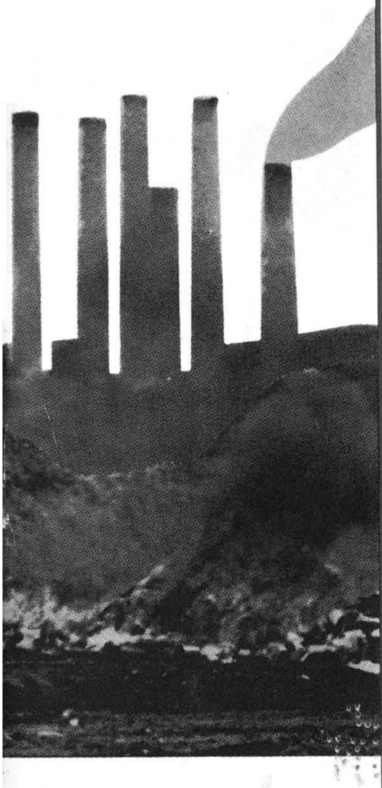
ENVIRONMENTAL
Science & Technology

Emphasizing
Water,
Air, &
Waste
Chemistry

AUGUST 1969



Open burning of solid wastes 711

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HEW's Vaughan: managing solid wastes 705

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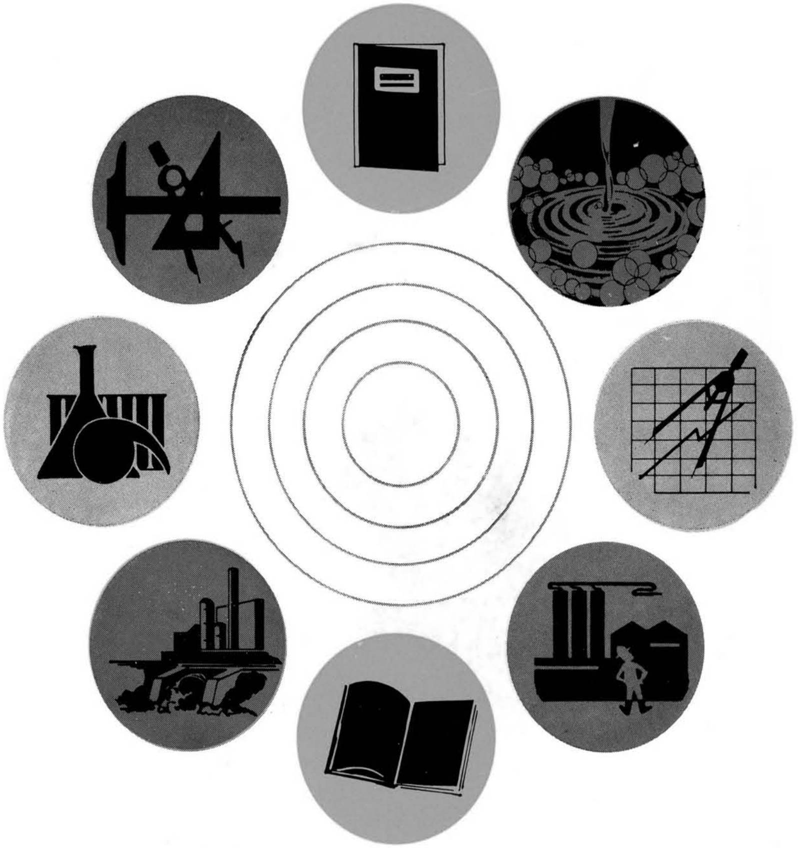

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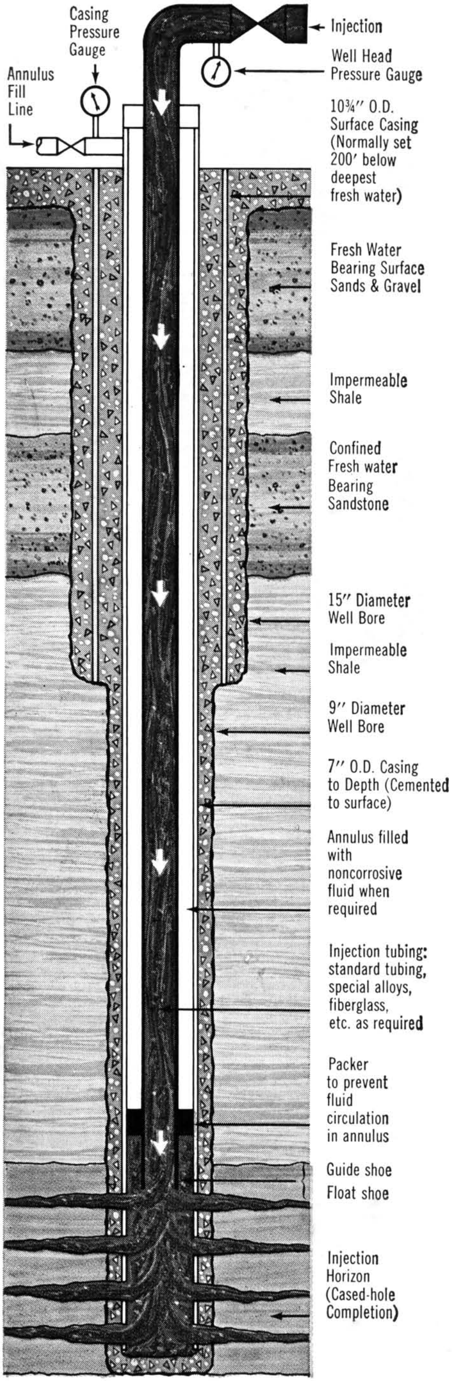
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Annulus Fill Line
Injection
Well Head Pressure Gauge
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Fresh Water Bearing Surface Sands & Gravel
Impermeable Shale
Confined Fresh water Bearing Sandstone
15″ Diameter Well Bore
Impermeable Shale
9″ Diameter Well Bore
7″ O.D. Casing to Depth (Cemented to surface)
Annulus filled with noncorrosive fluid when required
Injection tubing: standard tubing, special alloys, fiberglass, etc. as required
Packer to prevent fluid circulation in annulus
Guide shoe
Float shoe
Injection Horizon (Cased-hole Completion)

ENVIRONMENTAL
Science & Technology

Volume 3, Number 8
August 1969

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contents

Current research

Lead aerosols in marine atmosphere 737

T. J. Chow, J. L. Earl, and C. F. Bennett

The background level of atmospheric lead is still under scrutiny. Shipboard atmospheric samples (Apr.–May 1967) from remote areas in the north and central Pacific Ocean contain lead ranging from 0.0003–0.0015 μg. of lead per cubic meter of air, the air being less polluted in north temperate atmospheres. By having the exact background lead level, safe levels for industrial exposure can be reevaluated.

Determination of total nitrogen in water by microcoulometric titration 741

R. T. Moore and J. A. McNulty

The organic and inorganic nitrogen content in waste waters down to the 0.2 p.p.m. level can be determined in three minutes using a new technique. The analytical method can be used for industrial process control, sewage plant operations, and studies of crop fertilization, fresh water supplies, pesticide control, and ecology of water systems.

Air pollution from animal wastes. Determination of malodors by gas chromatographic and organoleptic techniques 744

W. E. Burnett

Adequate odor control methods include masking, modification, or elimination by mechanical, physical, or chemical means. Accumulated liquid poultry manure contains a number of important odor relevant compounds including mercaptans, sulfides, diketones, volatile organic acids, indole, and skatole. For animal odors, masking is not completely satisfactory. Some form of wastes elimination or prevention offers the greatest potential for poultry wastes' odors control.

Sedimentary phosphorus in lake cores—Analytical procedure 750

D. A. Wentz and G. F. Lee

The phosphorus content of lakes, probably the nutrient most often implicated in the biological production of a lake, now can be determined by an extraction procedure. This procedure is a useful tool for studying accelerated eutrophication of lakes. Data for available phosphorus from lake sediments—including sorbed phosphorus such as orthophosphate, phosphorus present as apatite and calcium phosphate, and certain organic forms of phosphorus—are obtained using the technique.

Sedimentary phosphorus in lake cores—Observations on depositional pattern in Lake Mendota 754

D. A. Wentz and G. F. Lee

Eutrophication—the progression from a deep sterile lake environment to a more shallow one characterized by high biological production—increases with nutrient influx into the lake. More than one half of the phosphorus in Wisconsin's Lake Mendota sediments (as defined by the above extraction procedure) is available for biological production of the lake. The complete mechanism of phosphorus deposit still is unclear.

Synergistic action of ozone-sulfur dioxide on peanuts 759

H. G. Applegate and L. C. Durrant

Damage to the peanut crop (1966–67) in Texas may be explained by synergistic action of air pollutants. Air pollutants in combination may cause more damage to vegetation than either pollutant separately. Such is the case with ozone (0.8–1.0 p.p.h.m.) and sulfur dioxide (2.3 p.p.h.m.) which in combination cause more damage to peanut plants than either pollutant separately.

Communications

Colorimetric determination of manganese in lake waters 761

J. J. Delfino and G. F. Lee

Classification of various manganese fractions in lake waters is made possible using colorimetric procedures. The accuracy of three colorimetric procedures—the persulfate, formaldoxime, and malachite green methods—for the determination of manganese in lake waters is compared; the persulfate method is the most efficient. The methods are useful in studies on water chemistry, limnology, and water treatment methodology.

Identification of bacteria by rapid spectrophotofluorometric methods 764

C. J. Rogers and T. C. Purcell

Bacteria present in polluted waters or waste processing operations can be classified by a new analytical method. Eleven strains of bacteria differed in their carbohydrate and esterase activities and in the esterase/carbohydrate (E/C) ratios, which form the basis for this method. The technique also may find use in process control for recycling or reuse of solid waste, and can be used to determine the activities at different time intervals.

An improved gas sampler for air pollutant analysis 767

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

The improved sampler consists of glass and Teflon parts and is easy to handle in field operations. The sampler is less subject to damage than its predecessor of all glass design, accommodates air flow rates from 0.5–2 liters per minute, and requires only 10 ml. of collecting solution.

A modification of the Bausch and Lomb aerosol dust counting system to automatically measure aerosol size distributions 768

P. M. Brown

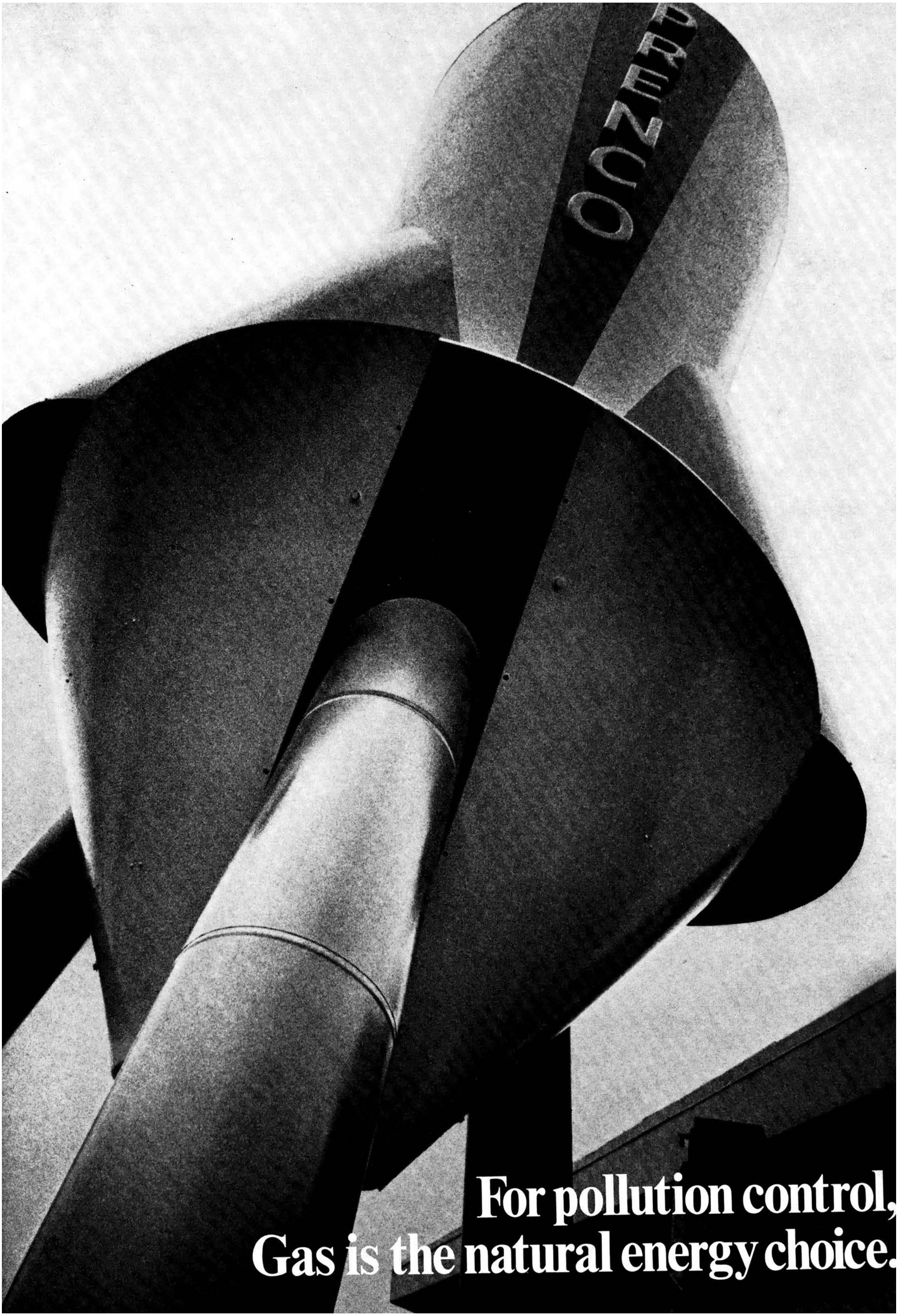
With additional circuitry, unattended automatic measurements of airborne particles can be determined with the Dust Counting System of Bausch and Lomb. The system has been operated successfully at ground level and at altitudes up to 20,000 feet.

Correction

Kinetics of substrate uptake in pure and mixed culture 769

R. I. Mateles and S. K. Chian

This article appeared originally in ES&T, June 1969, page 569.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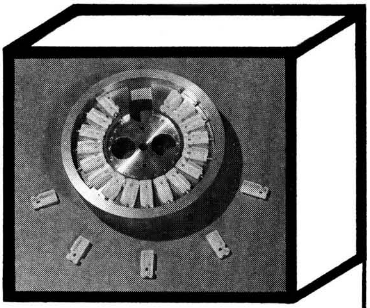

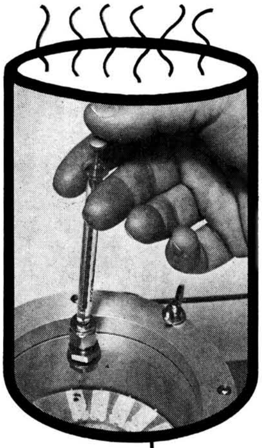

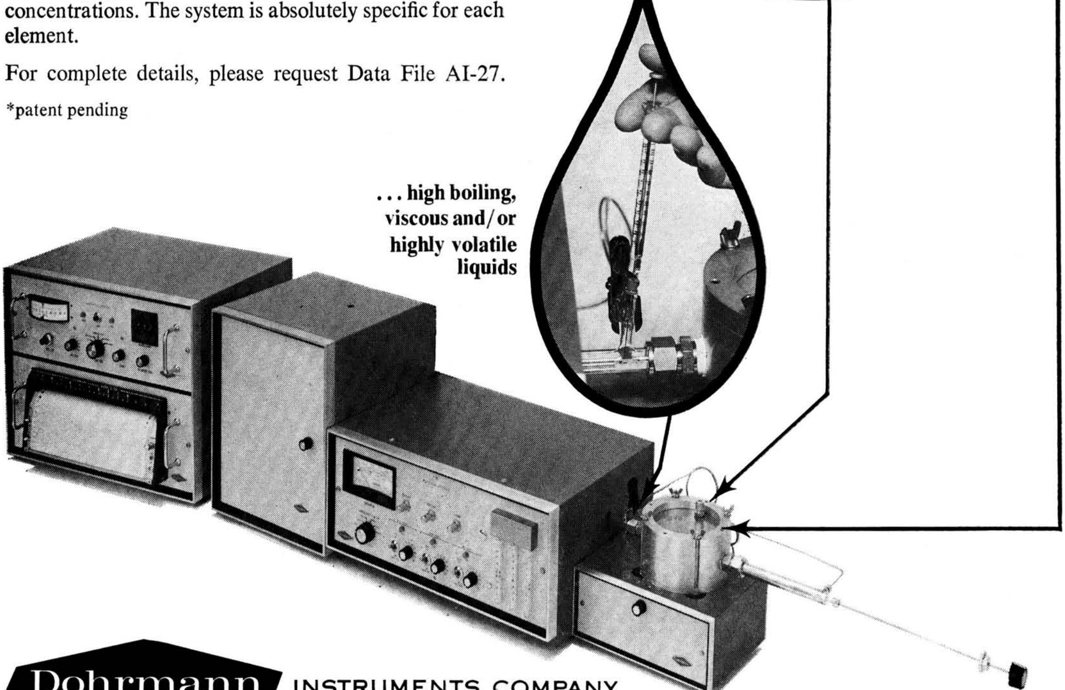

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Let's not perpetuate the myth
that natural resources are inexhaustible;
soon we will be forced to reuse them
or do without

Time to stop squandering resources

One of the most conspicuous features of civilization, American style, is its ravenous consumption of resources that are, for the most part, nonrenewable. In the early days of the American colony, tobacco planters found that they could get only a limited number of successive crops from a given plot of ground. When productivity from a plot declined, the planter simply moved on. There was plenty of land available so why not, he asked. At the same time, vast forests, abounding in game, covered the land. Timber was a resource that no one thought of as being anything but inexhaustible. Even when it became clear that timber resources were indeed exhaustible, the philosophy of "cut out and clear out" still remained the lumberman's cry. And there were so many game animals, surely the supply would never give out. Yet, buffalo were reduced in number from 60 million to the verge of extinction within two generations.

Today, we are much better informed about the finite extent to which resources are to be found on this earth. Soil conservation and reforestation are practiced in all so-called civilized countries. Hunting of game animals is controlled so that no species is shot out of existence. Yet, there still are some anomalies in our supposedly realistic view of the exhaustibility of resources. We continue to drill for oil and, although we should realize that there must be a limit to the amount of oil beneath the earth's crust, we are smug and complacent when told that known reserves are far greater in extent than was ever thought possible a mere 50 years ago. Perhaps supplies are inexhaustible after all? Whereas, in the administration of President Theodore Roosevelt, knowledgeable people advised the President that U.S. coal reserves were almost completely depleted, we know that 60 years later the U.S. Government is anxiously casting about for some way to use these coal reserves which have been comparatively neglected in the switch to petroleum based energy systems.

The successes of science and engineering in finding resources where none had been thought to exist may well have lulled us into a false sense of security. It is quite possible that we have begun to expect the impossible from technology: to find natural resources when none exists. It is becoming rather trite to say that we have allowed ourselves to be seduced by the apparent omnipotence of technology, but that seems to be exactly what has happened.

It is ironic to reflect that, although technology is commonly regarded as a panacea to man's problems, the development of a free enterprise system of economics actually is hindering the employment of technology where it could do some good. Take, for instance, the matter of water resources. Water is one resource that everyone seems to recognize as being limited—in fact, the media have carried numerous stories about imminent crises in water supply. But when we say "There's not enough water," what we actually mean is "There's not enough very cheap water." Having been accustomed, almost as a birthright, to using large quantities of water at next to no cost, we seem to feel that if we don't have cheap water we don't have any water. The fact is that existing technology would enable us to reuse, again and again, the water resources that do exist. Trouble is, it costs money to use the technology, and, apparently, we aren't yet willing to pay the price.

But the time is fast approaching when we either will pay the price or do without. The days of cut out and get out are gone forever. The sooner we learn that, the sooner we shall be able to come to terms with our decidedly exhaustible world.

D. H. Michael Bowen

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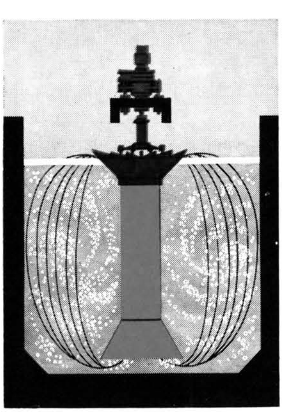

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Underwater storage system halts vessel pollution

A new system developed by Underwater Storage, Inc. (Washington, D. C.), under contract with the Federal Water Pollution Control Administration (FWPCA) promises to make a significant contribution to eliminating pollution in marina areas. Harold A. Quase and Sidney A. Silver of Underwater Storage (ES&T, August 1968, page 577) described the system at a demonstration on the heavily polluted Anacostia River in Washington. Cabin cruisers at the Anacostia marina are equipped with sewage holding tanks and small self-priming pumps. When a boat docks, the crew connects a flexible hose to the pump outlet and the boat's sewage is pumped quickly through dockside pipes to a 3000 gallon, nylon reinforced, rubberized tank built by Goodyear Tire and Rubber Co. (Akron, Ohio) and anchored to the river bottom. The contents of this underwater tank are periodically pumped out to a road tanker for delivery to a waste treatment plant. Ten boats at the Anacostia marina currently are taking part in the pilot program.

Aviation agency announces noise studies

The effects of aircraft noises and sonic booms on people and structures form the basis of recent contracts awarded by the Department of Transportation's Federal Aviation Administration to Stanford Research Institute (SRI) (Menlo Park, Calif.) and Wyle Laboratories (WL) (Hunstville, Ala.). Under a $129,893 contract, SRI will study and analyze unusual noise effects (including the sonic boom) upon special population groups. WL will study the effect of pressure waves on glass structures, under a $63,328 contract. Both studies were recommended in the "Report on Human Response to the Sonic Boom."

National Water Commission schedules public hearings

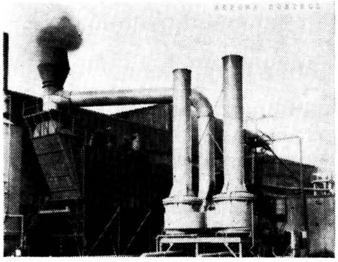
Late this month and early next month, the National Water Commisison (NWC) plans to hold six regional and one national conference so that the commission can develop its overall national water policy, and assignment charged to NWC under P.L. 90-515. Invitations to governors of the 50 states, representatives of water agencies and private organizations have been extended, according to NWC chairman, Charles F. Luce (ES&T, April 1969, page 303). NWC's newest member is Howell Awpling (Portland, Ore.).

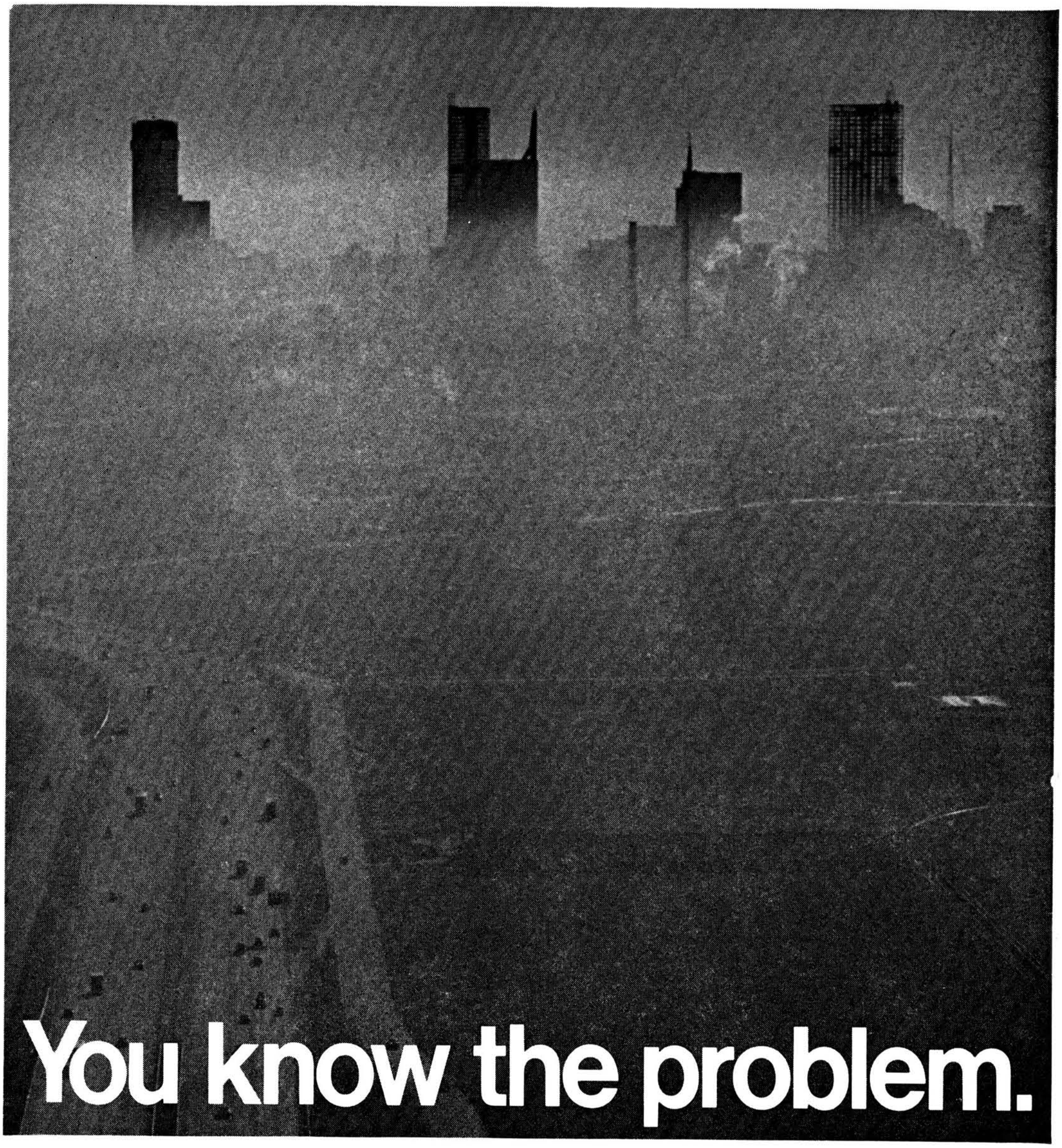
National Water Commission Conferences

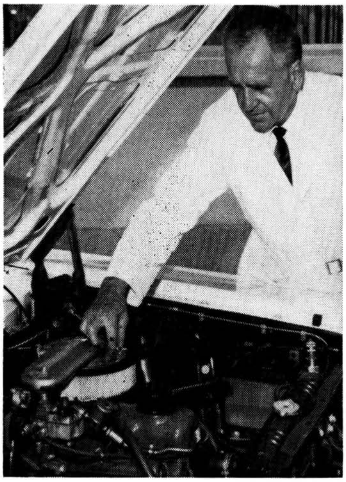
Portland, Ore	Aug. 29
Denver, Colo.	Sept. 26
Chicago, Ill.	Oct. 3
New Orleans, La.	Oct. 9
New York City	Oct. 16
Los Angeles, Calif.	Oct. 27
Washington, D.C.	Nov. 6–7

Commerce surveys smelters' air pollution abatement

In its series of air pollution control surveys, the Department of Commerce's Business and Defense Services Administration (BDSA) examined a representative 23 smelters of the secondary nonferrous metals industry, an industry primarily engaged in recovering nonferrous metals and alloys from scrap and dross. BDSA finds that the cost for such control equipment—usually dry baghouse, electrostatic precipitator, wet scrubber, or a combination of these devices—can be moderately significant elements of overall cost. BSDA finds that the annualized installed cost, plus the annual cost of operating and maintaining the systems, is less than 1% of the annual value of shipments ($1.6 billion in 1967), and is in the range of $1.35–1.70 per year for each cubic foot per minute of gas cleaning capacity. In the U. S., there are approximately 500 plants.




You know the problem.



Dual fuel unit reduces internal combustion emissions

A device that will permit an internal combustion engine to use natural gas in lieu of gasoline was announced last month by a new firm, Natural Gas Vehicles, Inc. (NGV) (Washington, D.C.). Carbon monoxide emissions will be controlled up to 90%. "No engine modification is required, and, initially, the device will be marketed to companies with fleets of vehicles," says Edward Falch, NGV's president. Another NGV official is S. Smith Griswold, president of Seversky Environmental Dynamics Research Assoc. (Washington, D.C.). The device, which sits on top of the caburetor and air filter (see photo), would cost about $350 per vehicle—$300 for the unit and $50 for a tank to hold the natural gas.

Westinghouse builds mine drainage treatment plant

With a contract from the State of Pennsylvania, Westinghouse Electric Corp. (Pittsburgh, Pa.) will build a plant capable of treating 5 million gallons of acid mine drainage per day. "This plant signifies a new concept in mine drainage abatement because it places the cost of treatment on a pay-as-you-go basis through sale of water, rather than placing the burden on the taxpayers," says Pennsylvania's governor, Raymond P. Shafer. Thus, manufacturers could easily locate on available land nearby and take this water directly from the treatment plant. At present, this quantity of acid mine drainage flows into the Susquehanna River. To be located near Wilkes-Barre, Pa., the plant will employ a flash evaporation process, similar to that used in desalting plants for conversion of ocean or brackish water to fresh water. To withstand the extremely corrosive effects of the mine drainage, the flash evaporative system probably will use titanium tubing.

Interior selects water resources programs for fiscal '70

Ten percent of the research proposals have been selected as projects, according to E. D. Eaton, acting director of Interior's Office of Water Resources Research (OWRR). Costing $2 million, the projects relate to urban or metropolitan waste problems (8), systems analysis development and application (8), water resources planning and management (5). Other projects will study the ecologic impact of water sources development, social objectives in water resources policy, and management of inland lake resources. The projects have been submitted to the Congress; after 60 days, final contracts and agreements will be executed, similar to last year's OWRR program (ES&T, July 1968, page 487).

Chicago looks at sludge disposal

Sludge disposal, the most expensive aspect of sewage treatment, is the subject of a $610,500 grant to the Metropolitan Sanitary District of Greater Chicago by the Federal Water Pollution Control Administration. Carl L. Klein, Interior's assistant secretary for water quality and research, noted that sludge disposal projects might be employed in the future to reclaim or revegetate strip mines or construction sites. In 1970, some 100 acres of land adjacent to the Calumet Expressway will be cultivated and fertilized with sludge. "The final goal at Chicago is the development by the year 2015 of a 21,500 acre tract that will have the capacity for using all of the digested sludge from Chicago's West-Southwest, Calumet, and North Side waste treatment plants," Klein says.

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environmental currents

Engineering firm will remove phosphate at plant

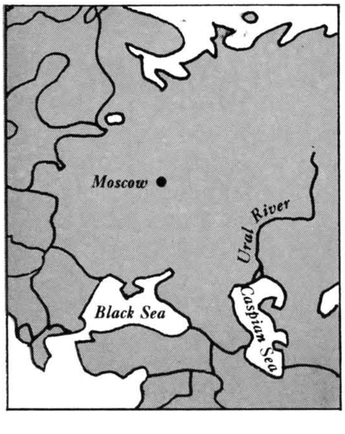
Roy F. Weston Co. (West Chester, Pa.) will investigate two 10 m.g.d. plants at the Back River Waste Water Treatment Plant (Baltimore, Md.) for phosphate removal techniques. One plant will be used as a control and the other will be used to evaluate various treatment techniques for phosphate removal. Under a $212,000 FWPCA grant, the study should be completed by mid-1970 and will possibly indicate whether chemical or biological action controls the phosphate removal process, according to M. N. Bhatla, Weston's project manager.

National environmental quality policy passes Senate

Last month, Sen. Henry M. Jackson's (D.-Wash.) bill, S. 1075, was passed by the Senate. Perhaps one of the most significant measures in the area of natural resource policy ever considered by any Congress, S. 1075 authorizes the Secretary of the Interior to conduct investigations, studies, surveys, and research relating to U.S. ecological systems, natural resources, and environmental quality. An independent and prestigious council also will be formed and will establish priorities and give expression to our national goals for enhancement of the environment. The only other national precedent for similar action was the Full Employment Act of 1946, which declared a national policy on management of the economy and established the highly successful Council of Economic Advisers.

Agriculture calls pesticide use halt

Last month, U. S. Department of Agriculture called for a suspension of pest control programs, pending a complete review of the project which is due within 30 days, according to J. Phil Campbell, Acting Secretary of Agriculture. The suspension affects programs of the Agricultural Research Service and Forest Service involving the use of nine persistent chlorinated hydrocarbon pesticides—DDT, dieldrin, endrin, aldrin, chlordane, toxaphene, lindane, heptachlor, and BHC. Meanwhile, FWPCA's thinking on degradation of pesticides in the environment includes a recent contract grant to the Aerojet General Corp. (El Monte, Calif.) for a catalyst which would cause DDT to decompose in the soil over a short period of time.



Polluted state of Russian river concerns Moscow officials

The Ural River in the central Soviet Union is so badly polluted that it "pleads for conservation," according to a report in the official communist party organ *Ekonomicheskaya Gazeta.* The report deplores existing conditions and cites several reasons for them: • Industries and cities have not embraced the multiple use principle. • Money from the USSR government is earmarked for pollution abatement equipment, but is dispersed too widely to make an impact. • Proliferation of government departments hinders agreements on joint treatment plants for plants and municipalities. • There is no central agency responsible for developing processes and equipment for waste treatment. • Construction contractors are dragging their feet, even though they have been paid to do specific jobs. The Soviet government certainly has the power to rectify the situation, and the impatient tone of the report on the Ural river suggests that the men in Moscow intend to get tough.


.750

Contract for SO_2 recovery unit granted

The first full-scale commercial application of Wellman-Lord's SO_2 recovery process will be at an Olin Mathieson sulfuric acid plant. Wellman-Lord's turnkey contract from Olin calls for design and construction of a unit similar to the demonstration plant now in the first stage of start-up at Baltimore Gas & Electric's Crane station (ES&T, May 1969, p. 421). Wellman-Lord says that the Olin unit will reduce SO_2 emissions at the 700 ton per day sulfuric acid plant in Paulsboro, N. J., to 500 p.p.m., one of the lowest levels experienced from this type of plant. Engineering for the project is already underway, and completion is scheduled for June of next year.

Solid-state technology aids electrostatic precipitators

Belco Pollution Control Corp., (Paterson, N. J.) has a NAPCA grant to develop a solid-state, high energy power supply for electrostatic precipitators. Belco president R. S. Herwig says that the goal of the project will be a 50% increase in efficiency of precipitator design by doubling the energy level now available with conventional power supplies. Belco predicts that such a unit will reduce the cost of new precipitators by as much as 40%, making them practical for smaller scale applications. The company further indicates that TVA, largest user of these collection devices, will test the prototype unit.

Pulp mill effluents are target of major grant

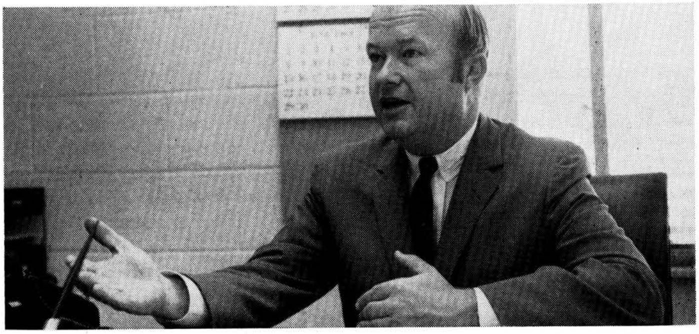
The largest industrial waste treatment grant ever tendered by FWPCA has been made to St. Regis Paper Co. (New York City) to study activated carbon treatment of pulp and paper mill effluents. One goal of the study is a kraft pulping process capable of reusing 90% of the primary water supply; another key phase will be aimed at plant site production of activated carbon as a byproduct of the kraft recovery process. Total funding for the three year project will be $1.4 million, with 60% of this covered by the FWPCA grant. Initial phases of the study will be done at the company's technical center (Nyack, N. Y.) and at Pensacola, Fla., site of St. Regis corporate laboratories and one of its major kraft process plants.

Joint venture formed to market SO_2 control process

Chemical Construction Corp. (New York City) and Basic, Inc. (Cleveland, Ohio), have jointly formed a new company, Chemico-Basic Corp., to promote and market a new flue gas SO_2 recovery process. The system to be offered by the joint venture is a central recovery plant approach, in which a single processing plant recovers sulfur from alkaline absorbants injected into the flue gas at a number of individual power plant boilers or industrial plants. In the process, magnesium oxide absorbs the SO_2 and converts it into magnesium sulfite, which is scrubbed from the flue gas along with the fly ash in a wet venturi scrubber. This material then would be shipped to the central processing unit where the sulfur is recovered—either in the elemental form or as liquid SO_2—for marketing; the regenerated absorbant then is recycled to the individual boilers. The central recovery process is the culmination of three years of development by Chemico; Basic's chemicals division conducted independent study on the magnesia chemistry involved.

Bureau attacks nation's solid waste

In an interview, the Bureau of Solid Waste Management's director summarizes the progress, goals, and priorities of federal activity



Richard D. Vaughan, BSWM's director

Today, the Bureau of Solid Waste Management (BSWM) is one of five operating bureaus within the Environmental Control Agency (ECA) of the Consumer Protection and Environmental Health Service (CPEHS). In fact, a solid waste health organization has been operating in the Public Health Service for the past three and one half years—originally, as an Office of Solid Waste (Washington, D.C.), then, after a reorganization, as the solid waste program of the National Institute of Urban and Industrial Health (Cincinnati, Ohio)—notes Richard D. Vaughan, BSWM's director. BSWM came into being about one year ago with the formation of the new federal agency, ECA.

Operating under the legal authority of P.L. 89-272, the Solid Waste Disposal Act of 1965, BSWM is responsible for the following functions:

- Initiating and accelerating a national R&D program with special emphasis on recovery and reuse.
- Giving financial and technical assistance to states, communities, private agencies, and the like. In the 1965 act, disposal is interpreted in a broad sense to include storage, planning, transporting, recycling, processing, and disposing of solid wastes.

In fiscal year 1969, BSWM operated at a budget level of $15.2 million; its budget request of $14.8 million for fiscal year 1970 is slightly less than last year's, Vaughan comments. Approximately two thirds—$10 million—will be allocated for grants, the remaining one third for the bureau's internal operations. At present, BSWM comprises 219 persons. The majority (170) is in Cincinnati; management personnel (26) are located in Washington, D.C.; a small research group (5) is situated in Johnson City, Tenn.; and regional office personnel (18) are located in nine solid waste field offices which correspond to the same nine areas designated for the National Air Pollution Control Administration's (NAPCA) regional activities for pollution abatement. Although the air pollution and solid waste regions in the U.S. are identical, they differ from the federal government's regions for the Federal Water Pollution Control Administration's (FWPCA) pollution abatement activities.

Priorities

BSWM's priorities for fiscal year 1970 are based on two criteria—urgent need and an apparent lack of progress in the past on certain items. The order of priorities is as follows:

- **First**—to make more progress in the reclamation of waste for recycle back into the U.S. economy.
- **Second**—to make progress in new methods for collecting and transporting solid waste.
- **Third**—to decentralize BSWM's training program, by putting it out into the field for operators and municipal officials.
- **Fourth**—to find ways to gain public support for good solid waste management practices in communities. "Unless people support and pass the necessary laws, bond issues, and the like, the U.S. will not get the job done," Vaughan warns.

National demonstrations

Demonstration grants are the largest single expenditure in BSWM's budget. Approximately 100 demonstration projects are complete or well under way, Vaughan notes. Normally, each runs for three years, with about 30 new projects started each year. Obviously, the most acute problems of accumulation of solid waste are in the high density urban centers. Still, some of the most difficult technical and economical problems are in the small communities, BSWM's director observes.

"In the demonstration programs, BSWM is looking at all types of grinders," Vaughan says. The Heil-Gondard grinder shows promise. This French hammer-mill type device is being used in a Maidson, Wisc., project to grind up all solid wastes, including glass bottles and metal cans, so that the waste can be placed directly on the land. Unfortunately, this disposal technique is more expensive than conventional landfill operations.

Other demonstration projects illustrate an economy of scale through regional operation. Several of these have been completed, Vaughan notes, including demonstrations in Des Moines (Iowa), New Orleans (La.), and the quad city area of New Jersey which includes the communities of Paterson, Passaic, Clifton, and Wayne. In these

cases, adjacent communities pool their financial resources to achieve an economy of scale. In other words, although what is the most effective solution to solid waste disposal in five cities combined may differ completely from the answer for each city separately, the answer for the five together probably will be more economical.

