished. However, others note that an increase in detergent degradation might result in the depletion of oxygen in effluents and the subsequent damaging of receiving waters.

Although problems have resulted from ungraded ABS detergents, they must be biodegradable at least in part since they can be reduced significantly by efficient waste treatment. Primary sewage treatment may give only 2-4% detergent removal, but conventional activated sludge processing can result in 30-80% degradation (an average of 50%). Laboratory studies conducted on ABS-seeded river water have shown reduction as high as 75% over a 30-day period.

The Illinois River

The Illinois River possesses many highly individual characteristics that distinguish it from other major rivers

(Text continues on page 198)

Laboratory scale studies, run at the Sanitary Engineering Research Laboratory of the University of California and reported in 1964, indicated that 95% of the LAS detergent applied to standard-rate activated sludge units was removed. In this instance a comparison of ABS and LAS showed that, "... in terms of intact detergent surviving the aforementioned wastewater treatment processes and contributing to the pollution of receiving waters, ABS proved to be five to eight times more resistant than LAS" (Klein and McGauhy, 1965).

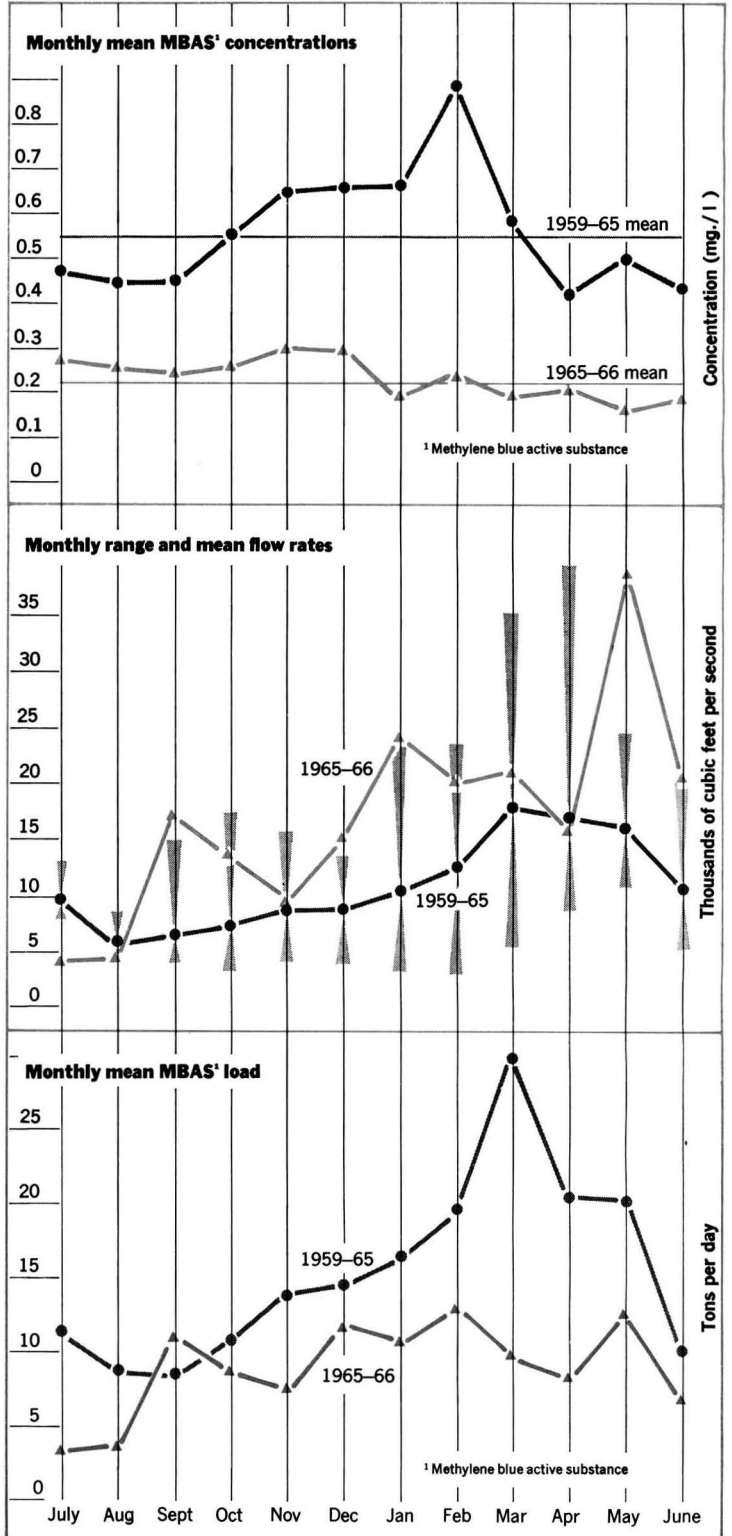
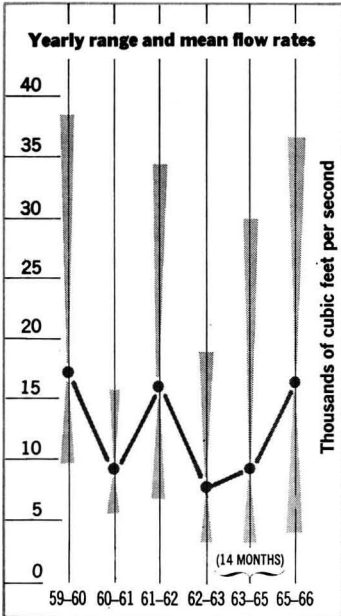
The production changeover in the U.S. was not abrupt since some manufacturers began modifying specific

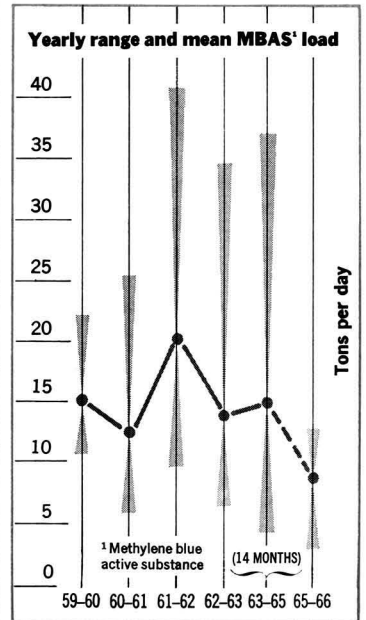
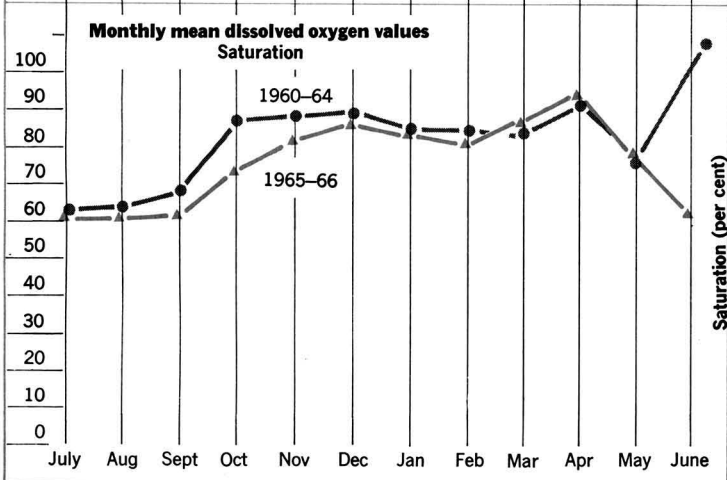
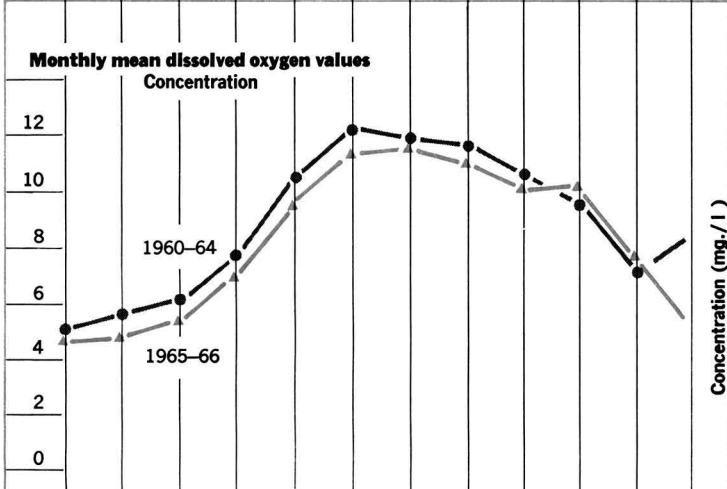
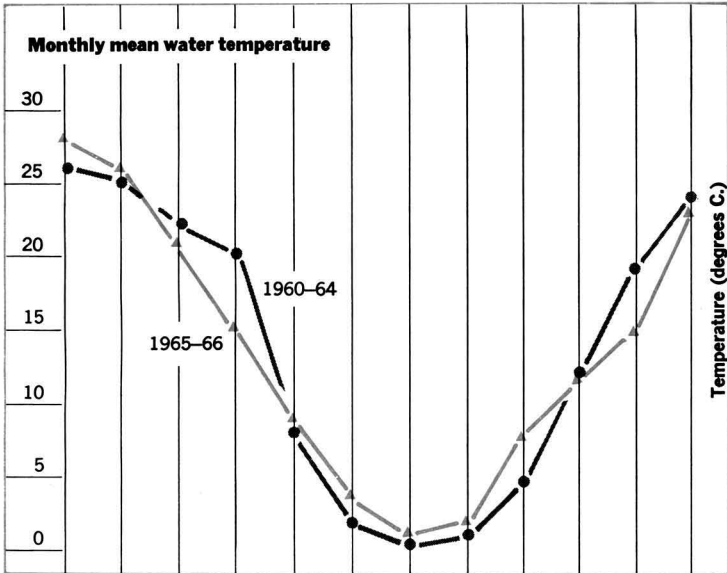
brands in the early fall of 1964. Distributors in the Chicago and Peoria areas received their first shipments of products containing LAS in October 1964. Some manufacturers had completed their conversion at the production level by April 1965. The entire soap and detergent industry had accomplished its change to more biodegradable detergents by June 30, 1965, six months ahead of its own target date.

Detergent buildup

The concern of health and sanitation authorities with the accumulation of intact detergents in waters used for human consumption has been more

Change in surfactant levels in Illinois River reflects switchover in surfactant use in bordering areas





of the U.S. A very old stream, it flows down an unusually flat gradient. The average fall for its entire 273-mile length is less than one third of a foot per mile (0.31 foot per mile). The upper stretch falls 65 feet in 40 miles (1.6 feet per mile), whereas the lower 233-mile sector falls only 20 feet to reach the level of the Mississippi River into which it flows. This lower section averages less than one-tenth foot of fall per mile.

For navigation and flood control purposes, the entire length of the Illinois Waterway consists of a series of eight pools extending 327.2 miles from the waterway's confluence with the Mississippi River. The first of these pools, the Alton Pool, is at the level of the Mississippi. Seven dams create successive retentions reaching back to Lake Michigan at Chicago.

Though the Illinois River properly originates at the juncture of the Kankakee and Des Plaines Rivers (nearly 54 miles downstream from Lake Michigan), the quantity and quality of flow originating in the Chicago area are of prime importance to communities located downstream. This flow, conveyed to the river mainly by the Chicago Sanitary and Ship Canal, consists principally of waters diverted from Lake Michigan and waste discharges from storm, sanitary, and industrial outlets.

The velocity of the Illinois River is quite low, with an average time of travel from Chicago to Peoria of 12.5 days (12.3 miles per day or 0.8 foot per second, at a flow at Peoria of 6945 cubic feet per second).

Contributions of tributaries, land drainage, and communities along the way increased this mean low flow of

the river at Peoria for the years 1959–65 to about twice the flow at its origin. This combination of low velocity of flow and increased dilution is believed to contribute to a reduction in the amount of organic matter and suspended solids.

The condition of the Illinois River has been the subject of many studies, beginning almost a century ago. Increasing use as well as an evolution in the composition of the effluents discharged into it is revealed by two studies conducted more than 60 years apart. The first, in 1899–1900, showed that 90% of the organic matter discharged into the Illinois River by Chicago had disappeared before reaching Peoria (153.5 river miles downstream). A 1963 study showed that close to 27% of the ABS detergent discharged by Chicago had been decomposed during a five-day period in which the river had flowed 75 miles.

Surfactant monitoring program

The initial phases of the monitoring program on the Illinois River at Peoria, first termed the ABS Sampling Program, were begun in September 1959. The post-conversion test period covered 12 calendar months, running from July 1965 through June 1966. Water specialists hoped that in 1966 the changeover to LAS would become detectable by alterations in undegraded detergent levels in the Illinois River.

Laboratory procedures

During much of the 1965–66 test period, the surfactant compounds analyzed were a changing mixture of ABS and LAS detergents. Because both substances are measurable by the methylene blue method, the research workers decided to use the term MBAS (methylene blue active substance) to denote the presence of either ABS or LAS, since the analytical technique did not distinguish between the two compounds.

The Illinois River was sampled on a twice-weekly schedule. Water was collected from below the surface of the river at the State Water Survey intake at Peoria (river mile 161.6). This location is 154.2 miles downstream from the main outfall of the Southwest Treatment Plant of the Metropolitan Sanitary District of Greater Chicago and 1.4 miles upstream from the out-

fall of the Greater Peoria Sanitary District treatment plant.

The majority of samples were analyzed within 24 hours of their collection. The procedure used to determine MBAS was the SEC modification of the methylene blue method. Data for the 1959–65 period were based on the analysis of 279 samples, and data for the 1965–66 period, on 99 samples.

Results and discussion

Monthly mean values for MBAS concentration in the Illinois River were determined for September 1959 through June 1965. During this essentially pre-LAS period, the mean value of 0.56 mg./l. MBAS was equaled or exceeded from October through March with a maximum of 0.87 mg./l. during February. The minimal value of 0.42 mg./l. was approached in the months of April through September, indicating a seasonal variation.

In the post-LAS period of July 1965 through June 1966, the concentration curve appeared much less variable with respect to the mean. The mean was 0.22 mg./l. MBAS with a maximum of 0.30 and minimum of 0.13 mg./l. A steadily diminishing trend in MBAS concentration may be detected in this post-LAS curve.

The Illinois River is subject to several variations caused by seasonal change. One of these variations is rate of flow. Monthly mean flows for the year 1965–66 displayed extreme variations from values for the preceding years. However, the mean and maximum flows for the year were roughly equivalent to those for two of the preceding five years. The period 1965–66 was clearly one of high and erratic flow on the Illinois River.

During times of maximum flow, dilution is maximal and retention is minimal. Increasing dilution would obviously lower the concentration of a solute. Because biological degradation is a function of time, greater retention would similarly result in a lower concentration of a biodegradable substance such as LAS.

To minimize the effects of flow variation, the quantity of MBAS transported by the Illinois River was presented in terms of tons of MBAS per day. The load values for the years 1959–65 had, as expected, an appropriate correlation with both the flow and concentration data for the

Mean MBAS loading in the Illinois River at Peoria decreases . . .

Year	MBAS load (tons/day)	Range	MBAS
1959-60	15.7	10.6-21.7	ABS
1960-61	13.0	6.4-26.2	ABS
1961-62	20.6	10.3-41.0	ABS
1962-63	14.5	6.7-35.3	ABS
1963-65	15.4	4.8-37.8	ABS and some LAS
1965-66	9.0	3.0-13.0	LAS and some ABS

. . . Although synthetic detergent sales continue to rise

Year	Total U.S. synthetic detergent sales (billions of pounds)	Increase over 1959-60 (Per cent)
1959-60	3.296	—
1960-61	3.375	2.3
1961-62	3.584	8.9
1962-63	3.807	15.5
1963-65	4.028	22.2
1965-66	4.206	27.9

Note: Data are based on reports from 40 leading U.S. manufacturers comprising approximately 85% of the soap and detergent industry. Values do not include packaged and bulk scouring cleaners.

same period. The MBAS load in 1965-66 showed levels which were, with the exception of September, distinctly lower than the mean for the corresponding months in the years 1959-65. Yearly summary data showed a mean value for 1965-66 that was notably less than the mean of the lowest of the preceding years (1960-61). In fact, the difference was nine tons per day compared with 13 tons per day. A summary of the MBAS load in the Illinois River at Peoria for the six-year period is shown in the table above.