In a rural, sparsely settled area where it just doesn't pay to collect the waste from every house (Chilton County, Ala.), a series of containers are being evaluated under another grant. These containers replace despoiled land areas, are filled up by local residents, then the containers' contents are transported to a central sanitary landfill. Perhaps, other rural areas will find this method of solid waste handling to their advantage.

Promising leads

A number of promising leads and processes are in the forefront of solid waste technology today. These include improved methods for collection and transportation, recycling and reuse, and disposal of wastes.

Perhaps one of the most advanced engineering concepts in solid waste management is being developed under contract by Combustion Power Co. (Palo Alto, Calif.). The unit consists of a fluidized bed incinerator which burns refuse at high pressure, producing hot gases to power a turbine, which in turn drives an electrical generator. Municipal solid waste has about one third the heating value of a good grade of coal. Combustion Power's president Richard Smith estimates that five similar units could process all wastes from the city of San Francisco and that 40 units would be required to handle New York City's wastes.

Usually, railhaul of wastes is a controversial topic because of citizen objection at the receiving end, Vaughan notes. One recommendation BSWM would stress to communities interested in this method of solid waste handling is to enlist the support of these citizens before proceeding too far with plans. Personally, Vaughan thinks the public should have a voice in the decision of whether some one else's solid waste is going to be placed in their area. Unfortunately, all do not share this view.

With a research grant to the University of Pennsylvania, Iraj Zandi and his colleagues are investigating pipeline technology for application in the collection and transportation of solid wastes. The hydrodynamics of slurried solid wastes appears practical. "The pipeline method is technically feasible and economically attractive under certain conditions, including high density areas and short haul transportation," Vaughan says. Under a research contract, Stanford Research Institute (SRI) is assessing the technical possibility of an air classification process for the separation of nonhomogeneous dry solid waste materials. "With SRI's pilot scale air classification system, BSWM has had modest success in separating five materials including glass and metal," Vaughan continues. SRI's pilot plant for the recycle and reuse of waste separates the items as to size, configuration, and specific gravity.

Development of another promising disposal technique is in progress under a demonstration grant to King County (Seattle, Wash.). Here, the county has constructed a machine that will compact refuse at 200 p.s.i. and extrude the waste below ground level. In California, under a BSWM fact finding contract, Dillingham Corp. (San Diego) is examining the feasibility of ocean disposal of solid wastes (ES&T, March 1969, page 205).

"A number of private contractors are in the business and are responsible for approximately one half of the solid waste management operations in the U.S. today," Vaughan adds. These contractors include the National Disposal Services, Inc. (Barrington, Ill.), headed by John Vanderveld, Jr., and Universal Bi-Products (Sun Valley, Calif.), headed by Richard Stevens. Two additional firms that are deeply involved in this business are Zurn Industries (Erie, Pa.) and Aerojet General Corp. (El Monte, Calif.). In addition, more than 50 consulting firms are actively participating in the development of effective solid waste management systems.

Survey

As part of state and interstate planning grants, each participating state surveys existing solid waste practices within its jurisdiction. Each state is at a certain stage in its development of data. During the past three and a half years, 40 states, the District of Columbia, and three territories—Puerto Rico, Guam, and the Virgin Islands—participated in BSWM's national survey of waste disposal practices in the U.S. "Approximately half of these are well along in their respective regional surveys," Vaughan says. By the end of fiscal year 1970, this half will have completed their studies. But the final survey for the entire U.S. probably will not be ready until 1971.

Meanwhile, an interim survey has been helpful in gaining more public awareness of solid waste management problems. The report released last September covers 40% of the U.S. population on a broad geographic basis, including southern, northern, coastal, and pacific states. This summary revealed that 94% of all landfills were unsatisfactory for one or more of the following reasons:

- Landfill was not designed to prevent ground or surface water pollution.
- Landfill burned at some time.
- Landfill was not covered daily with dirt.

BSWM doesn't expect the complete study to alter significantly the conclusion of the interim report, Vaughan notes, "But one area where data may be off is in the estimation of operational figures relating to collection."

Legislation

Sen. Muskie's solid waste bill, S. 2005 (ES&T, June 1969, page 517), places great emphasis on resource recovery. Under the provisions of the proposed legislation, grants would be awarded not only to states and their agencies, but, for the first time, to local areas and regional communities. Also, funds would become available for the implementation of state plans. "Now, some of the states are past the planning stage and are ready for action," Vaughan says.

Bureau of Solid Waste Management

Richard D. Vaughan, director
Hugh H. Connally, deputy director
Richard Lonegram, assistant bureau director, Cincinnati
William Frietsch, executive officer

Divisions

Research and development—Andrew Breidenbach
Technical operations—H. Lanier Hickman
Demonstration operations—Anton J. Muhich

Offices

Information—Ralph Black
Program planning and evaluation—Richard Eldredge

BSWM's budget request for fiscal year 1970

(millions of dollars)

Grants		Federal share
Demonstration	$5.5	66⅔%
Research	2.5	Up to 100
Training	0.5	Up to 100
State and interstate planning	1.5	50
Subtotal	$10.0	
Internal operations		
Contracts	$1.5	
Internal budget	3.3	
Subtotal	$4.8	
Total	$14.8	

At the recent one day hearing on S. 2005 (Jacksonville, Fla.), testimony was received from a broad spectrum of people interested in solid waste. These 38 witnesses included conservationists, mayors, public works officials, private enterpreneurs, research professors, consulting engineers, state government officials, and the like.

A strong advocate of field hearings on legislation, Vaughan adds, "When a bill has the impact that S. 2005 would have if passed, people who would have to face this problem must have their views considered. In this way, they let the committee know how the people actually feel about the problem."

Under the 1965 act, states were awarded planning grants. Now, the proposed legislation would supplement this activity and provide additional items. But one of the prime purposes of the original legislation—at least in Vaughan's opinion—was to build strong viable state agencies. BSWM will not be satisfied with a state's plan unless that plan gives the state regulatory agency a strong arm in implementing practices. Vaughan considers this a must. In most cases, the regulatory action will involve the state department of health. In other cases, the action will involve the state resource agency, pollution control agency, or a similarly constituted agency. In each case, the governor of the state makes the decision where the regulatory agency would be placed, according to BSWM's director.

Training

Similar to other environmental areas, including air pollution and water pollution, the field of solid waste management is plagued by a lack of adequately trained personnel. To help remedy the situation, BSWM funds training programs at 10 universities. In addition, one- and two-week training courses have been made available in Cincinnati to some 1200 persons over the last three years. "We are taking city engineers and making them quite knowledgeable about solid waste management practices," Vaughan says.

"Sometimes, BSWM is thought of as a pollution control agency," Vaughan adds. "This is wrong; BSWM is a waste management organization. A pollution control agency—such as the federal agencies for air and water pollution control—is concerned with the protection of one resource," Vaughan explains. "These agencies observe all activities that adversely affect the air and water and make regulations to protect that particular resource. They get laws passed and do many of the same kinds of things as BSWM. But it's for the regulation of the kind of activities that adversely affect the resource."

"Turn this around now," Vaughan says. "BSWM is an agency with a mission to manage a particular kind of waste. In fact, BSWM operates under the following three constraints:

- To prevent degradation of our natural resources.
- To prevent a threat to public health.
- To dispose of wastes economically."

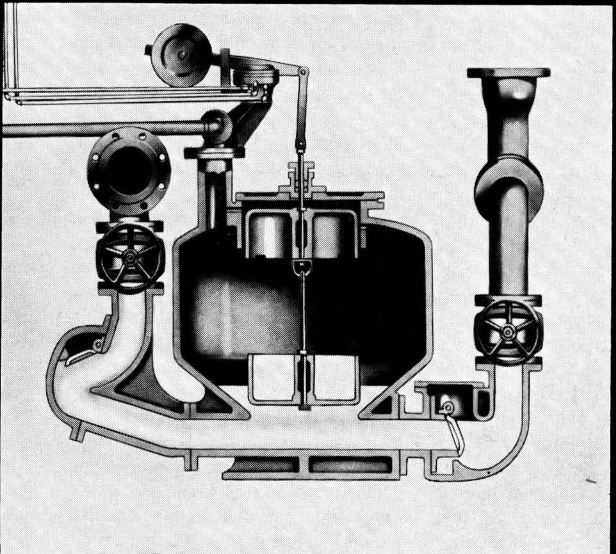
One example of BSWM's concern for public health is illustrated by the fact that, from a health standpoint, collection of solid waste by sanitation workers has been found to be one of the most hazardous occupations of any in the U.S., according to survey statistics of the American Public Works Association and National Safety Council. "For example, it is more hazardous than underground mining," Vaughan comments. "Actually, BSWM is interested in verification of these statistics and the development of positive action programs to reduce this accident rate. In this case, BSWM is actively pursuing this problem with occupational health and accident prevention agencies of the Public Health Service."

Other federal agencies

Other federal agencies and departments also are involved in the solid waste problem. Although some overlap of BSWM's program with those of other federal agencies is apparent, a forthcoming report of the Office of Science and Technology will recommend national solid waste R&D needs and make recommendations concerning them.

For example, under the 701 Grants Program, the Department of Housing and Urban Development (HUD) awards grants to communities for planning solid waste disposal systems. Agriculture, another federal department, is concerned with disposal of feedlot wastes. Interior, specifically FWPCA, concerns itself with preventive water pollution practices. Department of Defense installations have solid waste management problems since they must handle their own wastes.

BSWM is concerned with agricultural wastes when the agricultural waste problem adversely affects a community. When the feedlot becomes a community problem, BSWM looks for ways to effectively handle this kind of waste. Lacking any interagency group to exchange information, BSWM provides its expertise to other federal agencies on a consultative basis as needed, Vaughan comments. BSWM also serves as a consultative organization, providing technical information and advice to other federal, state, and local agencies when called upon to do so, Vaughan adds.



Waste waters yield to new development

Industrial and municipal waste waters have characteristic fingerprints which can be used to trace the sources of pollution in the nation's streams

Not only can specific water pollutants be detected, but now their point of origin can be traced with an advanced analytical instrument. The pyrographic analyzer provides unmatched chemical information necessary in water quality control, according to findings at the Federal Water Pollution Control Administration's (FWPCA) Southeast Water Laboratory (Athens, Ga.). Developed by the Rocketdyne Division (Canoga Park, Calif.) of North American Rockwell Corp. under an FWPCA research contract, the instrument serves to identify trace organics such as oil, pesticides, and the like in waste waters.

"The pyrographic method represents a dramatic departure from conventional analytical techniques which are normally carried out on a molecular level," says David W. Duttweiler, director of the Southeast Water Laboratory. "The enormous variety of pollutants that exist in the nation's streams have far outstripped the ability of conventional analytical procedures to adequately identify and quantify them. Time and manpower limitations dictate that faster, more comprehensive techniques be developed for routine monitoring as well as for special investigations."

Based upon a concept first proposed by Rocketdyne's Ihor Lysyj at a 1968 symposium on organic matter in natural waters (University of Alaska), the instrument is used for the direct analysis of multicomponent organic constituents in a water matrix. The method can be used for the gross characterization of water sources.

Operation

Following the controlled pyrolysis of organic pollutants in water samples, the unit's operation includes the following functions:

- Separation of the resulting products of pyrolysis by gas chromatography.
- Detection of eluted fractions by hydrogen flame ionization.
- Mathematical interpretation of the resulting pyrograms.

A waste water sample—without any special preparation—is injected directly into the unit's pyrolysis chamber which is maintained at a regulated temperature (800° F.) and constant steam flow. The use of steam as the carrier gas for the pyrolyzate allows the injection of large water samples, resulting in a high detection sensitivity. The sensitivity of the pyrographic technique was proved satisfactory at a concentration level of a few parts per million. The pyrograms obtained with the instrument are distinctive fingerprints of water pollutants.

Each industry discharges a waste having a composition distinctive to that industry's operation. These unique compositions offer a means for characterizing and tracing organic pollutants to their source. The composition of municipal wastes differs from that of industrial wastes, and these sources also can be distinguished and traced.

Field study

"Earlier this year, the prototype unit was field tested jointly by FWPCA and Rocketdyne personnel," says H. Page Nicholson, chief of water contaminants characterization research at the Southeast Water Laboratory. "The Middle Oconee River (Jackson County, Ga.) was chosen as the test site because of a favorable combination of pollution sources."

"Located in the headwaters area is a poultry processing plant that treats its wastes with aerobic and anaerobic ponds before release. About a mile downstream is another poultry plant that discharges untreated wastes, and still further downstream a textile mill," Nicholson elaborates.

This preliminary investigation indicates that new techniques apparently can be used to assess a number of aspects of such a water pollution situation. These include:

- Identification of the contributions made by the several upstream sources to the total pollution load.
- Detection of changes in water quality resulting from the various pollutants.
- Elucidation of the chemistry of anaerobic and aerobic waste treatment processes.
- Detection of incipient septic conditions in the river.
- Characterization of the chemical changes preceding and accompanying anaerobic and aeroic reversals in water bodies. More extensive examination of the river is planned later this year.

Ultimately, the pyrographic technique can be used in automatic monitoring systems. Then, pyrographic data on the waste composition of waterways can be telemetered to a central FWPCA facility for computerized data analysis and interpretation. Industries can benefit by having continuous control of the quality of their waste discharges.

Outfall. *Water effluents can be monitored under field conditions*

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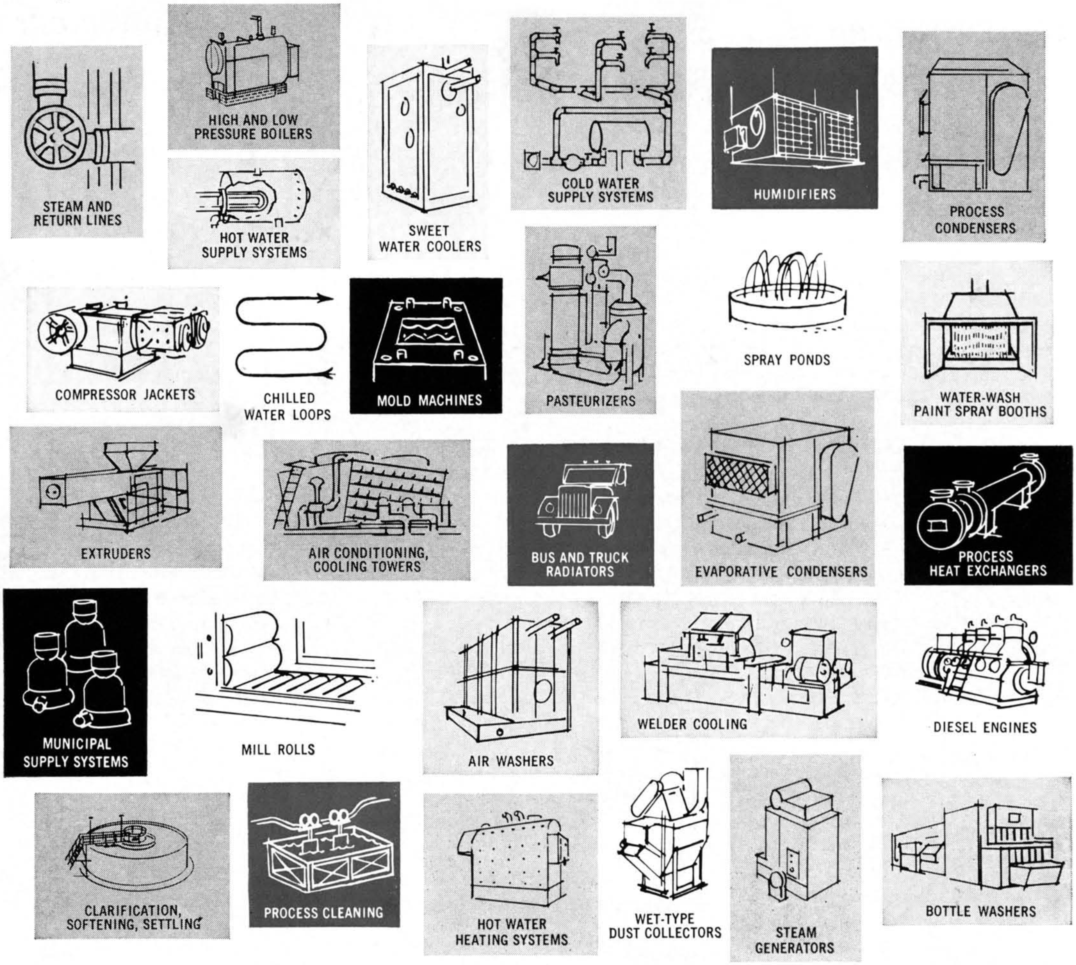

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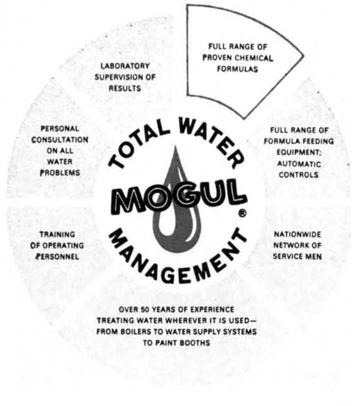

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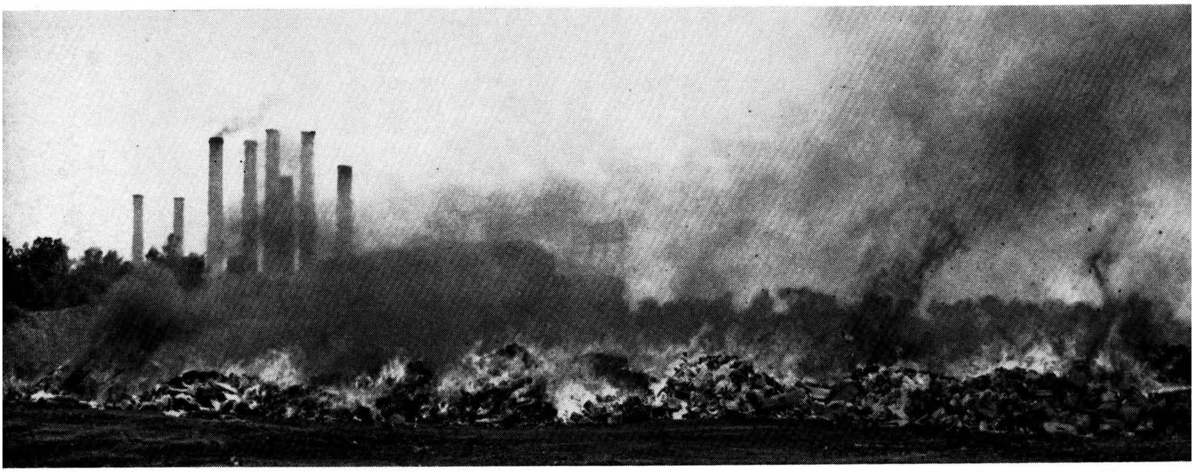
Open fires: a necessity?

The trend is away from open burning of solid wastes but, sometimes, there is no alternative



Open burning on a dump provides modern man with one of the most irritating eyesores imaginable. Moreover, this method for disposing of solid wastes is just as inefficient as it appears to the onlooker with smarting eyes. It is not possible to enumerate exactly the amount of particulate matter put into the air by the average open burning site, but 20 pounds per ton of solid waste probably is representative.

At the 62nd Annual Meeting of the Air Pollution Control Association (APCA) held recently in New York, air pollution officials from New York City and the San Francisco Bay area named some of the reasons why open burning still is practiced, even though it was roundly condemned by almost everyone years ago.

New York City experience

The basic problem in New York City, according to Harold Romer of the city's Department of Air Resources, stems from the city's characteristic frenetic building activity which produces huge quantities of oversized burnable demolition waste. In recent years, the waste has been loaded onto barges and burned in lower New York Bay. Disintegrating piers and other waterfront structures present still another disposal problem. In May 1967, New York City prohibited all open burning. A crisis quickly developed; barges laden with oversized wastes lined New York's docks, representing a somewhat ironic but, nevertheless, very real fire hazard. To avert the danger, the commissioner of the Department of Air Resources issued a temporary permit authorizing open barge burning in the lower bay.

The commisioner really had no choice since there is, at present, no practical alternative to open burning of oversized wastes. Shredding and cutting would enable the waste to be burned in municipal incinerators, but the nature of structural materials makes them extremely difficult to cut. Temporary storage at landfills also is unsatisfactory, because compaction of the waste is so hard to achieve. Properly designed open pit burning would be an acceptable solution to the problem, Romer opines. However, proper design has yet to be developed, although open pits produce smaller amounts of particulates than open dump or barge burning.

Bay area experience

In the San Francisco Bay area, one factor that is not present in New York enters the open burning picture—a sizable agricultural industry. More than a million acres in the bay area is agricultural. Open burning of crop stubble, orchard prunings, and range brush are commonly carried on, and weed control by burning is practiced, though this is giving way to chemical treatment.

H. C. Johnson of the Bay Area Pollution Control District said at the APCA meeting that, on Jan. 1, 1970, when all backyard burning in one- and two-family homes is prohibited, essentially the only open burning permitted will be agricultural. (There are some other exceptions, such as fire fighting instruction.) But in 1970, open burning is expected to contribute only 3-4% of particulates in bay area air.

Guidelines for open burning

Wherever it is practiced—in New York, or San Francisco, or elsewhere—it is likely that open burning will be permitted only under certain conditions. Typical of these are:

- Winds strong enough and in the right direction so that smoke is carried away from inhabited areas.
- No inversion conditions; days in which winds at higher altitudes are stronger than those at lower altitudes are the best.
- Burns to be started early in the day, so that fire can be subject to continuous surveillance and can burn out before sundown.

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Polymers vie for water treatment role

Polyelectrolyte use growing slowly, but optimism abounds

The emphasis on secondary treatment of municipal waste water inherent in federal water quality acts and pollution abatement enforcement conferences has been expected to have a significant effect on the demand for waste water treatment equipment and chemicals. But, in at least one area—the use of synthetic polymer flocculants, or polyelectrolytes—the boom has been rather slow in developing. Or, at least, somewhat slower than was expected 15 years ago, when these materials were introduced into the market as competitors to conventional inorganic coagulants.

To be sure, most industry observers agree on one point: The potential for increased use of polymeric flocculants in new treatment plant construction and in upgrading existing plants is considerable. To what extent, and how soon, the industry can effectively capitalize on this depends on a number of factors, some economic and some technical, some obvious and some subtle.

ES&T's first control directory (October 1968, page 799) lists more than 30 manufacturers of flocculant chemicals; a spot check of some of the firms that produce polymeric flocculants reflects the enthusiasm that prevails in these quarters. Dow Chemical, one of the earliest entrants into the field of synthetic polyelectrolytes, optimistically points to the recently released results of a Federal Water Pollution Control Administration (FWPCA) sponsored field test of polyelectrolytes in which Dow cooperated by supplying materials and technical assistance. Dow's R. G. Schuessler comments further that, although the market has been slow in developing, the future for these materials still looks bright. Basil Q. Welder, director of marketing for Calgon's water management division, points out that his company's production and sales volume of these materials have been increasing significantly. "There's no doubt that polymers will make significant contributions to water treatment capability, both in primary and secondary phases of conventional treatment plants and in advanced treatment methods," Welder says.

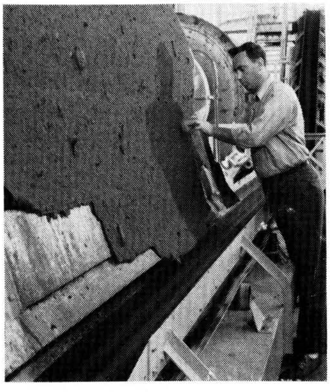
← Circle No. 31 on Readers' Service Card

There are also other indirect signs of optimism in the wind. National Starch and Chemical recently put on stream (Meredosia, Ill.) a new unit for manufacturing polyelectrolytes for municipal and industrial waste water treatment. In June, Vistron Corp., the chemicals division of Standard Oil Co. (Ohio), began production of acrylamide (a raw material for one class of polyelectrolytes) at a 15-million-pound per year plant (Lima, Ohio). Vistron's product supervisor, Tom Roth, singles out waste water treatment as the most attractive outlet for polyacrylamide, and he expects the market for this polymer to grow as much as 15% in the next five years.

Separation aid

Polyelectrolytes are used in waste water treatment as coagulants, or flocculating or filtering aids in carrying out the solids-liquid separations basic to primary solids removal and secondary biological treatment. Alum, ferric chloride, and lime have, up to now, dominated this field—one estimate is that only 5–10% of U.S. municipal waste treatment plants use polymeric coagulants.

Natural polymers, such as gum, proteins and starches, have been, and still are, used as flocculating agents, but the commercially more important types in waste water applications are synthetic polymers. The list of those available includes high-molecular-weight polyamines, polyacrylamides, polyalkyleneimines, and polyacrylonitrile.



First step. *Coagulation usually precedes vacuum filtration*

The most useful way of classifying polymeric flocculants is according to the electrical charge which the polymer molecule carries—which, in turn, determines the type of application for which the coagulant is best suited. Thus, cationic (positively charged) polymers generally are used for sludge conditioning prior to dewatering by vacuum filtration or other means, whether in primary or secondary treatment. Anionic polymers (negatively charged) are used as solids coagulants or settling aids in primary treatment. Nonionic polyelectrolytes which carry no net electrical charge have been developed and are available, but are used chiefly in treatment of water supplies, and find little or no waste water applications.

Theory

The exact mechanism by which flocculants perform their function is not definitely known; in fact, flocculation theory is perhaps one of the most fertile fields of waste water research. Two possible mechanisms have been proposed:

- **Charge neutralization,** in which the mutually repulsive electrostatic surface charges of the solid particles—called the Zeta potential—is counteracted. This allows inherent, but weaker, cohesive forces—known as Van der Waal attractions—to cause the particles to adhere to each other and agglomerate.
- **Particle bridging,** in which the polymers form a link between two or more solid particles at active sites along the polymer molecule. The active site may be caused by hydrogen bonding, chemical reaction, or electrolytic attraction.

Both of these mechanisms can be expected to be affected by such factors as particle sizes, concentration, pH, ionic strength, and other external forces in the solid liquid suspension. Thus, such matters as predicting whether polymeric flocculants will be effective in a given situation and choosing among the several types of available materials are difficult questions; by the same reasoning, the broader question of the ultimate impact of polymeric flocculants in the whole waste water field is highly problematical.

Whatever the operative mechanism, the main advantage of polymeric flocculants is their efficiency. Not only can greater solids separation be obtained in many cases, but the materials are effective at much lower dosages—as little as 20%—of that required with inorganic flocculants. Net result is a considerable savings in capital costs through a reduction in size of the sludge handling and treatment equipment required. Disposal problems are reduced also, since the amount of flocculant added ultimately increases the amount of sludge that accumulates. Where sludge is disposed of by incineration, polymers have an added advantage, since inorganic flocculants add to the amount of residual ash from the incinerator.

The major disadvantage in the use of polyelectrolytes is their cost. Prices for these specialized polymers often run between $1.00-2.00 per pound; conventional inorganic flocculants are available for literally pennies per pound.

Field studies

One example that illustrates the potential advantages of polymeric flocculants is the FWPCA study at Cleveland's 125-m.g.d. Easterly treatment plant. During a nine month evaluation of the use of polyelectrolytes in primary clarification, among the processing improvements noted were a 57% reduction in biological oxygen demand (BOD) in the first stage, a $3300 per month saving of aerator power cost—enough to pay 25% of the cost of the chemicals used—and a one third reduction in secondary effluent BOD. In discussing these results at a recent water treatment symposium, Dow's Schuessler projects that adding polymer treatment to the existing plant can effect the same degree of treatment as a planned expansion of Easterly's primary clarifiers; the annual operating cost for polymer treatment would be only $160,000, compared with $315,000 per year which will be required for amortizing the capital cost of the planned expansion.

Water treatment officials elsewhere are not so optimistic; one municipal treatment plant recently ran an evaluation on representative types of polyelectrolytes. Among the results, which have yet to be formally released, is this conclusion: Although some increased efficiency was achieved in the primary treatment step, the overall result in secondary effluent quality was not sufficient to justify the cost. Thus, as is evident in these two examples, the case for polymeric electrolytes is not at all clear-cut. Whether to use the electrolytes in a given application depends on balancing their high cost against a number of technical factors, including the characteristics of the waste to be treated, the specific design of the treatment plant, and the local water quality standards to which the effluent must conform. But, generally, the issue boils down to higher operating costs (in the case of polymers) compared with higher capital costs (in the case of the conventional flocculants).

Construction costs

Although the demand for water treatment equipment and supplies triggered by federal water quality legislation remains somewhat firm, some observers comment that the demand could be much greater were not the federal government lagging in fulfilling its commitments on grants for sewage plant construction. Over and above this general consideration, there are other effects of a slowdown in treatment plant funding on the future of polyelectrolytes. Most of the federal and state money available to municipalities for water treatment is tagged for meeting capital costs. Some states and FWPCA reportedly are considering making grants available to municipalities for operating costs. Most agencies are forced to run their plants with local funds. Thus, in preparing applications for grants for new facilities, or for upgrading existing ones, municipal plant operators naturally would be tempted to choose a process design in which the greatest share of the overall costs would be eligible for state or federal funds.

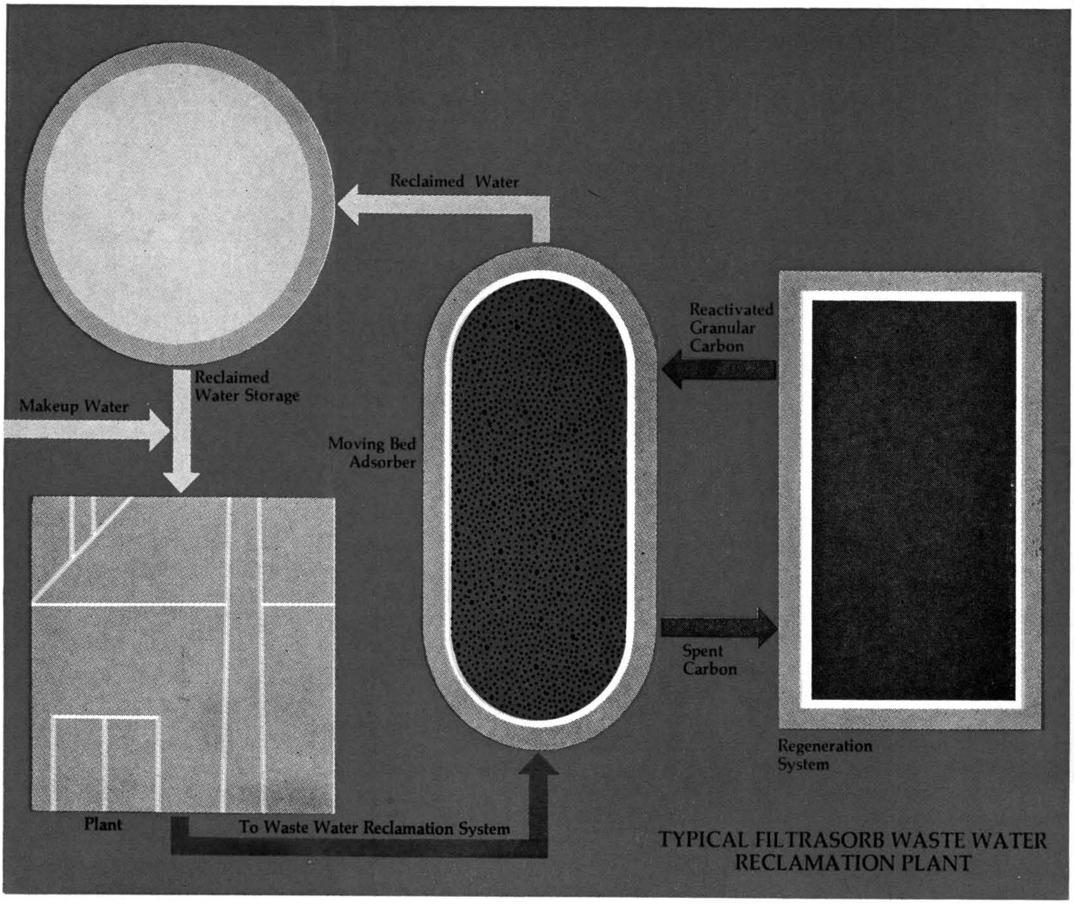
However, there are a few bright spots in the demand for polymeric flocculants. As in the Easterly plant, polymers can be useful in upgrading existing inadequate facilities to meet more stringent water quality standards, until more grants become available. However, the major impact in this regard will be in those communities which provide for little or no secondary treatment. Another area where polyelectrolytes show some promise is in the emphasis on phosphate removal from secondary effluents. Most phosphate removal processes rely on chemical precipitation of the phosphate, and polymeric flocculants can be useful in facilitating removal of the precipitates from the effluent.

Finally, polyelectrolytes may see significant service in advanced waste treatment applications. In this regard, Calgon's Welder mentions a 10 m.g.d. polymer/carbon process being designed by Calgon for construction at the Rocky River, Ohio, waste treatment plant. The basic feature of this process is the use of carbon adsorption in the place of conventional biological secondary treatment; but pretreatment of the waste stream with polymeric flocculants is a key step.

Industrial waste

Relatively speaking, synthetic flocculants have perhaps made greater inroads in industrial waste treatment than in municipal treatment. Flocculation, of course, has been a basic processing step in many manufacturing operations—mainly metal refining, pulp and paper manufacture, and chemicals and food processing—and it is natural that industrial firms would turn to flocculation technology to solve their own waste water treatment problems. This is particularly true in those cases where the materials can be obtained from captive sources. Furthermore, the funding of industrial waste treatment plants is not subject to the same constraints as municipal plant financing. Thus, industrial waste treatment plant designers are more sensitive to reducing overall treatment plant costs than to whether the saving is in capital investment or operating costs.

Thus, polymeric flocculants may be a far cry from the instant abatement possibilities which some proponents claim for them. They do, however, present another example where modern technology—in this case, polymer development and colloid theory—and the lure of a sizable commercial market can play a significant role in the problems of pollution abatement. For example, two Great Lakes abatement programs already include timetables for 80% phosphate removal from all discharges to the lakes.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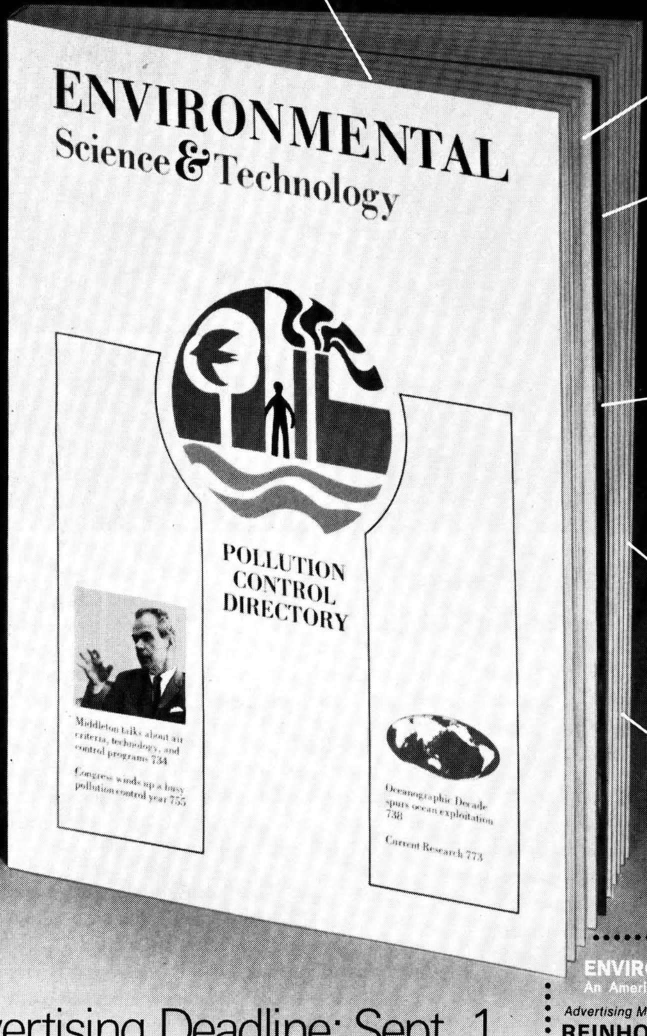

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Vegetation tames mine and smelter wastes

Chemicals, plants, team up in solid waste technique

Mine and smelter wastes, a 1.1 billion ton per year headache for the basic minerals industry, can generate severe pollution burdens. Winds can tease large quantities of air polluting dusts and particulates from mill tailings, and rainfall often leaches stream polluting acids from mine wastes. In the U.S., a major effort at coming to grips with the problem of mineral wastes is being undertaken by the Bureau of Mines, which was given this responsibility under the 1965 Solid Waste Disposal Act. Last month at the 16th Ontario Industrial Waste Conference (Niagara Falls, Ont.), Karl Dean, project supervisor of the bureau's mineral waste stabilization and utilization program at Salt Lake City, Utah, gave some insight into the progress being made on this problem.

The bureau's program includes some limited work on utilization of mineral wastes, but these approaches can be expected to be only marginally successful, and even then could not accommodate the total amount of waste generated. Thus, the major stress is on preventing these materials from becoming pollution sources.

Plants and chemicals

In this respect, the most innovative approach has involved a combined chemical-vegetative stabilization procedure for the mine wastes. Dean and two fellow workers at the bureau, Richard Havens and K. T. Harper, have successfully demonstrated such a procedure on a test plot of copper mill tailings at McGill, Nev. Key to the project is the selection of plant species adaptable to the prevailing climate of the area and the soil medium presented by the tailing wastes, and chemical treatment of the wastes to make them more suitable for germination. In the two years since an experimental plot was treated, the test area has been well stabilized against wind and water erosion, and vegetative cover appears capable of self-perpetuation. Total cost of the method offers no barrier to widespread use of the technique.

The problem of mine and mineral wastes is not a regional or local concern, but is truly national in scope. A 1965 land survey by the Department of Agriculture shows that the U.S. contains 2 billion acres of land that have been despoiled by surface mining. The problem is more serious in some areas than in others—the coal and iron mining regions of Pennsylvania and West Virginia, and the phosphate fields of Florida, for example—but, still, it is of some concern in almost all the states; half of them have more than 20,000 acres that could benefit from effective reclamation techniques.

Test project

Copper millwaste, the subject of the Bureau of Mines' McGill study, presents a serious problem, since the copper content of most ores being processed is so low that more than 98% of the ore mined must be disposed of after processing. Partly for this reason, copper mill tailings account for 40%—about 462 million tons per year—of the total mineral waste problem. At the Kennecott copper mill, where the bureau program was conducted, the tailings pond area comprises 3900 acres of waste.

Vegetative stabilization of these tailings had been attempted by Kennecott intermittently since 1946, without much success. Most of the failure occurred because of the abrasive action of airborne sand particles which buried the plants or cut them off at ground level. Thus, about two years ago, the Bureau of Mines set out to investigate chemical stabilization techniques which would control the sand movement until vegetation they had planted could take hold.

The McGill tailings, like most mineral wastes, contain no nutrients, have poor soil texture, and many fines. Thus, the major phase of the project involved evaluating chemical soil stabilizers that could overcome these factors. Previous work had shown that many materials, including cement lime, silicates, bituminous derivatives, and synthetic polymers were effective for stabilizing the tailing wastes, but most of these either were not compatible, or interfered with vegetative growth. Several water soluble elastomers proved effective but a commercial resinous adhesive reagent was selected as the cheapest material.

Various plant species also were evaluated for their effectiveness in providing vegetative stabilization. Winter wheat was chosen to supply a fast growing cover to supplement the effect of the chemical stabilizer; legumes were used because of their ability to fix atmospheric nitrogen; the Siberian pea tree was selected as a shrub-type plant to act as a windbreak;and wheat grasses were added to bind the soil and provide a permanent cover.

Evaluation of results of the chemical-vegetative stabilization project thus far indicates that the primary objectives of the program have been met. The stabilized tailings have been fully resistant to wind and water erosion, despite the many violent wind-thunderstorms which occur in the area. The vegetative cover requires no irrigation for two years; amount of fertilization required is still being studied.

Costs of the technique are reasonable. At the outset of the project, a liaison committee comprised of representatives of the mining industry had cited $250 per acre as a reasonable cost. Total costs of the McGill experiment were $135 per acre, which could be reduced if larger acreages were treated or suitable equipment was readily available.

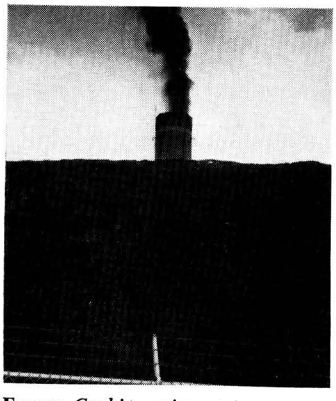
Wastes. *Copper mill tailings are largest share of mineral waste problem*

Can coal burn cleanly?