The 1965-66 diminution in both MBAS load and concentration occurred during what was at that time the highest period of synthetic detergent sales in the U.S. A steady rise in synthetic detergent sales and subsequent use marked the entire seven-year test period.

Though these data are not nationwide in scope, the segment of the national population from which MBAS in the Illinois River was derived is essentially typical in its patterns of surfactant purchase and use.

The extent to which MBAS is removed from the river by biodegradation *in situ* may be affected by water temperature. The temperature curve for 1965-66 varied little from the curve for 1960-64, indicating that water temperature variation is not responsible for the change in MBAS levels for the two periods.

The question of oxygen depletion subsequent to increased MBAS degradation was considered. Twice-weekly dissolved oxygen determinations were performed by the Alsterberg modification of the Winkler method during both the pre-LAS and post-LAS sampling periods. Levels were determined for DO as mg./l. and as per cent saturation. Neither measurement showed a notable difference between the pre-LAS or post-LAS sampling periods (with the possible exception of June 1966, when the curves diverged). The brief downward trend in 1966 was not sustained during subsequent DO measurements.

Any increase in biodegradation of MBAS in the post-LAS period does not appear to have resulted in a de-

crease in dissolved oxygen in the Illinois River at Peoria.

In brief, then, we have reached the following conclusions:

- A lower level of MBAS both in terms of concentration and load was observed in the Illinois River at Peoria after the conversion from ABS detergents to the more readily biodegradable LAS compounds.

- Lowest levels of MBAS concentrations and load in seven years occurred at the period of highest detergent sales and use.

- No interference with dissolved oxygen levels in the river resulting from increased biodegradation was found.

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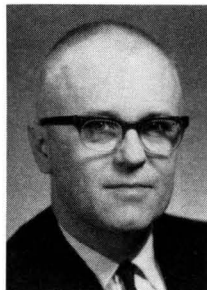
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"Synthetic Detergents and Water Quality; Part II: The 'Soft' Deter-



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A Simple Technique for the Absolute Determination of Atmospheric Oxygen

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■ A method is presented for the absolute determination of oxygen at concentrations near atmospheric. The oxygen in a sample is determined gravimetrically after reaction with either white phosphorus or a sodium-potassium alloy. The method requires little time and simple laboratory equipment and is capable of yielding values for oxygen concentrations having an over-all uncertainty of ± 0.1 mole %.

Several simple instrumental techniques for the determination of the oxygen content of the atmosphere are available which are capable of a reproducibility to within ± 0.01 mole %. Calibration of such instruments, however, requires analysis of a sample of air, the composition of which has been verified by an absolute method capable of an accuracy of 0.01 mole % or better. Absolute chemical methods usually depend on measurement of the volume change accompanying adsorption of oxygen with a suitable reagent. The classic study by Benedict (1912) is a good example of the accuracy which can be achieved. However, the complexity of the apparatus and the skill required of the operator are such that few laboratories are prepared to undertake such analyses.

The method described herein was developed in a search for a simple method requiring no other apparatus than would be found in any good laboratory. The method is extremely simple, has an accuracy adequate for a variety of problems, and requires little actual time for each analysis.

Method and Apparatus

The method consists simply in reacting the oxygen from the sample of air with either phosphorus or a sodium-potassium alloy. The nitrogen and argon are separated by pumping them away, and the oxygen is determined gravimetrically by the gain in weight of the vessel. The reagent is contained in a small flask (Figure 1), which is weighed against a similar flask on an equal arm balance. The flask is attached to a manifold through which the sample is admitted and through which the residual nitrogen and argon are pumped away.

Reagents

Stick white phosphorus is melted under warm water and broken up into small globules about 3 or 4 mm. in diameter which are stored under water in a small bottle until needed.

The phosphorus is introduced into the reaction flask through the barrel of the unlubricated stopcock. A slow stream of nitrogen is passed through a glass tube which also enters the flask through the stopcock barrel. The tube is removed after the phosphorus is in the flask, and the pregreased plug is quickly inserted. The flask is then connected to a vacuum system, evacuated, and gently warmed to melt the phosphorus and to vaporize the water. Care must be taken to prevent overheating which would vaporize too much of the phosphorus. The phosphorus is then agitated slightly by rotating the flask gently back and forth about the joint to produce a large surface of phosphorus while at the same time any occluded water is removed. Five or six grams of phosphorus are more than sufficient for about 10 determinations. The vapor pressure of phosphorus is about 0.07 torr at room temperature. Consequently, there is significant loss of phosphorus when the bulb is pumped at room temperature even for short periods. It was found, for example, that at ice bath temperature, 0.00020 gram of phosphorus was lost when the

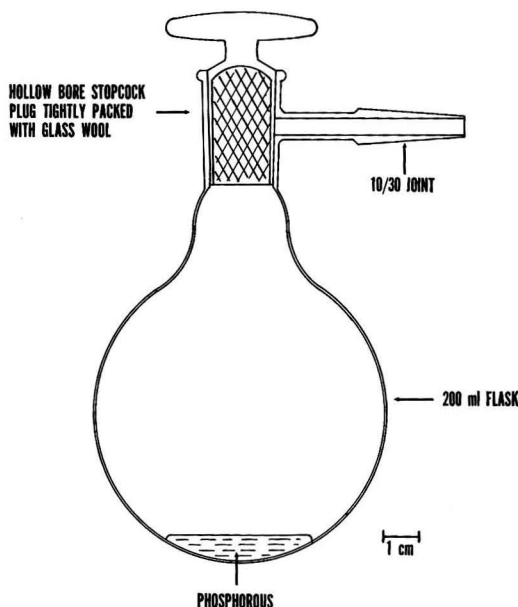


Figure 1. Reaction flask

bulb was pumped for 4 minutes. Therefore, it is necessary to cool the bulb much below 0° C. during the pumping operation. Cooling with dry ice was tried but this is not satisfactory because of poor thermal contact, mechanical difficulties, and the accumulation on the bulb of an oil film originating from the dry ice. Submerging the flask in liquid nitrogen to a point about 1 inch below the stopcock was found to be a satisfactory method for cooling.

The sodium-potassium alloy is prepared by cutting a piece of each metal of about equal size. The dimensions must be such that the pieces can be easily inserted into the flask as already described. Oil or other organic matter must be excluded from the surface of the metals. This can be done by first blotting any oil from the surface of the metal and then cutting with a knife blade that is wiped carefully after each slice is removed. An inert atmosphere is maintained in the flask until it is connected to the vacuum system for evacuation.

The flask is gently heated until the metals melt and coalesce. The resulting alloy, a liquid at room temperature, is agitated to remove any entrapped gas. It was found necessary to expose the flask to air two or three times before analytical use to condition the reagent. Small bubbles erupt from the surface of the mass of the liquid during pumping when the liquid alloy is disturbed. After several determinations, one of the constituents of the alloy is preferentially reacted and the liquid becomes a mass of small crystals which grow up out of a solid layer firmly fixed to the glass.

Vacuum System

Any system, even a fore pump and trap, which will reduce the pressure to about 5×10^{-2} torr is adequate. The vacuum system used for this determination consisted of an oil diffusion pump and a manifold with attached manometer and tilting McLeod gauge and was used primarily because of its availability.

Reaction Flask

The flasks are made by expanding the bulb on a right angle stopcock and sealing it to a 200-ml. round-bottomed flask. The glass wool plug is needed only when phosphorus is used to prevent loss of oxides during pumping.

The weight of the flask should be minimized. The total weight of a completed bulb is approximately 110 grams. Initially the weight of a bulb and its tare are adjusted to within 0.00010 gram using aluminum wire. The tare is another bulb filled in the same manner which can be used for analysis when the first bulb nears exhaustion. Some care should be taken to select flasks and stopcocks so that both the final volumes and weights of the two bulbs are reasonably close, so that buoyancy corrections are not required. The bulbs used in this study differed in volume by less than 5 ml. A change in barometric pressure of 1 torr would result in a weight change of approximately 7×10^{-5} gram if the difference in volume were as much as 5 ml. Because of the difficulty of determining the exact volume of the flasks, weights, and weight pan, a determination of the expected effect was made by weighing the undisturbed flasks periodically over a period of three days. During this period, the observed barometric pressures at the time of weighing varied by 1.5 torr. No change in weight was noted. The use of other flasks, not so for-

tuitously matched as the above, could introduce serious errors if changes in buoyancy are not accounted for.

Weighing

A semimicro equal-arm balance is used. The pans are removed and the bulbs are suspended by wire bails attached below the lip of the barrel of the stopcock. The maximum weight difference between the two bulbs before changing reagents did not exceed 0.7 gram. A small pan constructed of aluminum foil and aluminum wire is suspended from the side arm of the flask. Weights calibrated to an accuracy within ± 0.001 mg. are used.

A single weighing done after four hours of equilibration is enough to assure constancy. Bulbs left hanging in the balance case have shown no change over periods of several days, nor were any short-term changes observed when the bulb was weighed periodically over several hours' time. When changes were noted, they were always due to leaks around the stopcock or other observed problems.

The manipulation involved in filling and evacuating the bulbs introduced no significant error in the weighings. As an example, a bulb was weighed, attached to the manifold, pumped, removed, cleaned, and reweighed. This was repeated three times.

Original weight difference between bulb and counterpoise	0.11633
Weight difference after first pumping	0.11634
Weight difference after second pumping	0.11634
Weight difference after third pumping	0.11634

The total weight of oxygen retained in a bulb for each analysis is about 0.05000 gram, so that a change of 0.00001 gram is negligible in this situation.

Procedure

The evacuated bulbs were placed in the balance case and allowed to equilibrate. With volumes of this size, equilibrium is not attained rapidly. In fact, about four hours is required for equilibrium, and it has been found advantageous but not necessary to shield the balance case with an outer case. After attaining constant weight, the bulb is attached to the vacuum manifold for evacuation.

The sample of air, freed from water vapor by passage over a column of magnesium perchlorate (about 12×200 mm.), is admitted to the system including the bulb until a pressure of about 700 torr is reached. When phosphorus is used, only water vapor is removed. When the sodium-potassium alloy is used, it is necessary also to remove carbon dioxide by passage over Ascarite.

The bulb is removed from the system, and the joint is carefully cleaned of all traces of grease. First it is wiped with dry tissue followed by two wipings with tissue soaked in methylene chloride or other similar highly volatile solvent. The bulb is then returned to the balance case and weighed.

The next step involves the removal of nitrogen and argon. When the sodium-potassium alloy is used, it is only necessary to attach the bulb to the manifold and to pump on it for one minute after which it is returned to the balance for weighing. When phosphorus is used, a somewhat different procedure is followed. The bulb is first cooled for 10 minutes and then

evacuated for 15 minutes. The lengthy evacuation is due to the tightly packed glass wool plug in the stopcock. The bulb is then removed from the system and warmed. The spherical portion which has been immersed in liquid nitrogen is washed with distilled water, carefully dried, and hung in the balance case to attain temperature equilibrium.

Results

The method has been evaluated by determining the oxygen content of a cylinder of compressed air. Sixteen valid determinations were performed using phosphorus, and 20 determinations were completed using the sodium-potassium alloy. The results for the two methods are shown in Table I. The value obtained using phosphorus is high because the carbon dioxide was not removed and remained condensed in the flask together with the reacted oxygen. The carbon dioxide was found by mass spectrometry to be 0.0048 mole % or about 0.0075 wt. %. When this is subtracted from the above, the results by the two methods are identical.

The argon-to-nitrogen ratio of this sample of air was determined mass spectrometrically and was compared with that of atmospheric air. The ratios were found to be identical, and the molar concentration of argon in the sample is therefore assumed to be 0.93 mole %. Using this value, the measured value for carbon dioxide, and knowing that nitrogen is the only other gas present, the value 23.157 wt. % oxygen is equivalent to 20.959 mole %. The actual concentration of oxygen in the atmosphere is probably close to 20.945 mole % (Glueckauf, 1951). The value obtained by Benedict (p. 114, 1912), after correction (Glueckauf, 1951), is 20.952 mole %. These values represent the oxygen content of normal air containing 0.03 mole % carbon dioxide. If the sample of air used in this study contained this quantity of carbon dioxide, the oxygen concentration would be 20.953 mole %.

The difference between this value and the actual value for atmospheric oxygen may either be a real difference or the result of a systematic error in the method. Differences in the composition of commercial compressed air are known to occur. To determine whether this was true for the compressed air used in this study, it was compared with a sample of clean and dry atmospheric air. The method of comparison utilized an instrumental method which measures differences in oxygen content with a reproducibility of better than 0.005 mole %. The observed difference between the air contained in the cylinder and that of the atmosphere was $+0.008 \pm 0.003$ mole %. The limit is the 95% confidence limit for the average. The results indicate that a real difference does exist between the two samples and that the gravimetric method has no significant systematic error.

Table I. Summary of Results

Method	Average Wt. % Oxygen	Computed Standard Deviation	95 % Confidence of the Average
Phosphorus	23.165	0.064	0.034
Sodium-potassium alloy	23.157	0.038	0.018
Combined results ^a	23.157	0.050	0.017

^a With correction of phosphorus data for CO₂.

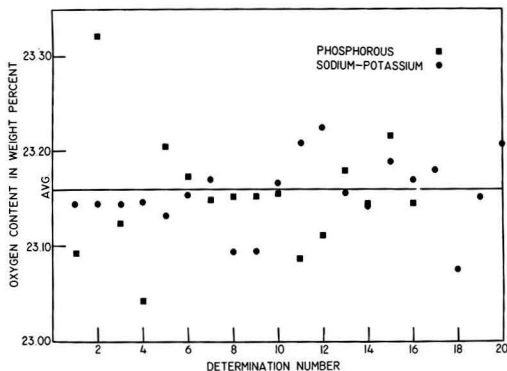


Figure 2. Graphical representation of the data

Many possible sources of error were investigated in an attempt to increase the accuracy. The results (Figure 2) indicate a random source of error. There is no connection between the condition of the bulb—that is the number of times it had been used—and the deviation of a result. For instance, determinations numbered one through eight for the sodium-potassium alloy were done using the same reagent. High results were not due to inadequate pumping as many of the determinations, both high and low, involved two or more pumpings. Back diffusion of pump oil was suspected at one time as a possible source of high results. A column of Molecular Sieves was inserted between the bulb and the manifold but was discarded when no effect on the results was noted.

Other Applications

Problems involving the determination of oxygen in other gases can be treated by this method. Analysis of respiratory gases, atmospheric research, and combustion analyses are several possible applications. The method should work equally well for both higher and lower concentrations of oxygen.

At present, the method is being used to analyze a series of mixtures approximating the composition of air which will be issued as a standard reference material.

Conclusions

A method has been presented which allows, in terms of the actual time involved, a rapid determination of oxygen over a wide range of concentrations without the need for elaborate equipment or specially trained personnel. The method has been used to analyze a single sample of air which is to be used as a primary standard for the calibration of the instruments for the determination of oxygen.

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Thin-Layer Chromatographic Separation and Spectrophotofluorometric Identification and Estimation of Dibenzo(*a,e*)Pyrene

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■ Hexacyclic polynuclear hydrocarbons are of interest to air pollution because of their carcinogenic activity and their presence in combustion sources. An investigation was made of both the one-dimensional and two-dimensional thin-layer chromatographic separation of these compounds using mixed substrates. Spectrophotofluorometry was used for identification and estimation purposes. Dibenzo(*a,e*)pyrene was identified as being present in urban airborne particulate matter obtained from composites of samples from the city of Birmingham and from a combination of various other cities in the state of Alabama. The concentration of dibenzo(*a,e*)pyrene in the composite from the combination of various cities in Alabama was estimated to be approximately 100 μg . per gram of benzene soluble.

Only two hexacyclic aromatic hydrocarbons containing the pyrene nucleus have been found in urban airborne particulate matter: dibenzo(*cd,fg*)pyrene, which is better known as benzo(*ghi*)perylene, and dibenzo(*cd,jk*)pyrene, which is better known as anthanthrene (Sawicki, 1964). The carcinogenic activity (Hartwell, 1951; Lacassagne, Buu-Hoi, *et al.*, 1963; Sawicki, 1964; Hoffmann and Wynder, 1966) of compounds of this type, as well as the presence of some of them in combustion sources (Oro, Han, *et al.*, 1967), particularly in automobile exhaust (Lyons, 1962) and cigarette smoke condensate (Carugno and Rossi, 1967), cause them to be of concern in studies of the constituents of ordinary urban air.