Within several years, new coal combustion and electricity generation processes promise reduced burdens of SO_x, NO_x, and waste heat

What effect some promising processes hold for reduction of pollution burdens from fossil fuel electric generating stations only time can tell. But fluid bed combustion of coal in electric generating stations promises greater SO_2 and NO_2 reductions than conventional operations. Magnetohydrodynamics may one day reduce the thermal pollution burden.

Fluid bed combustion of coal, the subject of the recent agreement between the U.S. and the United Kingdom (ES&T, July 1969, page 615), offers the potential for enhancing the use of coal, one of the most important energy resources in the U.S. British investigators already have accumulated a considerable amount of technological know-how on the subject. Lord Ro- a liaison committee comprised of rep- bens, National Coal Board chairman, noted that the board annually spends $1.5 million on R&D related to the fluid bed combustion process.



Energy. *Coal is a prime source*

Three combustion leads

Fluid bed combustion of coal operates at temperatures from 1400-1900° F.—an optimum range for reaction of limestone with SO_2—so that limestone additives for SO_2 emissions control should be especially effective. This operating temperature is substantially below peak flame temperatures in conventional boilers. Furthermore, long periods of effective contact between the limestone and SO_2 can be maintained. Perhaps, combustion systems may be designed to minimize the formation of nitrogen oxides.

In 1964, fluid bed combustion studies began at the British Coal Utilization Research Assoc. laboratory (Leatherhead, Eng.) Scaleup now is proceeding on two systems, both of which have coal firing rates of 800-1000 pounds per hour. The first, a small industrial shell-type (fire-tube) boiler, generates approximately 8000 pounds of steam per hour. The second, a pressurized unit, operates at five atmospheres, and will provide intermediate pilot plant data for a pressurized utility boiler which would be coupled with a gas turbine. These units promise sufficient engineering data for larger demonstration plants.

At the Coal Research Establishment (CRE) (Stoke Orchard, Eng.), fluid bed combustion studies began in 1966. By the end of 1969, CRE will have spent $3 million on the project.

At Esso Research and Engineering, Ltd. (Abingdon, Eng.), studies with limestone additive for SO_2 capture were undertaken about three years ago. Esso's work demonstrated the feasibility of limestone sorption under the following circumstances:

- **Oxidizing conditions** followed by reduction of the calcium sulfate to produce SO_2 and lime for reuse.
- **Reducing conditions** to form calcium sulfide followed by steam regeneration under reducing conditions to produce H_2S and lime for reuse.
- **Reducing conditions** to form calcium sulfide followed by regeneration of the calcium sulfide with air to produce SO_2 and lime for reuse.

Magnetohydrodynamics

A promising technique which coal-fired electric utilities may eventully find useful for thermal pollution abatement is magnetohydrodynamics (MHD), a term used to describe those electric generating systems which obtain power from conducting fluids as they move through magnetic fields. In addition, lower thermal pollution burdens are another benefit MHD promises for central stations power, according to a report, "MHD for Central Station Power Generation: A Plan for Action."

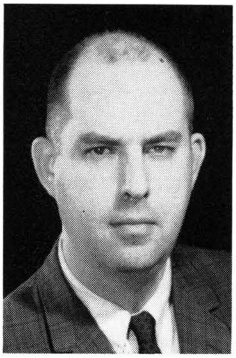
Prepared by a special Office of Science and Technology (Washington, D.C.) panel under the chairmanship of Louis H. Roddis, vice chairman of Consolidated Edison Co. (New York City), the report notes that MHD also offers the promise of improved efficiency and lower fuel costs in future central station power plants using fossil fuels. But additional research is needed before constructing a large prototype facility; this research would cost $2 million per year, and probably would take three years.

However, MHD's potential is considerable. For example, fossil fuel MHD would realize a savings in fuel of about one third, the panel concludes. Furthermore, MHD plants are predicted to achieve overall efficiencies of 50-60%. In comparison, the best fossil fuel cycles today operate at 40% efficiency, and nuclear powered ones at 33%.

An increase in thermal efficiency from 40% to 50% reduces the heat rejection per unit power output by one third, and an increase from 40% to 60% reduces heat rejection by 55%. Since conventional fossil fuel plants, and those with MHD topping cycles, will discharge roughly equivalent fractions of heat up the stack, the reductions in cooling water requirements are correspondingly large percentages. This reduction in heat rejection could mean a corresponding increase in power generating capacity that can be served by a given source of cooling water.

The question of air pollution and MHD operation is complex. Unfortunately, MHD's very high combustion temperature (4800° F., compared with conventional type boiler temperature of 3100° F.) produces more polluting oxides, not fewer, according to the report. So, gas cleaning appears to be an important requirement; sale of acid products could pay for cleaning.

Fluoride criteria for vegetation reflect the diversity of plant kingdom



D. C. McCune
Boyce Thompson Institute for Plant Research, Inc.

Discussion by:
R. H. Daines
Rutgers University
H. R. Hickey
Resources Research, Inc.

Air quality standards are a part of our present mandate to apply science and technology to the improvement of our environment. The selection of reasonable and adequate standards will depend on the development of air quality criteria that are useful and accurate summaries of our present scientific knowledge. The enforcement of standards will require the use of reliable air monitoring methods. Thus, the immediate technical significance of air quality standards lies not so much in the standards themselves as in the solution of technical problems that must precede and accompany them.

There are at least three areas in which problems will be met in the development of criteria and the application of standards:

- The nature and occurrence of the pollutant.
- The effects of the pollutant on a receptor and the factors that determine the dose-response relationship.
- The characteristics of present air monitoring techniques.

Atmospheric fluorides present specific problems in each of these areas, and illustrate some problems of general significance with respect to the effects of air pollution on vegetation.

Atmospheric fluorine is an omnibus term that commonly refers to various airborne fluorine-containing materials. Various emissions studies and analyses indicate that both gaseous and particulate fluorides can be present in the atmosphere. The gaseous fraction may comprise one or more compounds, while the particulate fraction may vary both in chemical composition and particle size. This heterogeneity of the pollutant implies variability in its potential effect on vegetation, because phytotoxicity is determined by physical and chemical characteristics. The limited information on particulate size is unknown, but cryolite particles greater than 0.5 μ in size have not damaged plants and, in general, the toxicity of particulate fluorides is probably related to solubility and characteristics of the ionic species.

Obviously, it could be difficult to devise a standard for atmospheric fluorine, but this problem is only apparent. The preponderance of data on the effects of atmospheric fluorine on vegetation has been obtained from experimentation with HF. Other gases, such as F_2, SiF_4, or H_2SiF_6, have been used occasionally, but they appear to be as toxic as HF. Thus, criteria can be established only for gaseous fluorides; but since these are the more important pollutants, the criteria should suffice. Conversely, standards that would consider total atmospheric fluorine might not be adequate nor scientifically based. The major problem, therefore, is the establishment of air monitoring techniques that can discriminate between particulate and gaseous forms, if the air quality standards are to be meaningfully evaluated and enforced. It would also seem unwise to assume that gaseous fluorides are a certain fraction of the total, if changes in industrial operations or the intervention of atmospheric processes affect the composition of the pollutant.

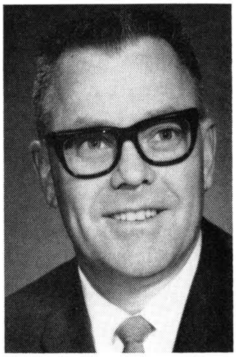
Distribution

The temporal distribution of atmospheric fluorine is another important factor in the development of criteria and standards. Estimates of atmospheric pollutant levels generally follow a log-normal distribution in urban areas; this is also true for fluorine. However, H. Stratmann has suggested that distributions for emission concentrations could range from the normal to the negative binomial, and there are few published data upon which postulates can be based concerning the distribution of fluorine. Moreover, it is possible that estimates of fluorine concentrations will reflect the distribution of analytical and sampling errors as well as the variability introduced by meteorological factors and operations of the source. It can be assumed that vegetation will be exposed to fluorine in recurrent periods of varying concentration and duration, although the exact distribution of fluorine is unknown.

Criteria or standards should consider three parameters—concentration, duration, and frequency—if they are to be soundly based. Unfortunately, published data on the effects of fluorine on plants are neither explicit nor abundant enough to allow this type of formulation. Much of our knowledge comes from continuous or intermittent fumigations at a constant concentration of HF or from exposures where only a weighted mean concentration is reported. Two approaches have been taken to collate these types of data for the effects of SO_2. The frequency of

(*Continued on page 727*)

Levels of toxicity to animals provide sound basis for fluoride standards



James L. Shupe
Utah State University

Discussion by:
L. V. Cralley
Aluminum Co. of America
John P. Jewell
Monsanto Co.

Fluorine is universally present in varying amounts in soils, water, atmosphere, vegetation, and animal tissues, and because of its reactivity, is found in a combined (fluoride) form. Livestock normally ingest variable amounts of fluoride, but no adverse effects are known to accompany low level ingestion. However, as long as the animal continues to ingest a constant or increasing amount of fluoride, it accumulates in mineralizing tissue. If amounts above the tolerance level (which varies with interacting factors) are ingested for long periods, fluorine toxicosis, or fluorosis, may result.

Fluorosis now can be correctly diagnosed and evaluated by qualified individuals, and many of the problems associated with fluorides and fluorosis in the past can be evaluated, controlled, and prevented. Proper differentiation between resultant economic and noneconomic effects, however, can be accomplished only by persons thoroughly familiar with the symptoms and lesions associated with fluorosis. The diagnostician must be able to differentiate the symptoms and lesions of this disease from similar ones characterizing other diseases.

Excessive atmospheric contamination by fluoride is relatively easy to recognize; however, it may be difficult to pinpoint the specific sources. Airborne materials are continually subject to variable winds and other atmospheric factors, and a given output of air pollutants may be hazardous only periodically and may not always be uniformly distributed. Thus, emission and ambient air analyses do not provide an accurate basis for evaluating the degree of fluorosis in livestock. Careful, comprehensive, and standardized sampling procedures are needed for accurate evaluations of atmospheric pollution within a given area.

Fluoride sources

Various sources contribute to the total fluoride intake of animals:

- Forage subjected to airborne contamination from industrial areas.
- High-fluoride water.
- Feed supplements and mineral mixtures rich in fluoride.
- Vegetation grown on high-fluoride soils.

Elevated levels of fluoride in vegetation usually result from excessive atmospheric fluorides which may be deposited on the surface of the vegetation. Hydrogen fluoride and silicon tetrafluoride are two phytotoxic gases encountered in atmospheric pollution. Particulate fluorides are more likely to accumulate on vegetation surfaces than gaseous fluorides; however, the particulates are usually relatively inert. Surface contamination may also occur when fluoride-laden dust or mud are deposited on vegetation. Some of the fluorides deposited on vegetative surfaces are removed by rainstorms; but in correlating and evaluating vegetative fluoride analysis with fluoride-induced symptoms and lesions in animals, one must consider that animals normally ingest unwashed vegetation.

Results of controlled fluorosis experiments and clinical experience with more than 77,000 animals in enzootic fluorosis areas confirmed that various factors govern the reactive processes of animals ingesting fluorides. The governing factors are: level or amount of fluoride ingested; duration of ingestion; type and solubility of fluoride ingested; age of animal at time of ingestion; level of nutrition; stress factors; and individual biological response. In turn, these factors are influenced by the variable responses they elicit from the body, such as elimination of fluoride in the urine, deposition of fluoride in mineralizing tissues, and reduction of fluoride intake because of anorexia.

Species

Since most cases of fluorosis of livestock in the U.S. have occurred in cattle, the majority of the fluoride studies in this country have involved cattle. Recent studies, however, have cited fluoride tolerances for sheep, swine, and turkeys. Varying degrees of fluorosis in horses have been observed in some enzootic fluorosis areas where cattle evidenced marked to severe fluorotic lesions. Other studies now underway are correlating fluoride tolerances for horses with fluoride-induced responses.

Normally, birds are more resistant than mammals to the toxic effects of fluoride ingestion. Rodents tend to be more resistant than larger animals on a body weight basis, while omivores are more resistant than herbivores. Fluorosis has also been noted in such wildlife as deer, elk, and fish, and in wild animals that have access to hot spring waters which may possess high fluoride content.

Diagnosing fluorosis

Fluoride has definite beneficial effects when ingested in small amounts, but adverse or toxic effects when ingested in excessive amounts, depending upon the interaction of the seven governing factors previously listed. Clinically, fluorine toxicosis is usually seen in two forms, acute or chronic.

Acute fluorine toxicosis most commonly results from accidental ingestion of high levels of fluorine compounds. The common sources of such livestock poisonings are rodenticides, insecticides, ascaricides, and water, vegetation, and feeds containing excessively high levels of fluoride.

Several different types of toxicologic responses may be seen. Signs of acute poisoning may appear one half hour after ingestion. The following symptoms usually are observed: excitement, high fluoride content of blood and urine, stiffness, anorexia, reduced milk production, excessive salivation, nausea, vomiting, incontinence of urine and feces, clonic convulsions, necrosis of mucosa in the digestive tract, weakness, severe depression, and cardiac failure.

Chronic fluorine toxicosis is the type most often observed in livestock, and complete understanding of its manifestations is essential to a correct diagnosis of the disease.

The onset of chronic fluorosis is insidious and often may be confused with chronic debilitating diseases such as osteoarthritis (degenerative arthrosis). In addition, each affected animal may have an individualized biological response. It is impossible, therefore, to define a precise point at which excessive continual consumption of fluorine induces a case of chronic fluorosis. The tolerance level may vary slightly in individual cases. In some cases the time lapse between ingestion of fluorides and manifestation of the symptoms of chronic fluorosis complicates the clinical picture.

No single criterion should be used in diagnosing and evaluating fluorosis, but the following symptoms and lesions are of particular importance:

- Mottling and abrasion of teeth.
- Degree of osteofluorosis.
- Intermittent lameness.
- Abnormal amount of fluorine retained in the bone.
- Abnormal amount of fluorine in the urine.

All findings must be carefully evaluated and interrelated before diagnosis and evaluation of fluorosis.

Dental lesions

One of the most sensitive reactions of the body to fluorine toxicosis occurs in the teeth. Fluorotic dental lesions are induced during tooth development and indicate the level of fluoride ingestion during the formation of enamel (amelogenesis) and dentine (dentinogenesis). Affected teeth erupt with characteristic fluorotic lesions such as mottling, staining, hypoplasia, and hypocalcification, and are more susceptible to excessive abrasion.

Both enamel and dentine are affected by elevated levels of fluoride ingestion during the formative stages of the tooth. When a tooth has fully formed and erupted, the tooth has no reconstructive ability to compensate for the fluorotic enamel lesions.

Dental fluorosis is usually diagnosed by examination of the incisors. Cheek teeth are also important, but are difficult to examine in live animals. Nevertheless, in fully evaluating dental fluorosis, the cheek teeth must be examined and evaluated along with the incisor teeth. However, the same criteria used in diagnosing and evaluating incisor fluorosis cannot be used in premolar and molar fluorosis, which are estimated by the degree of abrasion only.

The degree of dental fluorosis can be correlated with the amount of fluoride in the bones, degree of osteofluorosis, duration of exposure, age of animal during fluoride ingestion, amount of fluoride ingested during tooth formation, and other reactive processes of the body. Dental lesions, therefore, are useful diagnostic aids. However, to be most meaningful, the dental fluorotic changes must be correlated with other tissue responses and lesions that are indicative of fluorosis. In other words, dental lesions should not be used as the sole criterion.

Effects on bones

The amount of fluoride stored in the bone can increase, within limits, over a period of time without eliciting any demonstrable changes in structure and function. Eventually, high levels of fluoride will cause structural changes. Bone lesions characteristic of chronic fluorosis appear: porosis, sclerosis, hyperostosis, osteophytosis, and malacis, depending upon the interacting factors influencing the degree of fluorosis. Characteristic osteofluorotic lesions

subsequently may develop, and bone functions may be adversely affected.

The bone lesions are bilateral and are usually first observable on the medial surface of the proximate third of the metatarsal bones, the mandible, and metacarpal bones. They can be diagnosed and confirmed by radiography. Subsequently, bone lesions occur on the ribs. The degree of fluoride-induced bone changes can be correlated mong the various bones of the body and within certain anatomical and metabolic areas of specific bones. Therefore, in taking bone samples for chemical analyses and correlation studies, it is very important to use bones and specific bone areas for which standards have been established. The severity or degree of osteofluorotic lesions apparently is related to the structure and function of these bones and to the stress and strain imposed on specific areas of the bones. This is exemplified by the osteofluorotic lesions and fluoride contents of the ribs, mandible, and proximal and distal thirds of the metatarsal and metacarpal bones as compared to the diaphyseal areas of those bones.

Bones adversely affected by fluoride appear enlarged and chalky white, with a roughened irregular periosteal surface. Experiments with dairy heifers and cows indiate a close correlation between fluoride ingested, fluoride content of bone, and alkaline bone phosphatase activity. Studies indicate that low levels of fluoride ingested over prolonged periods may increase the breaking strength of bone and delay osteoporosis.

Effects of ingested fluorine on dairy cattle

			Chronic fluorosis			
Fluoride analysis (p.p.m.) of:	**Age (Years)**	**Normal conditions**	**No adverse effects**	**Borderline**	**Moderate**	**Severe**
Moisture-free diet	2-6	up to 15	15-30	30-40	40-60	60-109
Bone	2	401-714	714-1605	1605-2130	2130-3027	3027-4206
	4	706-1138	1138-2379	2379-3138	3138-4505	4504-6620
	6	653-1221	1221-2794	2794-3788	3788-5622	5622-8676
Urine	2	2.27-3.78	3.78-8.04	8.04-10.54	10.54-14.71	14.71-19.86
	4	3.54-5.3	5.3-10.32	10.32-13.31	13.31-18.49	18.49-25.63
	6	3.51-6.03	6.03-11.29	11.29-14.78	14.78-20.96	20.96-30.09
Milk	2-6	up to 0.12	up to 0.12	0.08-0.15	0.15-0.25	0.15 and above
Blood	2	up to 0.30	up to 0.30	0.15-0.40	0.30-0.50	0.50 and above
Soft tissue	2-6	up to 1.20	up to 1.20	up to 1.20	up to 1.20	up to 1.20
Other Effects						
Effect on incisor teeth[a]	2-6	0-1	2-3	2-3	3-4	4-5
Degree of wear on molars[a]	2	0-1	0-1	0-1	0-1	0-3
	4	0-1	0-1	0-1	1-2	1-4
	6	0-1	0-1	1-2	1-3	1-5
Periosteal hyperostosis[a]	2	0	0-1	0-1	0-2	0-3
	4	0	0-1	0-1	0-3	0-4
	6	0	0-1	0-2	0-4	0-5
Secondary changes[b]	2-6	absent	absent	occasionally noticed	present	present

[a] Classification: 0-normal; 1-questionable; 2-slight; 3-moderate; 4-marked; 5-excessive

[b] Loss of weight, reduced feeding and milk production, rough hair, or unpliable skin

The above table relates body fluoride levels and occurrence of secondary effects to fluoride content of dairy cattle diets for various degrees of chronic fluorosis. Acute fluorosis, which generally occurs with intakes of 250 p.p.m. fluoride or more, is characterized by a wide variety of symptoms, including high bood and urine fluoride, stiffness, anorexia, reduced milk production, excessive salivation, nausea, incontinence, clonic convulsions, necrosis of digestive tract mucosa, weakness, and cardiac failure. These data are based on controlled experiments, but can be correlated with numerous field cases that have been extensively studied and evaluated.

The most consistent measurement of fluorosis is the amount of fluoride retained in the normal mineralizing matrices of the body. About 96% of the total fluoride retained in the body is found in the bone, enamel, cementum, and dentine. The reactive processes and the concentration of fluoride in the normal mineralizing tissue depend upon all factors which influence fluorosis. Skeletal retention of fluoride is cumulative throughout the life of an animal, if the animal continues to ingest constant or increasing amounts of fluoride. Thus, the bones of young animals normally contain less fluoride than those of old animals. Aged animals raised on normal rations contain up to 1200 p.p.m. of fluoride in bones, calculated on a dry, fat-free basis.

Mechanisms

The exact and precise mechanisms of abnormal bone formation, modeling, and remodeling that are associated with fluorine toxicosis are not fully understood. However, it appears that three mechanisms are involved:

- Impairment of the mechanical properties of normally formed bones by excessive fluoridation.
- Precocious remodeling and excessive proliferation.
- Direct inhibition of normal osteoblastic activity by excessive blood and tissue fluid levels of fluoride.

Abnormal osteoblastic activity is thought to cause the formation of abnormal matrix with a resultant disorderly, defective, and irregular mineralization. In some animals that have developed marked fluorotic skeletal lesions, impairment of the normal blood supply also has been observed, and this further complicates complete understanding of the abnormal bone reactive processes. At present, it is believed that the fluoride ions replace a hydroxyl radical in the apatite-like crystal.

Intra-articular structures are not primarily affected in chronic fluorosis. In advanced cases that have fluoride-induced marked periosteal hyperostosis, there may be spurring and bridging that can eventully lead to marked rigidity and malfunctioning of the affected joints. It is diagnostically important to remember that the initial stages of the bone lesions associated with fluorosis are not intra-articular in nature. By contrast, the bone lesions associated with bovine osteoarthritis appear initially in the articular cartilage with compensatory marginal lipping and are intra-articular in nature. As osteoarthritis progresses, the lesions may become periarticular.

Lameness and stiffness are inconclusive measures of fluorine toxicosis. Intermittent lameness and stiffness seen in more advanced cases of fluorosis appear to be associated with the osteofluorotic lesions and mineralization of periarticular structures and tendon insertions. In turn, the intermittent lameness and stiffness deter the affected animals from properly standing, eating, or grazing. The subsequently reduced feed intake fosters lowered performance levels.

When ingestion of elevated levels of fluorine is suspected, but clinical symptoms are lacking, urine analyses can be used as a diagnostic aid. If mature cattle with permanent teeth are brought into an area where fluorosis is a problem, dental lesions, osteofluorosis, and the amount of fluoride in the bone do not adequately indicate fluoride ingestion levels. The amount of fluoride in the urine can be used in such cases to roughly estimate fluoride intake. The accuracy is enhanced when several animals from a herd are sampled, preferably in the morning, and, ideally, on more than one occasion. Urine of normal cattle contains less than 6 p.p.m. of fluorine.

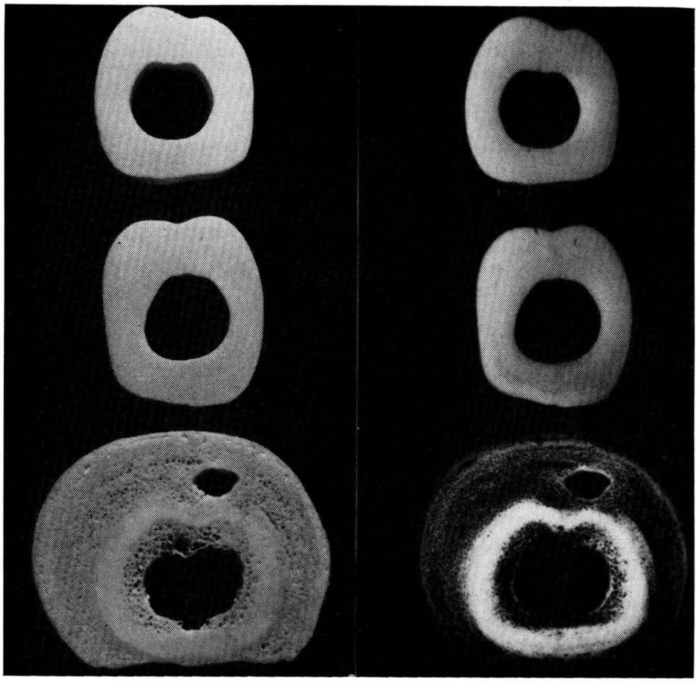
Characteristic pathologic bone changes have been observed radiographically in animals that have consumed high levels of fluorine for long periods of time. Porosis, sclerosis, hyperostosis, osteophytosis, and osteomalacia or any combination of these bilateral bone changes may occur. The roentgenographic findings will vary greatly depending upon the interrelation of a number of factors.

General condition

The general condition of experimental dairy cattle that received 93 or 49 p.p.m. of fluoride (NaF) for 7½ years was primarily affected during lactation periods. Some cows that received 93 p.p.m. evidenced general adverse effects after 2½ years; in some that received 49 p.p.m. adverse effects were observed after 4½ years. The general effects did not appear until after periosteal hyperostosis and intermittent lameness were discernible. Some of the findings include:

- **Hair and skin.** Some cows which received 93 or 49 p.p.m. of fluoride (NaF) for 7½ years had dry hair and thickened, nonpliable skin toward the end of the experiment.
- **Hoofs.** No adverse effects on the growth and shape of the cows' hoofs could be associated with ingestion of 93, 49, or 27 p.p.m. of fluoride (NaF) for 7½ years. Wide variations occurred within treatment groups, and advanced fluorotic cases did not reveal any correlation between fluoride intake and hoof growth.
- **Soft tissues.** Only small, insignificant amounts of fluorine (less than 2.5 p.p.m.) were retained in the soft tissues of cattle receiving up to 93 p.p.m. of fluoride (NaF) for 7½ years. No gross or histologic changes were noted in any of the major organs, and enzyme studies of selected soft tissues showed no significant effects except those related to renal clearance of *p*-aminohippuric acid.
- **Blood.** None of the cows that received up to 93 p.p.m. F for 7½ years evidenced any effect on blood morphology or the hemopoietic system. No correlation was found between fluoride in the diet and calcium, inorganic phosphorous, or alkaline phosphatase in the blood serum, although there was a correlation with amount of fluoride in the blood.
- **Placental transfer.** Fluoride passed through the placental barrier of cows that received various levels of fluoride for 7½ years. Bone fluoride of the calves correlated with the fluoride ingested by the dam and with the amount in her blood. In succeeding gestations, however, the amount of fluoride transmitted through the placental barrier did not increase, regardless of the duration of fluoride ingestion. There appears to be a barrier to the free passage of fluoride from maternal placenta to the fetal placenta.
- **Reproduction.** Prolonged ingestion of 93 p.p.m. fluoride for 7½ years had no effect on reproduction, as measured by services required per conception. The conception rates of experimental cows that received up to 93 p.p.m. of NaF for 7½ years were similar to those of the Utah State University dairy herd, which had higher conception rates than average for U.S. dairy cattle.
- **Milk production.** Milk production is not directly affected by ingestion of low levels of fluoride. Even in cases of marked fluorosis, effects on milk production are probably attributable to altered metabolic function, rather than to a direct interference with lactogenesis. Milk production of cows on 93 p.p.m. of fluoride (NaF or a fluoride of equivalent toxicity) apparently was adversely affected during the second lactation and was definitely reduced in subsequent lactations. Milk production of cows on 49 p.p.m. fluoride were adversely affected in the fourth and subsequent lactations.

Symptoms and visible or palpable clinical lesions sometimes are not definitive enough to warrant an unequivocal diagnosis of fluorosis. In such instances, or to substantiate a reasonably certain diagnosis, additional verification can be obtained in several ways. When carefully interpreted, urine analysis is a useful diagnostic aid. Bone radiographs can supply valuable information. Biopsies or necropsies can be used to obtain tissues for chemical analyses for fluoride content and for gross and histopathologic evaluations. Correlation of clinical findings with fluoride contents of the animals' water and forage often can help substantiate or disprove suspected fluorosis.



Metatarsal. *Visual* (left) *and x-ray* (right) *appearance of cattle bones show effect in increasing fluoride levels. Top specimens are from cattle on normal diet*

Alleviating fluorine toxicity

Although no substances can completely prevent the toxic effects of fluorides, some products can counteract or lessen the damage fluorides can cause. Aluminum sulfate, aluminum chloride, calcium aluminate, calcium carbonate, and defluorinated phosphate have reduced the toxicity of fluoride in animals. Heifers ingesting aluminum sulfate as a fluorosis inhibitor deposited 30-42% less fluoride in their ribs than did heifers on comparable diets without it. If animals must be fed hay which is high in fluoride, it should at least be combined with low-fluoride hay. If the drinking water available to the animals is unavoidably high in fluoride content, then it is advisable to feed roughage of low fluoride content. Soil high in fluoride should be planted to cereal or nonroughage crops, since grain does not accumulate fluoride as readily as forage crops do. In such cases, the necessary hay or roughage should be imported from low fluoride areas. All mineral mixtures fed to the animals should be defluorinated.

By way of summary, it should be noted that fluoride has beneficial effects when ingested in small amounts; trace amounts should be considered an essential nutrient. Toxic and adverse effects do occur when fluoride is ingested in excessive amounts; nevertheless, fluorosis can be prevented and controlled, but only when the complexity of the disease is realized and the symptomatology, pathogenesis, and lesions are properly correlated, interpreted, and evaluated.

Fluoride tolerances for young and matured livestock under various conditions have been established, and a comprehensive guide has been developed and compiled to facilitate diagnosing and evaluating fluorosis. The standards recommended are adequate to protect animals throughout their normal life.

Discussion

Jewell: Dr. Shupe has presented a concise and informative paper. Many industries which have had a problem with fluorosis in their area have taken steps to eliminate it, and the solution has taken time and large expenditures of capital. Industry has the responsibility to continue research in this area and, as technology of collection and scrubbing advances, to control air pollution whenever technically sound and feasible. For the foreseeable future, however, it will be necessary for industry and agriculture to exist in the same areas. A better understanding of the fluoride effects on cattle can only be obtained from research work such as Shupe described. If the data and knowledge now available on fluorosis had been in the literature 20 years ago, I am sure many of the misunderstandings between industry and agriculture could have been avoided.

Since the cattle experiments at the University of Utah are the basis of Shupe's paper, I have two general comments to make, based on my observation of the cattle:

- At times as I observed the cattle, I could not pick out, from general appearance, differences between the control group and the highest level of fluoride fed group.
- My classification of the animals' teeth, on the whole, would have been slightly lower than those of Shupe and other Utah State University workers.

Shupe points out that one of the sources of fluoride for cattle is pasture on a high-fluoride soil, but no reference was given. The University of Tennessee, in 1962, published a bulletin, "Bovine Fluorosis from Soil and Water Sources" which was a preliminary report on a continuing experiment. The publication brings out several of Dr. Shupe's points as to factors influencing occurrence of fluorosis and type and solublity of fluoride ingested. Also, I would like to bring out the wide range of values found for vegetation fluoride in pastures where industrial contamination is not a problem.

The data below are taken from this publication. Pastures were sampled monthly between 1955-60 on a planned cross sectional basis to cover the 10 acres in each pasture. Yearly averages of monthly samples of the same pastures by Monsanto personnel agree very closely with these data:

Low fluoride soil pastures

Fluoride in soil (p.p.m.)	Fluoride in vegetation (p.p.m.) April-Oct.	Nov.-March
488 (average)	28	70
594 (maximum)	456	356
384 (minimum)	5	10

High fluoride soil pastures

Fluoride in soil (p.p.m.)	Fluoride in vegetation (p.p.m.) April-Oct.	Nov. March
2997 (average)	143	486
4373 (maximum)	1993	2317
2044 (minimum)	11	14

The reason for bringing in these values is the importance of Shupe's statement: "In correlating and evaluating vegetative fluoride analyses with fluoride-induced symptoms and lesions in animals, one must consider that animals normally ingest unwashed vegetation." The question is: when we measure fluoride in vegetation, how much soluble and how much insoluble fluoride is present, and what compound or compounds of fluorine is present?

From the tables, we can see that even in the low fluoride soils, a considerable portion of the total fluoride must be present as the insoluble calcium fluorophosphate or fluorapatite.

The presence of dirt and dust on vegetation can account for the occasional odd ball result from areas of no industrial contamination.

The questions of alleviation by green pastures is also a factor. Hay brought from a contaminated area, although on a p.p.m. basis is equivalent to the toxicity of sodium fluoride, brings up the question of what did the hay run as green growing vegetation? Only one cattle experiment that I am aware of has been made on dairy cattle fed known amounts of fluoride as sodium fluoride in dry feed and then allowed free access to green pastures. The report of this experiment is given in a paper published in the *American Journal of Veterinary Research* (Apr. 1968), entitled, "The Effects of Feeding Fluorine as Sodium Fluoride to Dairy Cattle—A Six Year Study," by G. W. Newell and H. J. Schmidt of the Stanford Research Institute, Menlo Park, Calif. The objective of this experiment was to determine the effects of feeding fluoride to two year old heifers, under conditions of practical dairy management and practice. One difference here is the age of the dairy heifers at the start of the experiment—3-4 months old in the Utah study,

Fluorine tolerances in livestock diets

	Breeding or lactating animals (p.p.m.)	Finishing animals
Dairy and beef heifers	30	100
Dairy cows	30	100
Beef cows	40	100
Sheep	50	160[a]
Horses	60	...
Swine	70	...
Turkeys	..	100[b]

[a] Harris, et al., J. of Animal Sci. **20,** 51-55 (1963).
[b] Anderson, J. O., et al., Poultry Sci. **34,** 147-153 (1955).

These standards are adequate to protect animals from fluorosis throughout their normal life. The tolerances are based on sodium fluoride, or fluorides of similar toxicity, in the total moisture-free diet, and assume that the drinking water is relatively free of fluorides and two years old in the Stanford Research study. Another difference is that the Utah study was conducted under the rigor of dry lot feeding with no access to green pastures, while the Stanford study was conducted with cattle having access to irrigated pasture.

The alleviation factor on beef cattle is mentioned in another University of Tennessee Bulletin: "This indicates either a lower toxicity of fluoride from the smelter compared to that of NaF, or an 'alleviation factor' in pasture, or both."

Lactation

The Utah State study showed a reduction of milk yield after the second lactation period at the 93 p.p.m. F level, and at the 49 p.p.m. F level in the fourth and subsequent lactations. The Stanford Research study noted no adverse effect on milk production for five lactation periods begining with 2 year old heifers. The levels of fluoride fed in the Utah study were on a p.p.m. basis, and in the Stanford Research study in milligrams of fluoride per kilogram of body weight. Comparative data on a p.p.m. basis are:

Utah State

(Basel = no added flouride)

Group A Basel	12 p.p.m.
Group B Basel	27 p.p.m.
Group C Basel	49 p.p.m.
Group D Basel	93 p.p.m.

Stanford Research

Group I (control)	7.3 p.p.m.
Group II	33.6 p.p.m.
Group III	44.7 p.p.m.
Group IV	60.4 p.p.m.
Group V	85.6 p.p.m.

Schmidt and Newell report that within the limitations of their six year study, the boundary level at which toxicosis may be expected to occur over periods of prolonged ingestion of fluoride is 2.0-2.5 mg. of fluorine per kilogram of body weight per day (60.-85.6 p.p.m. in ration).

Suttie's experiments at the University of Wisconsin, where two year old dairy animals were fed up to 50 p.p.m. of added fluoride, showed a lactational effect in certain cows at 1.7-1.8 mg. F per kilogram of body weight. The cattle were kept in dry lot and allowed no access to green pasture.

I would agree with Shupe that his standards are adequate to protect animals throughout their normal life with the following provisions:

- That values quoted be used as the total ration of the livestock and not of green vegetation analysis alone in a fluoritic area, unless the growing vegetation furnishes the entire total diet.
- That the safe level of fluoride in the total diet not be considered a single value but as a range of values, as in Shupe's table and as recommended by the National Research Council:

	NaF or other soluble fluoride	Phosphate limestone or rock phosphate
Dairy cow	30-50 p.p.m.	60-100 p.p.m.
Beef cow	40-50 p.p.m.	65-100 p.p.m.
Sheep	70-100 p.p.m.	100-200 p.p.m.

- There should be a slightly higher range of safe values for beef cattle than dairy cattle. Results of experiments at the University of Tennessee on beef cattle indicated this is possible.
- Yearly averages of fluoride in growing vegetation should be used in conjunction with hay and other cattle feed used to arrive at the fluoride in the total ration.
- No single criterion, including tooth changes, should be used, unless correlated with other symptoms.

Cralley: A great amount of experimental work has been conducted in the U.S. on the effect of ingested fluorides in livestock, mainly at Utah State University, University of Tennessee, University of Wisconsin, and Stanford Research Institute. Dr. Shupe has presented an excellent review of this work in terms that can be related to air pollution standards. As he has indicated, fluoride is ubiquitous and is considered an essential element by many nutritionists. However, fluoride doses beyond tolerance levels result in economic damage in which the effects are general in nature and may readily be confused with responses to poor husbandry.

Shupe has noted that levels as high as 93 p.p.m. in the total ration, on a dry-weight basis, produce no effect upon soft tissue, blood, or reproduction: but a response is noted in milk production at the second lactation. Also, at ingestion levels of 49 p.p.m., an effect on milk production was noted, after more than seven years, during the fourth lactation. In some instances, on the 93 p.p.m. levels, cattle did evidence some general adverse effects after two and one half years on trial. These general effects, however, did not appear until after hyperostosis and intermittent lameness were discernible.

The main effect of fluorides on animals, at these low chronic levels, is upon teeth formation. Excess fluorides during this period lead to improperly developed teeth which later show excessive wear. Economic damage may result if the excess wear is sufficient to result in reduced food intake. However, once the teeth have been developed, they are not effected by subsequent high fluoride exposure.

Criteria

Shupe has shown that there are no adverse effects on dairy cattle when the fluoride content of the total ration is less than 30 p.p.m. The range of 30-40 p.p.m. represents a borderline zone, while 40-60 p.p.m. will result in moderate, adverse effects. These values are within the lower part of the range of 30-50 p.p.m. considered safe n a 1960 publication (No. 824) of the National Research Council. The above values refer to dairy, breeding, or lactating animals. Beef breeding cows, finishing animals, and other species have a greater tolerance to fluoride.

At the Air Pollution Control Association meeting (St. Paul, Minn.) June 1968, J. W. Suttie, of the University of Wisconsin, presented a paper entitled, "Air Quality Criteria to Protect Livestock from Fluoride Toxicity." Suttie's recommendations, which were based upon the fluoride content of forage instead of the total ration, were:

"After sampling on a monthly basis, the yearly average fluoride content of the forage should not exceed 40 p.p.m. (dry weight basis); or be in excess of 60 p.p.m. F for more than two consecutive months, or in excess of 80 p.p.m. F for more than one month."

When Shupe's and Suttie's recommendations are equated either in terms of fluoride in the total ration or in the forage, they are in agreement. This is because the total ration of dairy cattle generally includes low-fluoride components such as dry concentrates. Where excess fluoride dosage in livestock is suspected, it is necessary to obtain information on the fluoride content of the total ration. Under certain circumstances, some components—for example mineral supplements—can be high in fluoride unless the proper grade is utilized. However, for a general surveillance program, it is more practical to use standards in which the fluoride limit is expessed in terms of forage content rather than that of the total ration.

It is gratifying that this large amount of experimental work can be translated into terms of air pollution standards, and that there is such good agreement of the data.

(*Continued from page 720*)

occurrence of a given concentration has been used as a guideline in The Netherlands; the concentration-duration of exposure approach has been used for U.S. criteria. Either approach could be taken for the effects of fluorine, and one can be converted graphically into the other by a tranformation of the time axis, that is, the expression of duration as percent of a year.

However, it is doubtful that the two approaches would be equivalent in their description of the probable effects of fluorine on vegetation, and, therefore, in their specification of acceptable conditions. The effect of a continuous exposure to HF for seven days may be quite different from the effects of exposures to the same concentration for seven days spaced randomly in a month, a growing season, or a year. Indeed, Adams and Emerson concluded that the sequence of exposures may be more important than the actual level of fluorine within a certain range of concentrations. The origin of this problem lies in the accumulative nature of fluorine in the plant and the factors that influence its mode of action.

Reports of experimental fumigations or field observations indicate that several factors must be considered with respect to the effects of atmospheric fluorine on vegetation:

- Different types of fluorine-induced effects exist, and they can be generally categorized as visible markings such as chlorotic or necrotic lesions of the foliage; altered growth or reproduction of the plant; changes in physiological or metabolic processes; and accumulation of fluorine by the plant.
- Different species of plants and different varieties of the same species are not equally susceptible to fluorine-induced effects. For example, several publications list various plant species rated according to their susceptibility to foliar markings.
- Environmental factors, such as temperature, light intensity, water supply, mineral nutrition, or other pollutants may determine the type and degree of effect produced by fluorine.
- Susceptibility of a plant to fluorine varies with the stage of development. That is, the young or emergent plant foliage is most likely to show fluorine-induced markings, and seed production in sorghum is more susceptible during the period when the head is emerging.

Clearly, a plant's response to fluorine is complex, and criteria must take this into account to describe accurately the relationship of air quality to its probable effect. Yet, criteria must be sufficiently simple statements to be useful for the selection of reasonable air quality standards.

Criteria

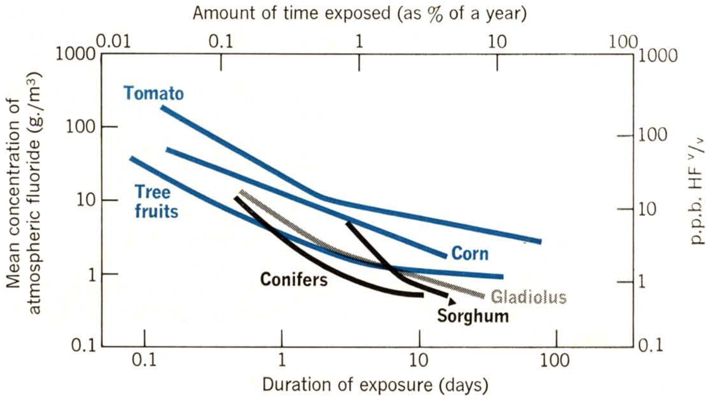
There are some ways data could be evaluated to achieve both simplicity and accuracy in criteria. Some types of effects might not be considered. For plants where fluorine accumulation is the primary concern—for example, in forage crops—sufficient data are not yet available to relate foliar fluorine levels to air quality. Thus, separate criteria or standards will have to deal with acceptable levels of fluorine in the plant. Physiological and metabolic changes have been found in the absence of visible symptoms or effects on growth, but it is doubtful whether this type of effect can be interpreted with respect to what could be called injury or damage.

It is with reference to these two terms—injury and damage—that foliar marking and altered growth or yield should be evaluated. Injury has been defined as any pollutant-induced effect, and damage as any reduction in value with respect to the intended use of the plant. Criteria for gladiolus, sorghum, and perhaps corn could be developed with respect to economic damage, as by reduced growth or decreased quantity and quality of yield.

However, data are not sufficiently abundant for other species, and criteria would have to deal with foliar markings. This type of injury could constitute aesthetic damage, but its relationship to economic damage depends primarily upon the biological and economic characteristics of the plant as well as the amount of injury present.

Plants possessing similar characteristics with respect to the significance of fluorine-induced effects could be grouped together, and the consideration of categories rather than individual species of plants would reduce the

Possible air quality criteria



Criteria. *One possibility for air quality criteria would be levels of exposure to HF which produce foliar markings (as in tree fruits, conifers, or tomato) or effects on growth and yield (corn, sorghum, or gladiolus).*

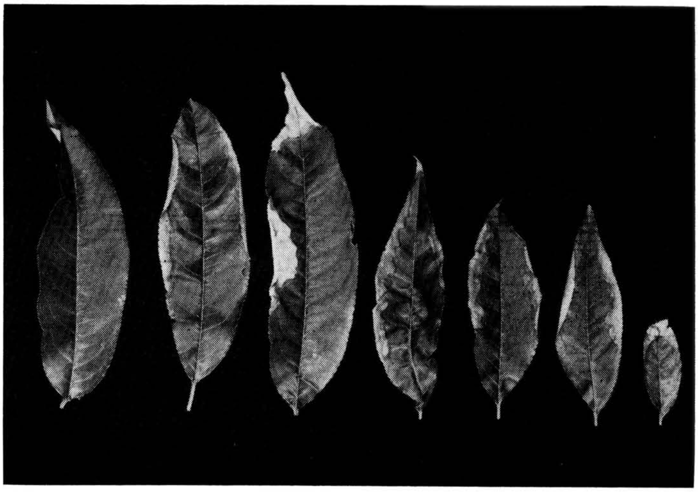
Source: API monograph 69-3, "Air Quality" by permission complexity of criteria. Plant species could also be grouped with respect to their susceptibility to fluorine, but differences in susceptibility within a species may be present. When information is available on more than one variety in a species, criteria could be based on the more susceptible varieties. This would assume that standards should allow varieties to be chosen for suitability to a certain agricultural situation and not for fluorine resistance.

When it is known that the availability of water or mineral nutrients can affect the plant's resistance to fluorine, criteria could be based upon sound agricultural practices. This would assume that standards should not protect methods or conditions that render a crop susceptible to fluorine and by themselves reduce crop yield. When a plant is more susceptible to fluorine during a certain stage of development, criteria for the time span equivalent to this period could be based upon the more susceptible stage. Criteria for longer periods, however, would be based upon the otherwise greater resistance of the plant to fluorine.

Other approaches can be used to consolidate data into criteria that could be represented graphically as lines or surfaces relating degree of effect to a time-concentration space. However, it is doubtful that continuous functions can describe the effects of fluorine on plants under given biological and environmental conditions. There is considerable uncertainty associated with any statement concerning the effects of fluorine, and one could judge an effect to be present when it is not or vice versa. Thus, a better form for presenting criteria suggested by Stratmann, Buck, and Prinz, is a dose-response surface for an effect of a certain degree and type in terms of the probability of its occurrence. Moreover, this type of formulation would be of value to those who must select standards and consider the probable costs and expected benefits of a certain degree of air quality.

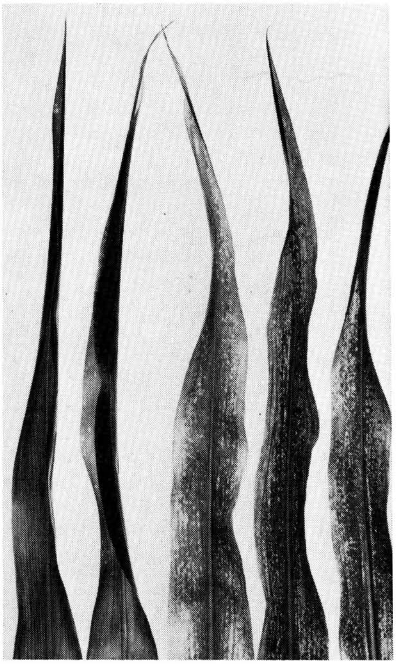
Fluoride monitoring

This problem of uncertainty is also important when measurements of air quality are used to enforce air quality standards. Here, the variability arising from errors in analytical and sampling techniques or from meteorological factors will determine the confidence with which one speaks about the observed air quality and its relationship to a standard. The accuracy of air

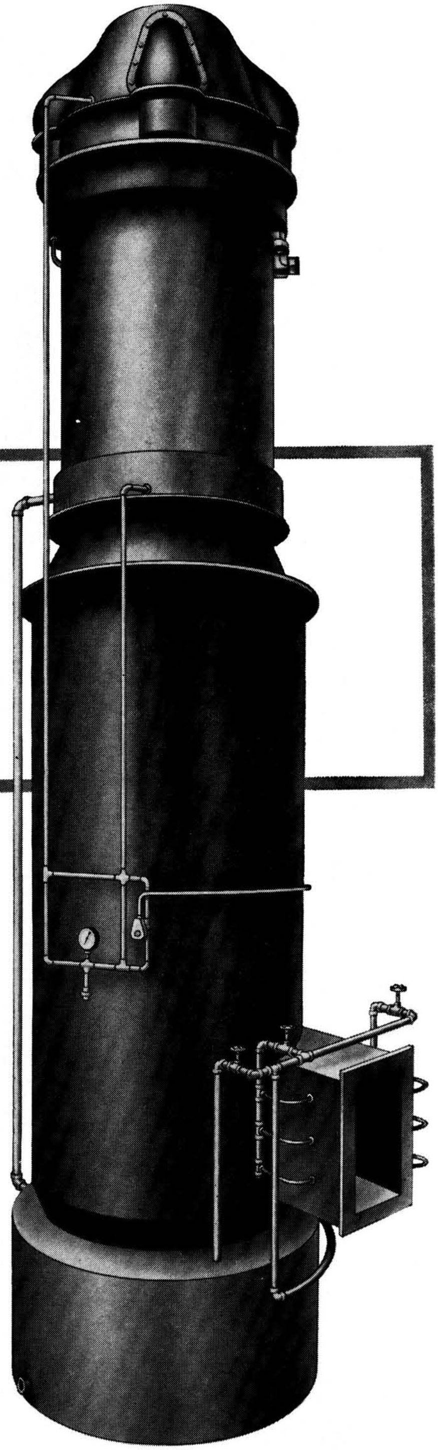


Peach leaves. *Marginal necrosis can be induced by HF. Control is at left; leaf age decreases to right. (A. E. Hitchcock)*

Sorghum. *Normal seed head development* (left) *is retarded by three-day exposure during anthesis to 10* (center) *and 27* (right) *micrograms of fluoride per cu. m. (Courtesy Boyce Thompson)*



Sweet corn. *Plant varieties show different degrees of HF induced leaf chlorosis (A. E. Hitchcock)*



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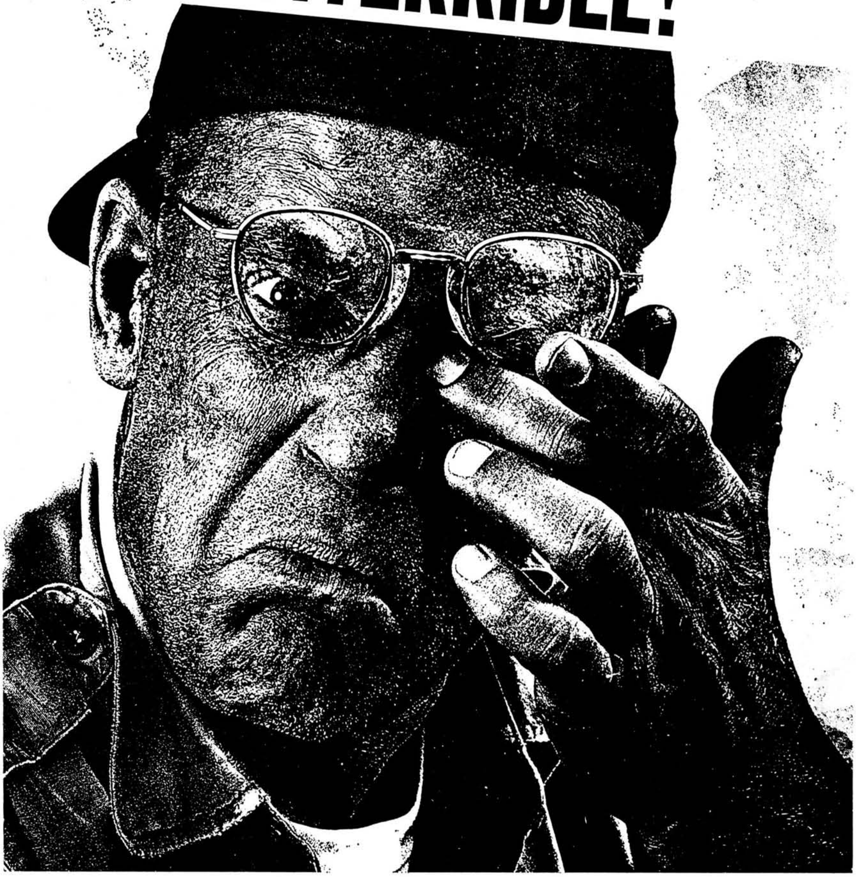

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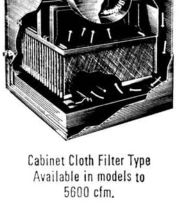

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monitoring methods for fluorine is not known. Sampling error may be greater than analytical error, and estimates of precision give relative errors of 5-20%.

Data on the temporal distribution of atmospheric fluorine are insufficient to determine the relationships of maxima, sampling or averaging periods, and mean values. Consequently, there are major advances to be made in the art of determining atmospheric fluorine levels, if standards are to be useful.

One major achievement would be the publication of acceptable standard monitoring methods which would consider both the equipment and operating procedures. Hopefully, this will result from the work of the Halogen Subcommittee of the Intersociety Committee on Manual of Methods for Air Sampling and Analysis. Standard methods of calibration also should be developed for all components of the air monitoring system. Standardization would include not only an initial calibration but also periodic checks during operational periods. Additionally, procedures should be developed for the evaluation of air monitoring data with respect to the values specified by an air quality standard. Stratmann has given some guidelines for determining the statistical significance of data in terms of the precision of the method. However, more guidelines may be needed to allow control agencies to judge the significance of their data and to determine the confidence they can enjoy in decisions about air quality. Variations in the methods used to acquire or evaluate data could be equivalent to the adoption of variable standards or misleading conclusions about control measures.

When air quality criteria are based on the results of experimental fumigations, there is always the question of how valid these criteria will be for plants growing in the field. A partial answer would be that the criteria are valid to the extent that the conditions met in experimentation are similar to the situation found in the field. However, the data that will come from air monitoring stations, if accompanied by observations on neighboring vegetation, could be used to determine the adequacy of air quality standards and criteria. Thus, air quality standards may acquire a new technical significance as an impetus for future scientific research. Furthermore, criteria and standards may undergo a continual revision as knowledge is gained and applied. In this respect, the establishment and use of reasonable standards will not only better air quality, but also aid in determining to what extent the environment must be improved.

Discussion

Hickey: The particular aspect of Dr. McCune's paper I wish to discuss is its foundation role in the problem of the ecological fit. McCune has sorted out the necessary considerations for establishing air quality criteria, and has identified the problems in putting these considerations to work. He points out that knowledge of concentration distributions is of great importance in assessing the probability of producing an effect, and that this is the link required to determine the appropriate ecological fit, or mix of activities. The problem of the engineer—to design or redesign emission sources—is an important responsibility, and must have as its basis the work of researchers such as McCune and his associates.

We are looking down the barrel of a high-caliber problem that gets tougher by the day: finding the proper fit for an increasing number of ecological interfaces. Locating design constraints is an elusive part of the problem because there are no satisfactory models to differentiate human wants from human requirements. Certainly, "do the best now possible" has been an extremely troublesome point to the design engineers. This dilemma should be partly resolved when the dust settles on criteria and standards. But the inconstant ecological fit of human activities has yet to be standardized.

There is a common ground in the dollar, but interfaces between the dollar and human wants are elusive, and someone has to decide some things arbitrarily. For instance, if a refuse disposal site must be designed to be suitable for location next to the White House, you've got a tougher problem than if it were located in a highly industrialized area. There are some locations where noise and light emission at night may preclude the location of some industrial plants, even before pollutant emissions are considered.

But some coexistence is inevitable, although intelligent zoning will ease much of the constraint-setting problem. Flexibility is desirable because technical innovation changes the meaning of some words or ideas. What an industrial plant is today may be quite unlike what it was many years ago.

The association between these notions and McCune's work is that, even when transfer functions are available to relate emissions to criteria for individual receptors, the engineer is still faced with the problem of deciding for which receptor he will design. If one is to construct a facility in a tomato and corn producing area, and must design for maximum economy, does this mean subsequent gladioli-growing should not be allowed for in the construction of the facility? On the other hand, should the engineer always protect for the most sensitive case, even at considerable extra expense?

McCune's data form a basis for some speculative design considerations. Consider that an exposure period of one day is to be used as a design basis. For a given source, we can assume single and constant conditions of emission distribution, meteorological characteristics, and topographical factors. Let us further assume that the mean 24 hour concentration is based on samples (or samples simulated by dispersion modeling) for a period of a year or more. The possible criteria thus indicate, approximately, these permissible 24 hour exposures:

Receptor	10^{-6} g F^-/m^3
Conifers	3
Fruit trees	4.5
Gladiolus	6
Corn	10.5
Tomato	12

The designer knows that exposure will be linear with emission rate, and we have specified other conditions for relative comparisons. If he allows a fixed percentage safety factor, the relative emission figures will not change, and are:

Receptor	Relative Emission
Conifers	1
Fruit trees	1.5
Gladiolus	2
Corn	3.5
Tomato	4

Thus, for conifers, the most sensitive case shown, emissions must be one fourth of those for tomato. Distance from the receptor, or emission height, may be selected to obtain the equivalent relationship. Thus, what is to be protected is highly consequential to the designer, and, given no constraints, he will make the decision that seems most sensible from all available information.

Some semi-arbitrary decisions on the ecological fit are apparently inevitable. Of course, there is not a continuum of design alternatives available to the engineer in terms of equipment, but meteorological and topographical factors, and simply the distance to the receptor, result in something approximately a continuum.

So it appears that zoning or ecological fitting of some sort is inevitable, and this will divide into at least two knotty problems; the appropriate ecological fit for already developed areas, and that for underdeveloped areas. Both are difficult, and not yet modeled to a satisfactory degree for our society. The work of McCune goes far in forming a basis for solutions.

Daines: Fluoride injury to plants has caused concern since the middle 1940's, as the result of substantial enlargement of industrial operations and the development of new products and processes from which fluorides were released. Those of us who had the opportunity in the 40's and early 50's to observe the rather extensive damage to many plant species are impressed with the excellent job that industry, in general, has done in reducing or correcting this problem.

Fluorides are extremely toxic to a few plant species and are much less toxic to others. The toxicity range embraces several orders of magnitude of exposure. For example, it is reported that some varieties of corn may be mottled at 3 p.p.b., and some varieties of gladiolus are even more sensitive. Furthermore, the phytoxicity of hydrogen fluoride is considerably increased when the leaves are wet.

Fluorides from soil

Fluorides occur naturally in almost all soils, wherever they are found. Available fluorides in the soil may be taken into plants through the roots—experiments have shown that rather high concentrations of fluorides may enter plants if soluble fluorides are added to the soil, sand, or solution cultures. However, there are reports that the addition of slag and phosphate rock containing high fluoride concentrations to the soil caused no increase in the fluoride content of vegetation grown therein. In this connection, in our own work, we have reduced the pH of Tennessee rock phosphate soils, containing several thousand p.p.m. fluoride, to 3.5 or 4.0 p.p.m., and, after raising the pH, have grown alfalfa and Sudan grass in these soils. These plants, despite the low pH history of the soil, contained a normal amount of fluoride.

Although soluble fluorides are accessible to vegetation, there seems to be no evidence that fluorides from the air build up in the soil solution in sufficient quantities to adversely affect crops. Experimental plants without increased fluoride content have been grown in soil from areas exposed for several years to airborne fluorides. In addition, other workers report an instance of a gladiolus fluoride content near an industrial plant of 243 p.p.m. when the plant was in operation; during a year when the plant was closed, the fluoride content of gladioli fell to 4 p.p.m.

Fluorides originating in the soil tend to accumulate in the roots. However, some fluorides in the foliage have their origin in the soil, and these are not removed by light washings in water. Root-acquired fluoride causes necrosis of internal areas of gladiolus leaves, whereas leaf-acquired fluoride causes marginal and tip necrosis.

Fluorides from the air

Studies have clearly demonstrated the ability of leaves to remove gaseous fluorides from the air with an accompanying accumulation in leaf tissue. This accumulation is greatest in leaf tips or in older leaves. Available data also indicate that some plant species absorb fluoride from the air more readily than others. For example, corn and tomatoes fumigated together, showed 39 p.p.m. of fluoride in the corn and 78 p.p.m. in the dried tomato foliage. In addition, old leaves on a tomato plant accumulated more fluoride than did young leaves. In general, the more sensitive plant species absorb less fluoride than do the more resistant species. A similar relationship exists for the young, most responsive, leaves and the older leaves on the same plant.

The routes of fluoride ingress to the leaf are not well elucidated. Certainly, open stomata provide an entry, but whether this is the only site of entry is somewhat in question. There has been a report of stomatal stiffness in pine needles from exposures to SO_2 that resulted in their remaining open, permitting absorption during light and darkness.

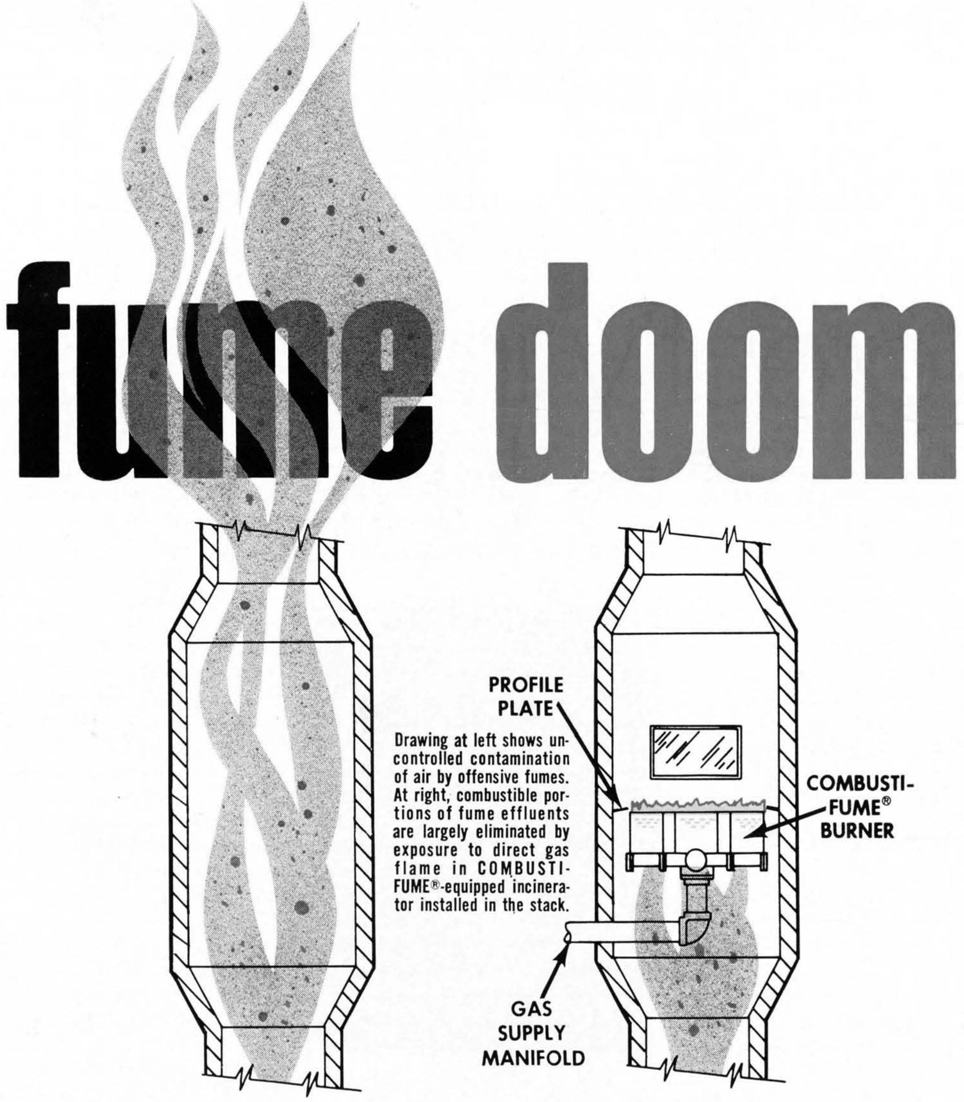
In this connection, other workers found no evidence of fluoride accumulation within the leaf from night fumigations of alfalfa plants whose stomata were closed, as revealed by porometer readings. The fluoride absorbed was shown to be externally attached since it could be readily moved by washing. However, fluoride concentrations both inside the leaf and on its outside surfaces increased significantly during daytime fumigations.

Wide variations in susceptibility to fluorides may exist among plant species, varieties of a given species, and individuals of a given variety. For example, certain varieties of gladiolus, Chinese apricots, prunes, blueberries, corn, and Ponderosa pines are very sensitive to fluorides; whereas ragweed, privet, and weeping willow can tolerate many times as much fluoride without visual response. One study that used 110 varieties of gladiolus showed a wide range of susceptibility among the varieties used; the varietal response varied from 4-83% of the leaf tissue killed. Similarly, seedings of *Pinus ponderosa* grown in a fluoride polluted area revealed a wide range of sensitivity to the pollutant. In this experiment, critical measurements of foliar samples from within two and one half miles of the source of fluoride pollution revealed a variation of 0-100% of the needles burned, and a variation of 0-86% of the total needle length burned on individual plants. During this 4 year study, some trees constantly manifested a high degree of sensitivity, other remained symptomless, and a third group fluctuated in response. Since resistant and susceptible plants were often found only inches apart, exposure, soil moisture, and fertility differences would not satisfactorily explain the wide variation in response. Uniform fluoride sensitivity would not be expected within a plant species, since nature has not provided environments that would select for this character.

Acute injury

Acute fluoride injury symptoms are the occurrence of necrotic tissue, usually along the margins and tips of the young leaves. Occasionally, streaking or spotting may occur. The affected tissue first appears as watersoaked areas which become buff to reddish brown on drying.

Of the monocotyledonous plants, some members of the lily family, such as gladiolus and tulip, are among the most sensitive. On these plants, the injury is usually characterized by necrotic areas at or near the blade tip; however, some gladioli respond with considerable intercostal streaking. Fluorine is absorbed over the entire leaf blade, but it moves to the tips, where injury ensues and may extend downward at or near the leaf edges somewhat beyond the more general tip inju-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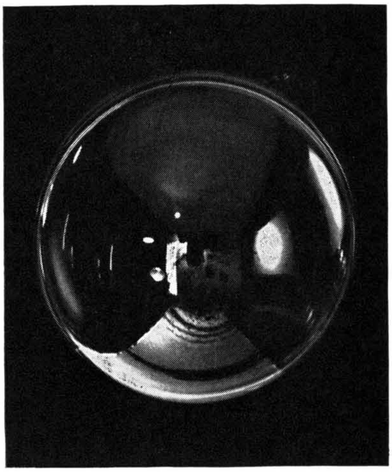

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ry. Necrotic tissue is tan to light brown, and frequently exhibits darker bands, probably separating tissue killed in succeeding exposures. This banding may appear on many species.

Among conifers, induced needle blight is characterized by brown or reddish-brown necrosis which begins in the tips of the needles and progresses towards the base. Occasionally, the injury appears as localized bands which are separated from the tip injury by bands of green tissue. In severe cases, the needles develop to about 25% their normal length and the tree retains the needles only 1 or 2 years instead of the normal 5 or 6 years. The needles are most sensitive during early development.

The usual response to excessive exposures of fluorides among the dicotyledonous plants is the appearance of marginal, buff-colored chlorosis. However, in some plants, such as apples, pears, and wild black cherry, necrotic tissue tends to be brown or reddish brown. In Chinese apricots and Italian prunes, mild expressions of disorder appear as light colored areas along the margins. These areas may appear at one or several points; in more severe cases, large areas of the margin show injury. With peaches and apricots, this necrotic tissue is readily separated from the rest of the leaf, and narrow misshaped leaves may remain. However, in peaches, the tendency is strong for the leaf to shed.

Although foliage symptoms are the most common fluoride injury, damage to other plant organs has been reported. Cyclamen flowers are more susceptible than the leaves, with the injury symptoms of the flower occurring on the margins of the petals and sepals. Soft red sutures and splitting of peach fruits along the sutures have been produced by fumigations and the use of fluorine-containing sprays. This symptom, which has been observed in nature, can be prevented by the use of lime or $CaCl_2$ sprays during pit hardening, according to investigators.

Chronic injury

Chronic injury expresses itself by a loss of chlorophyll, resulting in the development of a chlorotic or a mottled pattern on the affected foliage. The type of pattern is a characteristic of the plant species involved. Citrus, oaks, maple, and poplar exhibit chlorotic areas along leaf margins which often extend inward, between the veins, towards the midrib. The area bordering the veins of such leaves remains green. This injury resembles symptoms of mineral deficiency.

On corn, fluoride chlorosis is different from chlorosis caused by mineral nutrition. Chlorosis from low dosages of HF may exhibit small, irregularly shaped chlorotic spots at the tips and margins of the leaves. With an increased concentration or exposure period, more extensive mottling or bleaching results. While mottling may occur anywhere on the leaf blade, bleaching starts as a band along the margins especially towards the tip of the leaf. In severe cases, the bleaching may involve most of the leaf, leaving a narrow green band along the midrib. Before such intense chlorosis occurs, however, marginal necrosis (firing) will become evident.

At fluoride concentrations in excess of those that occur in nature, the calcium level of tomatoes affects the response to HF fumigations. Low calcium plants are more severely damaged than high calcium plants, and fluoride exposures result in necrosis of shoot tips of low calcium plants.

Tomatoes deficient in calcium have shown fruiting characteristics very similar to those caused by HF. Evidence has been found that fluorides interfere with fertilization by inhibiting pollen germination or pollen tube growth. Interference with normal fruit production by flower abscission has been reported even on plants showing very little foliage injury. It should be borne in mind that these results were achieved with excessive fluoride concentrations and that no such plant responses have yet been demonstrated with ambient concentrations.

While visible injuries from fluoride pollutants are recognized, there are reports of evidence of hidden injury in plants. For example, respiration increases in bush beans, as indicated by accelerated O_2 uptake, when plants are exposed to atmospheric fluoride at concentrations below those inducing visible injury. Growth of Douglas fir is reduced in a fluoride-containing environment. A study involving seven varieties of citrus showed the physiological effects to be out of proportion to the amount of photosynthetic area rendered inactive by necrosis from exposure to HF, indicating the occurrence of hidden injury. On the other hand, gladiolus leaves, damaged by crushing, induced increases in respiration comparable to that found in fluoride damaged tissue. Species grown for several weeks in an atmosphere containing a subphytotoxic concentration of fluoride revealed no detectable increase in respiration.

Atmospheric standards

More knowledge is needed on the influence of environmental factors on plant susceptibility to air pollutants, for the settling of air quality standards. Since the principal site of ingress to leaves by an air pollutant is the open stomata, factors that affect leaf ventilation are of major importance. In one investigation on this point, it was found that atmospheric humidity greatly modifies the permeability of the leaf—and as the permeability is increased, the response to an air pollutant is also increased. Using ozone as the pollutant, and Bel-W3 tobacco and pinto beans as test plants, the injury threshold was at least three times greater in air of low relative humidity as compared with high humidity exposures. In addition, air movement at a given humidity played an important role in determining the injury threshold concentration. For example, increasing the number of air changes in a plant chamber during fumigation has a tendency to increase phytotoxicity. One might expect plant response to this pollutant in nature to be modified by air movement, humidity, soil moisture, and fertility.

Thus, passing judgments on acceptable standards in ambient air, with its numerous and varied pollutants, from information on a single pollutant cannot be done without risk. Certainly, there are chemical compounds in the air that tend to modify, in both directions, the size of stomatal apertures and hence plant susceptibility. In addition, combinations of gases may result in altered phytotoxicity of the gas in question. Such has been demonstrated for ozone when it is mixed with SO_2.

Since the concentration necessary to evoke a given plant response will vary with the environment and plant species to be protected, acceptable concentrations should be based on plant response. Concentrations that produce demonstrable injury to the plants concerned are too high and should be prevented. If this approach is not satisfactory, and actual concentrations must be taken into account, the choosing of concentrations and time limits is complicated indeed. Certainly requirements necessary to protect vegetation in different parts of the country would vary considerably.


ONE WAY

Lead Aerosols in Marine Atmosphere

Tsaihwa J. Chow, John L. Earl, and Carrie F. Bennett

Scripps Institution of Oceanography, University of California at San Diego, La Jolla, Calif. 92037

■ Procedures for the shipboard sampling of marine air and the analysis of its lead content by the isotope dilution method are discussed. Marine air collected over the north and central Pacific Ocean between California, Midway Island, and American Samoa showed a lead concentration range from 0.0003 to 0.0015 μg. per cu. meter. This lead concentration range shows that marine air is the least polluted of north temperate atmospheres.

Increasing concern has been raised over the distribution of lead as a toxic pollutant in our environments (Patterson, 1965). The main sources of lead pollutants are the burning of antiknock additives in automotive fuels and the particulate lead emitted into the ambient atmosphere as industrial combustion effluents. Winchester, Zoller, *et al.* (1967) have observed that lead concentrations in aerosols from Fairbanks, Alaska, are correlated with high halide concentrations. Both lead and halides are antiknock additives. Altshuller (1967) has been reviewing biannually the existing literature regarding, among other pollutants, the atmospheric lead. However, most previous studies dealt primarily with metropolitan centers (Ludwig, Diggs, *et al.*, 1965). Limited data show, however, that even the remote rural regions could not escape the lead pollution (USPHS, 1966). To evaluate the degree of environmental lead pollution, it is essential to establish the "background level" of atmospheric lead. Therefore, the lead contents of the midocean air, thousands of miles away from the continents, were analyzed.

Sampling

The Pacific Ocean air samples were collected during the NOVA Expedition with the R/V Argo of the Scripps Institution of Oceanography. The ship departed from San Diego, Calif., on April 17, 1967, westward to Midway Island, then turned southward and arrived at Pago Pago, American Samoa, on May 15, 1967. The ship's cruise track and its local apparent noon positions are shown in Figure 1.

The sampling gear consisted of vacuum pumps which drew air through the filters. MF-Millipore cellulose ester membranes, type HAWP, 0.45-micron mean pore size were used, which had a retention efficiency of >95% for 0.05-micron particles. The filter holder was made of anodized aluminum with a gold-plated screen and clamp ring to support the filter. The filter holders were housed in inverted polyethylene cups for protection from sea spray and rainfall and were suspended from stainless steel poles extending forward horizontally from the top of the ship's flying bridge. The holders were approximately 9 meters above the quarterdeck and 12 meters forward of the ships' exhaust stack.

The sampling operation involved the simultaneous and continuous pumping of marine air through the filters for periods of 24- and 48-hours. Two types of vacuum pumps were employed in the sampling: for the 24-hour samples, the Gelman Little Giant air pump was used, while the 48-hour samples were collected with a Gelman Sentry air sampler. Air flow was monitored with a rotameter-type flowmeter placed between the pump and the filter holder. Flow rates averaged 1.0 cu. meter per hour for the Little Giant and 1.3 cu. meters per hour for the Sentry.

When a given sampling period was concluded, the filter holder was capped with a tight-fitting polyethylene cap and removed from the vacuum tubing. Then the exposed filter was removed from the holder with stainless steel forceps and placed in a previously acid-washed borosilicate glass beaker. The beaker was then sealed with Parafilm and stored in a polyethylene bag. All the above operations were performed by a polyethylene-gloved operator.

Contamination

It was difficult to avoid contaminating the filters during the sampling process aboard the research ship. During most of this trans-Pacific section of the NOVA Expedition, the ship was running with the prevailing trade winds which often exceeded the ship's cruising speed of 11 knots. Although care was taken to suspend sampling whenever changes in the ship's course or the relative wind direction might carry the exhaust plume near the samplers, still some of the filters showed black soot particles.

Another source of contamination was the lead paint which had been extensively used around the ship. At the present time, nonleaded paints are exclusively used for the Scripp's ships; however, old leaded paint may still occur on the hull of the ship. Portions of paint could be detached from such surfaces by natural processes of peeling, weathering, and ablation, but a more important agent of removal was the

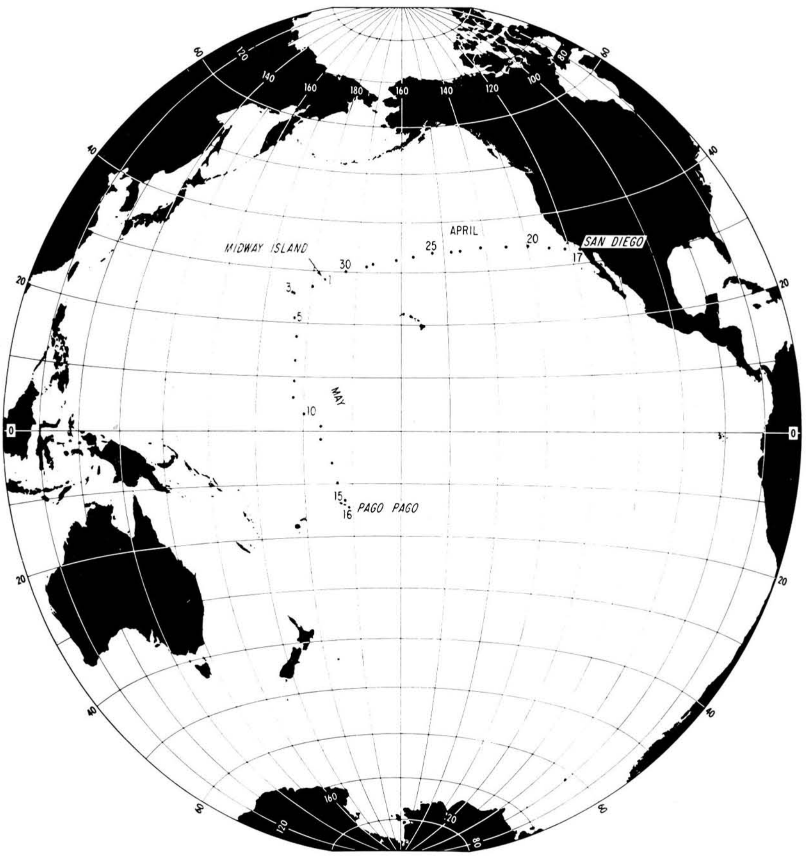

Figure 1. The cruise track and local apparent noon positions of the R/V Argo during the NOVA Expedition

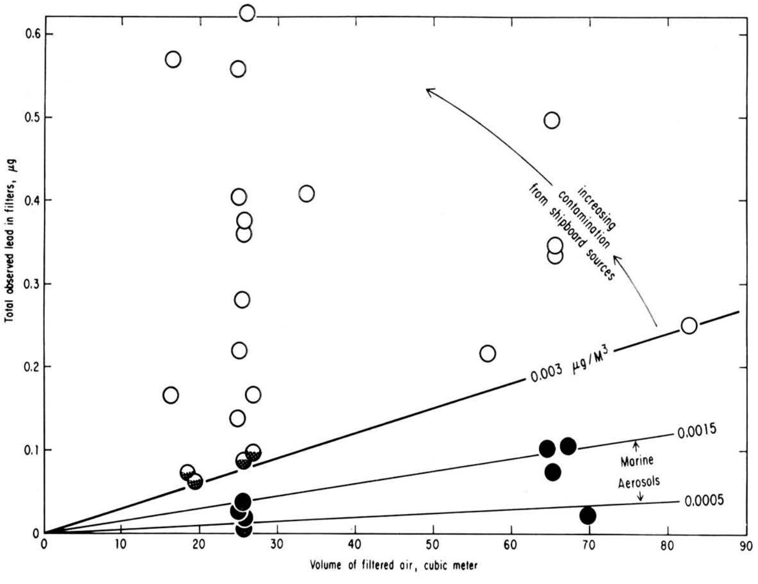

Figure 2. Lead concentrations in mid-Pacific air samples

The open circles represent samples visibly contaminated with soot. Half-solid circles did not contain visible soot, but were probably contaminated. Solid circles represent uncontaminated samples ship's crew, with their incessant paint chipping and repainting while at sea. To avoid any chance of contamination from this source, sampling operation was secured when the crew was working upwind or near the samplers. At the conclusion of each chipping, the decks and bulkhead were thoroughly and immediately hosed down with water to remove the paint debris.

Analysis

Usual techniques for the analysis of the atmospheric lead are colorimetric spectrophotometry (Cholak, Schafer, *et al.*, 1961) and atomic emission spectrography (USPHS, 1962). Neither of these two methods has sufficient sensitivity to determine the extreme low lead content in the marine atmosphere.

The lead concentration in these marine air samples was analyzed by the stable isotope dilution method using an enriched Pb^{206} tracer. Nitric and perchloric acids were doubly distilled under reduced pressure. Teflon and borosilicate glasswares were cleaned with concentrated nitric acid. Special precautions were taken in cleaning the apparatus. Reagents and Millipore filter blanks were periodically determined with the Pb^{206} tracer. The lead blank for fixed aliquots of chemical reagents averaged 0.03 μg. per run. Including the Millipore filter, the lead blank was 0.08 μg. per run.

The exposed Millipore filter was dissolved in concentrated nitric acid, spiked with Pb^{206} tracer and evaporated to dryness. Lead was isolated by standard ion exchange technique, purified by several dithizone extractions, and then converted to the sulfide form. Mass spectrometric analysis was performed on a 30-cm. radius, solid source instrument with an electron multiplier as described by Chow (1968). Square root of mass ratio correction is incorporated in the data to compensate for velocity discrimination in the electron multiplier. The lead aerosols were assumed to be common modern lead with a Pb^{206} to Pb^{208} ratio of 0.481.

Results

The analytical results for marine air as well as San Diego, Midway Island, and Pago Pago harbor air are listed in Table I.

Air samples (about 70 cu. meters) collected for a 48-hour period over the Pacific Ocean contained less than 1 μg. of total lead. This small quantity of lead came from three different sources: actual lead aerosols present in the atmosphere; contamination during the sampling operations aboard ship; and reagents and Millipore filter lead blanks of the chemical analysis.