Thin-layer chromatography and spectrophotofluorometry are highly valuable means for separating and identifying minute quantities of material in extremely complex mixtures. An investigation of the application of these methods to the identification of additional hexacyclic aromatic hydrocarbons containing the pyrene nucleus was undertaken to determine whether these compounds are indeed present in urban atmospheres before proceeding to quantitative analysis for them. Further experiments were conducted to produce a method of estimating the amount of dibenzo(*a,e*)pyrene in urban airborne particulate matter.

Experimental

Solvents, Reagents, and Instrumentation. Cyclohexane, *N,N*-dimethylformamide, anhydrous methanol, and anhydrous

ether were obtained commercially in the purest form possible. Pentane and dichloromethane were obtained commercially and redistilled; pentane was distilled at 35° C., and dichloromethane was distilled at 40° C.

An Aminco-Kiers spectrophotofluorimeter was converted to operate as a spectrophotofluorometer with slit arrangement No. 2 and an RCA 1P21 photomultiplier tube. The thin-layer chromatography apparatus is described below.

Two-Dimensional Thin-Layer Chromatography. Cyclohexane or cyclohexane saturated with *N,N*-dimethylformamide and then diluted was the solvent used in the first development. Aqueous *N,N*-dimethylformamide saturated with ether was used to develop in the second dimension. Standards were run on the plates, one-dimensionally as markers.

One-Dimensional Thin-Layer Chromatography. Two one-dimensional thin-layer chromatographic separations were carried out with aluminum oxide-cellulose acetate (2 to 1) plates to estimate the concentration of dibenzo(*a,e*)pyrene. Ten spots of 100 μl . each of the hexacyclic fraction in pentane were applied 1 cm. apart and three spots of 40 to 60 μl . each of a saturated pentane solution of dibenzo(*a,e*)pyrene were applied 1 cm. apart. Three centimeters separated the sample from the standard.

The plate was then developed with cyclohexane as the solvent. The area with the same R_f value as the dibenzo(*a,e*)pyrene standard was collected as described previously (Bender, Sawicki, *et al.*, 1964) and extracted with hot methanol, which was then evaporated. This entire sample was then spotted onto another plate using pentane as the solvent and checking for completeness by examining the fluorescent color of a pentane solution. Standard dibenzo(*a,e*)pyrene was added in the manner described earlier. The second plate was developed with aqueous *N,N*-dimethylformamide saturated with ether. The blue fluorescent area with the same R_f value as the dibenzo(*a,e*)pyrene was collected and extracted with hot methanol, and the methanol was evaporated. Pentane was added, and the fluorescence spectra were obtained.

Aluminum Oxide-Cellulose Acetate (2 to 1). Twenty grams of aluminum oxide G (E. Merck A. A., Darmstadt, Germany, distributed by Brinkmann Instruments Inc., Westbury, L. I., N. Y., batch No. F 3477) and 10 grams of cellulose acetate (Schleicher and Schuell 21% acetylated pulp 124/21 AC) were added to 90 ml. of water in a blender (Cole-Palmer Instrument and Equipment Co., Chicago, Ill.) and stirred for approximately 1 minute. The slurry was then placed in a spreader (Desaga-Brinkmann) and 5 plates (20 \times 20 cm. and 0.25 cm. thick) were made. The plates were allowed to air dry overnight.

DMF-H₂O (3 to 1), Et₂O-Saturated Solvent System. *N,N*-Dimethylformamide (60 ml.) and water (20 ml.) were placed in a separatory funnel and allowed to cool to room temperature. Ether (50 ml.) was added. The separatory funnel was shaken a few seconds and the layers were allowed

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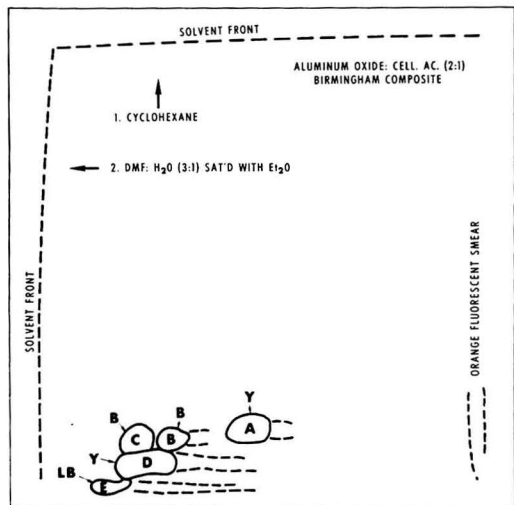


Figure 1. Two-dimensional, mixed-substrate, thin-layer chromatogram of urban airborne particulate

Y, yellow fluorescence. B, blue fluorescence. LB, light blue fluorescence. Fluorescence spectra of each lettered fluorescent area were run. B was identified as dibenzo(a,e)pyrene. See Figure 3 and discussion

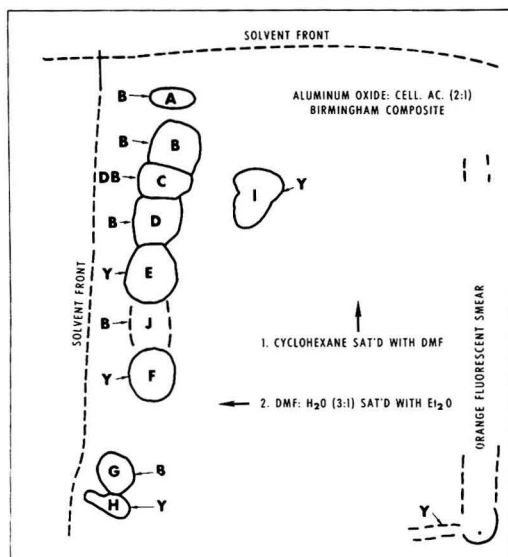


Figure 2. Two-dimensional, mixed-substrate, thin-layer chromatogram of urban airborne particulate

Y, yellow fluorescence. B, blue fluorescence. DB, dull blue fluorescence. Fluorescence spectra of each lettered area were run

to separate. The lower layer was drawn off and placed in the developing chamber to equilibrate for approximately 1 hour.

Cyclohexane, DMF-Saturated Solvent System. Cyclohexane (80 ml.) was placed in a separatory funnel, *N,N*-dimethylformamide (20 ml.) was added, and the mixture was shaken. The bottom layer was drawn off and discarded. Cyclohexane (30 ml.) was added to the top layer, and it was placed in the developing chamber to equilibrate for approximately 1 hour.

Samples. BIRMINGHAM COMPOSITE. A combination of particulate samples obtained on filter paper in Birmingham, Ala., was treated in the usual manner (Sawicki, Elbert, *et al.*, 1960a), and an aromatic fraction was obtained. It was then chromatographed on neutral alumina with various portions of various concentrations of ether in pentane (0, 3, 6, 9, 12, 15, 18, 25, and 100%) as the eluting solvent. Most of the 9% fraction and all of those above 9% (tubes 23 through 50) were combined to represent the hexacyclic fraction. This division was made spectrophotometrically by taking everything eluted after the benzo(a)pyrene fraction. The test tubes were washed into a beaker with dichloromethane as the solvent.

ALABAMA COMPOSITE. A number of urban samples from various cities in Alabama were combined, with dichloromethane as the solvent. A 0.6-gram portion of this composite was evaporated onto activated silica gel (Grace-Davison Chemical, Baltimore, Md.) and then placed on a 39-gram activated silica gel column. An aliphatic fraction was eluted with 120 ml. of pentane. An aromatic fraction was eluted with 3% ether in pentane and collected in four portions of 200 ml. and one of 100 ml. A higher-molecular weight aromatic fraction was eluted with 20% ether in pentane and collected in a 200-ml. portion and a 400-ml. portion; the latter portion probably contains the neutral oxy fraction.

The column was then washed with 300 ml. of chloroform-methanol (1 to 1). These portions were evaporated under vacuum. The first portion of the 20% ether portion was quantitatively transferred to a 10-ml. volumetric flask; this portion is referred to as the hexacyclic fraction of the Alabama composite.

Results and Discussion

Solvent Systems. The mixed solvent systems were saturated using the same relative amounts of the components each time because of the partitioning effects of the solvents involved. Extra cyclohexane was added to the cyclohexane-*N,N*-dimethylformamide system to prevent the *N,N*-dimethylformamide from producing a two-phase system as the plate development progressed. These systems were arrived at by running mixtures of a number of dibenzopyrenes.

Two-Dimensional Thin-Layer Chromatography. Two-dimensional thin-layer chromatography was used in exploratory research to find out whether any dibenzopyrenes could be found in the air. The general patterns (Figures 1 and 2) were not very reproducible. Dibenzo(a,e)pyrene, placed on the plate and developed one-dimensionally, gave a higher R_f value than was obtained with the same system in the two-dimensional procedure. Consequently, the two-dimensional method involved removing each of the fluorescent areas, extracting, and obtaining the fluorescence spectra.

The system shown in Figure 1 consists of a first development by cyclohexane followed by the aqueous *N,N*-dimethylformamide saturated with ether in the second dimension. The fluorescent areas are marked by letter. Fluorescent area B gave the fluorescence spectra shown in Figure 3. The emission and excitation spectra were compared with those of the available standards. These standards were dibenzo(a,e)pyrene,

dibenzo(*a,i*)pyrene, dibenzo(*a,l*)pyrene, 7-methyldibenzo(*a,h*)pyrene, naphtho(2,3-*a*)pyrene, dibenzo(*cd,jk*)pyrene (anthanthrene), and dibenzo(*cd,fg*)pyrene [benzo(*ghi*)perylene]. The general position and relative intensities of the absorption bands correspond only to dibenzo(*a,e*)pyrene. The exact positions of the wavelength maxima, as shown in Figure 3, correspond relatively close for fluorescence spectra in which the unknown is not pure. For this reason, this unknown has been identified as dibenzo(*a,e*)pyrene.

To achieve better separation, another two-dimensional system was developed using cyclohexane saturated with *N,N*-dimethylformamide then partially diluted with cyclohexane for the first development, and aqueous *N,N*-dimethylformamide saturated with ether for the second dimension. Although the fluorescent areas were better separated, dibenzo(*a,e*)pyrene could not be located. Fluorescent area *A* (Figure 2) possibly contains dibenzo(*a,i*)pyrene together with other components.

The identity of the components of each fluorescent area was investigated by collecting the fluorescent area and extracting. The fluorescence spectra were then obtained and compared with those of standards. All spectra were obtained in pentane to yield maximum fine structure for identification.

The fluorescence spectra obtained for the various fluorescent areas in the Birmingham composite sample (Figure 3) pro-

vide evidence for the presence of dibenzo(*a,e*)pyrene in urban airborne particulate matter.

Although this two-dimensional method provided faster thin-layer chromatographic separations than the one-dimensional methods, the need to obtain fluorescence spectra for each fluorescent area made it more time consuming; also one was less certain about where the desired compound should appear. For these reasons the two-dimensional method was used only for exploratory work, and the solvent systems that were developed were used as two one-dimensional systems to produce a more useful and more generally applicable method.

One-Dimensional Thin-Layer Chromatography. Since dibenzo(*a,e*)pyrene had been found in the Birmingham composite by use of the two-dimensional system, a method was developed to find it by using two one-dimensional separations and then obtaining the fluorescence spectra. The method, as described, was applied to the Alabama composite. The emission spectrum of dibenzo(*a,e*)pyrene was obtained along with some maxima at shorter wavelengths. The excitation spectrum was similar to that of dibenzo(*a,e*)pyrene, except that the 295- μ band was apparently mixed with a lower-wavelength band of an impurity to produce a maximum at 288 μ . The amount of dibenzo(*a,e*)pyrene was estimated by comparing the meter multiplier reading times the scale reading (as per cent transmission) of the unknown in pentane with that of a quantitatively prepared solution of dibenzo(*a,e*)pyrene in pentane containing 3% dichloromethane. The possible solvent effect was ignored. The amount of dibenzo(*a,e*)pyrene in the Alabama composite was approximately 100 μ g. per gram of benzene-soluble. This concentration was compared with those of other aromatic hydrocarbons reported during this same 3-month period in 1958-59. The concentration of benzo(*a*)pyrene in Birmingham was approximately 1900 μ g. per gram of benzene soluble and in Atlanta, approximately 730 μ g. per gram of benzene-soluble (Sawicki, Elbert, *et al.*, 1960b).

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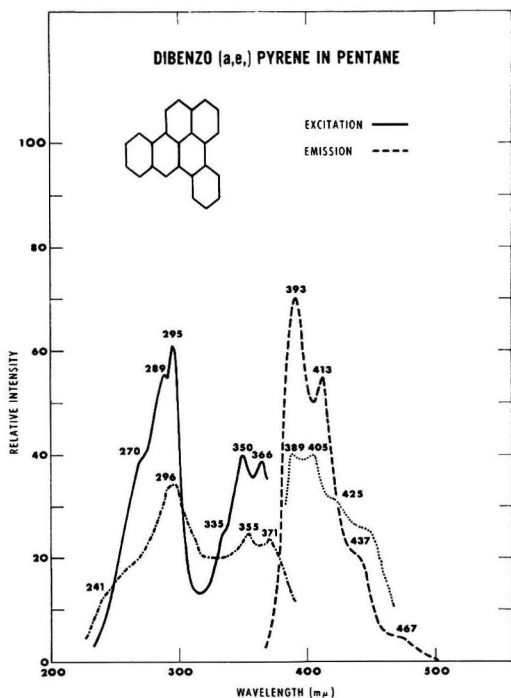


Figure 3. Fluorescence spectra of dibenzo(*a,e*)pyrene and extract of fluorescent area *B* (Figure 1) from thin-layer chromatographic separation of the Birmingham composite sample in pentane

- Excitation spectrum of dibenzo(*a,e*)pyrene
 - - - Emission spectrum of dibenzo(*a,e*)pyrene
 - · - · Excitation spectrum of unknown *B* in Figure 1
 · · · · Emission spectrum of unknown *B* in Figure 1

Kinetic Study of the Sorption of 2,4-D on Some Clays

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■ Relatively little is known regarding the kinetics of sorption of herbicides from solution on surfaces. For this reason, a detailed study of the kinetics of sorption of 2,4-D on three clay surfaces (illite, kaolinite, and montmorillonite) has been made. Rate constants, activation energies, free energies of activation, heats of activation, and entropies of activation have been calculated for the sorption process. The rate constants depended on the nature of the clay and fell between 2 to 22×10^{-7} second⁻¹. The rate constant decreased with an increase in the surface area. The amount of 2,4-D sorbed was minimum for kaolinite, whose surface area was also small. Temperature had little effect on the amount sorbed. Activation energies for the sorption process laid between 3 to 5 kcal. mole⁻¹, with clays of larger surface area giving higher activation energies. The over-all sorption process has been explained in the light of the structure of 2,4-D and the clay flocculates.

Relatively little is known regarding the kinetics of sorption of herbicides on clay. Owing to difficulties in experimentation and also in interpretation of data, very little information has been forthcoming. General considerations on the kinetics and thermodynamics of adsorption from solution have been given by Kipling (1965). Some interesting quantitative studies on the sorption process in solution on carbon have also been reported recently. This includes the work of Weber and Gould (1966) on the kinetics and thermodynamics of sorption of several pesticides on carbon and a similar study by Cookson and North (1967) on the adsorption of viruses on activated carbon.

In the use of chemicals as herbicides, much of the material

ultimately finds its way to the soil and is sorbed. Therefore, more should be known about this process. Owing to the biological activity of 2,4-dichlorophenoxyacetic acid (2,4-D) toward plants, the kinetics of its sorption on some water saturated clays was studied to aid the understanding of the herbicidal action of such chemicals.

Experimental

Materials. The clays used were the purest quality available of illite-35 (Ill.), montmorillonite-No. 26 (Upton, Wyo.), and kaolinite (Merck) (Table I). Solutions of C¹⁴ labelled 2,4-D were prepared by dissolving the crystalline material in distilled water.

To ensure that the clay was saturated with water, known weights were shaken with an excess of water at room temperature for 24 hours. After centrifugation of the suspension, the wet clay residue was again weighed. The amount of sorbed water was thus determined by difference.

Procedure. Weighed amounts of clay (5 grams of montmorillonite, 10 grams of kaoline, and 15 grams of illite) were saturated with water. A known quantity of radioactive 2,4-D solution (40 ml. of 1.266 p.p.m.) was added, and the mixture was shaken at constant temperature. The change in the concentration of 2,4-D in the bulk solution was determined by removing 0.1-ml. samples at appropriate time intervals, centrifuging, and determining the radioactivity in the supernatant by liquid scintillation counting.