Because of the difficulty in evaluating the individual random sampling contamination due to the ship's exhaust plume, the marine air samples were treated as a suite to determine their representative lead aerosol concentrations. The method of data analysis was as follows: a lead blank of 0.08 μg. was subtracted from each sample and the observed lead concentration in each filter was then plotted against its volume of air filtered as shown in Figure 2. The degree of increasing contamination is indicated by the counterclockwise arrow. The dimension of the points on the figure represents the measurement error. The air samples containing visible soot, all of which contained more than 0.003 μg. of Pb per cu. meter, are represented by the open circles. The half-closed circles represent samples with very light soot and/or sea spray contamination. The group of eight samples which are represented by solid circles did not exhibit any visible contamination. The lead content of this group ranged from 0.0003 to

Table I. Lead Concentration of Air Samples Collected during the NOVA Expedition

Sampler No. 1			Sampler No. 2	
Volume, M.^{3}	Pb[a] μg./M.^{3}	Date (1967)	Volume, M.^{3}	Pb[a] μg./M.^{3}
25.7	0.0034	April 17		
		April 18	65.6	(0.0051)
25.6	0.0015			
		April 19		
25.7	(N. D.)			
		April 20	65.4	0.0011
25.8	0.0007			
		April 21		
25.7	(0.014)			
		April 22	53.8	(0.020)
16.3	(0.010)			
		April 23		
24.8	(0.022)	April 24		
			33.7	(0.012)
26.9	(0.0062)	April 25		
			65.6	(0.0053)
25.1	(0.0088)	April 26		
25.7	0.0003	April 27		
		April 28	67.3	0.0016
20.2	(N. D.)			
		April 29		
19.3	0.0033			
		April 30		
16.4	(0.034)	May 1	82.7	(0.0030)
25.8	(0.066)	May 2		
18.8	0.0040	May 3		
		May 4	65.1	(0.0076)
25.9	(0.024)			
		May 5		
25.7	(0.014)			
		May 6	62.9	(N. D.)
11.9	(N. D.)			
		May 7		
12.1	(N. D.)			
		May 8	63.8	(0.018)
26.9	0.0036			
		May 9		
24.9	(0.0055)	May 10	69.9	0.0003
13.9	(N. D.)	May 11		
25.5	(0.011)	May 12	57.0	(0.0038)
25.0	(0.015)	May 13		
25.0	0.0011	May 14	64.7	0.0016
12.9	(N. D.)	May 15		
		April 15		
28.6	(0.18)[b]			
		April 16		
23.9	(N. D.)[b]			
		April 17		
8.4	(0.017)[c]	May 1		
8.4	(0.018)[c]	May 1		
25.6	(0.061)[d]	May 16		
25.6	(0.015)[e]	May 17		
26.2	(0.018)[e]	May 18		

[a] Lead concentration in parentheses indicates sample containing visible soot.
[b] San Diego Harbor
[c] Midway Island Harbor
[d] Pago Pago Dock
[e] Pago Pago Bay

0.0015 μg. of Pb per cu. meter. This range is considered as the uncontaminated midocean air lead concentration. The average of these eight uncontaminated samples is 0.0010 μg. of Pb per cu. meter.

The San Diego harbor air sample was collected when the ship was berthed on the west side of the San Diego Bay. The air contained 0.18 μg. of Pb per cu. meter. This sample was taken on a Sunday when lead pollutants from local sources were at a minimum, and also after a cold front had passed which brought a 1.65-cm. rainfall and onshore wind gusts up to 28 knots, leaving unusually clear air. The lead aerosol concentration of this sample was probably much lower than that for an average day at this location in mid-April. Lead concentrations obtained for the month of April at a San Diego downtown station ranged from 1.5 to 2.5 μg. of Pb per cu. meter. At Scripps pier station the average concentration was about 0.3 to 0.4 μg. of Pb per cu. meter.

The first of the three Pago Pago harbor air samples gave a lead concentration of 0.061 μg. of Pb per cu. meter. It was collected when the ship was docked alongside the Goat Island fuel depot. Many cars and trucks were active in the vicinity of the ship during the sampling period. The other two samples were collected while the R/V Argo was anchored at a mooring buoy in the bay, about 300 meters from the nearest land. The lead concentration of these two samples was 0.016 μg. of Pb per cu. meter. Several intermittent short rain squalls were accompanied by fairly constant trade winds of 3 to 15 knots from the direction of the open ocean during the collection of each of these samples.

Discussion

After the R/V Argo sailed away from the San Diego harbor heading toward the open ocean, the lead concentration of marine air decreased considerably to an average value of 0.0010 μg. of Pb per cu. meter which the authors believe represents the apparent upper limit of lead concentration in the mid-Pacific atmosphere.

Even the marine air samples which the authors have considered to be seriously contaminated and thus discarded, have lead concentrations that are still several orders of magnitude lower than that of the "cleanest" continental air ever reported.

Patterson (1965) estimated that the natural lead concentration for the atmosphere should be about 0.0005 μg. of Pb per cu. meter. The authors' observed average lead content of the mid-Pacific air is slightly higher than his estimate, but there are indications that the natural lead content should be much less. Prospero, Bonatti, *et al.* (1968) have sampled the continental dust in the atmosphere of the eastern Equatorial Pacific in the general area 8°N to 14°S and 80°W to 110°W during the spring of 1967. They reported the dust loads ranged from approximately 0.06 to 2 μg. per cu. meter with the highest concentrations occurring along a track 5°N and 8°N. The northern samples contained a plagioclase as the dominant mineral, whereas quartz was prevalent in the southern samples. All samples contained significant quantities of plant fibers, pollen grains, and fungal spores. The talc that is used as a carrier for pesticides was the predominating mineral in atmospheric dust collected over the Coral Sea (Risebrough, Hugget, *et al.*, 1968). Assuming that the natural lead content of the continental dusts is 15 p.p.m., the lead concentration of the Pacific atmosphere from the dust load was calculated to be 1×10^{-6} to 30×10^{-6} μg. of Pb per cu. meter. The authors' measured lead concentration of the midocean atmosphere is about 1×10^{-3} μg. of Pb per cu. meter, several orders of magnitude higher than that expected from the natural dust load. Therefore, this finding can be regarded as additional evidence for airborne lead pollution existing in the marine atmosphere.

The lowest atmospheric lead concentration the authors sampled on land was 0.004 μg. of Pb per cu. meter at Laguna Mountain, Calif., at an elevation of 6100 ft. That of the National Air Sampling Network was 0.1 μg. of Pb per cu. meter (USPHS, 1966). The present accepted "safe" level for industrial exposure to lead in air is 200 μg. of Pb per cu. meter (Amer. Conf. Governmental Indust. Hygienists, 1967) which is 200,000 times greater than the observed marine background lead level and perhaps 20,000,000 times greater than natural marine air. Presumably, this "safe" level was chosen without really knowing the exact background level of atmospheric lead.

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Determination of Total Nitrogen in Water by Microcoulometric Titration

Robert T. Moore and James A. McNulty

Dohrmann Instruments Co., 1062 Linda Vista Ave., Mountain View, Calif. 94040

■ A new and rapid instrumental technique has been developed to measure the total of both organically and inorganically bound nitrogen in water. Conceived as a replacement for normal Kjeldahl procedures, the system yields duplicate analyses down to 0.2 p.p.m. in under 10 minutes. The sample is pyrolyzed over a granular nickel catalyst in a stream of humidified hydrogen, the bound nitrogen in the sample being converted quantitatively to ammonia and subsequently titrated electrochemically in a pH-sensitive cell. Suitable for use with partitioning procedures, specific scrubbers, and gas chromatography, the technique is capable of rapidly revealing the organic and inorganic nitrogen spectrum in water samples. Equivalent results are obtained where the sample matrices are the typical hydrocarbons used in partitioning.

Many situations exist where it is important to know the total nitrogen content of a water system:

In industrial effluents where the level of nitrogenous contaminants must be monitored and controlled to prevent stream pollution

In industrial process control where efficiency or safety depend upon controlling total nitrogen in an aqueous medium

In sewage plants where knowing the total nitrogen content in conjunction with the ammonical nitrogen content at various stages gives a picture of total contaminants

In crop fertilization where nitrogen containing fertilizers are added to irrigation waters and the monitoring of total nitrogen in the drainage indicates fertilization efficiency as well as pollution levels

In fresh water supplies where the total nitrogen content must be specified according to usage

In pesticide control where nitrogen-containing pesticides may be monitored in drainage waters (Cassil, Stanovic, *et al.*, 1969)

In ecological studies of water systems where the existence of aquatic and fish life depends upon a range of concentration of total nitrogen

Total Kjeldahl nitrogen (A.P.H.A., 1965) includes ammonia and organic nitrogen, but does not include nitrate and nitrite nitrogen. To include the nitrate and nitrite nitrogen, a modified Kjeldahl procedure utilizing salicylic acid is recommended (A.O.A.C. 1960), but here it is not clear what percentage of the nitrite nitrogen will be recovered. These official Kjeldahl procedures require considerable time for the digestion and distillation of the sample, and great care must be exercised to avoid contamination at the low parts-per million nitrogen levels. The system described here is rapid, free from interferences, and gives the total nitrogen content, both organic and inorganic, for a given water system. Where suitable extraction procedures exist, specific nitrogenous species can be determined quickly. One might aptly describe this method as "the 3-minute Kjeldahl for total nitrogen."

Apparatus

Figure 1 shows a block diagram of the system, and Figure 2 gives the details of the pyrolysis tube. Figure 3 is a schematic diagram of the detection portion of the system, which consists of a microcoulometric cell (Martin, 1966), a microcoulometer, and a recorder. The total system described here is available from the Dohrmann Instruments Co. (Dohrmann Tech. Bull., 1968).

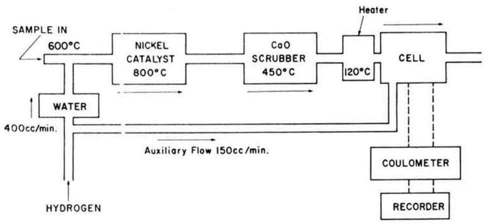

Figure 1. Block diagram of total nitrogen in water system

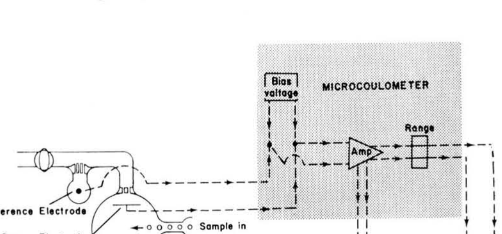

Figure 2. Pyrolysis tube and connections

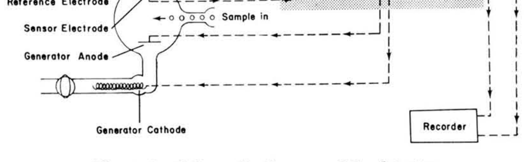

Figure 3. Schematic diagram of the detector

Discussion of Method

The water sample (typically 10 μl.) is injected with a syringe through the septum into the 600 °C. inlet section, volatilizes, mixes with humidified hydrogen, and is swept over the 20- to 50-mesh granular nickel catalyst at 800 °C. (Figure 2). The products of the pyrolysis for a hydrocarbon, R, containing halogen, sulfur, nitrogen, and phosphorus are scrubbed at 450 °C. with a CaO scrubber to remove CO_2 and other acidic gases like H_2S formed by the 800 °C. hydrogenation (Table I). The effluent from the pyrolysis tube then passes through the heated inlet capillary of the titration cell into the electrolyte, where the ammonia is titrated automatically with internally generated hydrogen ions.

In the slightly acidic cell electrolyte (0.04% Na_2SO_4), the ammonia molecule consumes a hydrogen ion according to the reaction

$$NH_3 + H^+ \rightarrow NH_4^+ \quad (1)$$

The sensor electrode (classical platinum-hydrogen pH electrode), in combination with a stable reference electrode, detects the change in hydrogen ion concentration (change in pH) and signals the microcoulometer to generate a hydrogen ion at the generator electrode, according to the reaction

$$1/2\ H_2 \rightarrow H^+ + e^- \quad (2)$$

which thus reestablishes the original pH of the electrolyte (Figure 3). This is therefore null-balance coulometry, wherein the concentration of the titrant (H^+ ions) is reestablished to its original level in performing the titration. Since the number of electrons involved in the above process equals the number of nitrogen atoms in the original sample, it is sufficient to measure the total charge (total number of electrons) which flowed in the generating loop during the analysis to determine the amount of nitrogen in the original sample. The data are typically displayed on a strip chart recorder as a single peak of generator current, I, *vs.* time, t, the area under the peak being the total charge, Q, transferred during the titration according to the equation

$$Q = \int i dt \quad (3)$$

A stoichiometric factor based on the Faraday, the molecular weight of nitrogen, and the particular recorder parameters of sensitivity and chart speed allows the total nitrogen content of the sample to be calculated from the peak area.

Procedure

Preparation of the Catalyst Section. The 20- to 50-mesh granular nickel catalyst must be specially conditioned for quantitation. A satisfactory procedure is the following: Heat the inlet, center, and outlet furnaces at 600°, 900° and 950° C., respectively, and condition the freshly charged combustion tube for 2 hours at a flow of 400 cc. per minute of ultrapure hydrogen; switch gas from hydrogen to high-purity argon and purge at 100 cc. per minute for 10 minutes; switch gas from argon to ultrapure or research grade oxygen at 200 cc. per minute for one hour; repeat argon purge for 10 minutes; switch back to ultrapure hydrogen and condition at a flow rate of 400 cc. per minute. Final overnight conditioning in ultrapure hydrogen is usually adequate.

Slightly sharper peak shapes will be noticed if the nickel catalyst is separated into 20 to 30, 30 to 40, and 40 to 50 cuts, and the pyrolysis tube is packed with the larger granules at the inlet end of the catalyst zone, although this is not essential. Peaks can be sharpened by increased hydrogen flow and reduced temperatures, but here higher background noise and incomplete reduction are possible. Since coking of the catalyst or accumulated impurities such as inorganic salts will tend to increase tailing and reduce yields, a one-hour oxidative burn-off as described above, once a week, is recommended for maintaining quantitation (here, the initial and final hydrogen conditioning steps are reduced to 1 hour apiece at the conditioning temperatures). The scrubber tube must not be placed in the outlet furnace during the catalyst conditioning period, as this contaminates the scrubber tube with low-boiling metal contaminants—such as zinc from the nickel catalyst.

Preparation of Scrubber. The quartz scrubber tube inlet section is filled with 2 inches of 20- to 50-mesh CaO held between quartz wool plugs. The scrubber tube is then baked at 950°C. for 2 hours by insertion in the pyrolysis tube within the outlet furnace section under a water-saturated hydrogen flow of 400 cc. per minute. This drives off water of hydration as well as acidic impurities which would interfere or cause noise during operation. Periodic 20-μl. injections of distilled water during the bake-out will help wash the CaO carrying off out-diffused impurities. The outlet furnace temperature is lowered to 450 °C., and the scrubber tube is withdrawn and allowed to cool to room temperature. The tube is then held vertically so that the CaO is in the uppermost position and tapped gently to settle the CaO packing, which has shrunk slightly during this conditioning process, the quartz wool plug is pushed back against the granules, and the outlet portion of the tube is scrubbed thoroughly with a wet cotton swab to remove carbon, CaO particles, or other impurities that have collected during the high-temperature conditioning. After the outlet portion is dried with a clean, dry, cotton swab, the tube is reinserted in the outlet oven at 450° C. operating temperature. This temperature is above the dissociation temperature of ammonium halides and below the 620 °C. dehydration temperature of $Ca(OH)_2$. Apparently, the hydrated form of CaO is the scrubbing agent, since scrubbing becomes effective only below 550 °C.

The procedure described above also constitutes the reconditioning cycle when recoveries fall off owing to scrubber tube contamination. The scrubber is regenerable for a period of weeks. Other alkaline earth metal oxides such as BaO, SrO, or MgO could have been used in place of the CaO to remove CO_2 and acid gases, but some special preparations would be necessary to produce these materials in a suitable form to prevent small particles from entering the cell and giving strong positive peaks. The choice of CaO was based on availability, convenience, and relative ease of scrubber conditioning.

Saturating the hydrogen with water performs these functions: it reduces coking (indicated by peak tailing) on the nickel which would trap nitrogen on subsequent samples reducing yields; it cleans up trace amounts of carbon in the system which normally contribute to the formation of CO_2; and it keeps the CaO-$Ca(OH)_2$ equilibrium established in the

Table I. Ideal Pyrolysis Products

R (Hydrocarbon)		CH_4, C_2H_6, ..., CO_2
O		H_2O
X (Halogen)	800 °C.	HX
S	H_2, H_2O	H_2S
N		NH_3
P		PH_3

scrubber tube for effective scrubbing of any CO_2 or other acid gases formed during sample injection. The heater on the inlet capillary prevents moisture condensation and subsequent tailing of the peaks, although care should be taken to use DC or shielded AC voltage to prevent electrical interference in the cell.

Other operating characteristics essential to quantitation are the following: the use of ultrapure hydrogen gas; an electrolyte made with high quality double-distilled water; the sample injection rate kept to 1/2 μl. per second or less, since faster injection rates rapidly upset the equilibrium in the combustion tube, tending to yield nonquantitative results; and samples injected at a regularly timed interval which will allow for re-equilibration of the baseline (three to five minutes is typical).

The system, properly conditioned, will also function satisfactorily on most hydrocarbon matrices if water is injected occasionally to keep the scrubber tube conditioned.

Results

Table II illustrates the variety of prepared standards that have been analyzed in this laboratory. Total nitrogen concentrations from 0.2 to 1000 p.p.m. in sample sizes up to 20 μl. are easily quantitated. For a well-conditioned system, variations of ±3% or ±0.2 p.p.m. (whichever is greater) are usual. Worthy of special notice is the fact that aminotriazole gave 90% of theoretical yield, even though it contains a single N—N bond which usually results in lower yields (Martin, 1966). Total instrumental time per analysis is on the order of 2 to 3 minutes. Combustion tubes or scrubber tubes which require reconditioning or very high parts-per-million nitrogen samples may increase measurement time to five minutes or more.

Figure 4 illustrates a typical sequence of injections of an actual industrial effluent independently measured at 35.0 p.p.m. nitrogen (primarily ethylene diamine).

Figure 5 shows typical duplicate recovery at the 10-p.p.m. nitrogen level on inorganic nitrogen in water.

Nonvolatile samples or liquids containing high percentages of nonvolatile material cannot be sampled using hypodermic syringes because the needle fouls. Samples with salt concentrations—such as 20% NaBr or the salts in sea water—do not interfere with quantitation, but they plug the syringe after the second injection. Techniques for the introduction of these samples at the 1/2-μl.-per-second rate have been developed and will be the subject of another paper.

It is advisable to run samples in increasing order of concentration if possible. At concentrations of 2 p.p.m. or below, samples can be run at random. Changing concentrations an order of magnitude may require two or three determinations to establish equilibrium in the pyrolysis furnace. Samples below 1 p.p.m. are best determined on a freshly conditioned scrubber.

Phosphorus and sulfur at levels of 10,000 p.p.m. do not

Table II. Results for Prepared Standards

Sample	Sample Vol., μl.	Known, P.P.M. N	(Mean) Found P.P.M. N	Relative Std. Dev., %	No. of Detns.
			Organics in H_2O		
Diethanol amine	8.4	1.14	1.14	1.6	7
Diethanol amine	5.4	11.4	11.1	0.4	6
Aminotriazol	5.6	18.1	14.7	0.6	4
Chloropheniramine	5.6	10.3	10.1	1.6	6
Ethylene diamine	5.8	35.0	35.1	1.8	4
Ethylene diamine	1.8	70.0	71.6	1.4	4
Ethylene diamine	1.6	140.0	143.0	2.5	4
			Organics in 0.1*M* NaOH		
Bovine albumine (Recrystallized)	5.6	23.6	23.3	2.5	3
Cystine (NBS std.)	5.6	10.8	10.3	2.7	3
Tryptophan	5.6	10.0	9.8	9.0	3
Valine	5.6	9.50	9.40	8.5	3
			Inorganics in H_2O		
Calcium nitrate	5.6	9.5	9.5	2.4	6
Manganous nitrate	5.6	10.0	10.0	2.0	4
Nickel nitrate	5.6	10.7	10.6	2.0	3
Potassium nitrate	5.6	10.5	10.3	2.9	4
Potassium nitrite	5.6	15.0	14.7	2.7	3
			Organic Pesticides in Benzene		
Linuron 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea	5.6	5.3	5.35	3.0	3
EPN (Ethyl P-nitrophenyl thionobenzene-phosphonate)	5.6	10.6	10.2	2.3	5
			Organics in Alcohol		
Diethanol Amine	5.6	15.8	15.9	1.5	3

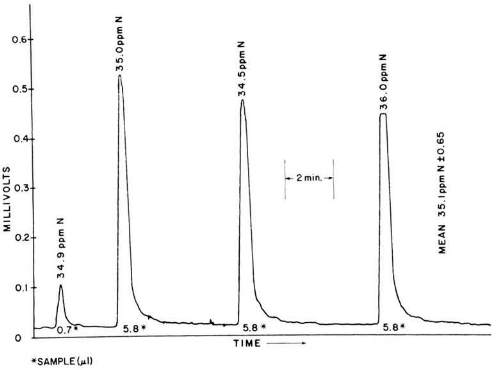

Figure 4. Analysis of plant effluent water

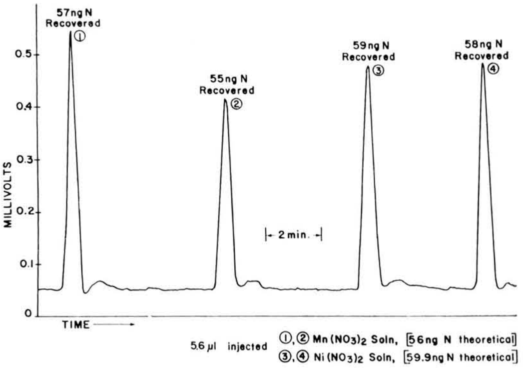

Figure 5. Total inorganic nitrogen in water

interfere. No interference has been encountered from halogen—for example, 20% sodium bromide—and metals such as sodium, potassium, magnesium, and calcium.

Conclusions

A system has been described for measuring the total nitrogen content in water down to 0.2 p.p.m. nitrogen in typically 3 minutes. The system is virtually free from interferences and its components are regenerable if contaminated. It is used in industrial effluent monitoring, water quality control, sewage plant processes monitoring, and as a replacement for total Kjeldahl nitrogen determinations where inorganic nitrogen is included.

Further experimentation should push the limits of detection down into the 0.01-p.p.m. range, since the theoretical blank caused by the dilution effect in the constant pH titration cell is 0.015 p.p.m.

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Air Pollution from Animal Wastes

Determination of Malodors by Gas Chromatographic and Organoleptic Techniques

William E. Burnett

Department of Food Science, Cornell University, Ithaca, N. Y. 14850

■ A combination of gas chromatographic and organoleptic techniques was used to determine the chemical compounds responsible for the offensive odor of accumulated liquid poultry manure. The volatile odorous substances were trapped and concentrated in short sections of gas chromatographic columns held at − 78° C., separated by gas chromatography and identified by the correspondence between relative retention time and the odors of the peaks for the unknowns and authentic compounds. Mercaptans, sulfides, and diketones were identified. Volatile organic acids and the nitrogen heterocycles, indole and skatole, were also identified, using direct injections of liquid manure supernatant and standard gas chromatographic techniques. The sulfur compounds, organic acids, and skatole were implicated as important malodorous components involved in air pollution. The prevention of the formation of the malodorous substances was suggested as the best means of control of air pollution from animal wastes.

Modern, high-density animal-confinement operations produce large quantities of manures which rapidly undergo microbial decomposition with the production of strong, obnoxious odors. When these odors are discharged into the ambient atmosphere by ventilation systems or when the manure accumulations are disturbed, as during cleaning and subsequent waste disposal operations, nuisances result which are incompatible with residential and recreational use of adjacent areas (ENVIRON. SCI. TECHNOL., 1968).

Very little information is available regarding the chemical nature of the odor of animal manures. Such information is vital for the intelligent management or treatment of wastes to prevent, minimize, and control odors during storage, handling, and disposal.

Previous workers have identified some of the components of the odor of animal wastes. The odorous gases, ammonia and H_2S, have been already identified by a number of workers (Day, Hansen, *et al.*, 1965; Lebeda, Day, *et al.*, 1964; Lebeda, 1965; Hammond, Day, *et al.*, 1968).

In some investigations on the odors from animal wastes, odorous compounds have been separated by gas chromatography. Deibel (1967) performed gas chromatographic analyses on the odor of fresh and accumulated poultry manure. He found butyric acid, ethanol, and acetoin (3-hydroxy-2-butanone) to be the chief volatile components in accumulated manure, while fresh manure was devoid of these compounds. Of these compounds, butyric acid is the most malodorous and evidently contributes to the off-odor of accumulated poultry manure.

Merkel, Hazen, *et al.* (1968), using functional group tests and gas chromatography, identified amines, amides, alcohols, carbonyls, sulfides, disulfides, and mercaptans as components of the total volatiles from accumulated swine waste. Of these groups, only the alcohols and carbonyls were separated into their individual components. The alcohols included methanol, ethanol, *n*-propanol, 2-propanol, *n*-butanol, and 3-methyl 1-butanol. The carbonyls identified were formaldehyde, acetaldehyde, propionaldehyde, isobutyraldehyde, heptaldehyde, valeraldehyde, octaldehyde, and decaldehyde.

Merkel, Hazen, *et al.* (1968) also performed some odor evaluations, using selective absorbants to alter the odor from swine waste. The alcohols and carbonyls were judged unimportant, whereas the amines and sulfides were considered the major malodorous constituents.

Except for this recent work of Merkel, Hazen, *et al.* (1968) on the odor of animal wastes, there have been no serious attempts to relate instrumental results to subjective odor responses. Relating instrumental analyses and subjective reactions is important because not all of the components of the volatile fraction from animal wastes separated by gas chromatography are odorous. Furthermore, although many compounds possess a characteristic odor, they may not contribute malodorous notes to the total odor. Therefore, a very useful technique is to smell each fraction associated with a peak on the developed chromatogram, noting those components which have strong or offensive odors. This can be accomplished by use of the technique of correlating sensory and gas chromatographic measurements which was developed by Fuller, Steltenkamp, *et al.* (1964) and successfully used by Guadagni, Okano, *et al.* (1966) to assess the role of various aroma fractions in Delicious apple essence.

This paper deals with the results of the application of gas chromatographic and organoleptic techniques to the determination of the important compounds responsible for the malodor of accumulated liquid poultry manure.

Experimental

Gas Chromatography. A Model 1520B Varian Aerograph gas chromatograph was equipped with dual-flame ionization detectors, a matrix temperature programmer, and a Varian Model 20, 1-mv., dual-pen recorder operated at a chart speed of 20 inches per hour. The flame detectors were operated using a hydrogen flow rate of 30 ml. per minute and an air flow rate of 300 ml. per minute. One of the column-detector systems was equipped with an effluent-stream splitter which split the effluent from the column so that 20% went through the detector and 80% through an exit tube which permitted an observer to describe the characteristic odor of each fraction that emerged from the column (Guadagni, Okano, *et al.*, 1966). An attendant stationed at the chromatograph recorder wrote down each of these odor descriptions near the peak which corresponded to the odorous fraction.

Two different columns and sets of chromatographic conditions were used for these separations. For direct aqueous injections, a 6-foot × 0.25-inch o.d., aluminum, Porapak-Q, 100- to 120-mesh column was used. The gas chromatographic conditions were as follows: injector temperature, 190° C.; detector temperature, 220° C.; column temperatures, 100° C. for 12 minutes, followed by a ballistic increase to 200° C., and held at 200° C. until completion of the analysis; carrier gas (helium) flow rate, 50 ml, per minute at 65 p.s.i.; electrometer range, 0.1 (most sensitive); and recorder attenuation, × 4. For samples concentrated by precolumn trapping (see Sampling Procedures), a 4-foot × 0.25-inch o.d., stainless steel, Porapak-Q, 50- to 80-mesh column was employed. A two-foot section of this column, attached to the other column section by a Swagelok union, was used as the precolumn. The chromatographic conditions were as follows: injector temperature, 230° C.; detector temperature, 280° C.; column temperature program, hold at 75° C. for 2 minutes, 10° C. per minute increase for 10 minutes, hold at 175° C. for 2 minutes, 10° C. per minute increase for 6 minutes and hold at 230° C. until completion of analysis; carrier gas (helium) flow rate, 20 ml. per minute at 65 p.s.i.; electrometer range, 0.1 (most sensitive); and recorder attenuation, × 4 (unless otherwise noted).

The second column-detector system in the instrument was used for conventional separations. The method of Hindin, May, *et al.* (1964) was used to determine volatile organic acids. A 4-foot × 0.125-inch o.d., stainless steel, 10% Carbowax 20M on 60- to 80-mesh, acid-washed Chromosorb-W column was used for the separations. The gas chromatographic conditions used were as follows: injector temperature, 240° C.; detector temperature, 280° C.; column temperature, 125° C.; carrier gas (helium) flow rate, 25 ml. per minute at 65 p.s.i.; electrometer range, 1.0; and recorder attenuation, × 4.

Indole and skatole were separated on a 5-foot × 0.125-inch o.d., copper, 5% SE-30 on 50- to 80-mesh, acid-washed, DMCS-treated Chromosorb-W column under the following instrumental conditions: injector temperature, 290° C.; detector temperature, 300° C.; column temperature, 100° C; carrier gas (helium) flow rate, 30 ml. per minute at 65 p.s.i.; and electrometer range, 0.1 (most sensitive).

Sampling Procedure. All of the analyses reported here were performed using accumulated liquid poultry manure collected from a commercial poultry farm from pits under caged White Leghorn laying hens. To prepare the waste for direct aqueous injections into the gas chromatograph, the manure was filtered through glass wool to remove feathers and large particles, and then centrifuged at 10,000 r.p.m. for 10 minutes. The clear, straw-colored supernatant was saved for injections into the gas chromatography instrument.

For the separations of indole and skatole, the liquid manure was steam distilled and the distillate extracted with chloroform according to the procedure of the A.O.A.C. (1960). The chloroform extract was evaporated in a rotating-film evaporator to 3-ml. volume, and samples were injected into the chromatograph.

In most cases, however, concentration of the liquid manure volatiles was necessary to provide sufficient quantities of the odorous components to give a measurable response by the flame detector. The precolumn trapping procedure of Hornstein and Crowe (1962) was used to concentrate the volatiles. Six hundred milliliters of liquid poultry manure, 150 grams of sodium sulfate, and a magnetic stirring bar were placed in a 1-liter Erlenmeyer flask. The flask, in a water bath held at 70° C., was connected to the assembly for collecting volatiles (Figure 1).

To begin the collection, the nitrogen gas was bubbled through the stirred manure. The volatiles in the headspace of the flask were carried by the sweep gas through a calcium

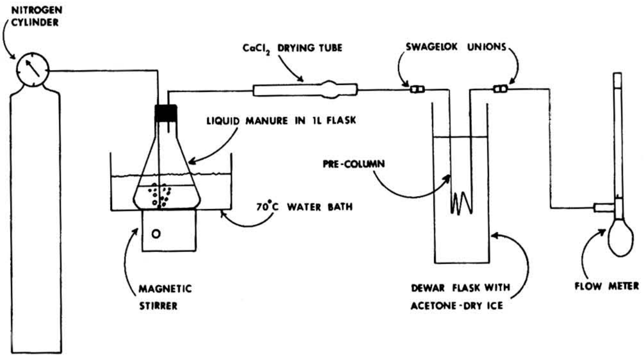

Figure 1. Precolumn trapping assembly

chloride drying tube and trapped in a coiled 2-foot precolumn held in a Dewar flask containing acetone and dry ice. The exit end of the precolumn was attached to a soap bubble flow meter. Flow rates were between 30 and 50 ml. per minute and sampling times between 45 minutes and 2.5 hours. At the completion of a run, the column was removed from the dry ice–acetone bath and immediately installed in the gas chromatograph. The column was then heated to the initial temperature (usually 75° C.). A small amount of methanol was injected as an internal standard to aid in identification of the volatiles. After a 5-minute equilibration, the carrier gas was turned on and the chromatogram developed. The organoleptic evaluation for each component was noted on the recorder chart as previously described.

Aroma Significance Tests. To provide information regarding the relationship of sulfur compounds to the offensive odor of liquid poultry manure, the effects of a reagent for sequestering sulfur compounds on the odor of liquid manure was observed, according to the procedure of Grill, Patton, *et al.* (1966). Fifteen milliliters of 6% aqueous $HgCl_2$ solution (to bind hydrogen sulfide, mercaptans, sulfides, and disulfides) was added to 5 ml. of poultry manure supernatant in each of three foil-covered, 125-ml., glass-stoppered Erlenmeyer flasks. These flasks and three untreated controls (5 ml. of supernatant + 15 ml. of distilled water) were submitted to an odor panel of 8 to 10 laboratory personnel, who evaluated the degree of similarity of the head-space aroma between a standard (untreated poultry manure) and the six unknown flasks, using the procedure of Schutz (1964). The panelists related the degree of similarity on an 8-point scale, where 8 signified similarity to and 0 meant no similarity to untreated liquid poultry manure. The panelists were asked for comments on the character of the aroma of each of the flasks. A sample data sheet is shown in Figure 2.

Results and Discussion

Separation and Identification of Volatile Acids. From 0.5 μl. of prepared supernatant injected directly into the gas chromatograph, six peaks were repeatedly obtained on the Carbowax 20M column. These were identified as acetic, propionic, isobutyric, *n*-butyric, isovaleric, and *n*-valeric acids. Identi-

Sniff the manure standard. Compare the unknowns with the standard in turn, and rate the degree of similarity on the following scale:

Extremely similar	8
	7
Very similar	6
	5
Moderately similar	4
	3
Slightly similar	2
	1
Not similar	0

Ignore any differences in intensity, and concentrate on odor quality.

Liquid Manure Standard Odor

Unknowns	Degree of Similarity	Comments
1	—	
2	—	
3	—	
4	—	
5	—	
6	—	

Name____________

Date____________

Figure 2. Aroma significance test

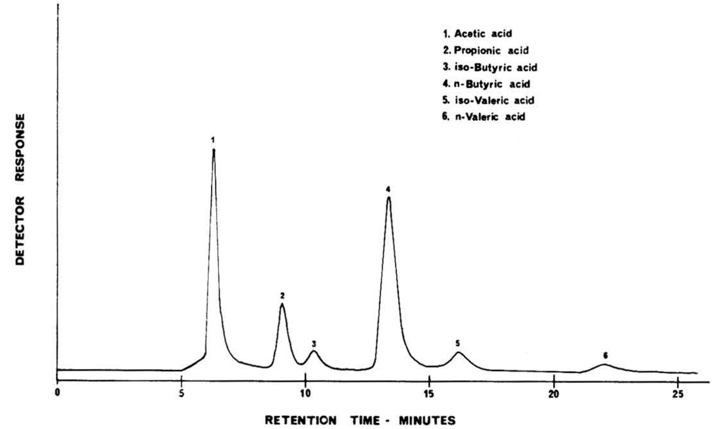

Figure 3. Typical separation of volatile fatty acids from poultry manure on a Carbowax 20M column

fications were made by comparison of the retention times of the unknowns with those of the authentic compounds. A typical separation obtained on the Carbowax 20M column is shown in Figure 3.

The volatile acids, especially the *n*-butyric, isobutyric, *n*-valeric, and isovaleric acids, have very disagreeable rancid or sweatlike odors. Merkel, Hazen, *et al.* (1968) were unable to detect organic acids in the vapors above storage pits containing liquid hog waste, probably because the pH of the waste was 8.0 or above. The pH of any waste would be an important factor in determining whether the organic acids contribute offensive notes to the odor. The pH of the liquid poultry waste in the current studies was usually between 7.0 and 7.4. As described later, the C_2 and C_3 organic acids were detected instrumentally and organoleptically, using direct injections of liquid manure supernatant.

Separation and Identification of Nitrogen Heterocycles. Two and one-half microliters of concentrated chloroform extract were injected into the gas chromatograph using the SE-30 column. Indole and skatole were identified by retention time comparisons with authentic compounds. A typical separation is shown in Figure 4. The presence of indole and skatole in liquid poultry manure was also confirmed by a colorimetric test (A.O.A.C., 1960).

The detection of the nitrogen heterocyclic compounds, indole and skatole, in animal wastes is significant. Indole is reported to have a powerful, harsh α-naphthylamine odor in large concentrations and an odor of jasmine upon dilution (Moncrieff, 1967; Givaudan, 1961). Skatole or methyl indole has been called "the odorous principle of faeces" (Moncrieff, 1967) because of its powerful disagreeable odor, which is present even upon great dilution. Both indole and skatole are very tenacious odorants which tend to cling to clothing and other articles and to persist for long periods. In the current study, approximately 18 times more skatole was found than indole [based on measurements of peak height (mm.) × attenuation]. Skatole, therefore, is evidently responsible for the strong fecal note in the malodor and probably is in part responsible for the tenacious character of the poultry waste odor.

Separations Using Effluent Stream Splitter. Using direct injections of 25 μl. of manure supernatant, five peaks of characteristic odor were recorded on the chromatogram. However, some additional odors were detected organoleptically where no peaks appeared on the chromatographic trace. This means that a number of compounds were present in sufficient quantities to give an odor, but not in sufficient quantities to give a response by the flame detector (Figure 5). Judging from the odor evaluations, these compounds were most likely volatile sulfur compounds which have offensive odors and rather low odor thresholds. Table I lists the odors associated with each peak in Figure 5 and the possible identity of each compound. These tentative identifications were confirmed to the extent that their odors were identical to the authentic compounds. These results agreed with the analysis of volatile acids by the method of Hindin, May, *et al.* (1964) reported above, and indicate that volatile organic acids do play a role in the malodor of liquid poultry manure.

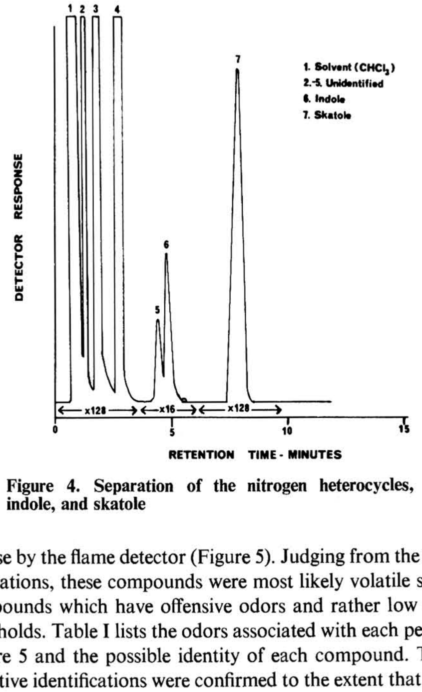

Figure 4. Separation of the nitrogen heterocycles, indole, and skatole

Table I. Organoleptic Evaluations of Eluted Components[a]

Peak No.	Odor	Possible Compound(s)
1	Ammonical	NH_3 or an aliphatic amine
2	Vinegarlike	Acetic acid
3	Picklelike	Propionic acid
4	Sweatlike	2-methylpropionic acid
5	Rancid odor	*n*-butyric acid

[a] Figure 5.

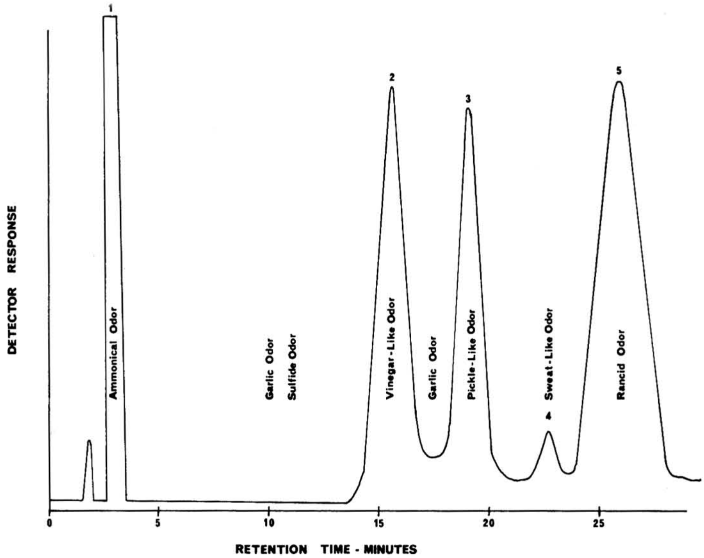

Figure 5. Chromatogram of liquid manure volatiles with organoleptic evaluations obtained from direct injection of prepared supernatant

Use of the precolumn trapping method of Hornstein and Crowe (1962) in combination with organoleptic evaluations of the volatile components separated by gas chromatography yielded the best results.

Fourteen peaks including methanol (internal standard) were obtained. Of the fourteen peaks, nine had a characteristic odor (Figure 6). By comparison of relative retention times (RRT) and odors of the unknown peaks with those of authentic compounds, a number of tentative identifications were made (Table II).

The presence of a number of highly volatile aliphatic mercaptans and sulfides in liquid poultry manure is also significant. These classes of compounds possess strong, highly offensive odors and evidently play a large role in the over-all odor blend. Incidentally, this finding is consistent with the recent findings of Merkel, Hazen, *et al.* (1968) relating to the odor of hog manure. They found that the offensive odor of accumulated liquid hog manure was due in part to the presence of thiol groups.

The aroma significance test gave a further indication of the very important role that the sulfur compounds play in determining the malodor of poultry waste. The addition of mercuric chloride to the liquid manure supernatant reduced the odor similarity from 7.3 (very similar for the control flasks) to a value of 4.3 (moderately similar). The panelists noted that the treated samples lost their offensive, putrid character and had instead a "sick-sweet" odor which probably was due to the organic acids and nitrogen heterocycles.

The diketones, 2,3-butanedione (diacetyl) and 3-hydroxy-2-butanone (acetoin), have rather pleasant, sweetish odors. They are largely responsible for the odor of fresh butter (Moncrieff, 1967). Although they evidently do not contribute any offensive notes to the malodor of poultry waste, they most certainly contribute to the total odor. The same might be said

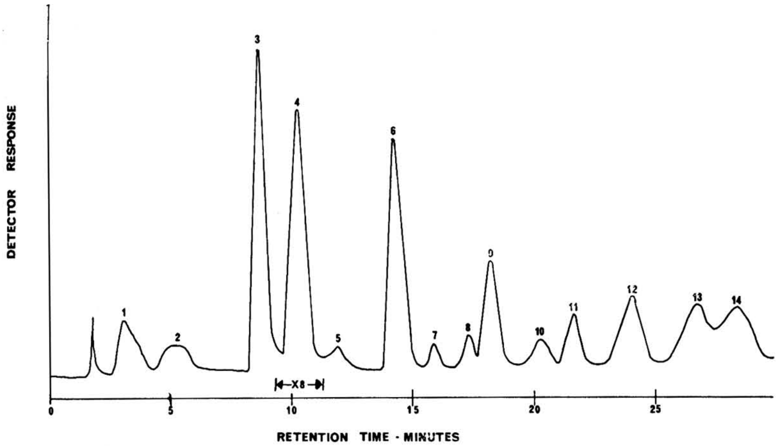

Figure 6. Chromatogram of concentrated liquid manure volatiles obtained by the precolumn trapping technique

Table II. Tentative Identifications of Unknowns[a]

Peak No.	Odor	RRT[b]	RRT[b] of Authentic Compound	Possible Compound(s)	Odor Confirmation with Authentic Compound?
1	Rotten eggs	. . .	. . .	Hydrogen sulfide	Yes
4	Rotten cabbage	1.22	1.29	Methyl mercaptan	Yes
6	Onionlike	1.77	1.97	Ethyl mercaptan	Yes
7	Putrid	1.97	1.98	Methyl sulfide	Yes
9	Butterlike	2.28	1.59	2,3-Butanedione (diacetyl)	Yes
10	Onionlike	2.57	2.56	*n*-Propyl mercaptan	Yes
11	Butterlike	2.75	2.82	3-Hydroxy-2-butanone (acetoin)	Yes
12	Putrid, garlic	3.07	3.08 3.24	*n*-Butyl mercaptan or Methyl disulfide	Uncertain

[a] Figure 6. [b] Relative Retention Time. Methanol (Peak No. 3) Internal Standard = 1.00.

for alcohols, aldehydes, amides, etc. which were found as components of the odor of hog waste (Merkel, Hazen, *et al.*, 1968). Although they were judged unimportant in determining the nature of the malodor, if present in suprathreshold concentrations, they would contribute to the total odor. Furthermore, even if some of these substances were present in subthreshold concentrations, they could contribute to the total odor owing to additive effects (Guadagni, Okano, *et al.*, 1963).

Merkel, Hazen, *et al.* (1968) found that aliphatic amines played a significant role in the odor of hog waste. Although aliphatic amines were not determined by gas chromatography in the current study, their presence in accumulated poultry waste is suspected. For example, when a trichloroacetic acid extract of accumulated poultry waste was steam distilled at alkaline pH, a characteristic foul, "fishy" odor of aliphatic amines was detected in the headspace of the flask containing the steam distillate.

The results of the current study and those of Merkel, Hazen, *et al.* (1968), emphasize the fact that the odor of animal wastes is not due simply to the presence of the gases, ammonia and hydrogen sulfide, or even to one or two odorous organic compounds, but to a very complex mixture of volatile organic compounds and odorous gases. Recent studies, the current study included, have not exhausted all of the possibilities of odorous compounds, but it is believed that most of the more important types of compounds that contribute to the obnoxious odor of manure accumulations have been accounted for. Future investigations will no doubt round out our knowledge of the chemical nature of the odor of animal wastes.

The identification of such powerful odorants as indole, skatole, mercaptans, and sulfides in accumulated liquid poultry waste helps to explain why the odors from such animal wastes carry over great distances, as during land spreading of the material, and emphasizes the need for adequate odor control measures. If animal industries are to coexist with their neighbors, such measures will have to be put into effect.

As reviewed by Lindemann (1964), the control of odors includes masking or modification and elimination by mechanical, physical, or chemical means. For animal wastes, masking is not completely satisfactory because there is no substitute odor that is completely inoffensive to everyone.

Some form of elimination or prevention seems to offer the greatest possibility of control of odors from animal wastes. For example, recent research by Ludington, Bloodgood, *et al.* (1967) has shown that the aeration of stored liquid poultry waste has been effective in preventing the formation of the odorous gas, hydrogen sulfide. In-house drying of poultry wastes during collection has been effective in controlling odors (Bressler, 1968). Launder (1968) found that the collection of poultry wastes in a mixture of cold water and phosporic acid effectively inhibited the production of obnoxious odors. Other practical methods of prevention should be within the realm of possibility.

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Sedimentary Phosphorus in Lake Cores—Analytical Procedure

Dennis A. Wentz and G. Fred Lee

Water Chemistry Laboratory, University of Wisconsin, Madison, Wis. 53706

■ A dilute HCl-H_2SO_4 extraction procedure for the removal of "available" phosphorus from lake sediments is presented. Sediment sample size, pH of the sediment-extractant mixture, and sample pretreatment (including drying and grinding) all significantly affect the amount of phosphorus removed. In theory, all sorbed orthophosphate should be leached from the sediment at the pH employed. In addition, fluoroapatite and calcium phytate show 88 and 11% recovery, respectively, while AMP and $FePO_4$ are not significantly recovered. FeS at a concentration of 22.3 mg. of Fe per gram of dry sediment does not interfere. There is a significant error resulting from color and turbidity leached from the sediment, but this is relatively constant. The phosphorus extracted is measured using a modified vanadomolybdophosphoric yellow color procedure. A wavelength of 420 mμ is employed to minimize the effect of iron and to obtain optimum sensitivity and adherence to Beer's law. The over-all technique may have application in the study of accelerated lake eutrophication.

Phosphorus is probably the nutrient most often implicated as a possible limiting factor in the biological production of a lake. In the watershed, it may exist in various organic and inorganic combinations (Degens, 1965; Jackson, 1964; Mortensen and Himes, 1964; Olsen and Fried, 1957; Tisdale and Nelson, 1966). Thus, there is no reason to expect that all the phosphorus entering a lake should be in a form which is amenable to utilization by the associated biota. One of the phosphorus fractions designated in the field of soil chemistry as "available," i.e., extractable by one of several different procedures and correlative to a positive field crop response, might have given an indication as to the past association of phosphorus deposition and biological production. A study was, therefore, undertaken in an attempt to elucidate this potential relationship.

The first portion of the investigation was devoted to the development and evaluation of a suitable analytical procedure, the results of which are reported here. The second paper in this series will discuss the application of the procedure to a sediment core taken from Lake Mendota, Wis.

Experimental

Numerous tests have been proposed for measuring the phosphorus fertility level of soils. These are primarily extraction procedures designed to provide an indication of the amount of soil phosphorus which is biologically usable. Actually, the tests measure certain operationally-defined fractions of the soil phosphorus, which are, in turn, correlated with crop growth responses.

Phosphorus fractions extracted in the above manner are known collectively as various forms of "available" phosphorus. The most common procedures presently in use are discussed in Jackson (1968), Nelson, Mehlich, *et al.*, (1953) and Olsen and Dean (1965). These procedures remove water-soluble, acid-soluble, and alkali-soluble phosphorus. Many of the extractants are buffered, and many contain an agent for releasing the tightly-bound iron and aluminum phosphates which may be present in some soils.

The manner in which phosphorus is bound should be similar for soils and sediments. Livingstone's (1957) and Livingstone and Boykin's (1962) work on Linsley Pond, a eutrophic glacial lake in southern Connecticut, implies a sorption mechanism to account for the apparent association of sedimentary phosphorus with mineral matter. The effect of pH on the sorption of phosphorus onto bentonite, Fuller's earth, and onto river, lake, and estuarine sediments is such that the sorption is maximum at neutral to slightly acidic pH's (Carritt and Goodgal, 1955; Jitts, 1959; Macpherson, Sinclair, *et al.*, 1958). Above and below this range the percentage of phosphorus sorbed decreases rapidly (apparently to zero at extreme values). The reaction appears to be reversible under usual environmental conditions.

The method of phosphorus extraction described in this investigation is a modification of the dilute HCl-H_2SO_4 procedure described by Olsen and Dean (1965). The extractant has a pH of 1.1, the lowest to be found in the literature. On this basis the procedure selected as maximum release of any sorbed sedimentary phosphorus should be provided via a pH-controlled desorption. Unless otherwise stated, any subsequent mention of available phosphorus shall refer to the operationally-defined phosphorus fraction extracted by this procedure.

The dissolved orthophosphate which resulted from leaching the sediment was analyzed by means of vanadomolybdophosphoric yellow procedure of Kitson and Mellon (1944). This procedure was taken directly from Jackson (1958), except that all measurements were made at 420 mμ after 20 minutes as suggested by Olsen and Dean (1965). Because of the high chloride concentration of the extractant, the color-forming reagent was prepared by replacing the HNO_3 with an equivalent amount of HCl.

The vanadomolybdophosphoric yellow procedure was selected over the more commonly used molybdophosphoric blue procedures (Jackson, 1958; Standard Methods, 1965; Strickland and Parsons, 1965) for several reasons: A pH adjustment is not required provided the aliquot taken for analysis would not produce an acidity greater than 0.2 *N* if diluted to 50 ml.; there is no reduction step; the color is stable for at least two weeks (Kitson and Mellon, 1944); and interfering ions are virtually nonexistent—even arsenate does not interfere below 125 mg. per liter (Kitson and Mellon, 1944).

Results and Discussion

Unless otherwise stated, all sediment samples were oven-dried at 105 °C. for at least 24 hours and were ground using a mortar and pestle; all reagents were prepared from ACS reagent grade chemicals; and all analyses were done with the aid of a Beckman DU spectrophotometer.

Phosphorus Determination. Studies of the visible spectrum of the yellow heteropoly complex, Perkin-Elmer Model 202 ultraviolet spectrophotometer, and of calibration curves constructed at various wavelengths indicated that 420 mμ provides both optimum sensitivity and adherence to Beer's law throughout the specified absorbance range of 10 to 75% transmittance (*T*). [An attempt was made to restrict all spectrophotometric measurements to the range of 10 to 75% *T*, to keep the absolute photometric error to a minimum and still allow a maximum range of phosphorus concentration to be analyzed (Meites and Thomas, 1958).] These facts, along with Shapiro and Brannock's (1962) suggestion that 420 mμ be employed to minimize the interference from iron [apparently a yellow background attributable to dissolved Fe(III)], provide the basis for utilization of this wavelength in all subsequent analyses.

Sensitivity, minimum detectable concentration (MDC), precision, and working range of the vanadomolybdophosphoric yellow color method were determined and are presented in Table I. The sensitivity is two to five times poorer than that suggested for the molybdophosphoric blue procedure, while the MDC is three to seven times higher (Standard Methods, 1965). The over-all working range of 0.2 to 18 mg. of P per liter, determined for various light paths at 420 mμ, compares favorably to the range of 0.75 to 20 mg. of P per liter indicated by Jackson (1958) for 1 cm. cells at wavelengths between 400 and 420 mμ. In 10 cm. cells, the lower limit of the working range is still an order of magnitude greater than that observed for the blue color method. The measured precision is better than that listed in Standard Methods (1965), for the blue color method, by a factor of three.

Phosphorus Extraction. All sediment-extractant mixtures were shaken in 50-ml. Erlenmeyer flasks for 5 minutes at 300 r.p.m. (Metabolyte Model G77 water bath shaker) and at a constant ambient temperature of 20 °C. No specific attempts were made to determine the effects of varying these conditions. However, evidence presented later, in regard to the effect of multiple extractions, indicates that further increasing the time or rate of shaking would not have resulted in increased phosphorus release.

Table I. Sensitivity, Minimum Detectable Concentration, Precision, and Working Range for the Vanadomolybdophosphoric Yellow Color Procedure

Light Path, Cm.	Sensitivity,[a] Mg. P/L./%*T*	MDC,[b,c] Mg. P/L.	^sC,[d,c] Mg. P/L.	Working Range,[e] Mg. P/L.
1	0.15	0.2	0.02	2–18
5	0.030	0.04	0.004	0.4–3.6
10	0.015	0.02	0.002	0.2–1.8

[a] The sensitivity is defined as the change in concentration which accompanies a 1% change in transmittance at a level of 50% *T*.

[b] $MDC = (\bar{A}/S - C)\sqrt{n}$, where $\bar{A}$ is the mean absorbance determined from *n* different solutions of a single known concentration, C, and S is the slope of the standard curve [see Wentz (1967) for derivation of the equation].

[c] Determined from 10.0, 2.00, and 1.00 mg. of P per liter standards for 1, 5, and 10 cm. cells, respectively; $n = 5$.

[d] ^sC is the standard deviation for concentration based on $n - 1$ degrees of freedom and is a measure of the precision of the method.

[e] Determined from the intersections of the 10 and 75% *T* lines with the standard curves.

If the phosphorus being extracted is sorbed phosphorus, then the extraction can be considered a desorption, for which there exists an equilibrium condition. This equilibrium should be achieved if the results are to be meaningful. As the rate of phosphorus desorption and the equilibrium phosphorus concentration are both proportional to the temperature at which the extraction is performed, increased time and/or rate of shaking would have no effect on the amount of phosphorus released if equilibrium had been attained at the specified temperature. Precipitated phosphorus compounds would be expected to behave similarly to sorbed phosphorus forms, except that the mechanism of release would be dissolution rather than desorption. In any event, the released phosphorus is an operationally-defined fraction of the total, and incongruities are kept to a minimum by maintaining the extraction conditions as nearly constant as possible.

Olsen and Dean (1965) recommend filtration through a Whatman No. 42 filter for clarification of the sediment-extractant mixture. This method was compared with centrifugation and membrane filtration techniques by suspending samples of subsurface marl from Lake Mendota in distilled water and measuring the turbidity spectrophotometrically at 420 mμ.

Filtration through a 0.45-micron membrane filter and centrifugation at 10,500 r.p.m. (Servall type SS-4 centrifuge) for 30 minutes provided similar results; both were superior to filtration through a Whatman No. 42 filter. The membrane filtration technique was selected for use in all studies except those involving successive extractions of the same sample. Centrifugation for 30 minutes at 10,000 r.p.m. was used for the latter.

The Darco G 60 quality charcoal suggested by Olsen and Dean (1965) is apparently intended as a decolorizing agent as dilute HCl-H_2SO_4 extracts of lake sediments are yellow and have visible spectra similar to those of the vanadomolybdophosphoric yellow color. However, because of dilution, the contribution of this yellow color to the final absorbance is relatively small. For this reason, use of the charcoal was eliminated from the procedure. An analysis of the error thereby introduced is presented later.

The effect of sample size on the amount of available phosphorus extracted is shown in Figure 1. The general shape of the curve (Figure 1a) indicates maximum available phosphorus at low sample weights (approximately 0.05 gram) and a

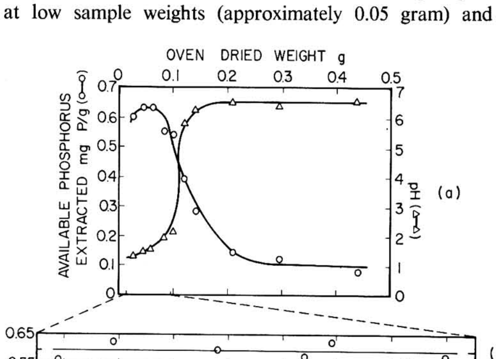

Figure 1. Effect of sample size on the amount of available phosphorus extracted from the subsurface marl of Lake Mendota (a), and a detailed analysis of the plateau (b).

sharp decrease to a constant minimum value above 0.25 gram. A detailed examination (Figure 1b) of the gently-rounded peak suggests that it is actually a plateau extending from 0.03 to 0.08 gram. This amounts to an extractant per sample ratio of 1.5-to-4 when expressed on a milliliter per milligram basis. Throughout this plateau the amount of available phosphorus extracted is not a function of sample size.

The pH's of the extracts are also plotted in Figure 1a. The equivalence point, which is indicated at 0.11 gram of sediment, results from the titration of the acid extractant by the carbonates of the marl. Rough calculations based on the pH of the extractant and the amount of sediment required to titrate it, indicate that the sediment is 58% carbonate by weight. Calculations for the surface sludge of the same core (based on a similar curve showing a plateau in the range from 0.03 to 0.06 gram and an equivalence point at approximately 0.2 gram) suggest a value of 32% carbonate. These values compare favorably with the averages of 62.7 and 32.3% carbonate reported by Murray (1956) for the marl and sludge, respectively, of Lake Mendota.

The sharp pH increase causes an inhibition of phosphorus desorption and a curtailment of the plateau. An example of a situation wherein the pH effect is inoperative is represented by the subsurface organic (peat-like) sediments of Comstock Lake in Marquette County, Wis. (Figure 2). In this case, the plateau is seen to be much larger than that found in the Lake Mendota sediment. Its curtailment apparently results when the volume of extractant used is no longer sufficient to hold all the potentially extractable phosphorus in solution.

To determine the efficiency of the extraction procedure, five successive extractions were completed on each of two samples from the subsurface Lake Mendota marl. Sample sizes were based on previous results. There was no indication of a significant increase in available phosphorus removed after the first extraction (Figure 3). The cumulative available phosphorus appears to increase slowly after the first extraction; this is because the amount removed by each successive extraction falls within a background, which may be due, at least partially, to a combination of color and turbidity.

The results also indicate that for one extraction, the selected time and rate of shaking are sufficient to allow the attainment of equilibrium at the temperature employed.

Effect of Sample Pretreatment. Having established the conditions of the actual extraction step, the effects of sample preparation were examined. The two pretreatments investigated were drying sediment samples and increasing sample homogeneity. Two different sediment types, subsurface marl from Lake Mendota and subsurface organic sediments from Comstock Lake, were utilized.

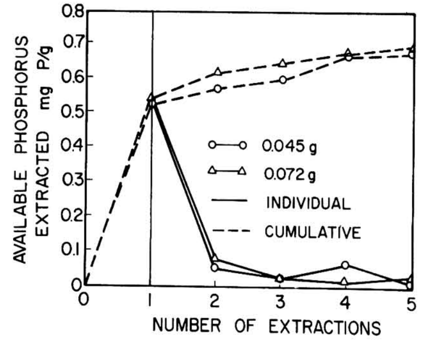

Figure 3. Effect of multiple extraction on the amount of available phosphorus removed from the subsurface marl of Lake Mendota

According to Jackson (1958), freshly-taken, moist soil samples should be extracted, as the available phosphorus can be increased from between 10 and 30% to greater than 100% by air-drying and oven-drying, respectively. He indicates that these effects appear to be most pronounced in acid soils.

Replicate analyses of available phosphorus were determined on wet, air-dried, and oven-dried samples of the Mendota and Comstock sediments. The wet samples were hand-mixed with a glass stirring rod, while the dried samples were gently ground using a mortar and pestle. Moisture content was determined on the wet and air-dried samples. The results are presented in Table II.

Both the mean available phosphorus ($\overline{AP}$) and the precision (s_{AP}) of the extraction appear to have increased on drying. The available phosphorus increase resulting from air-drying is 16% in both cases and compares favorably with the range of 10 to 30% suggested by Jackson (1958) for soils. On the other hand, Jackson indicates a 100% increase in the available phosphorus of soils after oven-drying. A range of 19 to 22% was found for the two lake sediment types studied in this investigation.

In an effort to improve the precision of the extraction procedure, attempts were made to increase the sample homogeneity. Wet samples were ground as fine as possible using a tissue grinder. Oven-dried samples were ground to pass a 270-mesh sieve (53-micron opening) using a mortar and pestle. Table III lists the results.

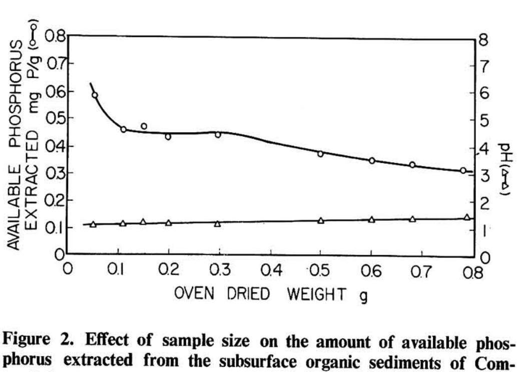

Figure 2. Effect of sample size on the amount of available phosphorus extracted from the subsurface organic sediments of Comstock Lake, Marquette County, Wis.

Table II. Effects of Drying on the Available Phosphorus Extracted from Lake Sediments

Sediment Type[a]	Pre-treatment	Available Phosphorus[b] Mg. P/G. Mean, $\overline{AP}$	Available Phosphorus[b] Mg. P/G. Std. Dev.,[c] s_{AP}	No. of Replicates n
LM	Wet	0.55	0.170	4
LM	Air-dried	0.64	0.075	5
LM	Oven-dried	0.67	0.043	5
CL	Wet	0.37	0.116	5
CL	Air-dried	0.43	0.033	4
CL	Oven-dried	0.44	0.026	4

[a] LM = Lake Mendota subsurface marl; CL = Comstock Lake subsurface, organic sediments

[b] All results are expressed on an oven-dried weight basis

[c] Based on $n - 1$ degrees of freedom

Table III. Effect of Increasing Sample Homogeneity on the Available Phosphorus Extracted from Lake Sediments

Sediment[a]	Pretreatment	Available Phosphorus,[b] Mg. P/G. Mean, $\overline{AP}$	Std. Dev.,[c] s_{AP}	No. of Replicates n
LM	Wet, hand-mixed	0.55	0.170	4
LM	Wet, homogenized	0.60	0.139	5
CL	Wet, hand-mixed	0.37	0.116	5
CL	Wet, homogenized	0.48	0.019	5
LM	Oven-dried, mortar and pestle	0.67	0.043	5
LM	Oven-dried (270-mesh sieve)	0.66	0.037	4

[a] LM = Lake Mendota subsurface marl; CL = Comstock Lake subsurface, organic sediments.
[b] All results are expressed on an oven-dried weight basis.
[c] Based on $n - 1$ degrees of freedom.

The increase in mean available phosphorus and precision of both the wet samples after homogenizing is apparently due to increasing the sample homogeneity. The more drastic changes of the Comstock Lake sample are probably the result of the greater ease with which this soft, organic sediment could be homogenized. The Lake Mendota sediment which is more mineral in nature, resisted homogenizing with the tissue grinder. Grinding the oven-dried sample from Lake Mendota to pass a 270-mesh sieve affected neither the mean nor the standard deviation.

Based on the above results, it appears the optimum results can be obtained with oven-dried samples which have been gently ground using mortar and pestle. The four- to five-fold increase in precision on drying overshadows the increase in available phosphorus of approximately 20%.

As the sediment extraction procedure is much longer than the actual phosphorus determination, it was decided that a method of stockpiling the clarified extracts would be useful. The method of preservation and storage recommended by Jenkins (1965), i.e., freezing at −10 °C. in the presence of 40 mg. Hg^{2+} per liter, was chosen since no significant changes in phosphorus forms were reported for at least 31 days.

Indications are that the color development is unaffected by the above method of storage. Standard curves of freshly-prepared and of preserved and frozen (27 days) standards yielded identical slopes. A check on the precision, s_C, determined from five preserved and frozen replicates at a concentration of 1.00 mg. of P per liter, yielded a value of 0.002 mg. of P per liter in 10-cm. cells. This is the same as that determined for freshly-prepared standards (Table I).

A fair amount of the dissolved solids in the extract precipitated upon freezing. These were readily redissolved, however, by periodic shaking during the time that the extracts were equilibrating to room temperature.

The finalized procedure for the extraction and analysis of available phosphorus in lake sediments, based on the above results, is presented in detail in Wentz (1967).

Phosphorus Forms Extracted. In addition to the sorbed phosphorus which should be extracted, it is desirable to know what types of phosphorus compounds are broken down and brought into solution.

Four phosphorus compounds—phosphate rock (presumably fluorapatite), $FePO_4$, calcium phytate, and AMP (adenosine-5′-monophosphate) were chosen, and known amounts of each were added to separate known weights of an oven-dried sample of subsurface marl from Lake Mendota. The Lake Mendota sample contained 0.66 mg. of available P per gram, initially. Mixing was accomplished in 2-ounce, cylindrical, capped jars which were rotated on a device similar to laboratory ball-mill rollers. Both the phosphorus compounds and the sediment sample had been previously ground to pass a 270-mesh sieve to insure mixing, rather than demixing, during the rotation of the jars (Campbell and Bauer, 1966).

The per cent recoveries listed in Table IV are based on the differences between the phosphorus concentrations found and that of the unaltered sediment, as compared to the concentration of phosphorus added. The meaningfulness of the per cent recovery values is dependent on a comparison of the mean concentration found with that of the unaltered sample. This comparison can be made using a modified test (Bauer, 1960). Application of the test indicated no difference, at the 5% level, between the available phosphorus of the unaltered sediment and that of the sample with either the $FePO_4$ or the AMP added. The inclusion of some of the phosphorus from the calcium phytate may be due to a partial acid hydrolysis of the P-O-C linkages.

Interferences. According to Shapiro and Brannock (1962), "... each 4% total iron as Fe_2O_3 in the (sediment) sample will ... cause the value of P_2O_5 to be high by 0.01%. ..." In terms of milligram per gram dry sediment, this correction becomes

$$+\Delta \text{ 640 mg. Fe per gram} = +\Delta \text{ 1 mg. P per gram.}$$

The highest known reported total iron value for Lake Mendota is about 24 mg. of Fe per gram (Bortleson, 1968). Such an iron concentration would cause any phosphorus value to be 0.03 mg. of P per gram too high, provided all the Fe was brought into solution. This value is less than the standard deviation for five replicates of oven-dried Lake Mendota subsurface marl (Table II) and is negligible.

An experimental check on the above conclusion was made by adding 22.3 mg. of Fe per gram as FeS (not ACS grade) to a sample of Lake Mendota subsurface marl and determining the available phosphorus. The substitute test showed no significant difference, at the 5% level, between the available phosphorus of the sample, to which the FeS had been added, and that of the unaltered sediment.

The turbidity and yellow color imparted to the extract by the sediment samples have been found to present potential

Table IV. Types of Phosphorus Compounds Extracted by the Available Phosphorus Procedure

Phosphorus Cmpd.[a]	Concn. Added, Mg. P/G.	Concn. Found Mg. P/G.	% Recovery
Phosphate rock[b]	2.18	2.58[c]	88
$FePO_4$	1.58	0.73[d]	4.4
Calcium phytate[e]	1.49	0.83[d]	11
AMP[f]	1.86	0.66[d]	0.0

[a] Not ACS grade chemicals.
[b] NBS No. 120a from Florida; apparently predominantly fluorapatite.
[c] Two replicates.
[d] Three replicates.
[e] $C_6H_6(OPO_3H_2)_5(OPO_3Ca)$.
[f] Adenosine-5′-monophosphate.

interferences. If, for example, a 0.06-gram sample of subsurface marl from Lake Mendota were to be extracted, the interference from turbidity and color would be expected to be 0.1 mg. of P per gram. This is the maximum potential interference to be expected from any of the sediments studied. The error should be relatively constant because of the severe restrictions as to the weight of the sample which may be extracted when using 20 ml. of extractant.

Conclusions

The above procedure allows the extraction of relatively loosely-bound forms of phosphorus. These include sorbed phosphorus, phosphorus present as apatite (and presumably any calcium phosphate, also) and certain organic forms. At the time, they entered a lake basin, these phosphorus forms may have been readily available for use by the lake biota. If phosphorus were limiting biological production, then the above forms might effect an increase in the rate of the natural eutrophication process. Thus, this extraction procedure represents a potential tool for studying accelerated eutrophication. The positive error due to color and turbidity extracted by this procedure would not affect its use in the above regard, as the error appears to be fairly constant: changes in available phosphorus would be more important than absolute concentrations.

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Sedimentary Phosphorus in Lake Cores—Observations on Depositional Pattern in Lake Mendota

Dennis A. Wentz and G. Fred Lee

Water Chemistry Laboratory, University of Wisconsin, Madison, Wis. 53706

■ An available phosphorus extraction procedure was used to analyze a core from the deepest portion of Lake Mendota, Wis. The rate of available phosphorus deposition was constant in the marl, increased concomitantly with the change from marl to sludge, reached a maximum about 30 cm. below the sediment-water interface, and decreased gradually thereafter toward the surface. The initial increase probably corresponds to man's first appearance in the watershed; the decrease may be associated with the removal of sewage effluent from the lake in 1899. The available phosphorus comprises about one-half of the total and appears to be associated with the carbonate portion of the sediment.

The study of lake eutrophication, i.e., the progression from a relatively deep, sterile environment via an increased nutrient availability to a more shallow environment characterized by high biological production, has recently received considerable impetus because of the recognition that the urbanization of a lake's watershed can greatly increase the rate of nutrient influx into the lake. The nutrients contained in wastewater effluent and agricultural runoff, predominantly phosphorus and nitrogen, can cause an accelerated or "cultural" eutrophication and an enhancement or commencement of its associated problems (Anderson, 1961; Beeton, 1965; FWPCA, 1966; Hasler, 1947; Lawton, 1961; Sarles, 1961).

The present investigation was designed to test the effectiveness of an available phosphorus extraction procedure, evaluated in the first paper in this series (Wentz and Lee, 1969), as a potential tool for studying accelerated eutrophication. The investigation was restricted to Lake Mendota, Wis., for reasons of convenience, prior research concerning its chemistry and sedimentation regime, and its exemplification of the glacial lakes which dominate the region surrounding the Great Lakes.

Sample Collection and Storage

The sediment-coring apparatus and techniques employed are the culmination of research and experience accumulated by the University of Wisconsin Water Chemistry Program since it began its coring operations in the summer of 1964.

Essentially the sampler consists of the core barrel from a large-diameter (3.5-inch i.d.), hand-driven piston corer and the mainweight from a free-fall gravity corer. It is lowered and raised from the stern of a U.S. Army 2.5-ton 6 × 6 amphibious truck (GMC Dukw-353) by means of a power-driven winch and collapsible A-frame (Wentz, 1967).

The core studied was collected on October 26, 1966. It was extruded immediately, and 5-cm. lengths were placed in small polyethylene bags. The samples were frozen until commencement of the analyses three months later.

Description of Lake Mendota

Lake Mendota, with a surface area of 3940 hectares and a maximum depth of 25 meters (Wisconsin Conservation Div. Publication No. 218-64), is located in south-central Wisconsin. It was formed by the damming of a preglacial valley with a terminal moraine of the Wisconsin Glaciation (Hutchinson, 1957). The drainage of the area surrounding the lake consists of calcareous glacial deposits of Pleistocene age and of sandstones, dolomite, and dolomitic sandstone of the Lower Paleozoic Era (Murray, 1956). The city of Madison borders the southern and eastern shores of the Lake. The rest of the shoreline is of a rural nature, being occupied by summer homes, farms, permanent residences, wetlands, and undeveloped land. The lake receives agricultural drainage from the surrounding area, and some of its tributary streams receive sewage treatment plant effluent.

Lake Mendota is a hard-water lake and is considered to be eutrophic by most standards. The hypolimnetic waters become anoxic during summer stratification, and they approach this condition toward the end of the winter months. Obnoxious algal blooms and odors are not uncommon during the summer.

The physical characteristics of Lake Mendota sediments have been studied by Murray (1956). He reports that the most common stratigraphic section of the deep-water sediments consists of one-half to 14 inches of black sludge underlain by buff marl. The contact is reported to be knife sharp.

Murray studied primarily the organic matter, carbonates, and clastic content of the Lake Mendota sediments. Typical analyses of deep-water cores are listed in Table I. The organic matter and carbonate data have recently been corroborated by Bortleson (1968).

Table I. Organic Matter, Carbonate, and Clastic Content of Deep-Water Cores from Lake Mendota (Murray, 1955)

Core No.	Depth Below Sediment-Water Interface, Inches	Organic Matter, %	$CaCO_3$, %	Clastics, %
M-40	0–10[a]	14.3	35.0	57.0
	10–16[b]	11.0	65.5	23.5
	16–24[b]	11.4	64.9	23.7
M-48	0–13[a]	13.6	29.8	56.6
	13–21	11.6	60.1	28.3
	21–29[b]	11.9	62.9	25.2

[a] Sludge.
[b] Marl.

Results and Discussion

Profile WC-89, examined in this investigation, was taken from Lake Mendota at a depth of 23 meters. It was 92 cm. long. The uppermost 57 cm. was black sludge, followed by a transition zone to buff marl, which was dominant in the lowermost 30 cm. The contact appeared to be diffuse. Duplicate analyses (four replicates on the uppermost section) of available phosphorus were determined according to the procedure of Wentz and Lee (1969). The results are presented in Figure 1 where the values were plotted at the midpoint of the 5 cm. section analyzed. As the upper 2 cm. of the core contained less than 1% solids, this section was not analyzed.

The available phosphorus concentration remains constant at approximately 0.6 mg. of P per gram within the marl (lower 30 cm.), through the marl-sludge transition zone (62 to 57 cm.), and into the sludge. A gradual increase occurs thereafter (55 to 35 cm.), yielding a range of 0.7 to 1.0 mg. of P per gram in the upper 35 cm. of the sludge. Superimposed on this general trend of increasing available phosphorus concentration is what appears to be peak at about 35 to 25 cm.

A correlation of the general increase in available phosphorus concentration with the changing character of the sediments is indicated. However, this does not necessarily mean that the rate of deposition of available phosphorus has increased. Such a conclusion would be valid if the total sedimentation rate has remained constant.

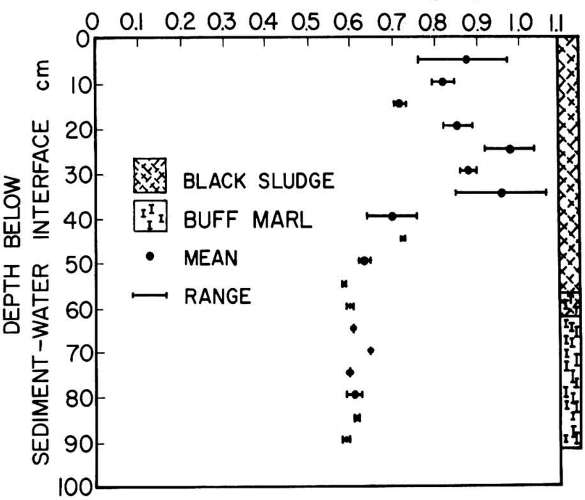
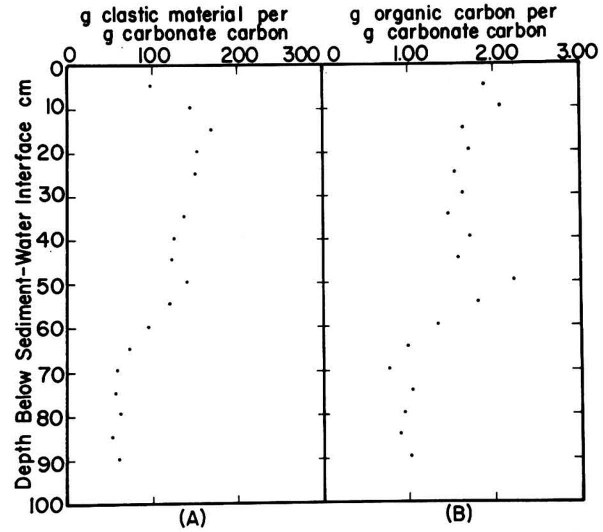


Figure 1. Stratigraphic distribution of available phosphorus in Lake Mendota sediments (Core WC-89)

Figure 2. Relationship of (A) clastic material and (B) organic carbon to carbonate carbon in profile WC-89 (based on data of Bortleson, 1968)



Sedimentation in Lake Mendota. According to Murray (1956), the sludge and marl of Lake Mendota are two separate sedimentary units, the former being neither derived from, nor a percursor of the latter. Both units are composed of the same three basic fractions–carbonate, organic matter, and clastics–in different relative proportions (Table I). The depositional mechanisms of the three fractions are apparently independent.

The abrupt change in sedimentation from marl to sludge is explained by Murray as being the result of increasing rates of clastic and organic matter sedimentation superimposed on a constant carbonate depositional pattern. Murray postulated that the increased rate of clastic deposition resulted from increased erosion during the middle of the 19th century, when extensive areas of land in the drainage basin were cleared for farming; and the lake level was raised five feet, exposing a new shoreline to wave action. The increased rate of organic matter deposition, which had to occur for the organic matter concentration to remain constant, is explained by Murray as being due to increased biological production in the lake. This, in turn, is attributed to the increased domestic drainage accompanying the urbanization of the drainage area. Thus, it appears that Lake Mendota has been affected by cultural changes.

If Murray's conclusion regarding the constant rate of carbonate deposition in Lake Mendota is valid, then the concentrations of the other constituents of the sediments, when referred to carbonate-carbon concentration, should provide an approximation of their relative rates of deposition. This has been done for clastics and organic matter (Figure 2) for profile WC-89 from data presented by Bortleson (1968).

Available Phosphorus Deposition. Figure 3 presents the available phosphorus data of Figure 1 recalculated on the basis of carbonate-carbon concentration. There is a gradual increase in the deposition rate beginning with the zone of transition from marl to sludge. The maximum rate of deposition occurred at 35 to 25 cm.; it has been decreasing since that time.

To discuss the factors believed to be controlling this pattern, a review of the various possible methods of phosphorus deposition in fresh-water lakes is necessary. Mackereth (1966), in his studies of the soft-water lakes of the English Lake District, was concerned with 1) sedimentation in combination with autochthonous organic matter; 2) erosion of phosphorus-containing minerals from the water-shed and deposition in unaltered form; and 3) coprecipitation with iron and manganese. There are three additional modes of deposition which should be considered for the hard-water lakes of Wisconsin. These are 4) sedimentation in combination with allochthonous organic matter; 5) sorption; and 6) association with carbonates. In this study, methods 1, 3, and 4 can be eliminated, as the extraction procedure used removed negligible amounts of phosphorus held in organic combination or phosphorus precipitated with ferric iron (Wentz and Lee, 1969). (Any ferrous iron would have been oxidized before extraction because of the sample pretreatment procedure which was used.) In addition, method 2 is not likely to be important as a mechanism for increasing available phosphorus deposition as there is no significant source of natural phosphorus in the drainage basin of Lake Mendota (Ostrom, 1968). This leaves only methods 5 and 6 to be considered. Some insight into the importance of method 6 can be gained from the ratio of available phosphorus/carbonate carbon at various depths (Figure 3A). Figure 3B shows the ratio of available phosphorus/clastic material while Figure 4A shows the ratio of available phosphorus/iron. These latter two curves help to interpret the importance of method 5.

The curve in Figure 3A is best discussed in three separate sections: the period of constant available phosphorus deposition (90 to 70 cm.); the period of increasing available phosphorus deposition (70 to 30 cm.); and the period of decreasing available phosphorus deposition (30 to 5 cm.).

Period of Constant Available Phosphorus Deposition. The interval from 90 to 70 cm. probably represents the period prior to man's influence. During this time, the rates of deposition of available phosphorus, clastic materials, iron (Figure 4B), and carbonate carbon are all relatively constant. Little can be inferred concerning the mechanism of available phosphorus deposition; however, it is probably safe to assume that it is primarily the result of erosion and deposition of unaltered phosphorus-containing minerals. This provides the background concentration of available phosphorus in the sediments.