A 0.1-ml. aliquot of the supernatant was mixed with 10 ml. of scintillation media (2 to 1, toluene and methyl cellulose mixture) in a scintillation vial, the radioactivity measured in a Packard Tri-Carb Liquid Scintillation Spectrometer. From a knowledge of the specific activity of the starting material, the concentration could be determined. Count data were measured under conditions to give an accuracy of $\pm 1\%$.

Table I. Properties of Clays

Clay	Source	Surface Area, Sq. Cm./Gram	Net Charge, Meq./Sq. Cm.	Particle Size, Mm.	Amount of Water Sorbed by Clay, Gram of Water/Gram of Clay
Illite	No. 35 Fithian, Ill.	0.5 to 3×10^6	-3×10^{-7}	~ 0.83	0.5
Kaolinite	Merck, NFV	0.04 to 0.8×10^6	-2×10^{-7}	0.24 to 1.68	0.75
Montmorillonite	No. 25 John C. Lane Tract Upton, Wyo.	4 to 9×10^6	-1×10^{-7}	~ 0.83	8.0

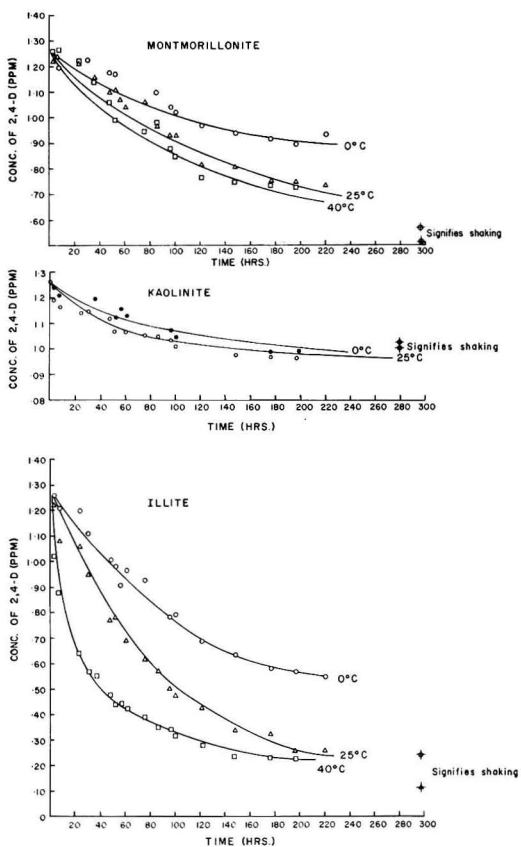


Figure 1. Rate of sorption of 2,4-D on illite, montmorillonite, and kaolinite, as shown by the decrease in the concentration of 2,4-D in the bulk solution with time

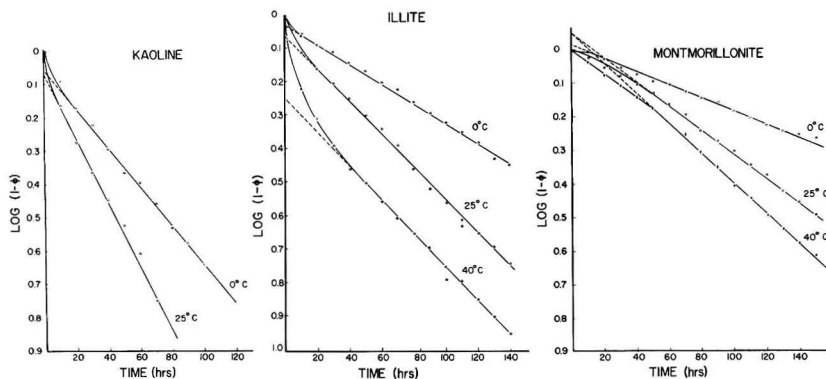


Figure 2. Plot of $\log(1 - \phi)$ vs. time for the sorption of 2,4-D on clays

Results

Typical data for the sorption of 2,4-D on these clays are shown in Figure 1, by plotting the change in the concentration of 2,4-D in the bulk solution as a function of time. Evidently, (Figure 1) the sorption is quite slow. The change in the concentration of 2,4-D with time is due to the combined effect of adsorption on the clay surface and diffusion inside the clay flocculates.

If q_t and q_∞ , respectively, are the amounts sorbed at time t and infinity—i.e., equilibrium—then ϕ can be defined as the fraction sorbed at a certain time. Thus

$$\phi = q_t/q_\infty \quad (1)$$

The quantity ϕ can also be represented in terms of the concentration of 2,4-D in solution. If C_0 , C_∞ , and C_t , respectively, are the concentrations of 2,4-D at the beginning, at equilibrium, and at an arbitrary time t , then

$$\phi = (C_0 - C_t)/(C_0 - C_\infty) \quad (2)$$

Evidently, when there is no sorption at $\phi = 0$ the whole surface is available for sorption, and when $\phi = 1$ the sorption is complete. The quantity $(1 - \phi)$, which denotes the approach fraction of unsorbed surface analogous to the concentration of a reactant in solution, can be defined as

$$\frac{-d(1 - \phi)}{dt} = k'(1 - \phi) \quad (3)$$

where k' denotes the rate constant for sorption.

If a large enough surface is used and the concentration of 2,4-D is relatively small, then it can be assumed that the reverse reaction, the rate of desorption, is small enough to be neglected. If ΔG^\ddagger is the free energy of activation required, then k' can be written in terms of absolute rate theory as:

$$k' = \frac{kT}{h} \exp \frac{-\Delta G^\ddagger}{RT} \quad (4)$$

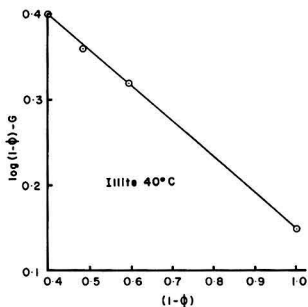


Figure 3. $\log(1-\phi)-G$ vs. $(1-\phi)$ to estimate γ

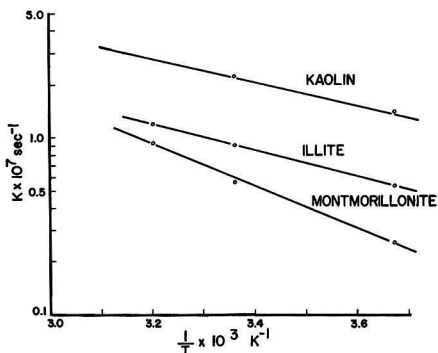


Figure 5. Arrhenius plot of rate constant vs. temperature

where k is the Boltzmann constant, h is Planck's constant, T is the absolute temperature, and R is the gas constant.

According to Equation 3, a plot of $\log(1-\phi)$ as a function of time t should be a straight line, but Figure 2 shows it as nonlinear, at least at the initial time values. This kind of behavior for a unimolecular process in the condensed phase has been explained by Eley (1953) on the assumption that the free energy of activation ΔG^\ddagger changes with ϕ

$$\Delta G^\ddagger = \Delta G_{\alpha}^\ddagger - \gamma(1-\phi) \quad (5)$$

where $\Delta G_{\alpha}^\ddagger$ is the free energy of activation at equilibrium and γ is a constant. Substituting ΔG^\ddagger in Equation 4 gives the results

$$\frac{-d(1-\phi)}{dt} = (1-\phi)A \exp\left[\frac{\gamma(1-\phi)}{RT}\right] \quad (6)$$

$$A = \frac{(kT)}{h} \exp\left[\frac{-\Delta G_{\alpha}^\ddagger}{RT}\right]$$

Integrating Equation 6 and assuming that $\gamma(1-\phi) < RT$:

$$\ln(1-\phi) - \frac{\gamma(1-\phi)}{RT} = A't + \text{constant} \quad (7)$$

According to Eley, the straight line at longer times corresponds to $A't + \text{constant}$ (Figure 2). To obtain γ , $\ln(1-\phi) - G$ is plotted as a function of $\ln(1-\phi)$, where G is the

extrapolated value of the straight line obtained by drawing a tangent to the curve in Figure 2 at different times. In every case, this plot gave a reasonable straight line whose slope

corresponds to $\frac{\gamma}{RT}$ (Figure 3). The value of γ was substituted in Equation 7 and another graph was plotted, which also gave a reasonable straight line (Figure 4). From the slope of this straight line, the rate constant was calculated. The activation energy was calculated from the Arrhenius plot of the rate constant vs. the reciprocal temperature (Figure 5).

The heat of activation ΔH^\ddagger is related to the activation energy ΔE as

$$\Delta E = \Delta H^\ddagger + RT \quad (8)$$

The entropy of activation ΔS^\ddagger and the free energy of activation ΔG^\ddagger can be calculated from the following:

$$k' = \frac{(kT)}{h} \exp\left[\frac{-\Delta H^\ddagger}{RT}\right] \exp\left[\frac{\Delta S^\ddagger}{R}\right] \quad (9)$$

and

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (10)$$

A summary of the rate parameters calculated for the sorption of 2,4-D on these clays is given in Table II.

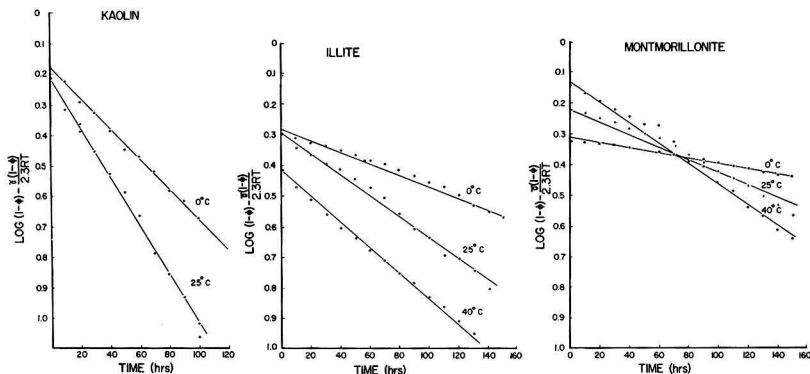


Figure 4. Eley's plot of $\log(1-\phi) - \frac{\gamma(1-\phi)}{2.3RT}$ vs. time

Table II. Rate Parameters for the Sorption of 2,4-D on Clays

Clay	Temperature, ° C.	Rate Constant, k' Second ⁻¹	Energy of Activation, ΔE Kcal. Mole ⁻¹	Heat of Activation, ΔH^\ddagger Kcal. Mole ⁻¹	Entropy of Activation, ΔS^\ddagger , E.S.U.	Free Energy of Activation, ΔG^\ddagger Kcal. Mole ⁻¹	γ Cal.
Illite	0	5.0×10^{-7}					358
	25	8.8	3.5	4.1	-76.2	1.9	398
	40	11.8					595
Kaolinite	0	13.6×10^{-7}					220
	25	21.9	3.2	3.8	-75.5	1.5	296
Montmorillonite	0	2.5×10^{-7}					400
	25	5.5	5.5	6.1	-70.5	4.0	310
	40	9.2					209

Discussion

The rate constant for the sorption of 2,4-D on these clays can be interpreted from the structure of the clay and the chemical. The adsorbate 2,4-D is a weak acid with the dissociation constant value of $K_D \sim 10^{-4}$ in aqueous solution where it exists in the molecular form as well as in the ionic species. In the present study, the pH of the solution is nearly neutral, and hence, the amount of 2,4-D in the molecular form will be very little. Therefore, the bulky anion takes part in the sorption process. The clay surface consists of a two-dimensional silica-alumina matrix (van Olphen, 1963). The structure of kaolinite, montmorillonite, and illite are different. Kaolinite consists of one silica layer (silicon tetrahedrally coordinated with four oxygen atoms) and an adjacent alumina octahedron (aluminum octahedrally coordinated with two oxygen atoms and four hydroxyl groups). The exposed planar clay surface of kaolinite consists of a layer of oxygen and a layer of the hydroxyl groups. In contrast, a 2 to 1 clay mineral, montmorillonite, contains a layer of silica tetrahedrons (silicon coordinated with four oxygen atoms) on each side of an alumina octahedron. In this structure, each exposed planar surface consists of an oxygen atom. Illite contains two different minerals, mica cores and vermiculite. Both the mica and vermiculite are silica-alumina type minerals in a ratio of 2 to 1. The mica contains potassium, which exists in a chemical bond between the two adjacent silica tetrahedra, while vermiculite contains no potassium in the inner layer position.

Kaolinite, montmorillonite, and illite have markedly different cation exchange capacities and water expansion characteristics, and isomorphous substitution occurs in both the tetrahedral layer and octahedral layers of montmorillonite, vermiculite, and mica. The net negative charge develops primarily in the tetrahedral layer in the mica and vermiculite and in the octahedral layer for montmorillonite. Because of the difference in charge density and the difference in charge source, mica binds potassium sufficiently to eliminate both an effective cation exchange capacity and water expansion

characteristic. Vermiculite will expand slightly with the absorption of water and has sufficient charge to collapse on addition of potassium ions. However, montmorillonite, with a lower charge density will absorb water and expand readily but will not completely collapse with potassium saturation. Since kaolinite has essentially no isomorphous substitution and a low charge density, it will exhibit a very small water expansion characteristic and a very low exchange capacity.

In the presence of water, the clay particles associate in different ways, depending on the spatial charge distribution, and form flocculates. The flocculation can be of either the face-face, face-edge, or edge-edge type. The electrical interaction energy involved in the formation of these flocculates and the rate of sorption and diffusion through different types of flocculates will also be different (Vold, 1958). Kaolinite usually forms edge-face type flocculation (Schofield and Samson, 1954), while in montmorillonite two different types of swelling takes place depending upon the amount of water present (Norrish, 1954). When the amount of water is of the range of 0.5 gram of H₂O per gram of clay, a crystalline type swelling occurs. With the further increase in water concentration, the clay swells with a several-fold increase in its volume.

When 2,4-D comes in contact with the clay, it can adsorb on the surface and also diffuse in the flocculates. The rate of adsorption will be faster than the rate of diffusion, and this rate will be influenced by the amount of 2,4-D adsorbed. In the present study, the rate is represented as the rate of sorption, which includes adsorption as well as diffusion. The value of the rate constant reported here is of the order of that of diffusion. Because of a certain isomorphous substitution, the clay has a net negative charge; consequently, the adsorption of the 2,4-D anion, which usually takes place at the edges of the clay particle, is small (Table III). The amount adsorbed can be expressed by the Freundlich isotherm:

$$X = KC^n \tag{11}$$

where X is the amount sorbed, C is the equilibrium concentration, and K and n are constants. For pesticide interaction,

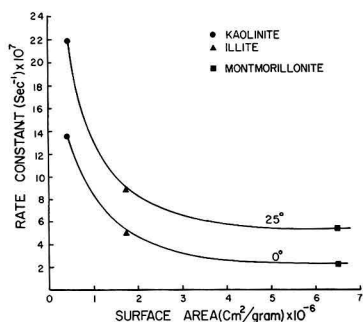


Figure 6. Relation of surface area vs. the rate constant

Value of the surface area (average of upper and lower limits) taken from Tab. e I

at the low concentration of pesticide, n is very close to unity (Lambert, 1967). K is an estimate of the tendency of sorption analogous to the equilibrium constant:

$$K = X/C \quad (12)$$

The value of K obtained from Equation 12 is also included in Table III. There is no direct correlation between the amount sorbed and the surface area. The surface area in these clays varies as montmorillonite > illite > kaolinite. However, the K values roughly vary as illite > montmorillonite > kaolinite. The relatively high value of K for sorption of illite may be due to the effect of K^+ ions. The tendency of illite to sorb more 2,4-D has also been reported by Frissel (1961). However, kaolinite, having a smaller surface area than the other two, sorbs a considerably less amount of 2,4-D. There are few temperature effects on the K values except for illite, indicating thereby negligible enthalpy change. The two processes involved in the sorption—namely, adsorption and diffusion—usually have an opposite sign in the temperature coefficient. With an increase in temperature, the amount of adsorption usually decreases, while the diffusion increases. Hence, the effects of temperature are balanced in these two processes and give little change in K . There are also very few correlations between K and k' . However, kaolinite, whose K value and surface area are small, has a higher rate constant. The specific rate constant decreases nonlinearly with an increase in the surface area (Figure 6). The rate constant for montmorillonite is considerably smaller than the other two clays. This is reasonable because montmorillonite has a large surface area, and absorbs a large amount of water, resulting in more diffusion, and hence a slower rate.