Period of Increasing Available Phosphorus Deposition. During the interval from 70 to 30 cm., the rate of available phosphorus deposition steadily increases. Two subintervals can be discerned.

In the first, from 70 to 55 or 50 cm., there is a rapid increase

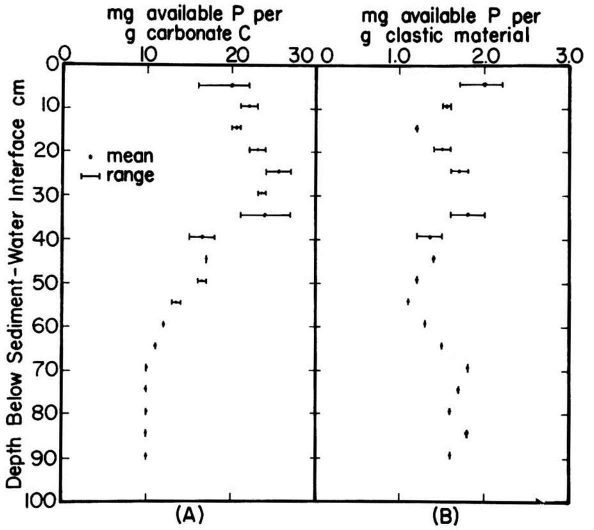


Figure 3. Relationship of available phosphorus to (A) carbonate carbon and (B) clastic material in profile WC-89 (based on data of Bortleson, 1968)

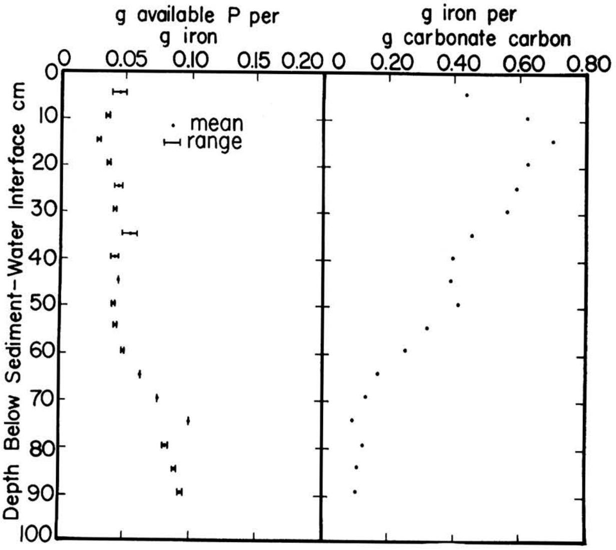


Figure 4. Relationship of (A) available phosphorus to iron and (B) iron to carbonate carbon in profile WC-89 (based on data of Bortleson, 1968)

in the rate of deposition of clastic materials and organic carbon, presumably due to man's first appearance in the watershed. There are concomitant decreases in the ratios of available phosphorus/clastics and available phosphorus/iron.

Let us consider the possibility of sorption onto clastic materials (e.g., clays) or iron compounds as controlling available phosphorus deposition. For this purpose, the classical Freundlich equation serves as a useful tool of presentation. Its use makes no implications concerning mechanisms involved. The Freundlich equation is given as:

$$\frac{X}{m} = kc^{\frac{1}{n}},$$

where X is the mass of sorbate taken up, m is the mass of sorbent, c is the final concentration of sorbate, and k and n are constants. In terms of the problem at hand, X represents the amount of phosphorus sorbed, m represents the clastic materials or iron compounds being deposited, and c represents the phosphorus in solution in the lake water.

Considering the clastic materials first, it is seen from Figure 3B that there is a decrease in the ratio of X/m between 70 and 55 cm. This would require a decrease in c, a situation which might be possible if the increased rate of organic matter deposition suggested by Figure 2B were due to in situ organic production. (It would also mean that something other than phosphorus was limiting production at this time.) For the rate of available phosphorus deposition (X per unit time) to increase (Figure 3A), the rate of clastics deposition (m per unit time) would have to increase simultaneously, and to a greater extent. Indeed, this is the case (Figure 2A).

For the sorption of phosphorus onto ferric hydroxide (the most logical compound of iron to consider), the same reasoning would be used, and similar conclusions would be drawn.

On the other hand, it is more likely that the aforementioned increase in organic matter deposition was due to allochthonous materials carried into the lake as man began clearing the watershed for farming. It is also likely that the phosphorus influx, and thus presumably the phosphorus concentration in the lake water, was increasing at this time. If the available phosphorus being deposited were associated with the carbonate portion of the sediments, either via a sorption or a precipitation mechanism, then this would explain the increasing ratio of available phosphorus/carbonate carbon.

In the second subinterval, from 55 to 50 cm. to 30 cm., the increasing rate of available phosphorus deposition is associated with a slightly-increasing rate of clastics deposition and a relatively constant rate of organic matter deposition. The rate of available phosphorus/clastics has reversed and is increasing; the ratio of available phosphorus/iron remains relatively constant. During this period, the available phosphorus deposition could be the result of sorption onto clastic materials or an association with the carbonate portion of the sediment. Either mechanism would require an increase in the concentration of phosphorus in the lake. This would most probably have been sustained by an increasing phosphorus influx due to urbanization.

Period of Decreasing Available Phosphorus Deposition. The rate of available phosphorus deposition generally decreases from 30 cm. to 5 cm. In the subinterval from 30 cm. to 15 cm., the ratios of available phosphorus/clastics, available phosphorus/iron, and available phosphorus/carbonate are all decreasing. These phenomena cannot be accounted for by sorption onto clastics, or iron, or by an association with carbonate, if the phosphorus concentration in the lake is to be increasing. We are, therefore, forced to conclude that there was either sudden decrease in the rate of phosphorus influx into the lake or a major shift in the mode of phosphorus deposition. Whichever conclusion is accepted, the change appears to have begun approximately 85 years ago, i.e., in the early 1880's. This is based on an estimated sedimentation rate of 3.5 mm. per year for the recent sludge of Lake Mendota (Bortleson, 1968).

Considering all the additional sources of phosphorus usually accompanying the urbanization of a lake's watershed, the first alternative would seem unlikely, and the latter quite plausible. However, from 1884 to 1899, Lake Mendota received the effluent from Madison's sewage treatment plant (Sawyer, 1947). Until this time, the phosphorus influx was probably gradually increasing. Then what probably amounted to a significant portion of this influx was suddenly removed. If the time estimates based on Bortleson's sedimentation rate were only slightly in error, the two events could easily have coincided.

The decreasing rate of available phosphorus deposition levels off at about 15 cm. and remains more or less constant from there to the 5-cm. level. The ratios of available phosphorus/clastics and available phosphorus/iron are both increasing within this subinterval. Thus, if sorption of phosphorus onto clastics or ferric hydroxide were the controlling factor, one would expect an increasing phosphorus concentration in the lake. However, the increasing ratios could easily be reflections of the decreasing rates of clastics and iron deposition during this period (Figures 2A and 4B). If this were true, an association with the carbonate portion of the sediments would be implied. This, in turn, would require a more or less constant concentration of phosphorus in the lake.

The previous discussion assumes that the mechanism of sedimentation is not reversible under the normal conditions encountered in fresh-water lakes. This would probably be true for sorption onto clastics or for an association with carbonate. On the other hand, phosphorus sorbed onto ferric hydroxide and deposited in the sediment during turnover or early stratification, may be released as the Fe(III) is reduced to Fe(II) toward the end of stratification. If, however, the efficiency of the phosphorus release is less than 100%, the reasoning probably still holds true.

Another assumption which is made is that of no diagenesis after deposition. The most likely possibility for exception here would be phosphorus associated with carbonate. This phosphorus could be deposited via sorption (Marshall, 1964) or precipitation, with subsequent diagenesis to apatite (Degens, 1965; Kardos, 1964). Also, the direct precipitation of apatite (calculations by the authors indicate that Lake Mendota is presently supersaturated with respect to this compound) should not be overlooked (Corsaro, Lauderbach, *et al.*, 1964). But, any apatite, however formed, would be expected to be intimately associated with the carbonate of the sediments, thus leaving the discussion essentially unaffected.

The ratio of available phosphorus to total phosphorus is

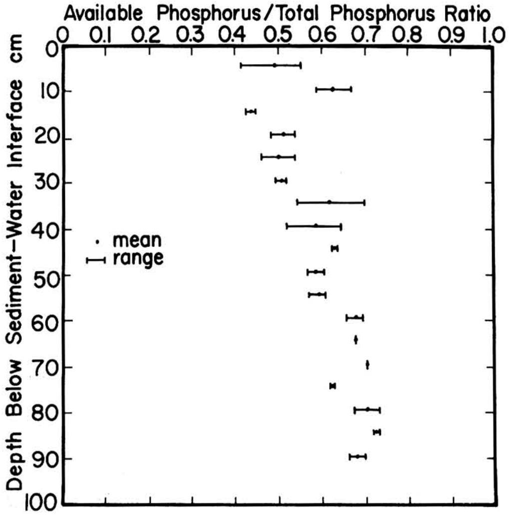


Figure 5. Relationship of available phosphorus to total phosphorus in profile WC-89 (based on data of Bortleson, 1968)

given in Figure 5. It has gradually decreased from about 0.7 at the 90 cm. level to about 0.5 at the 5 cm. level.

Conclusions

Since man produced his first significant effect on the watershed, the rate of available phosphorus deposition has been continually changing. Although the mechanism(s) of deposition is still unclear, two points seem apparent. The available phosphorus is most likely associated with the carbonate portion of the sediments; and general trends in available phosphorus deposition seem to correlate with significant events in the recent history of the lake. A discussion of the micro changes in available phosphorus deposition might yield more enlightening results. This was not undertaken in the present investigation because of the poor precision attained for analyses of available phosphorus from the sludge, as compared to those from the marl.

Generally more than one-half of the phosphorus in the sediments of Lake Mendota is available as defined by the procedure used in this investigation.

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Synergistic Action of Ozone–Sulfur Dioxide on Peanuts

Howard G. Applegate and Lane C. Durrant

Department of Plant Sciences, Texas A&M University, College Station, Texas 77843

■ Peanut plants were fumigated with ozone and sulfur dioxide singly and together. Both gases, when applied separately, induced characteristic damage to the plants. A synergistic action not characteristic of individual gases was found when the two gases were administered simultaneously.

In 1966 and 1967, the peanut crop in Texas suffered damage from an unknown disorder. Attempts to isolate a causal pathogen proved fruitless. Since the damage appeared after passage of weather fronts, some gaseous pollutant was suggested as the cause. Ozone, produced by lightning as fronts passed over the fields, appeared to be a possible cause of the damage. Since the amount of ozone generated would be small, some other gas might act synergistically with the ozone to induce damage. Previously reported synergism between ozone and sulfur dioxide (Menser and Heggestad, 1966) in inducing plant damage led to testing ozone, sulfur dioxide, and ozone-sulfur dioxide gases on peanuts.

Materials and Methods

Spanish peanuts cv. Starr (*Arachis hypogaea*) were germinated in sterilized sand. When 28 days old, the plants were placed in two growth chambers. One chamber received only carbon filtered air; the other chamber received carbon filtered air plus the experimental gases. Each chamber had a volume of 96 cubic feet plus a plenum at either end. Conditioned air entered a 16-cubic foot plenum at one end of a chamber and was exhausted through a similar plenum at the other end of the chamber. There were 9 complete air changes per minute through the chambers. Experimental gases were introduced into an air duct after the air conditioning equipment, but before the plenum. The chamber atmosphere was monitored by pulling gas samples from the exit plenum. Each plenum was separated from the fumigation chamber by a fiber board. The board has one-half-inch diameter holes every 6 inches through which air or air-gas mixtures entered and left the fumigation chambers.

While in the fumigation chambers, the plants were given a 14 hour photoperiod (2,000 foot candles of light at plant height). The light quality, as judged by a scanning spectroradiometer, closely approximated that of sunlight. During the photoperiod, an 85° ± 2 °F. temperature and a 54 ± 3% relative humidity were maintained. During the nyctoperiod, the temperature was 70° ± 2 °F. with a relative humidity of 50 ± 3%. One-third of the plants were grown in beakers in which water covered the roots; a third of the plants received normal watering; a third were allowed to wilt before receiving enough water to permit limited growth.

Ozone was generated by passing oxygen through a high voltage arc (Menser and Heggestad, 1964) and monitored by the potassium iodide method (ASTM, 1959). Sulfur dioxide was reagent grade gas and was monitored by the disulfitomercurate method (West and Gaeke, 1956). Unpublished data gathered from Houston and vicinity (approximately 30 miles southest of an area in which peanut plants were damaged) showed ozone and sulfur dioxide concentrations ranging up to 3 parts per hundred million (p.p.h.m.) and 15 p.p.h.m., respectively. It was decided, therefore, not to exceed these concentrations in fumigation studies. Each fumigation treatment was repeated three times over a four month period.

Results

At ozone concentrations of 2 to 3 p.p.h.m., injury occurred on high-moisture plants 24 to 48 hours after the start of fumigation. The most mature leaflets turned chlorotic, starting at the midrib, and progressing towards the margins if fumigation continued. Ultimately, while chlorotic but not necrotic, the leaflets abscissed. If fumigation stopped after the first symptoms appeared, the leaflets recovered their green color.

At sulfur dioxide concentrations of 5 to 12 p.p.h.m., injury occurred on high-moisture plants 4 to 8 hours after the start of fumigation. The youngest leaflets turned a light tan along the margins. The color later changed to a darker brown. If fumigation continued the necrosis progressed along the veins into the middle of the leaflet. The entire leaf abscissed when necrosis was complete. If fumigation stopped after the first symptoms appeared, no further necrosis occurred.

Plants were fumigated with both gases—ozone at 0.8- to 1.0-p.p.h.m. and sulfur dioxide at 2- to 3-p.p.h.m. The first symptoms appeared 4 to 5 hours later on high-moisture plants. A chlorosis, similar in color to ozone injury alone, appeared on the youngest leaflets. In contrast to ozone-induced injury, however, the chlorosis started at the margins and slowly progressed to the midvein. Forty-six to 50 hours after fumigation had started, the marginal chlorotic areas turned a light tan similar in color to the sulfur dioxide-induced injury. The necrosis slowly progressed inward and ultimately the leaf abscissed.

In all fumigation treatments the visible symptoms of injury were identical on high-, medium- and low-moisture plants. The symptoms appeared first on high-moisture plants, followed in 8 to 10 hours on medium-moisture plants, and 10 to 14 hours later, on low-moisture plants.

Plants grown in a chamber receiving no ozone or sulfur dioxide showed no damage at any time.

Discussion

The data presented here show that ozone and sulfur dioxide can act synergistically to induce damage which, while superficially similar to either gas alone, is in fact distinctive. That such synergism has been shown under controlled conditions does not prove that the same phenomenon occurs in the field. The possibility of such a phenomenon has been demonstrated, however.

In these experiments, injury induced by the synergistic action of the two gases appeared within hours after the fumigation had started; in the field, injury was not noted until 2 to 3 days after passage of the weather front. This time difference could be due to several factors. The concentrations of the gases were higher in the environmental chambers than in the field and reluctance of growers to enter wet, muddy fields may have delayed seeing the damage. A third possibility is that high ozone-content air was brought down from above as the low pressure systems passed over the fields (Dobson, 1930).

Both ozone and sulfur dioxide enter plants via the stomates (Brandt, 1962). Plants growing under low-moisture conditions presumably had their stomates closed. This could account for fact they showed injury last. Two possibilities exist to explain that plants grown with their roots submerged in water showed injury the quickest. Their stomates were wider open (or more stomates were open than on the other plants), or stresses imposed on the plants by growing them with submerged roots made them more susceptible to the additional stress imposed by the gases.

The ozone and sulfur dioxide injuries reported here are similar to those found by other workers (Altman and Dittmer, 1966; Brandt, 1962). Concentrations of the two gases used in this study are found in polluted air in cities (Altman and Dittmer, 1966; Linnell, 1965). This does not mean, of course, that these concentrations exist in the countryside. Field data are needed to discover if ozone-sulfur dioxide synergism is in fact the agent which injured peanut plants in Texas in previous years.

Symptoms induced by the synergistic action of ozone and sulfur dioxide on peanuts in the controlled fumigations were identical to those initially observed in field grown plants. Plants in the field, however, did develop a bronzy color on leaflets which did not abscise. This coloration developed several days to several weeks after the initial symptoms. Efforts to induce a similar bronzy coloration in controlled fumigations were unsuccessful.

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Colorimetric Determination of Manganese in Lake Waters

Joseph J. Delfino[1] **and G. Fred Lee**

Water Chemistry Laboratory, University of Wisconsin, Madison, Wis. 53706

■ The persulfate oxidation, formaldoxime, and malachite green colorimetric methods for Mn in lake waters were evaluated. The persulfate and formaldoxime procedures gave essentially the same results in membrane filtered samples. Turbidity in unfiltered samples resulted in the formaldoxime method giving higher results than the persulfate method. The malachite green method did not yield consistently useful data unless a lengthy modification was employed. The persulfate method proved to be the most efficient and adaptable method in a study of the chemistry of Mn in lake waters.

Analysis of natural waters for the trace metal manganese is usually performed according to one of the procedures in Standard Methods (1965). The procedures involve oxidation of lower valent Mn (oxidation states II, III, IV) to permanganate. The MnO_4^- absorbance is then measured colorimetrically. This method is sufficient when the total Mn content of a water sample is desired. Total Mn is understood to be Mn in all of its possible oxidation states in an unfiltered sample. Under certain circumstances, more detailed data concerning the oxidation state(s) and physical form(s) of Mn (soluble or particulate) may be desired. Research in water chemistry, limnology, and water treatment methodology is an area where such data could be utilized.

This communication describes how relatively simple colorimetric procedures can be used to yield information concerning the chemistry of Mn in lake waters. The application of the techniques described in this paper have been presented by Delfino and Lee (1968). The increasingly popular atomic absorption method of analysis is not treated here. The reader is referred to papers by Fabricand, Sawyer, *et al.* (1962) and Brooks, Presley, *et al.* (1967) for further information.

A scheme for a comprehensive analysis of aqueous Mn has been published (Morgan and Stumm, 1965). Colorimetric methods were given for the determination of total Mn by oxidation to MnO_4^- in an acidic medium and by reaction of Mn with formaldoxime reagent in a strongly basic medium. The total equivalent concentration of oxidized Mn was determined by reaction of Mn(III) and (IV) species with orthotolidine reagent. Morgan has recently employed crystal violet as a reagent in place of orthotolidine in the evaluation of Mn oxidation states in sediment pore waters, as reported in Presley, Brooks, *et al.* (1967). Another procedure for total Mn is the catalytic method which makes use of the formation of the dye malachite green (Strickland and Parsons, 1965). No specific method for Mn(II) in dilute aqueous solutions is yet known but Mn(II) can be estimated from the difference between total Mn and the equivalents of oxidized Mn (Morgan and Stumm, 1965).

Separation of the physical forms of Mn into "soluble" and "particulate" fractions can be done by membrane filtration. Mn(II) standard solutions have consistently passed through filters with an average pore diameter of 0.22 microns without detectable loss of Mn(II) on the filters (Morgan and Stumm, 1965). In contrast, when suspensions of oxidized Mn were filtered, no oxidized Mn was detected in the filtrates. Membrane filtration is useful when an operationally defined classification of Mn according to its physical form(s) is desired.

Experimental Procedures

Sample Collection. Water samples were collected from two Wisconsin lakes, Lake Mendota and Cox Hollow Lake, using a 4-liter capacity Van Dorn sampler. Samples were poured into 2.5-liter glass bottles, previously rinsed with 1-to-1 HCl, distilled water, and a small volume of the water sample being collected. Analyses were generally completed within 6 to 12 hours after collection.

Analytical. Total Mn was determined by the three colorimetric methods described below. A Bausch and Lomb Spectronic 20 spectrophotometer was used with cells providing light paths of 1.27 and 2.54 cm. All lake water samples were analyzed at least in duplicate.

Procedure 1 involved the oxidation of Mn to MnO_4^-. Ammonium persulfate, with Ag^+ catalyst, was chosen as the oxidant since it was the most rapid and efficient oxidant available. The Standard Methods procedure was followed. Common interferences were minimized by use of a special acid reagent originally developed by Nydahl (1949). A sensitivity of 0.05 mg. per liter was obtained when 100-ml. samples were analyzed. However, by employing a simple evaporation-concentration technique, larger samples yielded sensitivities as low as 0.01 mg. per liter. Generally, 500-ml. samples to which 5 to 10 ml. of the special acid reagent were added were concentrated to 25 ml. by evaporation on a hot plate. The presence of the acid reagent prevented precipitation of $CaCO_3$ during heating since the samples contained 25 to 35 mg. per liter of Ca and 2.80 to 3.90 meq. per liter of total carbonate alkalinity. The MnO_4^- absorbances were measured at 525 $m\mu$.

Many water samples contained algal and detrital debris. The two lakes sampled are eutrophic and have abundant plankton communities. This debris was not removed prior to the total Mn determinations. Boiling in the presence of the acid reagent destroyed much of the planktonic material. However, undecomposed cell fragments and particulate inorganic detritus remained. The suspended material created enough turbidity to interfere with the MnO_4^- absorbance measurement after the addition of the oxidant. This was corrected by measurement of the initial absorbance, including turbidity, followed by the addition of a few milliliters of 30% H_2O_2 and subsequent measurement of the absorbance after

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[1] Present address, Department of Chemistry (DFC), U. S. Air Force Academy, Colo. 80840

the reduction of MnO_4^- was complete (pink color was destroyed). The difference between the initial and final absorbance readings was taken as the MnO_4^- absorbance.

The volumetric concentration factor had no effect on Mn recovery. Experiments with dosed Lake Mendota water showed that concentration of samples having initial volumes anywhere from 500 ml. to 50 ml. yielded the same final concentration of Mn per liter. Care was exercised with respect to the final volume of the solution following evaporation and just prior to addition of the oxidant. When sample volumes were concentrated to a final volume less than 20 ml. in the presence of the acid reagent, development of the MnO_4^- color was inhibited. Richards (1930) noted this and suggested that excess acidity caused the reduction of MnO_4^- to lower oxidation states.

Procedure 2 was the reaction of Mn with formaldoxime reagent to form the orange-red colored Mn-formaldoxime complex which has an absorption maximum at 450 mμ. Sandell (1959) and Morgan and Stumm (1965) discussed the preparation and properties of the formaldoxime reagent. The main interferences in the procedure are Ca, Mg, and Fe due to the high pH (9 to 10) at which the Mn compex is formed. The interfering species form precipitates resulting in undesirable turbidity. Also, Fe forms a weakly colored formaldoxime complex with an absorption maximum near 525 mμ. To control the interferences, Bradfield (1957) recommended the use of a 10% solution (w./v.) of the complexing agent N-(carboxymethyl)-N′-2-hydroxy-ethyl-n,N′-ethylenediglycine (HEEDTA).

This procedure was carried out in two steps. First, 50- to 100-ml. aliquots of lake water samples, in addition to 10 ml. of HEEDTA solution, were heated for 1 hour at 65 °C. in a water bath. This resulted in complexation of Ca, Mg, and Fe with HEEDTA. The HEEDTA did not affect the recovery of Mn as determined from separate lake water samples dosed with Mn. After heating, the samples were cooled to room temperature. In the second step, 2 ml. of formaldoxime reagent and 5 ml. of 5*N* NaOH were added and the solution mixed. The pH was between 9 and 10, the optimum range for color development. Fifteen minutes were allowed before the absorbance was measured at 450 mμ. Failure to include the HEEDTA complexation step resulted in extensive precipitation of any of the interfering ions present.

In addition to the above-mentioned chemical interferences, background turbidity of lake water samples affected the procedure. Water sample blanks did not adequately overcome the turbidity since some of the colored Mn complex apparently adsorbed onto the particulate matter. Therefore, the formaldoxime procedure was used primarily on membrane filtered samples. The formaldoxime method is more sensitive than the permanganate procedure and should be considered when the main interferences can be controlled. In addition, an evaporation-concentration step can be used if boiling is carried out with sufficient HEEDTA to prevent precipitation. Additional NaOH may then be required to adjust the pH to the optimum range prior to color development. An automated modification of the formaldoxime method was reported by Henriksen (1966) but was not included in this study.

Procedure 3 has a reported sensitivity of 0.1 μg. per liter, making it one of the most sensitive colorimetric methods known for aqueous Mn. The method employs oxidation of leuco-base of malachite green by periodate at pH 4 with Mn acting as a catalyst. The absorption maximum of the oxidized malachite green species is 615 mμ. Strickland and Parsons (1965) outlined the procedural technique as applied to sea water samples, and the method has been used in oceanographic work (Wangersky and Gordon, 1965). The procedure occasionally led to spurious results, however, since the catalytic reaction involving the periodate, malachite green, and Mn is complex. Fernandez, Sobel, *et al.* (1963) studied the reaction in detail and suggested the use of a kinetic approach to determine the Mn concentration rather than the method based solely on colorimetry.

The kinetic method as described by Fernandez, Sobel, *et al.* (1963) requires about eight hours to complete the analysis. The method follows the rate of decomposition of the malachite green color, which is linear, rather than the initial color formation reaction, which is nonlinear. The time factor is a deterrent when large numbers of samples are to be processed soon after collection. One reasonably good set of Mn data taken from lake water samples was obtained with the procedure according to Strickland and Parsons (1965) (Table I). The Fernandez, Sobel, *et al.* (1963) method was not applied to actual lake samples in this study, primarily due to the time consideration. Depending on the Mn concentration, sample volumes were often 1 ml. or smaller with the malachite green method. Except for the one set of data reported in Table I, most results obtained with this method were not retained or reported due to lack of reproducibility. If the time factor is not critical, the procedure as given by Fernandez, Sobel, *et al.* (1963) is recommended.

Results

Analytical. The accuracy of the three procedures was determined by dosing lake water samples with known amounts of standard Mn solutions followed by a comparison of absorbances with values from distilled water standards. Mn recovery was complete within the limits of precision. MnO_4^- absorbances resulting from the persulfate oxidation of Mn(II) solutions compared very well with MnO_4^- solutions standardized by titration with standard oxalate. The precision was estimated by conducting replicate analyses on selected samples as shown in Table II. The data for the malachite green procedure in Table II represent the best results obtained as mentioned above. The precision of most replication experiments was much poorer.

Field Studies. A comparison of the colorimetric procedures as applied to the two lake water systems at different times of the year is shown in Table I. Time did not allow the use of all of the methods on any one sampling date. Columns B, C, and E contain data which were obtained after an aliquot of the original water sample was passed through a membrane filter of the specified pore sizes (Millipore Filter Co., Bedford, Mass.).

Discussion

The analysis of Cox Hollow Lake samples collected on August 16, 1966, compared the persulfate and formaldoxime procedures for total Mn in unfiltered samples. The formaldoxime procedure yielded higher values at each depth. The higher formaldoxime data were the result of natural turbidity which the HEEDTA complexation step could not eliminate. Both procedures were carried out with reagent blanks using lake water samples. However, the persulfate method easily compensates for background turbidity as discussed previously, whereas the formaldoxime procedure does not. Thus, in the formaldoxime analysis of the Cox Hollow samples, turbidity resulted in higher absorbances and yielded higher apparent Mn values. Planktonic and detrital debris at all depths in the lake added to the turbidity.

Table I. Comparison of Analytical Results from Lake Water Samples Using Three Colorimetric Procedures

Sample Depth, Meters	Total Mn Unfiltered, Mg./L.	Total Mn After 0.45-μ Filtration, Mg./L.	After 0.10-μ Filtration, Mg./L.	Total Mn Unfiltered, Mg./L.	After 0.45-μ Filtration, Mg./L.	Malachite Green Total Mn Unfiltered, Mg./L.
	Persulfate Oxidation			Formaldoxime		
	A	B	C	D	E	F
			Cox Hollow Lake—August 16, 1968			
1	0.15	[a]	[a]	0.20	[a]	[a]
2	0.20	[a]	[a]	0.30	[a]	[a]
3	0.20	[a]	[a]	0.25	[a]	[a]
4	0.20	[a]	[a]	0.25	[a]	[a]
5	0.20	[a]	[a]	0.30	[a]	[a]
6	0.35	[a]	[a]	0.40	[a]	[a]
			Lake Mendota—February 10, 1967			
5	0.01	0.01	0.01	[a]	[a]	0.01
19	0.21	0.21	0.21	[a]	[a]	0.17
20	0.40	0.40	0.40	[a]	[a]	0.30
21	0.52	0.51	0.50	[a]	[a]	0.45
22	0.56	0.56	0.56	[a]	[a]	0.50
23	0.75	0.73	0.75	[a]	[a]	0.68
			Lake Mendota—April 5, 1967			
7	0.04	0.04	[a]	[a]	0.04	[a]
11	0.04	0.04	[a]	[a]	0.05	[a]
17	0.05	0.05	[a]	[a]	0.05	[a]
19	0.05	0.05	[a]	[a]	0.05	[a]
21	0.04	0.05	[a]	[a]	0.05	[a]
23	0.05	0.04	[a]	[a]	0.05	[a]

[a] Denotes no analysis made on sample

No analytical differences were seen in the Lake Mendota samples from April 5, 1967. A comparison was made between the persulfate and formaldoxime procedures using samples which were first filtered through 0.45-micron membrane filters. The two procedures yielded essentially the same data. Differences of 0.01 mg. per liter were within limits of precision. Removal of excess turbidity was the key to obtaining comparable data. However, this was not always necessary as shown in Table II. The average of replicates determined by the persulfate procedure was very close to the average of formaldoxime replicates. The replicates for both procedures were carried out on the same unfiltered water sample. In that particular sample, there was not enough turbidity in the unfiltered water to affect the results. Whenever use of the formaldoxime procedure is desired, particularly on unfiltered samples, a few trial runs should be made to assure no interference is caused by the particulate matter in the water.

The persulfate and malachite green procedures were compared using Lake Mendota samples collected on February 10, 1967. The malachite green values were lower for each depth except the 1-meter level. This was probably due to a large conversion factor since the malachite green analyses were run on aliquots of 1 ml. or less compared to 100-ml. aliquots for the persulfate oxidation. Calculations on a milligram per liter basis magnified at least 100 times any small error in the malachite green analyses, as compared with the persulfate oxidation. Taking this into consideration, the results were reasonably comparable. However, on almost every other occasion, comparison between the malachite green and either of the other two procedures resulted in larger discrepancies.

Application. If analyses of some of the Mn fractions in a lake water sample are desired, the following approach is suggested. Measure total Mn in an unfiltered aliquot by persulfate oxidation. Filter aliquots of the sample through 0.45-, 0.22-, or 0.10-micron membrane filters and measure the Mn in the filtrates either by persulfate oxidation or the formaldoxime method. No significant difference existed in the results from samples filtered through 0.45- or 0.10-micron membrane filters as shown by data in Table I from Lake Mendota on February 10, 1967. This observation is also supported by

Table II. Precision of Analytical Procedures

Procedure	No. of Replicates	Av. Concn., Mg./L.	Std. Dev., Mg./L.	Sample Source	Date	Depth, Meters
1. Persulfate Oxidation	10	0.57	0.02	Lake Mendota	9/19/67	22
2. Formaldoxime	6	0.55	0.01	Lake Mendota	9/19/67	22
3. Malachite Green	6	0.68	0.02	Lake Mendota	2/10/67	23

data from other sampling dates as reported elsewhere (Delfino and Lee, 1968). However, the membrane filtration results will vary from lake to lake depending on the nature of the particulate matter present, pH alkalinity, and other environmental variables. Check aliquots of the membrane filtrate solutions for the presence of equivalents oxidized Mn, using the crystal violet reagent, buffered at pH 4. The filtered samples listed in Table II all gave negative reactions with crystal violet indicating the absence of detectable oxidized Mn in the filtrates. Semiquantitatively determine the presence or absence of particulate Mn oxides trapped on the 0.45-micron membrane filters according to the procedure of Ormerod (1966). The formation of blue-green colored spots on the filter when tested with a solution of malachite green in 0.1 *N* HCl indicates the presence of hydrous Mn oxides in the particulate fraction of the water with particle sizes greater than 0.45.

Completion of the above procedures gives data for total Mn, total "soluble" Mn in 0.45-micron filtrates, equivalents of oxidized Mn in 0.45-micron filtrates, and the presence or absence of Mn oxides in the particulate fraction. In addition, an estimation of reduced Mn(II) can be obtained by comparison of the difference between total "soluble" Mn and equivalents of oxidized Mn in the 0.45-micron filtrates.

In conclusion, this report has described some useful and sensitive colorimetric procedures, combined with membrane filtration, which allow a reasonable classification of various Mn fractions in lake waters. The versatility of the persulfate oxidation method should not be overlooked while the search continues for newer, more rapid, and even more sensitive procedures for the complete analysis of Mn in lake waters.

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Identification of Bacteria by Rapid Spectrophotofluorometric Methods

Charles J. Rogers and Thomas C. Purcell

U. S. Department of Health, Education, and Welfare, Public Health Service, Consumer Protection and Environmental Health Service, Environmental Control Administration, Bureau of Solid Wastes Management, 222 East Central Pkwy, Cincinnati, Ohio 45202

■ There is a genuine need for additional characteristics, based on either biochemical properties or cellular composition, of microorganisms to establish their taxonomic relationships. The present study represents an attempt to provide additional characteristics applicable to the identification of certain species of bacteria. The methods described are rapid, sensitive, and, when applied in the analysis of carbohydrates (*C*), esterases (*E*), and *E*/*C* ratios of 11 strains of bacteria, give information to aid in identification of species. The characteristics are reported in tabular form for two separate incubation periods and, when taken into consideration with other identifiable properties of the organisms, can be used to further the classification and taxonomy of clinically significant bacteria present in polluted waters or waste processing operations.

The separation of bacterial esterases by starch gel electrophoresis revealed characteristic enzyme patterns that have been employed to identify a number of bacteria including *Bacillus thuringiensis* (Norris, 1964), certain mycobacteria (Cann and Willox, 1965), and Vibrio species (Willox and Shewan, 1963). This difference in electrophoretic patterns prompted the present study to identify bacteria by determining carbohydrate content and esterase activity and by calculating the esterase/carbohydrate (*E*/*C*) ratios of several bacterial species. Using these simple but sensitive methods, application of this technique would aid in rapid identification of bacteria isolated from polluted waters and compost. The technique might also be employed to detect contaminative or mutational changes in fermentation processes designed for recycling or reuse of solid waste.

Materials and Methods

Many methods have been used for determination of esterases. The methods most commonly reported are colorimetric (Ellman, 1961; Mendel and Rudney, 1943), manometric (Gal and Roth, 1957), or electrochemical (Kramer, Cannon, *et al.*, 1962). Since the present investigation involved measuring the esterase activity with as few cells as possible, a fluorometric method was considered because of its greater sensitivity. The fluorometric technique used is described by Guilbault and Kramer (1965) for the hydrolysis of indoxylacetate to a stable fluorescent compound, indigo white. The method, was modified, however, by using a lower concentration of the esterase substrate and a longer period of time for enzymatic reaction.

Carbohydrate contents of the bacteria were determined fluorometrically employing a method sensitive enough to measure nanogram quantities as previously reported by Rogers, Chambers, *et al.*, (1966).

The results from an examination of 11 strains of bacteria are presented in this report.

Indoxylacetate was purchased from Nutritional Biochemicals Co., Cleveland, Ohio, and para-dioxane from Eastman Organic Chemical Co., Rochester, N. Y. All other compounds used were analytical grade commercial products. Trypticase soy broth (TSB Baltimore Biological Laboratories) was prepared by dissolving 10 grams of media in a liter of water. Five-milliliter quantities of this broth were placed in test tubes and were sterilized for 15 minutes at 115°C. Eleven bacteria obtained from the Taft Center Collection in Cincinnati were grown in the sterilized trypticase soy broth (TSB), and were analyzed for esterase activity and carbohydrates after incubation intervals of 6 and 16 hours, respectively, at 35°C.

The 11 bacteria were washed three times by centrifugation at 12,100*g* for 8 minutes with 0.05*M* phosphate buffer at pH 7.0. Suspensions were prepared to give a reading of 50 in the Klett-Summerson colorimeter using filter No. 42.

The esterase substrate was prepared daily by dissolving 5.0 mg of indoxylacetate in 5.0 ml of dioxane.

Esterase Assay. A 1-ml. bacterial suspension was added to 4.0 ml. of 0.05*M* phosphate buffer, pH 6.5. One-tenth milliliter of indoxylacetate was added to each sample tube and to 5.0 ml. of buffer (reagent blank). At the end of 15 minutes the resulting fluorescent compound, indoxyl, was measured in the Aminco-Bowman spectrophotofluorometer. Slit arrangements in the spectrophotofluorometer were as follows: cell No. 2, ${}^{1}/_{16}$-inch slit; No. 3, ${}^{1}/_{8}$; No. 5, ${}^{1}/_{16}$; and No. 7, ${}^{3}/_{16}$-inch. The activation and fluorescence wavelengths used were 390 and 490 mμ as described in the Guilbault and Kramer technique (Guilbault and Kramer, 1965).

Carbohydrates were determined as follows: 1.0 ml. of the bacterial suspension, 4.0 ml. of HCl, and 0.5 ml. of resorcinol reagent (50 mg. of resorcinol/20 ml. of 66% HCl) were placed into 25-ml. screw-cap borosilicate glass tubes. The tubes were heated for 30 minutes in an oil bath to 100°C. followed by the procedure previously described (Rogers, Chambers, *et al.*, 1966). The fluorescence was measured using activation and fluorescence wavelengths of 488 and 508

Table I. Spectrophotofluorometric Analysis of Differences in Carbohydrates and Esterase Activity of Bacterial Species After 16 Hours Incubation in TSB at 35° C.

Days	Genus	Species	Carbohydrate[a]	Esterase[a]	*E/C*
1	*Staphylococcus*	237	0.184	0.290	1.6
2	*Staphylococcus*	237	0.227	0.325	1.5
3	*Staphylococcus*	237	0.265	0.435	1.6
1	*Staphylococcus*	*hemolyticus*	0.099	0.390	3.9
2	*Staphylococcus*	*hemolyticus*	0.107	0.350	3.4
3	*Staphylococcus*	*hemolyticus*	0.104	0.385	3.7
1	*Staphylococcus*	227	0.145	0.440	3.0
2	*Staphylococcus*	227	0.130	0.395	3.0
3	*Staphylococcus*	227	0.153	0.540	3.5
1	*Escherichia*	*coli*, AR-1	0.358	0.066	0.18
2	*Escherichia*	*coli*, AR-1	0.384	0.039	0.10
3	*Escherichia*	*coli*, AR-1	0.328	0.064	0.19
1	*Escherichia*	*coli*, GM-3	0.199	0.034	0.17
2	*Escherichia*	*coli*, GM-3	0.244	0.027	0.11
3	*Escherichia*	*coli*, GM-3	0.265	0.050	0.19
1	*Streptococcus*	*faecalis*	0.373	0.550	1.5
2	*Streptococcus*	*faecalis*	0.324	0.455	1.4
3	*Streptococcus*	*faecalis*	0.335	0.714	2.1
1	*Streptococcus*	*hemolyticus*	0.248	0.054	0.22
2	*Streptococcus*	*hemolyticus*	0.314	0.080	0.25
3	*Streptococcus*	*hemolyticus*	0.350	0.084	0.24
1	*Streptococcus*	*bovis*	0.289	0.033	0.11
2	*Streptococcus*	*bovis*	0.329	0.054	0.16
3	*Streptococcus*	*bovis*	0.297	0.056	0.12
1	*Streptococcus*	*liquefaciens*	0.294	0.405	1.4
2	*Streptococcus*	*liquefaciens*	0.217	0.320	1.5
3	*Streptococcus*	*liquefaciens*	0.320	0.730	2.3
1	*Bacillus*	*cereus*	0.243	0.105	0.43
2	*Bacillus*	*cereus*	0.184	0.096	0.53
3	*Bacillus*	*cereus*	0.193	0.070	0.36
1	*Bacillus*	*globigii*	0.200	33.94	170
2	*Bacillus*	*globigii*	0.181	35.38	193
3	*Bacillus*	*globigii*	0.153	31.90	208

[a] Fluorescence readings expressed as meter multiplier times transmission.

mμ, respectively, expressed as meter multiplier times transmission.

Results

Data from three of the five experiments using bacteria grown on TSB at 35°C. after 16 hours were charted (Table I). The values listed were carbohydrates, esterase activity, and esterase/carbohydrates (*E*/*C*) ratios. When these three values for the staphylococci were compared, quantitative differences between the three bacteria could be observed.