The activation energy for these rate processes has been obtained from the Arrhenius plot between k' and temperature, and in most cases the value of the rate constant has been determined for three temperatures. The value of the activation energy is small, and ranges from 3 to 5 kcal. mole⁻¹, which is a characteristic of diffusion controlled processes. Here, the value of the activation energy decreases with de-

Table III. Equilibrium Data for the Sorption of 2,4-D on Clays

Clay	Temperature, °C.	Equilibrium Concentration of 2,4-D, P.P.M.	Amount Sorbed, μgram/Gram of Clay	K
Illite	40	0.11	1.52	13.8
	25	0.11	1.52	13.8
	0	0.24	1.40	5.8
Kaolinite	40	1.02	0.41	0.4
	25	1.01	0.43	0.43
	0	1.03	0.40	0.39
Montmorillonite	40	0.57	0.43	7.6
	25	0.52	0.47	9.0
	0	0.51	0.47	9.2

crease in the surface area. The entropy of activation is negative, indicating thereby a lesser degree of freedom for 2,4-D in the transition state.

Table II shows that the value of the constant γ depends on temperature as well as the nature of the clay. The value itself ranges from 200 to 600 cal. and can be compared with the values reported (Eley, 1953) for the extension elasticity of silk fibre ($\gamma = 580$ cal.) and for potash silica glass (480 cal.).

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On the Mechanism of Activated Silica Sol Formation

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■ Activated silica sols have had a long history as coagulant aids. These activated sols differ from stabilized sols primarily in that the polymerization of the silicate is not halted to give a stable particle. The rate of polymerization is changed by dilution before gel formation takes place. By following pH and light scattering changes within the sol systems, conclusions have been drawn as to the mechanism of polymerization and the effect of dilution upon polymerization. In forming the activated sols, sulfuric acid and ammonium sulfate were used. These two reagents give significantly different polymerization behavior to warrant modification of the polymerization mechanism in the presence of ammonium ion. Flocculation tests conducted with kaolin clay, using the activated sols as coagulant aids, mirror the fundamental behavior measured by pH and light scattering. Thus the fundamental data obtained on the sols themselves can be applied to practical jar test procedures in a meaningful way.

The effectiveness of activated silica sols in the coagulation of suspended matter in aqueous systems has been known for three decades. Pioneering work was done by Baylis, who used sulfuric acid to prepare the silica sols (Baylis, 1936, 1937, a,b, 1938). Hay found that a variety of reactants could be used to obtain active sols, including acid gases, ammonium salts, and acid salts such as sodium bicarbonate and sodium bisulfate (Hay, 1944a,b, 1948).

The silica sols have usually been used in conjunction with primary coagulants, such as alum, lime, or ferric salts, and are considered coagulant aids. In some unusual cases, they have brought about flocculation without the help of the primary coagulants. The clarification of a wide variety of natural waters and waste streams has been made easier by their use.

Gel time studies have been made, in which the effect of variables such as pH, type of reactant, mole ratio of reactant to silicate, etc. on the gel times of the silica sols have been outlined (Hurd, 1938; Merrill and Spencer, 1950; Spencer, Middleton, *et al.*, 1951; Baxter and Bryant, 1952; Bergman and Nelson, 1962). Basic studies of the polymerizing silicic acid system have been done by Audsley and Aveston (1962), and by Greenberg and Sinclair (1955), using light scattering, conductivity, and centrifugation methods.

In a recent paper, Stumm and co-workers have outlined the pH-concentration domains in which the various species of silica are found (Stumm, Hüper, *et al.*, 1967). They have also evaluated parameters that influence the activity of the poly-

silicates and have compared the coagulating properties of the polysilicates with those of silicic acid. Stumm *et al.* paid particular attention to the effect of pH and dilution upon the polymerization of silicic acid and the manner in which the degree of polymerization affects the coagulation behavior relative to aluminum oxide and the silver bromide sols. In interpreting the results, these authors pointed out correctly that the electrostatic effects may be outweighed by sorption of the negatively charged polysilicate sol on the surface of a similarly negatively charged sol particle, resulting in flocculation. That study did not consider in detail the role of neutral electrolyte, except to show that sodium sulfate results in much greater scattering intensity as compared with sodium nitrate, so far as the silver bromide sols themselves are concerned in the presence of polysilicate.

The present study differs from that of Stumm *et al.* in that the growth of the sol particles has been observed in the presence of two electrolytes, the one being generated by the neutralization of silicate solution using sulfuric acid and the other being added, this rate of polymerization having been observed at several pH levels, the system pH being a contributing factor in the polymerization. In addition, the silicate used was already in the multimeric domain, having an average molecular weight of 325 (by light scattering) as supplied. Before consideration can be given to the detailed results on sol particle formation and the consequent behavior of these sols relative to coagulation, the terms and concepts used in discussing the general subject must be made clear.

Mechanism of Gelation of Silicates

The gelling of silicates is normally conducted by the addition of a mineral acid to the silicate solution. When this is done, one has a system which contains the acid added, the silicate anion at some stage in the polymerization process, water and neutral salt derived from the neutralization of the alkali metal silicate by the acid. That the nature of the gelation process is strongly dependent upon the neutral salt has been long recognized. As an extreme example, one can form a Graham sol by means of dialysis or ion exchange which consists of discrete, low molecular weight particles, comprising a system which is stable for long periods of time without forming a gel structure. At the other extreme, the addition of a strong mineral acid such as hydrochloric will result in gel structure within a short time, that time depending upon pH, concentration, and the type of acid used. The authors find, for example, that the gel time is lengthened as one goes from hydrochloric to sulfuric and then to phosphoric acid even when conditions of pH and silicate concentration are kept constant. The primary difference between these systems is the neutral

salt that is produced, sodium chloride being much more effective than sodium sulfate or sodium phosphate (Figure 1).

A gel consists, in this context, of a three dimensional structure that develops between sol particles as a result of hydrogen bonding within the system. That the extent of the hydrogen bonding and the strength of these bonds depends upon the anion present is not surprising. The judging of the gel time is, however, usually subjective, dependent upon the existence of thixotropy within the system. Before the gel structure is observed, the system is said to consist of an activated sol. An activated sol is differentiated from a stabilized sol in the sense that the polymerization process in the latter has been brought to a halt. Furthermore, the stabilized sol particles have about them a layer of ions that prevent interparticle hydrogen bonding and, therefore, prevent gelation.

Polymerization of Silicates

The neutralization to silicic acid must be considered in the context of the polymeric or monomeric condition of the starting silicate. The neutralization of sodium metasilicate may naively be written as:



yielding a monomeric species with the empirical formula H_2SiO_3 . The degree to which monomer exists in solution is a function of pH and dilution, but the polymerization process does advance at a significant rate and polymers of undetermined molecular weight are largely present.

The polymerization process is described in terms of the functional groups that may be present and their reactions. The polymerization reactions that may occur are:



Reaction 2 is well recognized, involving only the condensation of silanol groups to siloxanes with the production of water molecules. Reaction 3 is offered without direct proof but with the evidence shown in Figure 2. The pH at zero time is considerably lower than that after the polymerization has progressed indicating that a stronger base has been generated than was originally present in the solution. The production of hydroxyl ions according to Reaction 3 probably gives rise to the pH increase that is noted. At low initial pH's, no such increase is observed (Figure 2) suggesting that Reaction 2 is the predominant reaction under those conditions.

Activated silica sols are usually prepared under alkaline conditions in pH ranges where the pH does increase with time and where it is, therefore, likely that Reaction 3 contributes to the polymerization process as well as Reaction 2.

Ammonium salts have a specifically high polymerization or sol formation effect on sodium silicates. Ammonium silicates are not known although it has proved possible to partially stabilize silica sols with ammonium ion or with amines (Neundlinger, 1931; Balthis, 1952). The addition of ammonium salts to sodium silicate solutions does not follow a disproportionation reaction such that ammonium silicates are produced, but rather the silicate is polymerized and eventually gels (Vail and Wills, 1952). This is particularly observable at high pH values, and a reaction probably takes place according to:

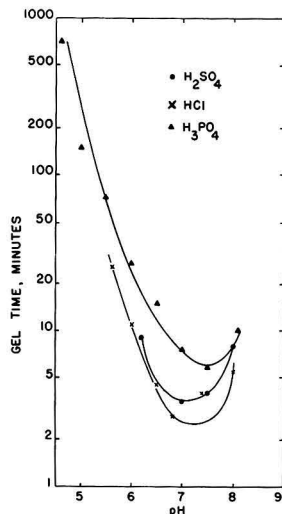


Figure 1. Gel times of sodium silicate (3.2 SiO_2 - Na_2O , 2.0 grams of $\text{SiO}_2/100$ ml.) neutralized with HCl, H_2SO_4 , and H_3PO_4 .

which is analogous to the evolution of ammonia by the addition of strong base. If this reaction does indeed take place, a source of silanol groups is found that can then take part in either Reactions 2 or 3, thus promoting polymerization of the silicate.

By delineating the difference between the reactions to be expected from ammonium salts and those to be expected by the addition of acid, with the consequent production of neutral salts of alkali metals, a qualitative difference is expected to exist within the two systems so far as the rate of sol formation and the rate of gelation are concerned. This paper shows these differences and gives some indication of how the flocculation of a clay soil is affected by silica sol formed in these two manners.

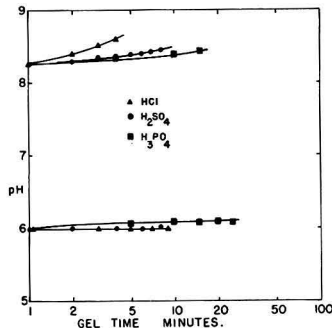


Figure 2. Change in pH with time after addition of mineral acids to Na silicate (3.22 SiO_2 - Na_2O by wt.; concentration, 2.0 grams of $\text{SiO}_2/100$ ml.)

Experimental Procedure

Sols were made by reacting either ammonium sulfate or sulfuric acid with E sodium silicate (Philadelphia Quartz Co., Philadelphia, Pa.). The silicate (8.69% Na₂O, 27.92% SiO₂; SiO₂-Na₂O weight ratio of 3.22) was a clarified commercial solution. The reactants were reagent grade chemicals. The alum was also a reagent grade Al₂(SO₄)₃ · 18 H₂O.

Stock solutions of the silicate and reactants were combined to obtain sols having the compositions shown in Table I. Turbidities, dissymmetry, and depolarization data on the sols were obtained using a Brice-Phoenix Light Scattering Photometer, Model 2000, as were turbidities of the supernatant suspensions from the jar tests. A 30-mm. square cell was used for the latter readings, and a 40-mm. semi-octagonal cell for the former. The pH changes were followed with a Beckman Model 76 Expanded Scale pH Meter, using a standard 0 to 14 pH glass electrode and a sleeve-type calomel reference electrode.

Sol activities were judged by a semiquantitative jar test based on a method described by Henry (1952). One-liter portions of a suspension of fine kaolin clay were flocculated, using silica and alum dosages of 10 and 25 p.p.m., respectively. Agitation was provided by a Phipps and Bird multiple stirrer. The silica sol was added to the suspension and stirred at about 100 r.p.m. for 30 seconds. The alum was added, and rapid stirring was continued for an additional 2.5 minutes, followed by 10 minutes' stirring at about 15 r.p.m. At this point the suspensions were allowed to settle for exactly 1 minute, and were then sampled about 1.75 inches below the surface of the water. This sample was stirred with a high speed blender, to redisperse any floc particles in it, after which the turbidity ratio was measured using the Brice-Phoenix instrument.

Barden clay (J. M. Huber Corp.), a hard, air-floated kaolinite, was used in the flocculation tests. Although very fine, it was further treated to obtain a stock suspension of the finer particles. About 0.1 ml. of sodium silicate solution (3.22 SiO₂-Na₂O ratio) was added to a 1% suspension of the clay in distilled water, which was transferred to a 250-ml. graduated cylinder. The coarse particles settled out, but the silicate kept the finest material in suspension, and, after a 1 hour settling period, the upper half of the system was decanted. This portion formed a stock clay suspension, which was added to cold tap water to give test suspensions containing 18 p.p.m. clay by weight.

The general plan of the work was to prepare the sols (Table I), and to measure the changes taking place as they aged by the light scattering, pH, and sol activity (flocculation test)

methods. Tests were continued for some time after gelation. At approximately half the gel time, portions of the full strength sol were diluted to lower silica levels; the changes in these dilutions were followed in the same way. The full strength sols were filtered through Millipore Corp. HA membranes (0.45-micron average pore diameter) immediately after preparation, and dilutions were made with filtered distilled water.

Sol activity was determined after various periods of aging, either at full strength or at diluted strength. Appropriate volumes of the various sols were taken, to give the desired 10-p.p.m. SiO₂ dosage—i.e., 0.5 ml. of the full strength sols, 1.0 ml. of the 1.0-gram SiO₂ per 100-ml. dilutions, 10 ml. of the 0.1-gram SiO₂ per 100-ml. dilutions, etc. were added to 1-liter portions of the turbid water immediately before the start of the flocculation tests.

Activated Silica Sol Formation

The starting silicate at a weight ratio of 3.22 SiO₂-Na₂O was initially diluted to contain 8 grams of SiO₂ per 100 ml. Either sulfuric acid or ammonium sulfate was then used to reduce the pH and cause gelation using proportions such that the gel time would lie between 100 and 200 minutes. The actual concentrations used and the actual gel times of the mixtures are shown in Table I. The normal practice in conducting this process when using activated silica sol as a coagulant aid is to interrupt the gelation procedure some time before the actual gel time by dilution. Both the parent solution and the diluted portions were studied by means of light scattering and pH as a function of time as shown in Figures 3 and 4 for the sulfuric acid system and Figures 5 and 6 for the ammonium sulfate.

As might be expected, the turbidity of the parent solution increases with time as the system proceeds toward gelation both for the sulfuric acid and the ammonium sulfate derived sols, but the sulfuric acid system results in higher turbidities. The pH behavior in both cases shows the expected increase in pH with time as the system proceeds toward gelation, this increase in pH being expected on the basis of Reaction 3 playing an important part in the polymerization process. The increase in pH when using sulfuric acid is a very marked one, and this increase is by no means duplicated when using ammonium sulfate. This lends support to the mechanism proposed above according to Reaction 4 which would lead to the production of silanol groups and dissolved ammonium hydroxide with a lower base strength than the sodium hydroxide postulated according to Reaction 3. For this reason, ammonium sulfate probably promotes polymerization by means of Reaction 2 to a greater extent than by means of Reaction 3, while sulfuric acid favors Reaction 3.

Dilution is often practiced at about one half the gel life, since this is the time interval during which an activated silica sol is effective for flocculation purposes. Consequently, portions of the starting solution were diluted to various levels of SiO₂ concentration as indicated in Figures 3 through 6 with both light scattering and pH measurements being made. Again the ammonium sulfate sols showed generally lower levels of light scattering than do the sulfuric acid sols, implying a lower degree of polymerization. The turbidity was expected to drop initially simply because of dilution, however, the subsequent decrease in turbidity with time over long time spans is strongly indicative of depolymerization of the particles. This occurs far more rapidly with the ammonium sul-

Table I. Activated Silica Sols

Reactant	Reactant Added		Gel Time, Min.
	Wt. g./100 ml.	Moles/mole Na ₂ O	
H ₂ SO ₄	0.83	0.85	120
(NH ₄) ₂ SO ₄	1.32	1.00	200

Temp. = 25° C.
 Silicate composition:
 3.22 SiO₂-Na₂O by wt.
 Concentration used: 2.0 g. SiO₂/100 ml.
 0.62 g. Na₂O/100 ml.

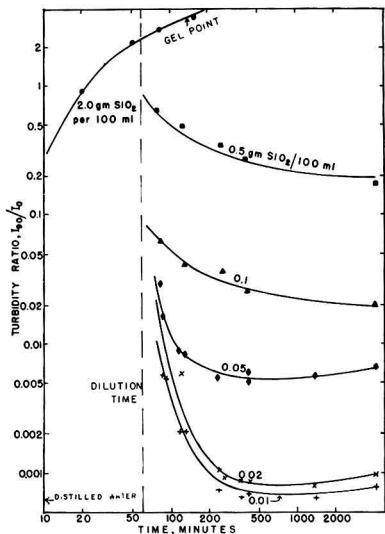


Figure 3. Changes of 90° light scattering with time

Silicate (3.22 SiO₂-Na₂O wt. ratio) treated with H₂SO₄, diluted at 60 minutes to concentrations shown, 2.0 grams of SiO₂/100 ml., sample undiluted

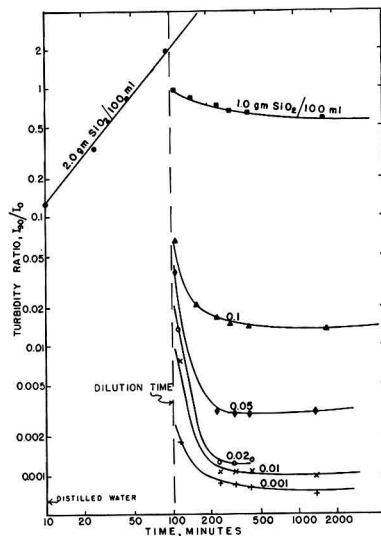


Figure 5. Changes of 90° light scattering with time

Silicate (3.22 SiO₂-Na₂O wt. ratio) treated with (NH₄)₂SO₄, diluted at 100 min. to concentrations shown, 2 grams SiO₂/100 ml., sample undiluted

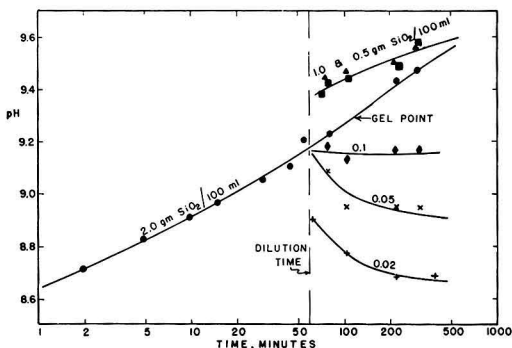


Figure 4. Changes in pH with time

Silicate treated with H₂SO₄, diluted at 60 minutes to concentrations shown, 2 grams of SiO₂/100 ml., sample undiluted

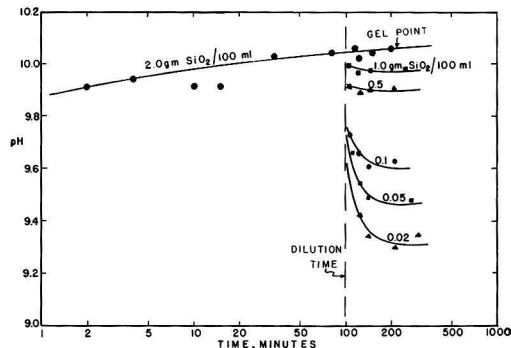


Figure 6. Changes in pH with time

Silicate treated with (NH₄)₂SO₄, diluted at 100 minutes to concentrations shown, 2.0 grams/100 ml., sample undiluted

fate sols, but the extent for the two systems is about the same after 500 minutes or so. The more rapid rate of depolymerization on the part of the ammonium sulfate sols is expected, based upon the generally higher pH of this system.

The pH changes observed in Figures 4 and 6 reflect the light scattering behavior, except for the sulfuric acid sols at 1 and 0.5 gram of SiO₂ per 100 ml. concentrations. Here the pH actually increases upon dilution indicating that the polymerization-depolymerization process occurring results, at this concentration, in the release of hydroxide ions or of silicate ions. This observation is not easy to reconcile with any known mechanism and is thought to be due to the absorption of hydroxyl ions on or within the structure of the sol particles,

with the release of these ions upon depolymerization of the particles.

Flocculation of Clay

The clay suspensions that have been described in Experimental Procedure were flocculated using a system involving alum as the primary coagulant and activated silica sol as coagulant aid. Alum dosage was kept constant throughout to obtain results meaningful in terms of the activated silica sol alone. The results for the two systems that were studied are shown in Figures 7 and 8. The parent sol at 2 grams of SiO₂ per 100 ml. concentration reached its optimum flocculation ability at about one-half the gel life as expected. Shortly before gelation the activity dropped severely as shown by the

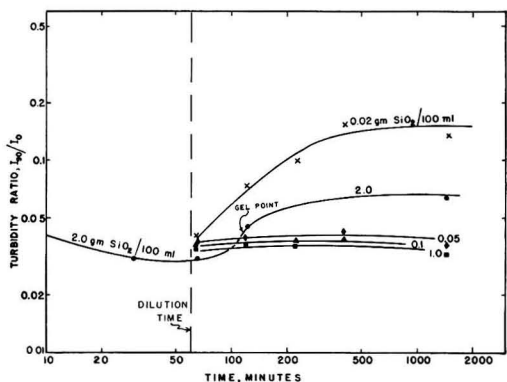


Figure 7. Jar test results, clay suspension, 25 p.p.m. of alum, 10 p.p.m. of SiO_2 using H_2SO_4 treated silicate

Silicate diluted at 60 minutes to concentrations shown, 2.0 grams of $\text{SiO}_2/100$ ml., sample undiluted

increase in turbidity ratio on the part of suspension. This is as expected in view of the fact that interparticle bonding to form the gel structure begins well before the subjective recognition of the gel point based upon thixotropy. The difference between the sulfuric acid and ammonium sulfate derived sols is not great at this concentration so far as total effectiveness is concerned.

After dilution, the difference between the two systems is very marked at intermediate concentrations of 0.1 and 0.05 gram of SiO_2 per 100 ml. Here the ammonium sulfate derived sol is very much less active, showing a fairly sharp loss of activity with time as the particles depolymerize. This mirrors the behavior shown in Figures 3 and 5, where the rate of change of the ammonium sulfate sol is much greater than for the sulfuric acid sol, using light scattering as the measurement. Similarly, it mirrors the behavior in Figures 4 and 6 regarding the rate of change of pH with time after dilution. At extreme dilution of 0.02 gram of SiO_2 per 100 ml., the differences between the two systems are not as sharp although the rate of change of the ammonium sulfate system is still the greater.

In practice, as various acidification techniques may be considered for water clarification needs, based upon the present data, a study over a fairly wide concentration range is needed to ensure that one system is really better than another, since dosages will vary with the seasons and the quality of the raw water being treated. On the basis of the above results, the sulfuric acid derived activated sol would seem to be superior since the total activity is not as dependent upon concentration changes at levels which are reasonable for practical flocculation. Clearly, this study did not concern itself with other variations that are possible, such as changes in alum concentration, temperature, etc.

Discussion

Comparison of the two widely different methods of preparing silica sols of the activated type, by the addition of sulfuric acid on the one hand and of ammonium sulfate on the other, shows that qualitative and quantitative differences exist in the behavior of these activated sols. These differences, based upon the sol structure itself as measured by light scattering and pH techniques, can be carried over into actual flocculation tests with meaningful results.

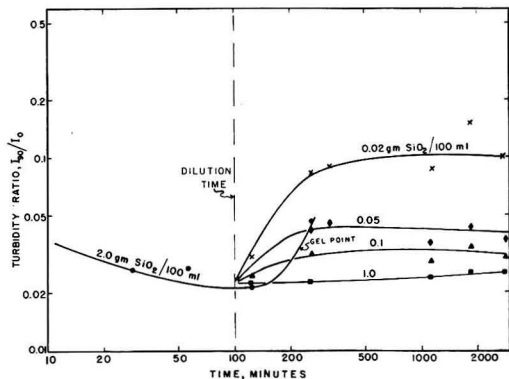


Figure 8. Jar test results, clay suspension, 25 p.p.m. of alum, 10 p.p.m. of SiO_2 using $(\text{NH}_4)_2\text{SO}_4$ treated silicate

Silicate diluted at 100 minutes to concentrations shown, 2.0 grams of $\text{SiO}_2/100$ ml., sample undiluted

While this study does not go into the delineation of a lyotropic series for silica sol formation, the nature of the salt present in the system has a profound effect on the rate of polymerization of silicate to form sol particles. Ammonium ion acts sufficiently differently from sodium ion so that a reaction is postulated such that silanol groups are formed by the association of the ammonium ion into ammonia with the transfer of a proton to the silanolate anion.

The polymerization of silicate is thought to be the result of two reactions that occur concurrently, but one reaction may be favored over the other depending upon the salt present and the pH range in which the reaction is conducted. One of these reactions concerns the condensation of silanol groups with the production of siloxane and water; the second reaction involves a silanol group and a silanolate anion condensing to siloxane with the production of a hydroxyl ion. These postulated reactions are supported by the data presented.

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CORRESPONDENCE

Gas Chromatographic Analysis of Polycyclic Aromatic Hydrocarbons in Soot Samples

SIR: We refer to the article of Chakraborty and Long (1967) in which Figure 7 shows comparative spectra for a pyrene standard and an unknown from the gas chromatograph. Although, in the text, they do not claim coincidence, the figure may leave some readers with this impression.

We would like to suggest that the spectrum for the unknown shown in Figure 7 is actually either 1- or 3-methylpyrene or a mixture of the two. The table below gives important wavelength positions for 1-, 3-, and 4-methylpyrene and pyrene as determined in this laboratory with a Cary 14 spectrophotometer. These are compared with the values given by Chakraborty and Long for pyrene and the GLC unknown.

Wavelength ^a Positions for Pyrenes					
Pyrene	3-Methylpyrene	1-Methylpyrene	4-Methylpyrene	Pyrene Std.	Fraction B
371.2				334	378
361.3				319	
356.6				307	358
351.0				307	
335.3	343.3	343.4	337.0	334	346
319.3	326.7	326.6	321.0	319	330
305.0	312.5	312.5	306.7	307	316
278.6	275.8	275.9	275.9	372	277
262.1	265.0	264.5	265.0	262	267
252.0	255.0	253.5	255.0	252	257
240.6	242.5	244.7	244.5	240	244
231.5	233.0	234.6	234.0	231	236

^a Wavelengths in m μ .

The bands shown for fraction B at 378 and 358 m μ are a mystery. The log ϵ values for pyrene and methylpyrene are very similar for corresponding absorption bands:

Pyrene	M μ	log ϵ	
	371.2	2.30	* α
	361.3	2.73	
	356.6	2.76	
	335.3	4.74	* ρ

If the bands shown in the spectrum for fraction B in the positions 378 and 358 m μ belong to the methyl derivative of pyrene as we assume, then these bands should not appear in this spectrum. The ratio of the absorbances of the α band at 378 and the ρ band at 346 is about 1 to 100. Notice the lack of α structure in the standard pyrene spectrum.

Allowing for slight instrumental variations of wavelengths between laboratories, it is clear that the unknown is *not* pyrene.

Literature Cited

Chakraborty, B. B., Long, Ronald, ENVIRON. SCI. TECHNOL. 1, 828 (1967).

R. S. Thomas
J. L. Monkman

Department of National Health and Welfare
Ottawa, Ontario, Canada

SIR: We have considered the comments of Thomas and Monkman on Figure 7 of our paper (Chakraborty and Long, 1967).

We hoped it was clear that, although there is a striking resemblance in the absorption maxima of the substance(s) responsible for fraction B corresponding to peak 9 in the gas chromatogram to those of pyrene, there is a bathochromic shift of the maxima. We concluded that the p.c.a.h. responsible for this spectrum "is a derivative of pyrene" but we could not identify it.

The resemblance between the important wavelength positions for 1-, 3-, and 4- methylpyrene reported by Thomas and Monkman and those of the GLC unknown is of interest and supports our view that this is a pyrene derivative. However, we have evidence that GLC peak 7 corresponds to a mixture of the methylpyrenes. The absorption spectrum corresponding to this GLC peak is compared with that of a mixture of 1-methylpyrene and 4-methylpyrene in Figure 1 of this letter.

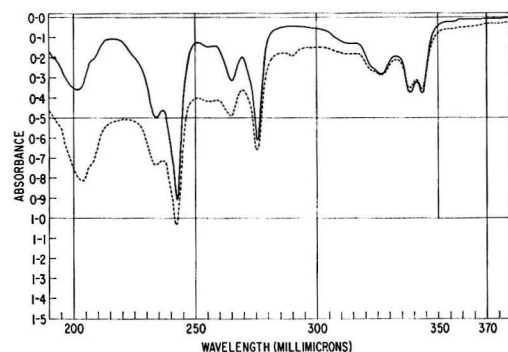


Figure 1. Ultraviolet absorption spectra of a mixture of 1-methylpyrene and 4-methylpyrene and that of gas chromatographic peak 7 in Figure 1 of the original paper

--- GLC peak 7
— Mixture of 1-methylpyrene and 4-methylpyrene

(This was not published in our paper in the interests of brevity.) It can be seen that there is close agreement between the absorption maxima.

Consequently, if GLC peak 7 corresponds to a mixture of the methylpyrenes, then peak 9, with longer retention time, might be expected to correspond to a mixture of substances, including the unidentified pyrene derivative, of higher molecular weight than the methylpyrenes.

Literature Cited

Chakraborty, B. B., Long, Ronald, ENVIRON. SCI. TECHNOL. 1, 828 (1967).

R. Long
B. B. Chakraborty

The University of Birmingham
Birmingham, England

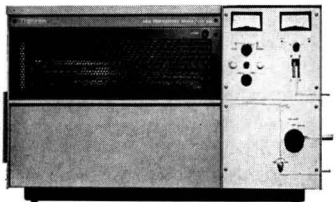
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BOOKSHELF

Book fills insecticide data niche

Insecticides: Action and Metabolism. R. D. O'Brien. xi + 332 pages. Academic Press, New York, N.Y. 10003. 1967. \$14, hard cover. *Ernest Hodgson is with the Department of Entomology, North Carolina State University, Raleigh, N.C. 27607*

By Ernest Hodgson

It is indeed pleasant, in this era of excessive publication of unnecessary books, to find one which is needed and which adequately fills the niche for which it was created. Its two major predecessors in English are now 15 and 11 years old, time enough for both to be obsolete. Such a book is necessary for the bookshelf of every toxicologist, especially those working on pesticides. But it is also important for anyone interested in the quality of the environment.

When one reflects on the origin of environmental pollutants, it is apparent that many—industrial wastes, automobile exhaust fumes, and domestic effluent, for example—are released to the environment after the fact. Thus, the act of dissemination is itself amenable to control and represents a convenient point of attack on the problem. This can be done by research if more data are needed, by legislation if it is apparent that the available knowledge is not being used, or by law enforcement if the existing laws are being ignored.

With pesticides there is a critical difference in that distribution into the environment is an essential preliminary to obtaining the desired effect. Although alternate nonchemical methods of agriculture are being pursued with enthusiasm, it is clear that they are, in the main, impractical at present, and likely to remain so for some time.

These methods will undoubtedly contribute to the long term solution of the problems involved in pesticide use.

However, when these problems are considered, together with the worldwide need for increased food production, there is no doubt in my mind that the immediate need is for additional, less persistent, more selective pesticides so that more of these compounds can be used than ever before, both in the United States and around the world. Thus, all interested in the quality of the environment should be aware of the chemical nature of the different types of pesticides, their modes of action, and the nature of their degradation products.

Dr. O'Brien's book is an excellent one for providing this kind of information about the insecticides, quantitatively the most important group of pesticides. In 1966, U.S. manufacturers also produced 1.25 billion pounds of pesticides with a manufacturers' value of \$800 million. Of this total, approximately 60% were insecticides.

Author's intent

The author states that it was not his intent to produce a historically complete reference work covering all aspects of insecticides (the time when this could be done by a single author is probably past), but to "provide a rather complete account of today's knowledge of the action of insecticides and a survey of their metabolism." Utility, modes of application, and formulation are not treated, nor are detailed synthetic routes provided for the compounds discussed. Hypotheses which have not stood the test of time are also omitted. Within this self-imposed framework, the author succeeded very well and, although there are occasional lapses both of emphasis and style, there are no omissions of material essential for an understanding of present knowledge of the action and metabolism of insecticides.

The book commences with a background chapter covering certain as-

pects of chemistry and neurobiology deemed essential for comprehension of the book. This is the weakest chapter in the book. Compressing the large amount of material into 21 pages leads to a deceptive oversimplification. The reader who uses the excellent references given can easily compensate for this.

This is followed by 12 chapters which cover the insecticides in one chemical class after another. These chapters are all very good while the two on organophosphates are outstanding, as one might expect. The book ends with four chapters covering aspects of a general nature, namely: synergism, antagonism, and other interactions; resistance; selectivity and penetration; and insecticides and environmental health.

The last chapter may be hard for wildlife enthusiasts to swallow conceptually. The facts therein are presented clearly and are not easy to refute, but the bird mortalities accepted so cheerfully by the author may not be

acceptable to all. One doubts that the proposed substitution of methoxychlor for other chlorinated hydrocarbons would prove to be effective in the majority of cases.