When the staphylococci were compared with the *Escherichia coli*, the esterase values and *E*/*C* ratios of the *E. coli* were much lower. In comparison with the values for other bacteria, these values were lowest except for *Streptococcus bovis*.

Data obtained from the analysis of the streptococci showed a reproducible difference in esterase activity and *E*/*C* ratios of *S. bovis* and *S. hemolyticus*. *S. faecalis* and *S. liquefaciens* showed no significant difference. No significant differences in carbohydrate value were observed when a comparison of the two bacilli were made. The esterase activity of *B. globigii*, however, was contrastingly greater than *B. cereus* and all other bacteria studied.

Values for carbohydrates, esterase activity, and *E*/*C* ratios of bacteria after 6 hours of incubation were determined (Table II). Three replicate experiments in each case showed the same order of esterase activity as seen in the 16-hour data (Table I). The values of the carbohydrates at 6 hours were higher, however, than the values obtained after 16 hours of growth.

Discussion

The information that may be obtained from a determination of carbohydrates, esterase activity, and *E*/*C* ratios presents a new technique to aid in the identification of bacteria.

Data shown in Tables I and II clearly demonstrate a semiquantitative difference in the bacteria studied. These differences in carbohydrates and esterase activity values are empirically valid since initial experiments were carried out in conjunction with the determination of equivalent cell numbers. Comparable cell numbers for each of several bacterial species were employed to demonstrate that the carbohydrate and esterase values were authentic.

This approach to the identification of bacterial cultures may be considered a rapid technique in that both analyses may be completed within 1 hour. In electrophoretic studies of bacterial esterases, the major disadvantage is the long and tedious process of preparing the enzymes prior to separation.

These methods also offer the advantage of determining the carbohydrates and esterase activity of bacteria at different time intervals to establish a given time in which the greatest difference may be observed in values of the bacteria being studied.

Table II. Spectrophotofluorometric Analysis of Carbohydrates and Esterase Activity of Bacteria After 6 Hours Incubation at 35° C. in TSB

Bacteria	Species	Carbo-hydrates[a]	Esterase[a]	*E*/*C*
Escherichia	*coli*, AR-1	0.445	0.051	0.11
Escherichia	*coli*, GM-3	0.345	0.048	0.14
Streptococcus	*faecalis*	0.415	0.294	0.71
Staphylocoecus	*hemolyticus*	0.215	0.364	1.70
Bacillus	*globigii*	0.310	7.080	22.50

[a] Fluorescence readings expressed as meter multiplier times transmission.

Since the total number of bacteria required for each determination are approximately 5.0 × 10^7, an incubation period of 6 hours using only 5 ml. of TSB was generally more than sufficient for most of the bacteria used in this study.

In the development of this technique, the bacteria were cultured in selected media which would allow certain species to reach a sufficient population for measurement within four to six hours while suppressing the growth of other organisms. Determination of equivalent cell numbers or cell weights is quite tedious and imposes a rather severe time problem. A waiting period of 18 to 24 hours would be needed for cell growth. By using an arbitrary optical density percentage reading, this waiting period is reduced four-fold.

In the application of this technique for the characterization of clinically significant bacteria isolated from polluted waters and other such sources, a presumptive identification would first be made by culturing the organism on a specific medium. Nonspecific media would yield mixed cultures.

Consequently, in studying mixtures of bacteria, it will be required initially that each organism be isolated and transferred to a specific, selected media. In a process which employs certain pure strains of bacteria, this technique may prove invaluable in indicating mutational changes and for spotting contamination by periodic monitoring.

Factors which may influence the values obtained by the methods proposed are incubation period, concentration of nutrient, and autoclaving time. In the present investigation, the esterase activity was increased by using longer incubation times. Preliminary data give some indication that esterase activity can also be increased by using higher media concentrations and by using longer autoclave periods.

Perhaps the best reproduction may be obtained by growing bacteria on a solid medium. Potentially, this technique of identifying bacteria may be clinically significant, since *Staphylococcus hemolyticus* and *Streptococcus hemolyticus* were readily distinguished in these studies. *Staphylococcus hemolyticus* esterase activity was approximately seven times that of the *Streptococcus hemolyticus*; the *Streptococcus hemolyticus* carbohydrates were approximately twice the staphylococcus in all experiments. These methods may also provide rapid identification of other streptococci, of which some members are pollution indicators.

A limited number of bacteria have been subjected to the methods reported. A more complete survey may result in similar values for entirely different microorganisms using a particular culture medium. In these instances, careful selection of more specific media could provide another useful parameter for differentiating *E*/*C* ratios.

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Received for review December 30, 1968. Accepted May 9, 1969. *Mention of commercial products does not imply endorsement by the U. S. Public Health Service.*

An Improved Gas Sampler for Air Pollutant Analysis

Arthur F. Wartburg, John B. Pate, and James P. Lodge, Jr.

Laboratory of Atmospheric Sciences, National Center for Atmospheric Research, Boulder, Colo. 80302

■ A gas sampling bubbler, consisting of easily assembled and replaceable glass and Teflon components, has been designed to replace prior designs, which are both expensive and fragile. The new bubbler has proved to be rugged, and easy to handle in the field. It is far less subject to damage than all-glass designs, but equally efficient in pollutant collection. Instructions for its use in the field are presented.

Probably the most widely used form of fritted glass bubbler for sampling gaseous air pollutants is a form derived from designs by (Cauer, 1935) through modifications by (Haagen-Smit, 1958) and Kinosian (Calif. State Dept. of Public Health, Air and Indus. Hygiene Laboratory, 1967). Kinosian's design had a very long bottom tube to accommodate reagents prone to serious foaming. The present form was developed in the U.S. Public Health Service laboratories between 1957 and 1960, but was not reported in the literature until 1965 (U.S. Dept. of Health, Education, and Welfare, 1965). This all-glass bubbler is adequately efficient for collecting nearly all polar gases at an air flow rate of 0.5 to 2 liter min.$^{-1}$, and requires only 10 ml. of collecting solution.

The design, though excellent, has three major drawbacks. First, the configuration is too fragile to withstand damage in the field and during washing. Breakage of the central stem inside the cap is frequent and expensive to repair. Second, the upper and lower parts of the bubbler are not interchangeable unless built with great precision. Finally, a separate bubbler is required for each sample to be taken, since there is no easy way to transfer exposed samples to another container in the field.

The improved glass and Teflon design, now available commercially at a cost comparable to the all glass version, shown in Figure 1 eliminates all three of these problems. Its geometry and dimensions are the same as the glass version, since these are satisfactory in the latter; the identical dimensions permit the same holders, connectors, etc., to be used interchangeably on either version.

Details of the new bubbler are shown in Figure 2. The top is accurately machined from a single block of Teflon (Type TFE) and grooved on the inside to accept a silicone rubber O-ring. A Teflon straight union is modified by removing one cap and machining a groove to take a smaller silicone rubber O-ring. The bubbler's top is bored and threaded for this part, and for a Teflon male connector. Both the tube fittings are screwed in place and secured with epoxy cement.

The two ball joint members are cut to length and bent. The stem, which may be any kind of gas disperser desired such

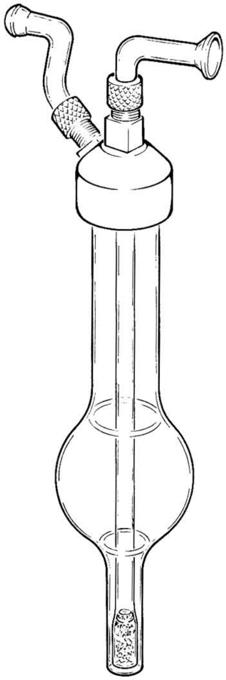

Figure 1. Bubble with Teflon top

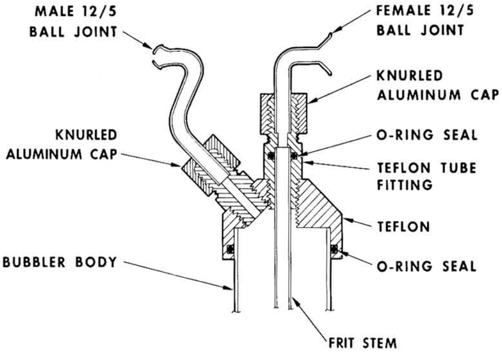

Figure 2. Detail of Teflon top

as a fritted or a capillary glass tube, is cut to length. The bottom of the bubbler is shaped as in the earlier model. None of the sections in the upper part should be seriously out of round. The only critical dimensions are the overall length, which must allow inserting the fritted tube to 2 mm. from the bottom; and the diameter of the upper part of the bottom section, where an O-ring seals it with the top part.

Both O-ring seals are easily disassembled, yet leakage through them is negligible. Assembled bubblers, with the knurled aluminum caps tightened, will routinely maintain an internal vacuum of one-half atmosphere for 24 hours without noticeable loss.

After a sample has been collected in the field, the top of the bubbler is removed. The fritted tube is slipped out, and the reagent is blown out of it with a rubber bulb. A polyethylene cap is placed on the bottom part, making an airtight closure that protects the reagent from contamination. The fritted tube is put into a plastic bag and is not reused until thoroughly washed. The Teflon top is rinsed, fitted with a fresh fritted tube, and attached to a new bottom. (The bottom sections can be conveniently filled with reagent in advance in the laboratory and sealed with the polyethylene tops.) Thus, only bottoms and fritted tubes, both relatively inexpensive, are needed in large numbers.

The bubblers may be completely disassembled for transporting or cleaning. This decreases breakage substantially. Even when fully assembled, the bubblers are less fragile, since the protruding parts are set in somewhat yielding plastic. Finally, if the entire glass portion does break, its replacement costs less than 25% of the total cost of the bubbler.

Tests made to compare the new bubbler with the all-glass version have shown that no pollutant is lost during its very brief contact with Teflon in the inlet. None of the usual sampling reagents attack Teflon. In brief, the plastic-topped bubbler offers advantages with no loss of sampling performance.

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A Modification of the Bausch and Lomb Aerosol Dust Counting System to Automatically Measure Aerosol Size Distributions

Paul M. Brown

National Center for Atmospheric Research, Boulder, Colo. 80302

■ Circuitry has been added to a Bausch and Lomb Dust Counting System to allow unattended, automatic measurements from which size distributions of airborne particles can be determined. The system has been tested and operated up to altitudes of 20,000 feet MSL.

Circuitry has been added to a Bausch and Lomb Dust Counting System consisting of the Dust Counter 40-1, Printer, and Digital Readout to allow unattended, automatic measurements from which size distributions of airborne particles can be determined.

The Bausch and Lomb Aerosol Dust Counting System (as described in the Dust Counter 40-1 operation manual) is used to monitor airborne particle concentrations. Particle detection is done by light scattering, and the system is capable of detecting particles 0.3μm.-diameter and larger. Light scattered by aerosol particles is concentrated by an optical system onto a photomultipler tube. The signal, in the form of pulses, from the photomultiplier tube is then amplified and the pulses counted and recorded. The pulse rate is also displayed by a meter on front of the Dust Counter 40-1. Sample times of 10^2, 10^3, or 10^4 seconds can be selected on the digital readout; and, at the end of the sample time, the printer records on paper the total count. The printer then resets to zero and begins to accumulate counts, the total of which will be printed at the end of the sample time, etc.

On front of the Dust Counter 40-1 is a size selector switch which may be set at one of several size ranges, and only particles equal to or larger than the range selected will be detected and counted. To determine the size distribution of airborne particles, the size selector switch must be manually changed to the various size ranges. In this note, a simple, inexpensive circuit is described which can carry out the switching function from size range to size range automatically and continuously.

A diagram of the switching circuit which allows automatic (or manual) operation is shown in Figures 1 and 2 and works as follows:

A solenoid plunger is energized in the printer when it prints the accumulated count at the end of the sampling time. This signal is used to energize a relay (24 VDC, 1000 ohm coil), the contacts of which are used to furnish power to a

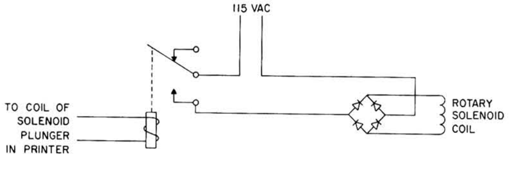

Figure 1. Diagram of the switching circuit

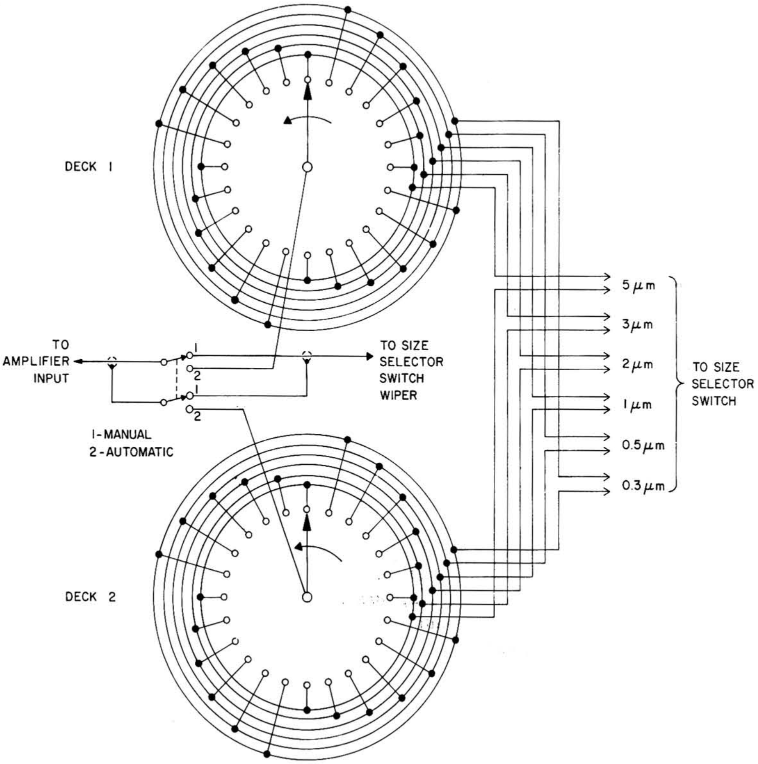

Figure 2. Wiring detail of the rotary switch

rotary solenoid connected to a 24-position, 2-deck switch (Ledex, Inc., Dayton, Ohio 45402). Each deck of the 24-position switch is wired as four 6-position switches. (A 6-position, 2-deck switch could be substituted.) The corresponding positions on each deck are then connected to corresponding positions on the size selector switch of the Dust Counter 40-1. We chose the sequence of 5.0, 3.0, 2.0, 1.0, 0.5, and 0.3μm. (10.0μm. omitted due to the small number of particles of this size range in the atmosphere) for convenience in determining the size distribution by subtraction of successive numbers recorded by the printer.

The modified Bausch and Lomb Aerosol Dust Counting System has been successfully operated as a ground based system and has been flown to altitudes to 20,000 feet MSL. Sampling times of 100 seconds were used, but additional changes in the circuitry to alter the sampling times can be made to suit the particular needs of the investigator.

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Correction

KINETICS OF SUBSTRATE UPTAKE IN PURE AND MIXED CULTURE

In this article by R. I. Mateles and S. K. Chian [ENVIRON. SCI. TECHNOL. **3,** 569 (1969)] in the legend for Figure 6, the triangle for lactose fed alone, and that for lactose in second stage in the legend for Figure 7 should be solid. Figures 11 and 12 should be transposed, but the numbers, titles, and legends should remain as printed.

Environmental quality—costs vs. control

The Economics of Air Pollution. Edited by Harold Wolozin. 318 pages. W.W. Norton & Co., Inc., New York, N.Y. 10003. 1966. $2.95, paper. *Colin Wright is assistant professor of economics, Northwestern University, Evanston, Ill.*

By Colin Wright

The literature dealing with economic problems associated with the existence of air pollution can be most easily classified into three general categories:

- The theoretical literature dealing with what economists call externalities, of which air pollution is an example.
- Articles and reports emanating from government and university groups interested in environmental quality.
- Books and magazine articles issued by the popular press. Much of what appears in this category—serious efforts to understand the economic problems raised by the existence of air pollution—may best be interpreted as polemics called forth by the increased demands for air pollution papers occasioned by the coverage of air pollution "crises" in the news media.

Articles appearing in the first category, though not dealing specifically with air pollution, represent the most sophisticated attempt to come to grips with the air pollution problem and are, accordingly, not publicly accessible.

Articles appearing in the second category may be further classified as either (a) restatements of propositions developed in those articles classified as theoretical literature, (b) empirical analyses of specific air pollution problems, or (c) suggestions on how air pollution can, or ought to be controlled when more realistic (usually taken to mean political) aspects of the problem are taken into account than those which are usually considered in the theoretical papers. Insofar as this classification is correct, the general public will find the literature in the second group best suited for obtaining an intelligent understanding of the economic aspects of air pollution and, more particularly, of its control.

"The Economics of Air Pollution," which falls into the second category, has much to recommend it. The volume consists of a preface by Gardner Ackley, formerly chairman of the President's Council of Economic Advisors; a forward by V. G. Mackenzie, chief, Division of Air Pollution, U.S. Public Health Service; a staff report on air pollution by the Committee on Public Works; a copy of the Clean Air Act and its 1965 amendment; and 10 articles, mostly by economists, emanating from a graduate seminar at American University.

The articles by Kneese and Mills are, in my view, the most rewarding for the general reader—especially when the expectations of the purchaser of a book called "The Economics of Air Pollution" are taken into account. Both men are well known economists who have made significant contributions to the professional literature. Their contributions to this volume are not what one would normally expect of papers presented at a graduate seminar, rather, they are quite readable summaries of how economists visualize some of the problems associated with air pollution. In this way, they are well suited for a volume which I take to be directed toward a nonprofessional market. Both Kneese and Mills articulate several important concepts and relationships without resorting to symbols

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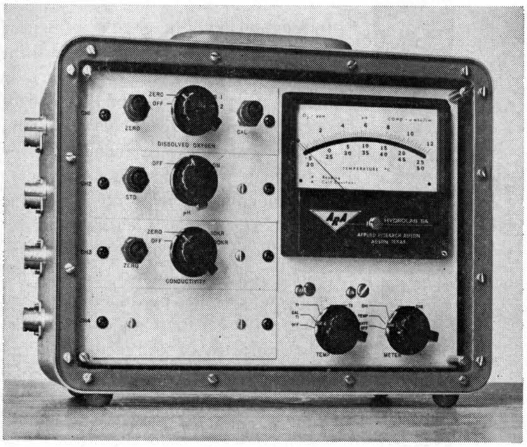

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or geometry—though the reader may wish to dust off his college economics text to review economic principles.

Economists' view

The essence of Kneese's and Mills' papers, and of the general framework within which economists view air pollution, can be summarized as follows: Most of the goods and services individuals consume are obtained via the market place. This means that we usually pay a price for items (or receive payment when we sell factor services such as labor). Implicit in such circumstances is the fact that the consumer initiates the transactions, though, as Galbraith is fond of emphasizing, such transactions may be greatly influenced (meaning initiated?) by advertising techniques. There are, however, an increasing number of goods and bads (i.e. something individuals would rather not have) that are encountered by individuals which come to them quite independent of their activity in the market. (This is not entirely correct for, in the examples of air pollution discussed below, pollutants exist as byproducts of the production process which produces those goods demanded either directly or indirectly by consumers.) Such encounters are external to the market place and are, appropriately enough, called externalities. Externalities may be good or bad. If your neighbor's kids played rock music which you didn't like, you would experience an external cost—a cost because you have a lower level of well being than you would if the music didn't exist.

An interesting way to view the existence of non-optimal levels of air pollution is to see this pollution as resulting from one segment of the population using a factor of production at a nonoptimal price. The atmosphere has attributes desired by producers and consumers. For producers, it may serve as a depository of waste products, thus, being a factor of production just as clearly as janitorial services would be. For consumers, the atmosphere has life giving and aesthetic properties, both goods for which people would, under certain circumstances, be willing to pay a price. An air pollution problem exists insofar as property rights to the atmosphere are not defined, or if defined not enforceable, or if defined and enforceable not in an optimal manner. Employing the value judgment most commonly adhered to in our society we would conclude that consumers and not producers have property rights to the atmosphere. Consequently, in the absence of pollution control, the producer uses the (factor) atmosphere to that point where the increment in the benefits of doing so are zero. He does this because he is, in effect, charged a zero price for its use. Kneese and Mills contributions are elaborations of how, through governmental action, the appropriate price may be imposed upon the polluting firms. Such a price would be equal to the dollar value of damages resulting from the pollution.

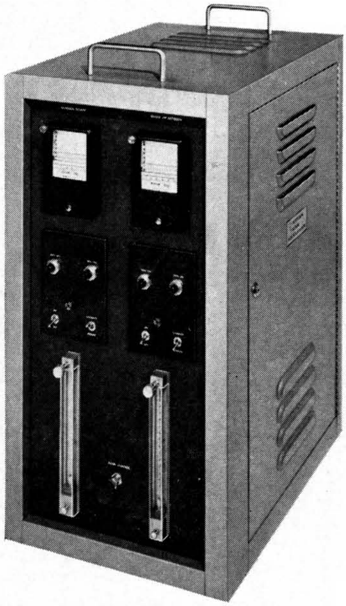
Other aspects of the problem

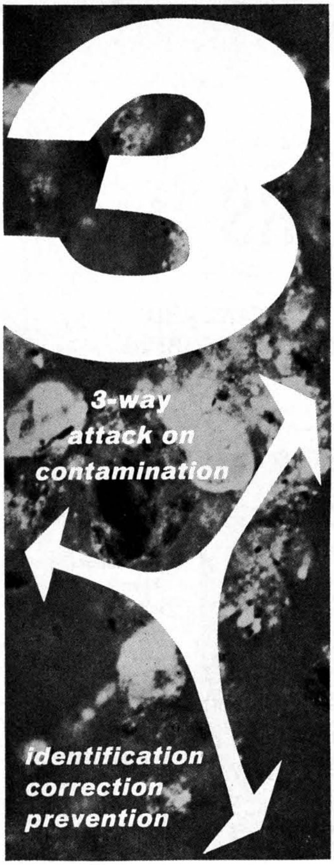
The article by Crocker also elaborates many of these points with some emphasis on the consequences to agricultural damage and problems of optimizing control over time. The contribution by Ridker is noteworthy in that it is, to my knowledge, the only piece of work that attempts to get at the sticky problem of measuring the actual costs of air pollution.

Both economists and non-economists will find the article by Goldner absorbing. He gives an account of Boston's attempt to formulate and effect an air pollution control ordinance. As any professional group mostly employed by universities, economists have been much maligned for living in their ivory towers. Goldner's article should be noted in passing, however, for attempting at least a partial defense of economists—that in recent years, an increasing number have been working in the twilight zone between economics and political science and have been breathing some political realism into their models.

Other articles in this volume discuss the appropriate criteria for pollution control in a benefit-cost framework (Wolozin); strategies for getting measures of economic consequences of pollution (Crowder and Lamale); thoughts on biological consequences of pollution (Chambers).

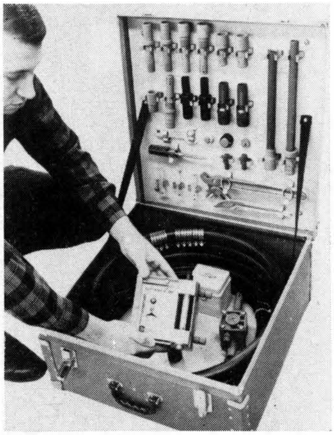
One should come away from this book with the thought that, for all practical purposes, many of the economic problems of pollution control have been solved (at least to the point where some control programs could be implemented). What remains are the political battles over consumer interest vs. producer interest. What seems to be required now is some activity by the likes of a Nader and perhaps a companion volume, "The Politics of Air Pollution" (edited by Sen. Muskie?).





Filter papers

Three new types of MN filter papers for special applications are available. Hydrophobic filter papers are phase separation papers for the removal of water from organic liquids. Polyester and PVC filter papers can be used for the filtration of corrosive liquids. Ion exchange filter papers are suitable for nuclear research applications. Papers can be cut to order in a wide range of sizes in circles, folded filters, sheets and rolls. Gallard-Schlesinger Chemical Mfg. Corp. **61**

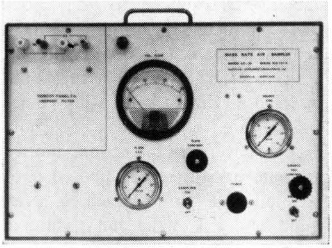


Emergency water treatment

Designed for emergency chlorination of water wells, reservoirs, tanks, and polluted streams, the Advance Emergency Chlorinator Kit is portable and easy to operate. Contained in a polyethylene carrying case, the kit features the Model 201 first line gas chlorinator, as well as all tools and accessories necessary for operation. Controls Co., Inc. **62**

Dust collectors

A line of high-efficiency cyclone type dust collectors is suitable for three classes of service. The company says one model enables meeting of air pollution control standards when very fine particles are involved; a second model collects fine dusts and is used as a primary collection unit; a third model is used as a primary unit for medium sized dusts or highly concentrated loads. Combustion Equipment Assoc., Inc. **63**

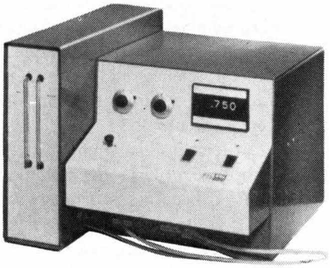


Air sampler

A new air sample rate controller for use in air pollution measurement operates to hold the mass flow rate constant, according to the manufacturer. The Model 69-3L compensates for changes in temperature, barometric pressure, filter clogging, and pump characteristics, and is equipped with a flowmeter for setting desired flow rate. National Instrument Laboratories, Inc. **64**

Water reuse

A continuous ion exchange system will continuously treat and recover polluted waters on a 24 hour a day basis, according to the company. The C.I.X. system enables economic recovery of a broad range of polluted water that previously had been treated but then discarded. Industrial Filter & Pump Mfg. Co. **65**



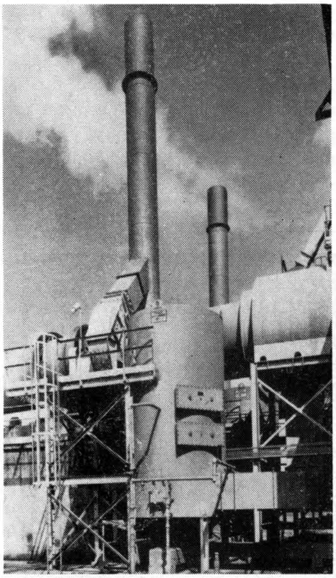
Nitrogen oxide monitor

A new instrument provides continuous monitoring of NO_2 or NO in the atmosphere, indicating the concentration on a panel mounted digital display, according to the manufacturer. The NO_2 Monitor features a built-in binary coded decimal output compatible with data gathering facilities and terminals for connection to a conventional electronic recorder. The device can operate unattended. Precision Scientific Co. **66**

new products digest

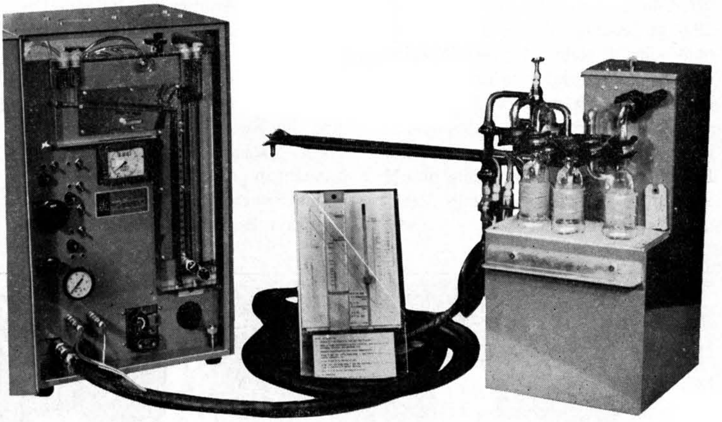
Flotation waste treatment

The Favair Mark II is a flotation waste treatment system which achieves double the capacity of existing conventional designs, according to the manufacturer. Developed in Sweden, the system uses lamels to permit high flow without turbulence for an increase in loading rates, resulting in improved operational stability and performance and improved influent quality in a compact unit. The Favair Mark II can be used for mill process water, as well as in pulp and paper mills, textile plants, and food processing plants. Permutit Co. 67



Gas scrubber

The Impinjet Wet Gas Scrubber employs a pre-codling sieve plate and an impingement baffle type scrubbing stage to clean, cool, and absorb gases for industrial air pollution abatement, the company says. Design involves venting rotary kilns in a lightweight aggregate process. Since the design features no moving parts, maintenance is at a minimum; also, additional stages can be added without an increase in water consumption. The units are available in capacities from 1000 c.f.m. to 500,000 c.f.m. W.W. Sly Manufacturing Co. 68



Testing water. More than 100 water analysis kits are included in a 92-page brochure. The catalog is intended as a buyers' guide to a complete line of portable test kits for water and waste water analysis. General information on test kits is included in the brochure, as well as directions for use, and special features of the line. Hach Chemical Co. **91**

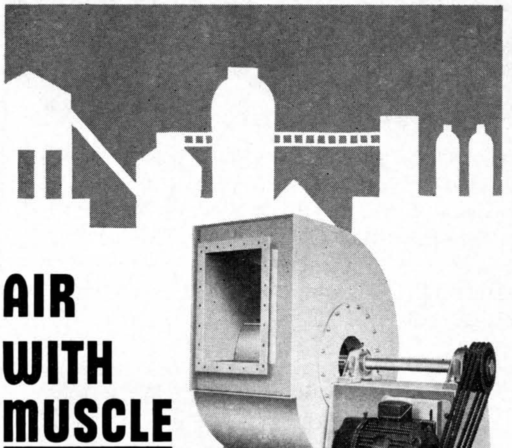
pH Meters. Bulletin 7147-A is a 20-page brochure describing the company's line of eight pH meters. Specifications and descriptive information are listed for each unit—including the solid-state Zeromatic-33, Expandomatic SS-2, Century SS, Electromate, and Digital meters—as well as data on pH accessories and ordering details. Beckman Instruments, Inc. **92**

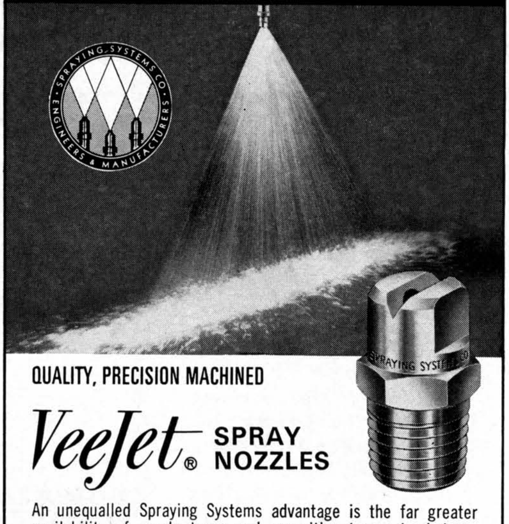
Gas separation. A technical bulletin describes a low pressure approach to liquefaction and separation of gases. "Curve Bending" (Bulletin CD-69) includes discussion of the Process Patent #3,358,460, which the company claims permits operation at low pressures, as well as the use of economical centrifugal compression and expansion equipment. Airco/BOC **93**

Magnetic flowmeters. Bulletin DS-7700 describes a series of solid-state magnetic flowmeters with integral signal converters. Units of the 7700 series—which mount directly into the pipe line without special cables or wires—feature accurate flow range adjustment in producing a DC signal that is linear with flow rate, the manufacturer says. Brooks Instrument Div. **94**

Water pollution abatement. Two booklets describe the company's capabilities in solving water pollution problems. The first discusses a biological process which the company claims can remove 99% biological oxygen demand in waste water, at the same time, requiring less acreage than is necessary either for high rate trickle filter systems or conventional activated sludge processes. The company's deep well injection system for handling wastes not amenable to biological treatment is described in the second booklet. Monsanto Biodize Systems, Inc. **95**

Water clarification. Designed for recovery and treatment of chemical and process wastes, tertiary sewage treatment, softening and clarifying water supplies, recovery of fibers and filler





from white water, and pollution abatement, the Uni-Floc Clarifier features the advantage of basic unit construction which can be modified with standard components to meet changing demands, according to the manufacturer. Because of this modular design, heavy initial engineering and design costs are eliminated, while wide latitude in meeting user requirements is achieved. The 12-page brochure (No. 17.33) includes specifications and advantages of the units, as well as details and illustrations. Crane Co. **96**

Refuse incineration in Europe. Four technical papers describe recent European experiences in incineration of mixed municipal refuse. Providing data on refuse per capita, analysis of refuse, and heat recovery, Paper #11 concerns European practices in refuse burning, giving special attention to grate configuration. Paper #16, which discusses principles of stoker design, burning rates, boiler design, and high-efficiency dust collection, presents information on plants of European design. A recently completed incinerator in Munich, Germany (300,000 ton per year capacity), is described in Paper #17. Paper #18 discusses long-term European incineration experiences, emphasizing heat recovery. International Boiler Works Co. **97**

Air pollution instrumentation. A 10-page bulletin describes and illustrates instruments available from the company for the detection and measurement of major pollutants involved in air monitoring, stack analysis, and auto exhaust analysis. Bulletin 0700-4 provides specifications, capabilities, and diagrams of the LIRA Model 200 nondispersive infrared type analyzer, the Total Hydrocarbon Analyzer, and the Total Combustibles Analyzer. Mine Safety Appliance Co. **98**

Pollution conference proceedings. "Systems for the Control of Sulfur Oxides" (Engineering Extension Series #12) is the proceedings of the 1st Annual Air Pollution Conference (Nov. 19, 1968). Sponsored by the College of Engineering and the Extension Division of the University of Missouri, and the Missouri Air Conservation Commission, the conference aimed to review the state of the art relating to processes which appeared to offer feasible systems for sulfur oxides control. Among the topics covered were the dolomite process; policies and regulations of St. Louis; and SO_2 control: involvement of National Air Pollution Control Association. College of Engineering, University of Missouri, Columbia, Mo. 65201. (Write direct)

Science careers. A 12-page, two-color brochure describes the scientific services and functions of the Environmental Science Services Administration (ESSA). "Science and Service: A Career in the Commissioned Officer Corp" also includes proposed programs and ESSA's relationship to a career in the commissioned officer corps. U.S. Department of Commerce, Washington, D.C. 20230. (Write direct)

FWPCA in Ohio. "Ohio Basin Region" is a 10-page brochure describing the role of the Federal Water Pollution Control Administration (FWPCA) regional office in the fight against water pollution in the area. Boundaries of the region are defined and illustrated in a map. Regional programs are outlined, as well as national programs. In addition, the brochure includes information about FWPCA, its objectives and its function. Office of Information, Ohio Basin Region, Federal Water Pollution Control Administration, 4676 Columbia Pkwy., Cincinnati, Ohio 45226. (Write direct)

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meeting guide

August 4–8
Engineering Foundation

Research Conference on Particulate Matters Systems

Deerfield Academy, Deerfield, Mass.

Designed to bring together people interested in all aspects of particulate science, the conference will feature discussion of such topics as pipelining of solids, particle size measurement, and surface chemistry applied to dispersion, agglomeration, and flotation. Attendance limited. For information: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

August 4–8
Engineering Foundation

Research Conference on Technology Assessment

Proctor Academy, Andover, N.H.

The sponsors define technology assessment as the process of identifying and studying the special, economic, and environmental consequences of the application of science. Such problems as automotive air pollution, sonic boom, and oil spills from offshore installations fall within this category. The conference will feature reports and discussion in an informal atmosphere for the purpose of defining the state of the art, proposing studies, and soliciting new approaches to methodology. Enrollment limited.

August 11–13
Soil Conservation Society of America

24th Annual Meeting

Colorado State University, Fort Collins

This year's meeting will include a student symposium, as well as six symposia on such topics as soil and land management to meet conservation goals, urban-suburban conservation, wastes in relation to agriculture and forestry, and water resources utilization and management. A general session will consider frontiers in conservation.

August 18–20
Environmental Health Science Center, Department of Agricultural Chemistry, and Department of Fisheries and Wildlife, Oregon State University

Symposium on Biological Impact of Pesticides in the Environment

Oregon State University, Corvallis

The 3-day symposium will attempt to assess the significance of pesticides in relation to ecological problems and health. Sessions will include presentation of papers, panel discussions, and open forums on such topics as pesticide movement in ecosystems, effects of pesticides on health and neurophysiology of mammals, and factors contributing to pesticide usage and affecting choice of remedies to resultant problems.

August 18–22
Engineering Foundation

Research Conference on Water Pollution

University of California, Santa Barbara

National Goals in Water Pollution Control is the theme of this year's meeting. More than 100 leaders in engineering and related disciplines will discuss the deficiencies in national policies, especially in the areas of beneficial water uses, establishment of water quality standards, financial incentives, government support for facilities, and public involvement in the problem.

September 17–24, 1969
Czechoslovak Academy of Sciences and Austrian Academy of Science

International Conference on Condensation and Ice Nuclei

Prague (Sept. 17–20), Vienna (Sept. 22–24)

Topics to be discussed are the physics and physical chemistry of aerosol nucleation, methodology of measurement of condensation and ice nuclei, and condensation and ice nuclei in cloud formation. Further information from Dr. J. Podzimek, Institute for Physics of the Atmosphere, CSAV, Bocni II, Praha-Sporilo, Czechoslovakia, or Prof. O. Preining, 1st Physics Institute of the University of Vienna, Strudlhofgasse 4, A-1090, Vienna, Austria

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Courses

August 11–23
University of Wyoming
College of Law

Short Course in Water Resources Law

Land and Water Law Center, Laramie, Wyo.

The two-week course is aimed at nonlawyers, including scientists, engineers, economists, administrators, and graduate students in water resources management. Some of the topics to be covered are riparian rights, pollution control, groundwater law, and public rights to waters. Two hours credit will be given. For information: Michael V. McIntyre, P.O. Box 3035, University Station, Laramie, Wyo. 82070

September 15–17
Environmental Science Services Corp.

Intensive Course on Profits in Environmental Management

The Sagamore, Bolton Landing, Lake George, N.Y.

The 3-day course is designed for management personnel having responsibility for industrial pollution abatement problems. Faculty will present conferences with a program for dealing with air, water, and solid pollutants.

September 22–26
University of California

Short Course on Combustion-Generated Air Pollution

University of California, Berkeley

The 5-day intensive course is planned to cover fundamental knowledge and current practice, and will include lectures and discussion on such topics as combustion and combustion kinetics, environmental effects of air pollution, control techniques, and emissions sources. For information: Continuing Education in Engineering, University Extension, 2223 Fulton St., Berkeley, Calif. 94720

Call for Papers

September 1 deadline
Cornell University

Agricultural Waste Management Conference

Ithaca, N.Y.

Abstracts may be submitted for presentation at the conference, scheduled for Jan. 19–21, 1970, on the theme The Relationship of Agriculture to Soil and Water Pollution. The conference will focus on possible contamination involved in the application of agricultural wastes and chemicals to the soil, as well as possible solutions. Areas of emphasis include runoff, groundwater contamination, management to maintain environmental quality. For information: Fred N. Swader, 154 Emerson Hall, Cornell Univ., Ithaca, N.Y. 14850

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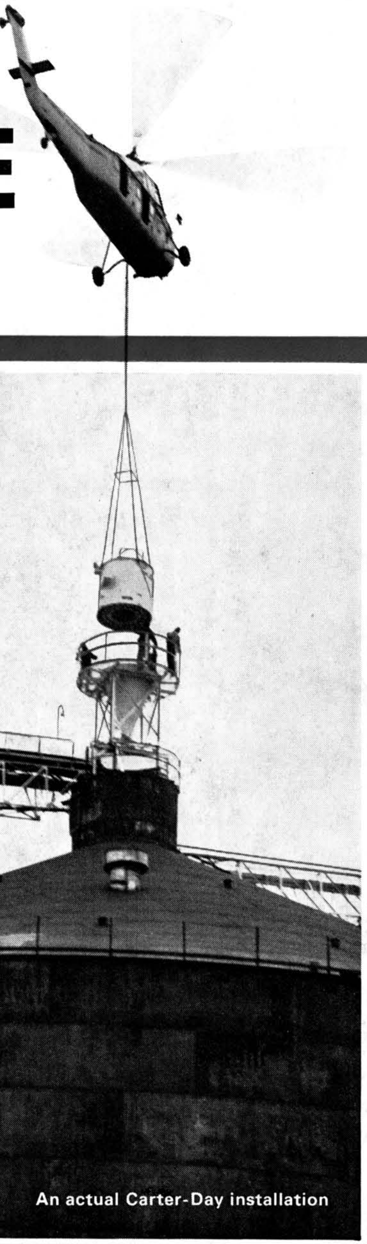

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