The style is more colloquial than that usually found in scientific treatises. This approach and the author's evident enthusiasm make the book refreshingly easy to read. This same enthusiasm can lead to excesses, however, which may irritate the reader. Words such as splendid, excellent, astonishingly, and extensive are used frequently enough and often in more than one context, that their effect is diluted. As an example we may refer to page 292 where a study of residues in human foods involving DDT and DDE analyses of 19 meals is described as extensive. In the next paragraph a study involving analyses for 40 pesticides in 216 composite samples is also described as extensive. Perhaps extensive would have been more meaningful if reserved for the latter.

The work is singularly free from

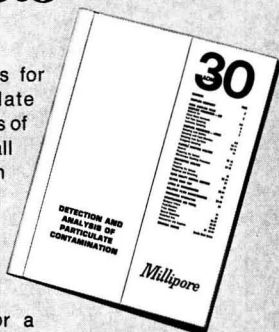
major errors, although one can discern areas which would have benefited from a little more attention from the author. The first paragraph of the section on metabolism (page 97) in Chapter 5 is, to me, the most glaring example of a lapse of attention. Before using such phrases as "enzymes in the usual sense of the word" he should state in precise terms what the usual and unusual senses are.

With regard to the warning in the last sentence of this paragraph, if a tissue contains a protein which catalyzes the hydrolysis of a carbamate and if there is no reason to suppose that this protein does not act *in vivo*, it is an academic question whether this hydrolysis would be enzymatic in the usual sense or the unusual sense, regardless of what these terms might mean.

In summary, this is a needed and important book, well written by a knowing and enthusiastic author. The faults are minor and do not seriously detract from the value of the book. ■

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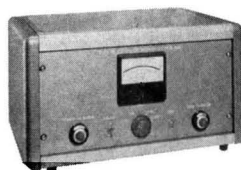
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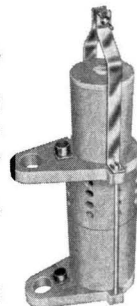
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A selected look at the subject of high-energy batteries

High-Energy Batteries. Raymond Jasinski. xv + 313 pages. Plenum Publishing Corp., New York, N.Y. 10011. 1967. \$17.50, hard cover. *Henry B. Linford is professor of chemical engineering, Columbia University.*

By Henry B. Linford

This book is devoted to the fundamental chemistry and elucidation of some of the performance characteristics of high-energy batteries. The title indicates an arbitrary decision about the battery systems that are discussed. In the preface, this decision is spelled out clearly to include systems of at least 100 W-hr./lb. for primary batteries and 50 W-hr./lb. for secondary batteries.

As is so common with such books, the reader is not necessarily assured a good detailed coverage of certain phases. This deficiency is understandable since the author is prone to more complete coverage in those areas in which he is highly specialized. An example of this tendency is illustrated in the presentation of separators (membranes). This very important component of any battery system is compressed to four pages. Anyone expecting a complete discussion in this area will be sadly disappointed.

It is unfortunate when a volume such as this is produced and no table of nomenclature is supplied. Since the nomenclature used by writers in the field of electrochemistry is not uniform, it makes reading a manuscript without such a table a burden. This volume does contain large amounts of useful tabulated data. However, they are spread throughout the text and not too easily located by the indexing system. It would be impossible to list the tables of data included in this work. In fact, just to list by title the 11 tables in the section of Chapter 3 dealing with fused salt electrolytes would be too cumbersome. These tables deal with the physical, chemical, and electrochemical properties of the more interesting fused salt systems.

The possible electrode-electrolyte

systems that have been investigated and could result in batteries that the author classifies as high-energy are discussed as to specific electrode and electrolyte materials in a very orderly manner. In Chapter 2 the author discusses aqueous systems; in Chapter 3 nonaqueous inorganic systems; and in Chapter 4 nonaqueous organic systems. In this discussion, the theoretical maximum energy capacities calculated from thermodynamics data are given along with actual performance in working cells.

Where information is available, the author spends a considerable portion of the total content of the book in the construction and operation of various types of batteries. Thus, much battery technology is included.

There is no question that anyone interested in the field of batteries, primary or secondary, must include this volume in his library. ■

Solvent Emission Control Laws and the Coatings and Solvents Industry. A Techno/Economic Study. 56 pages.

Environmental Science Services Corp., Stamford, Conn. 06902. 1967. \$35.00, paper.

This study contains an evaluation of the solvent emission regulations which are now firmly established in the air pollution codes of Los Angeles County (Rule 66) and the Bay Area (Regulation 3). Three key elements of these recently-passed codes are:

- Restriction of emissions of various photochemical reactive solvents during their use.
- Prohibition of sale of surface coatings which contain these solvents.
- Restriction of emissions of these chemicals during their manufacture.

The Bay Area code contains all three elements; the Los Angeles code contains only the first two; both of these codes are based on data from smog chambers and other sources.

Whereas the conditions for the formation of photochemical smog by the interaction of sunlight, nitrogen oxides, and certain hydrocarbons exist

more often in California than other parts of the U.S., the same conditions are found on occasion in other locations throughout the U.S. For this reason, regulations containing one or more or all of the above elements, or others, are expected to spread across the entire country within the next five years. Already representatives from other important industrial regions in such states as Michigan, New York, Massachusetts, and Texas have indicated an interest in establishing regulations containing similar provisions.

Major effect

This study discusses the probable effects of these California codes upon the coatings and solvents industry. The first major effect will be upon the formulation of surface coatings. The second major effect will be upon the chemical solvents industry.

For formulations to meet the requirement of these codes, changes will be required that are more serious than reformulation of many of the present

It should be required reading for anybody involved in air pollution, environmental control or meteorology.

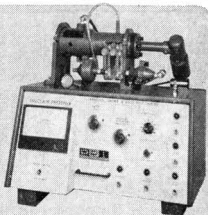
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surface coatings by the mere substitution of solvents. These changes will necessitate new solid concentrations, drying techniques, application techniques, resins, and others.

If the chemical solvent industry is to meet the requirements of these codes, photochemically reactive solvents such as mineral spirits, naphthas, substituted aromatics, branched ketones, olefins, and trichloroethylene are all adversely affected in that their emissions would have to be controlled during both manufacture and subsequent use.

Some 70 chemicals and solvents are covered in this study. Alcohols, esters, odorless mineral spirits, and glycol esters are expected to gain important solvent markets at the expense of photochemically reactive solvents.

Also, there is a hidden threat to the manufacture and storage of important bulk organic chemicals such as ethylene, propylene, butadiene, styrene, vinyl chloride, formaldehyde, and acetaldehyde. Under the provisions of the Bay Area code, emissions from these manufacturing and storage operations are restricted so that an additional capital and operating expense would be incurred by the chemicals' manufacturers and distributors. ■

Proceedings of the 6th Annual Sanitary and Water Resources Engineering Conference. Technical Report No. 13. Edited by Edward L. Thackston. iv + 193 pages. Vanderbilt University, Department of Sanitary & Water Resources Engineering, Nashville, Tenn. 37203. 1967. \$4, paper. *To obtain copies, write directly to: Dr. Edward L. Thackston, Box 133, Station B, Vanderbilt University, Nashville, Tenn. 37203.* ■

Analyses of Natural Gases, 1966. Bureau of Mines Information Circular 8356. B. J. Moore and R. D. Shrewsbury. 130 pages. U. S. Government Printing Office, Washington, D. C. 20402. 65 cents, paper.

The information circular contains analyses and related source data for 374 natural gas samples which were collected during 1966. This circular, the ninth in a series, presents data on 7244 natural gas samples gathered and analyzed between 1917 and 1966, as part of BuMines' continuing search for new sources of helium-bearing natural

gas. Samples were collected from 24 states and five foreign countries and analyzed for methane, ethane, propane, nitrogen, oxygen, argon, and hydrogen, in addition to helium. Heating values are also reported for the samples. This circular contains the first report of analyses of samples from Austria, Bolivia, Canada, Columbia, and The Netherlands. ■

Connecticut Water Law: Judicial Allocation of Water Resources. Robert I. Reis. 215 pages. Institute of Water Resources, University of Connecticut, Storrs, Conn. 06268. 1967. \$3, paper. ■

Four areas of water use are examined by Prof. Reis in this discussion of Connecticut water law: riparian rights in nonnavigable waters, doctrines of public and private rights in navigable waters, ground water, and surface water. The six appendixes contain valuable information about sewage discharge, the removal of gravel and sand from tidal waters, the protection and acquisition of pure water supplies, and the 1967 Pollution Control Act (Conn.). Although restricted to Connecticut law, the principles and opinions will be a valuable guide to persons engaged in planning, developing, or allocating water resources, according to William C. Kennard, Director of the Institute of Water Resources, who wrote the foreword to the volume. ■

Power Systems for Electric Vehicles. A symposium. vi + 323 pages. U.S. Department of Health, Education, and Welfare, Bureau of Disease Prevention and Environmental Control, National Center for Air Pollution Control, Cincinnati, Ohio 45237. 1967. No charge, paper. *A summary of the symposium appeared in ES&T, May 1967, page 394.* ■

Water Is Everybody's Business: The Chemistry of Water Purification. A. S. Behrman. viii + 229 pages. Doubleday & Co., Inc., New York, N.Y. 10017. 1968. \$4.50, hard cover; \$1.45, paper. ■

Air Pollution. Vol. I. Air Pollution and Its Effects. 2nd Edition. Edited by Arthur C. Stern. xix + 694 pages. Academic Press, New York, N.Y. 10003. 1968. \$28, hard cover. ■

Dust Detective

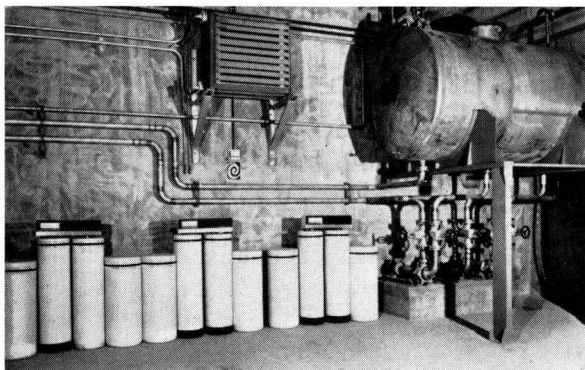
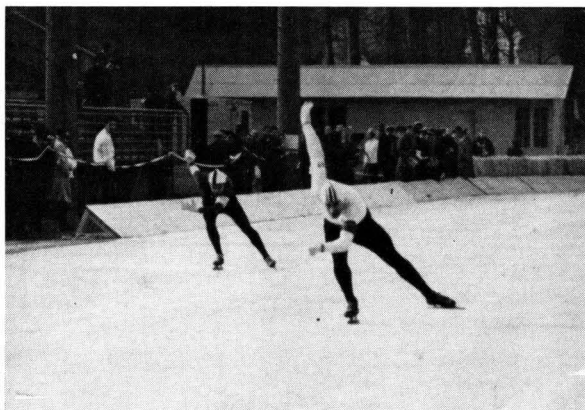


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61

Cooling Water Systems Treatment

Dearcide 713 is a broad spectrum bacteriostat and algacide for control of microorganisms in open recirculating cooling water systems. The phenolic amine treatment is effective against sulfate- and iron-reducing bacteria as well as algae, fungi, and slime-forming bacteria. The noncorrosive treatment is compatible with other treatments and is not appreciably affected by pH changes, according to the manufacturer. W. R. Grace & Co.

62

Coliform Test Kit

The Coliver II kit for testing contaminated water consists of disposable polystyrene tri-sectioned fermentation tube assemblies (five tubes per assembly) containing dehydrated culture media in tablet form in two of the three sections. The third section is a reservoir for the fermented products. A precisely engineered orifice permits interchange of actively growing coliforms between presumptive and confirmed tubes. Hach Chemical Co.

63

Anionic Surfactant

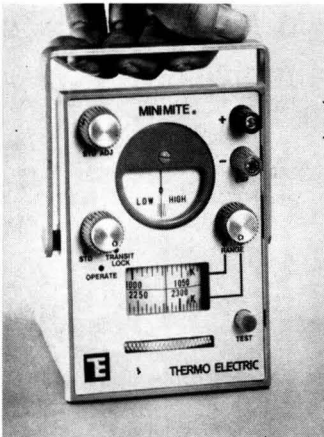
Bion KNa, a new anionic surfactant based on a quaternary ammonium salt, is an aqueous solution used to dilute specimens for subsequent potassium and sodium determinations by flame spectrophotometry, and to clean glassware. Pierce Chemical Co.

64

Air Pollution Primary Standards

A series of primary standards is available for air pollution studies. The 10 liquid chemicals, sealed in inert FEP Teflon tubes to ensure stability, are: sulfur dioxide, nitrogen dioxide, hydrogen dioxide, butane, propane, benzene, butene-1, *cis*-butene-2, *trans*-butene-2, and isobutylene. The standards will provide a basis for establishing the exact quantity of these 10 substances in an unknown sample to the p.p.m. level. PolyScience Corp.

65



Portable Potentiometer

Model 31101 portable potentiometer, the MiniMite, utilizes a null balance measuring circuit, which the company says is accurate to 0.25% of full scale, for measuring temperature and millivolt input signals. The 23.6-inch-long double range scale allows widely

spaced graduations. Temperature scales range from -450° F. to $+3200^{\circ}$ F. and millivolt scales range from 0 to 100 millivolts. More than 100 double range scales are available. Thermo Electric Co., Inc. **66**

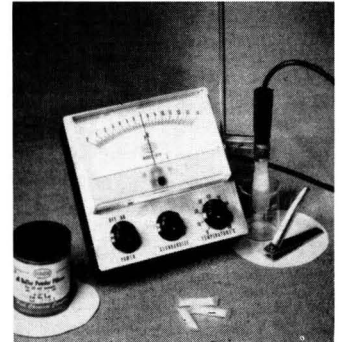
Automatic Sampler

The Surveyor automatic sampler for sewage or industrial waste sampling is light (15 pounds), self-cleaning, and clog-resistant, according to the company. It may be programmed to collect from 2 to 20 samples per hour (from 150 ml. to more than a liter per sample), and may be battery operated in areas remote from electric power. N-CON Systems Co., Inc. **67**

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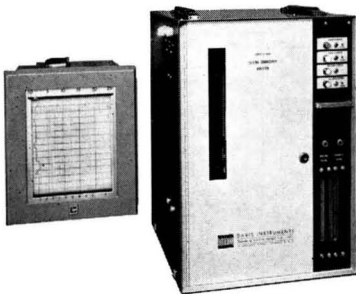
the adhesive force of mud, silt, and sediment to one ten-thousandth of untreated particles. Test results cited by the manufacturer show that one gallon of the chemical will remove one ton of mud. W. E. Zimmie, Inc. **68**



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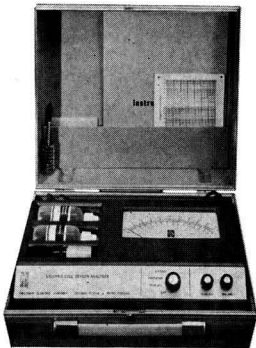
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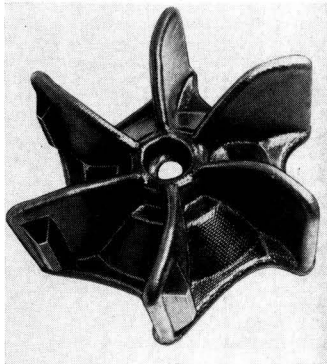
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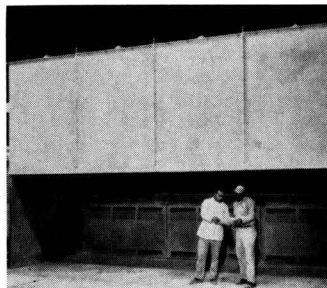
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Rubber-Coated Fans

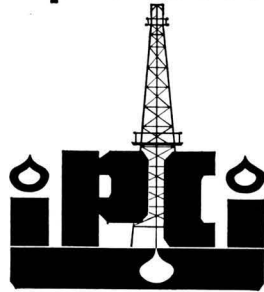
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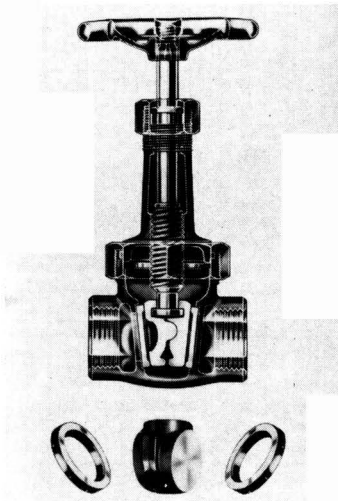
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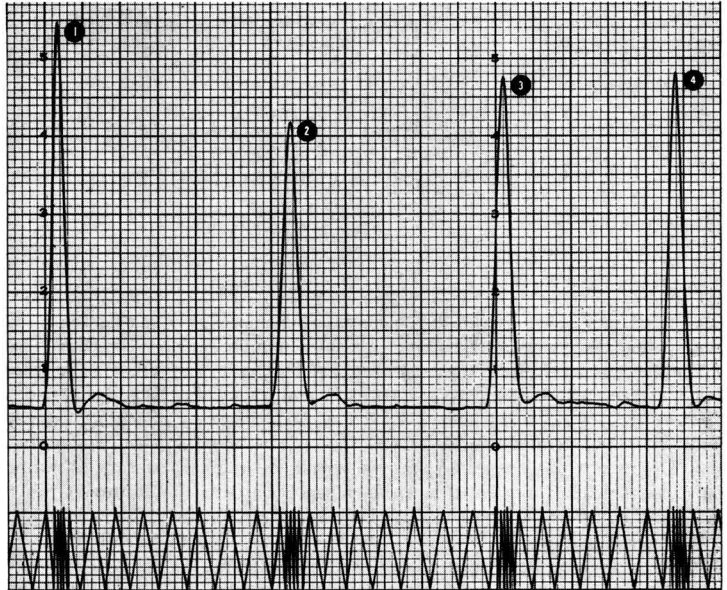
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A 13-minute, super-8mm., color film, "Solid Waste Worldwide—A Burning Issue," is available to consulting engineers, municipalities, and government agencies. The film is produced and narrated by Frank P. Sebastian, president of BSP Corp. Last year Sebastian toured various European countries and Japan as head of a San Francisco Chamber of Commerce-sponsored refuse disposal task force and head of the first U. S. Department of Commerce-sponsored advanced waste water treatment trade mission to Japan. In Japan, Sebastian presented a report on the strides made at Lake Tahoe, Calif., to prevent pollution.

Although the film shows solid waste disposal facilities in England, France, Germany, and Japan, it features the revolu-

tionary Japanese methods for converting incinerated sewage sludge residue to salable products.

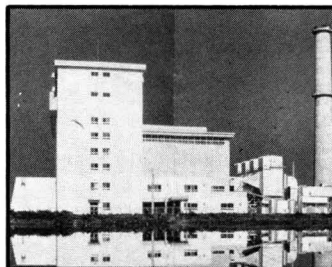
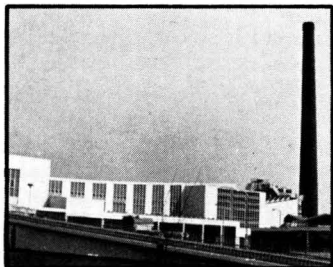
The Essen (Germany) plant burns a mixture of refuse and other fuel to generate steam and electricity. The burning refuse supplies 20% of the heat. The Issy les Moulineaux plant in Paris converts 1400 tons of refuse per day to steam and valuable byproducts. The Dusseldorf (Germany) plant produces steam and electricity by burning refuse. In addition the plant sells residual ash and magnetically separated scrap.

Requests to borrow the film should be sent to Frank P. Sebastian, president, BSP Corp., P. O. Box 8158, San Francisco, Calif. 94128. For a fact sheet describing the film, please circle 91 on Reader Service Card.

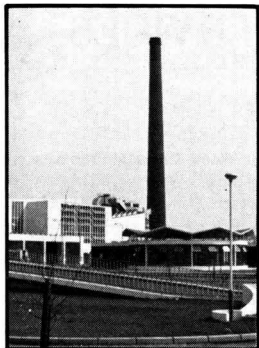
Early. *The Castle Bromwich (Birmingham, England) incinerator was designed in 1962. Thus, according to the film's producer, Birmingham was the first English town to see incineration as the best solution to disposal of solid waste*

Controls. *The incineration plant in Dusseldorf (Germany) produces steam, electricity, salable residual ash, and magnetically separated scrap and requires an elaborate control room to monitor the daily refuse load of 960 tons*

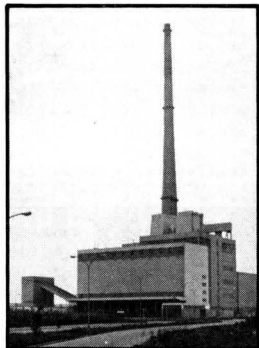
Beauty. *Yao City (Osaka), Japan, has located its incinerators near a body of water, much in the manner in which Atami City located its sewage treatment plant (ES&T, February 1967, page 173)*



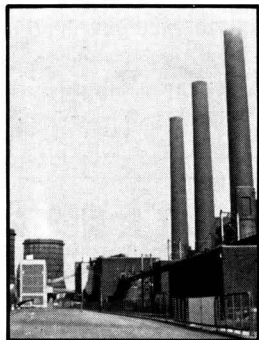
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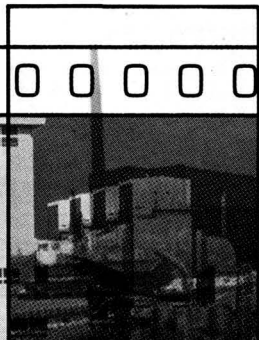
Reception. Reached by ramps, the platforms for unloading refuse at the Castle Bromwich incinerator are dubbed the "Reception Hall"



Odorfree. The Mannheim (Germany) plant can process as much as 800 tons of refuse per day. To ensure odorfree operation, all air in contact with refuse in the storage bunkers is fed through the plant's combustion chambers

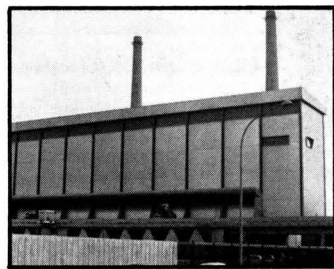
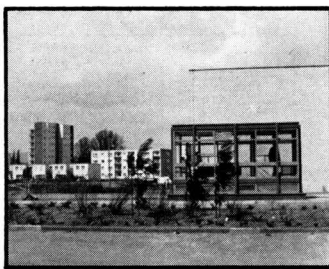
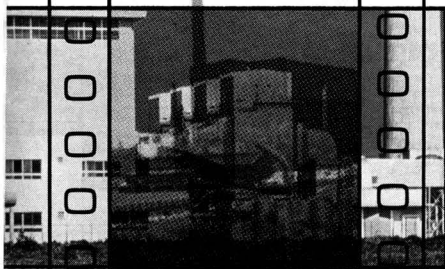


Generator. The Essen (Germany) incinerator, with a capacity of 1440 tons of refuse per day, burns a mixture of refuse and other specially added fuel to generate steam and electricity



Good neighbor. The Frankfurt (Germany) incinerator has a capacity of 600 tons of refuse per day, and is near some modern high-rise apartments

Sophisticated. At the Issy les Moulineaux (Paris) plant, a sophisticated installation which converts 1400 tons of refuse per day to steam and valuable byproducts, electrostatic filters are used to clean the exhaust gases to limit air pollution



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MEETING GUIDE

April 1-3 Technical Association of the Pulp and Paper Industry

5th Water and Air Conference

Portland-Hilton Hotel, Portland, Ore.

The conference will include sessions on water supply, water treatment, air pollution, waste water control, and waste water treatment. Tours to water and waste facilities at nearby pulp mills are planned.

April 3-5 Pollution Control Exposition and Conference

Astrohall, Houston, Tex.

Sponsored by the Houston Junior Chamber of Commerce, the exposition is aimed at potential users of pollution control equipment and will feature exhibits of equipment for all kinds of pollution—air, water, noise, and solid waste. The associated conference will have technical reports from many of the industries and organizations concerned with pollution control.

April 8-11 American Geophysical Union

Eastern National Meeting

Sheraton Park Hotel, Washington, D.C.

The hydrology section will hold sessions on the analysis of water resources systems, analytical techniques in hydrology, and surface water, ground water, and general hydrology. Other sections are presenting a variety of papers on topics of interest to environmental specialists, including geochemistry of the hydrosphere and sedimentation, climate modification and air chemistry, marine ridges, rifts and spreading, and crystal chemistry.

April 9 Ground Water Resources Institute

4th Ground Water Seminar

Shoreham Hotel, Washington, D.C.

In keeping with the theme of the seminar "Communicating the Ground Water Story—The Role of Ground Water in Total Water Management," the morning seminar program will feature papers on water resources for smaller cities, trends in state water well legislation, and the potential and problems of ground water recharge. The afternoon session includes papers on ground water hydrology for the layman and applications of aircraft and spacecraft surveys to ground water investigations.

April 9-10 Water Resources Research Institute of Mississippi State University

The Mississippi Water Resources Conference

Auditorium, Woolfolk State Office Building, Jackson, Miss.

A symposium devoted to state water resources, the conference comprises papers on reforestation and national forests, sediment travel and channel changes, flood damage legislation, watershed development, application of the equations of unsteady flow to water resources, and water resource management as related to water pollution control.

April 16-18 Air Force Cambridge Research Laboratories

5th Symposium on Remote Sensing of Environment

University of Michigan, Ann Arbor

The symposium will include presentations on sensors and vehicles, needs for remotely sensed data, data analysis programs and techniques, and problems limiting the use of remote sensing techniques. AFCRL cosponsors are the Office of Naval Research, Army Research Office, and U.S. Department of Agriculture.

April 16-18 University of North Carolina, and North Carolina State and Duke Universities

17th Southern Water Resources and Pollution Control Conference

Chapel Hill, N.C.

The conference will feature the technology of water resources and water quality management with particular reference to the southeastern U.S. Topics include the characterization of industrial wastes, tertiary treatment, instrumentation for determination of water quality, and a session on the problems of adoption and implementation of federal water quality standards by representatives of the southeastern states water quality agencies.

April 16-19 Engineering Extension and the College of Engineering of the University of California (Berkeley)

Water Resources Engineering Educational Series (WREES)

University of California Extension Center, San Francisco, Calif.

Program V, "Economics and Public Policy in Water Resources Development," includes discussions of economics and public policy for agricultural water use, water pricing and water use, the role of public water districts, competing uses for water, economics of reservoir operation, planning and economics of recreational water use, input-output analysis of water use patterns, locations and factors influencing economic development, demand theory for water, and economics and public policy of ground water basins. Water developments and problems of California will be emphasized.

April 19-20 Extension Division and Environmental Health Research Center of the University of Missouri

Environmental Engineering Conference

University of Missouri, Rolla, Mo.

The areas of water resources, water pollution, air pollution, solid wastes, urban affairs, and environmental health planning will be discussed at this conference, whose theme is "Man, Engineering, Environment." Write: Dr. S. G. Grigoropoulos, Environmental Health Research Center, University of Missouri, Rolla, Mo. 65401

April 26 Air Pollution Control Association—Mid-Atlantic States Section

1968 Spring Conference

Hotel Dupont, Wilmington, Del.

The theme of the semiannual technical conference is "The Legal Road to Cleaner Air." The morning session includes papers on Delaware and federal air pollution legislation and the legal aspects of air pollution control from the state level. The afternoon session features papers on compacts and legislative

(Guide continues on page 234)

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MEETING GUIDE continued

April 28-May 1 Institute of Environmental Sciences 14th Annual Technical Meeting and Equipment Exposition

Chase-Park Plaza Hotel, St. Louis,
Mo.

The theme of the meeting centers on new horizons and places emphasis on the application of environmental technology to the fulfillment of man's desire for a healthier, happier, and more peaceful life. Topics include space, earth, and marine environments; human factors; management; and others.

April 29-30 American Medical Association

5th Congress on Environmental Health Problems

Drake Hotel, Chicago, Ill.

The congress will focus attention on the goals and recommendations of the special report, "A Strategy for a Livable Environment." Commonly called the "Linton Report," this report to Secretary Gardner of HEW offers suggestions for solving environmental problems. The purpose of the congress will be to review and evaluate recommendations contained in the report and to examine the role of the medical profession in implementing some of the goals.

May 5-8 Incinerator Committee of ASME

3rd National Incinerator Conference

N.Y. Hilton Hotel, New York City, N.Y.

Sessions are planned on air and water pollution control, refuse and residue qualities and characteristics, incinerator planning, incinerator design, and industrial incineration. Write: Mr. Leo Cohan, program chairman, 1968 National Incinerator Conference, % Combustion Engineering, Inc., Windsor, Conn. 06095

May 30-31 Vanderbilt University

7th Annual Sanitary and Water Resources Engineering Conference

Noel Hotel, Nashville, Tenn.

Sponsored by Vanderbilt University School of Engineering, the State Department of Public Health, and the State Water Pollution Control Board, this conference is devoted to the design and operation of treatment processes for municipal and industrial wastes, hydraulic and hydrologic aspects of waste water collection, and disposal systems. A 1-day session on atmospheric pollution and control will be held concurrently.

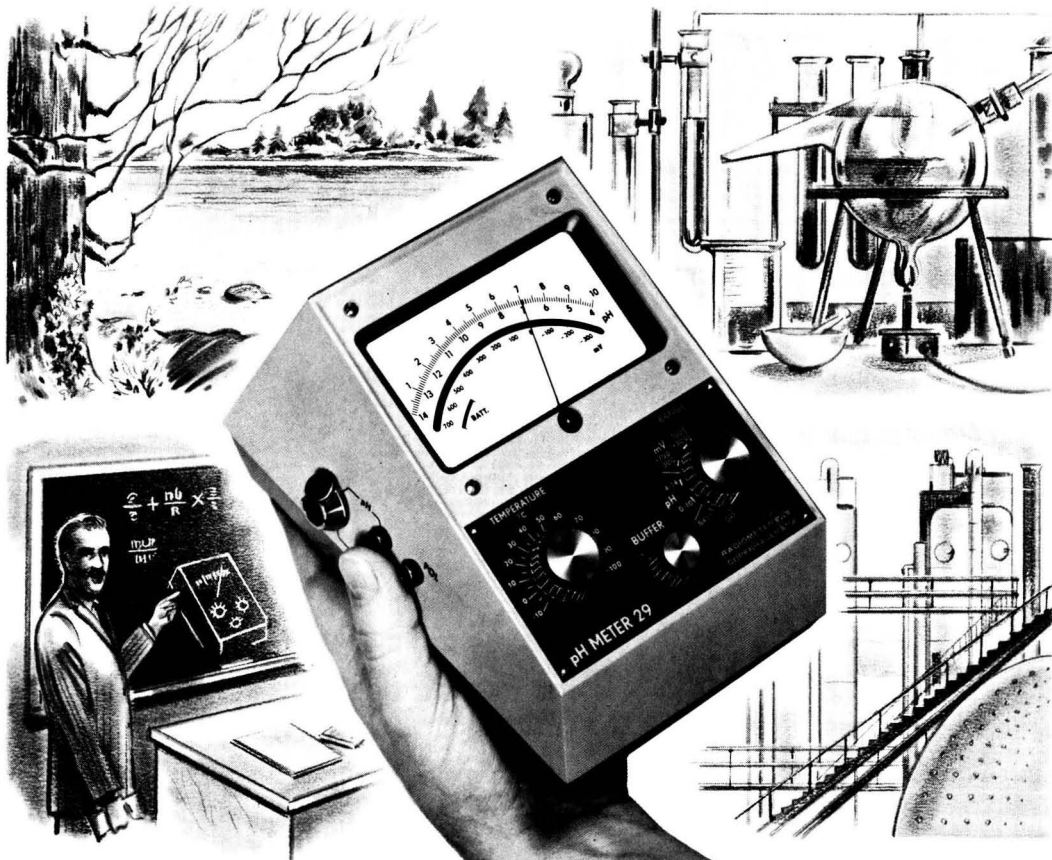
June 6-7 Texas Water Pollution Control Association

8th Industrial Water and Waste Water Conference

Koko Inn, Lubbock, Tex.

The theme of the conference will be water reuse management and measurement in industry. Conference topics will include industrial water systems, waste water treatment, pollution control, and problems of feed lot operations.

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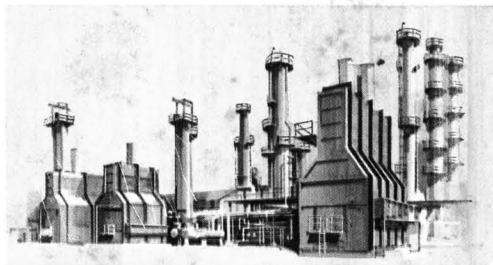
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