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Acid mine drainage 1237

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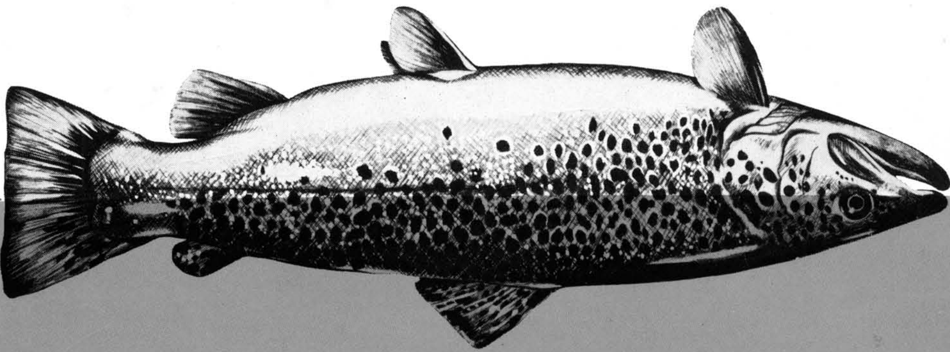

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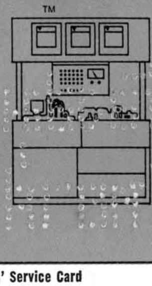

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ENVIRONMENTAL Science & Technology

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Volume 3, Number 12

December 1969

contents

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Current research

Communication

letters

Automobile industry project support

Dear Sir:

The July issue of ENVIRONMENTAL SCIENCE & TECHNOLOGY contains an excellent selection of articles of interest to those concerned with solutions to the air pollution problem, including the report "NAPCA checks emissions of new autos" and the symposium material on "The technical significance of air quality standards."

With reference to the article "Odors from industries need controls," we note with interest the reference to several projects in odor identification which are in progress. In these instances, credit for the support of these research efforts is given to the National Air Pollution Control Administration (NAPCA), the American Petroleum Institute (API), and "the automobile industry." I would like to call to your attention that the automobile industry support for the funding of these types of projects is being provided through the Automobile Manufacturers Association, in the instances where NAPCA and API have joined to support the Coordinating Research Council's Air Pollution Advisory Committee efforts.

William F. Sherman
Automobile Manufacturers Assoc., Inc.
320 New Center Bldg.
Detroit Mich. 48202

More on carbon monoxide

DEAR SIR:

I dislike adding more discussion to the confusion that many readers must be experiencing regarding the "Carbon monoxide hazards" letters (October 1969, page 876). However, both Silver and Weinstock could benefit from editorial assistance and more recent information.

I do not feel constrained to edit, but would urge them (and other readers) to read the following publications on carbon monoxide:

R. Beard and G. Wertheim, *Amer. J. Public Hlth.*, **57**, 2012 (1967).

D. Bartlett Jr., *Arch. Environ. Hlth.*, **16**, 719 (1968).
J. R. Goldsmith and S. A. Landaw, *Science*, **162**, 1352 (1968).

These papers should provide a more up-to-date familiarity with the subject of low level toxicity of carbon monoxide. I have no idea where Silver's "review" can be found and he is apparently not sure either.

M. Y. Longley
Institute of Gas Technology
IIT Center
Chicago, Ill. 60616

Correction: *The standard for CO industrial exposure has been lowered from 100 p.p.m. to 50 p.p.m., and not 5 p.p.m. as printed in Silver's letter*—**Ed.**

Trichloroethylene and smog

DEAR SIR:

We would like to comment on the Stanford Research Institute (SRI) study on the smog forming capabilities of trichloroethylene—highlighted on page 869 of your October issue.

Considering the differences in experimental procedures used by SRI as compared to those of the Los Angeles County Air Pollution Control District—differences in light intensities, hydrocarbon:NO_x ratios, residence times, and the use of dynamic conditions for some experiments—which make direct comparison of the data somewhat difficult, we feel that the SRI data confirm out findings regarding the relative activity of the hydrocarbons tested.

We do not agree with many of the conclusions that SRI has drawn from the data presented to us; for example, that "any contribution of trichloroethylene to photochemical smog manifestations would be negligible," or that comparison shows "that nearly identical effects resulted from the addition of *n*-paraffins and trichloroethylene." Our evaluation of the SRI data leads us to the conclusion that, photochemically, trichloroethylene more closely resembles olefins or xylenes than it does *n*-paraffins.

Our conclusion of the data in the report is that they essentially confirm the findings of the Los Angeles County Air Pollution Control District that trichloroethylene is a photochemically reactive solvent—a solvent that Rule 66 was designed to control.

Robert L. Chass
Los Angeles County Air Pollution Control District
Los Angeles, Calif. 90013

People pollution

Unchecked population growth threatens to destroy the quality of life just as surely as unchecked pollution

One of the most frightening things one can do these days is to read projections of population growth on this planet. According to the University of California's Walter E. Howard, writing in the September 1969 issue of *Bioscience,* world population is growing at a rate of 2% per year. This sounds innocuously slow, but, in reality, this is staggering growth that would, if unchecked, push total population from 3.3 billion to 25 billion in only 100 years. In the U.S. alone, if the birthrate of the 1950's were to be reestablished, it would take only 150 years for the population to reach the current *world* population, and, in another 500 years (that is, by the year 2620), there would be so many Americans that each one would be able to occupy only one square foot of this once empty country. One thousand years after the Declaration of Independence, there would be no place free of human bodies to plant the flag.

If these projections appear ludicrous to you, it is probably not because you argue with the inexorable logic of mathematics. It is because you will say, and rightly so, that before this horrendous crush of people could accumulate, some calamity would occur—as calamities have repeatedly occurred through history—to curtail population drastically. But at what level of human population will this happen? Man has been successful in conquering many of the diseases and hazards that for millennia kept his numbers in check. His success has resulted in the world's increasing birthrate and, more important, to the much greater number of children who survive long enough to reproduce. Unfortunately, the knowledge and skill that were brought to bear on man's traditional enemies were not accompanied by any foresight into a future in which birthrates continually outstrip death rates.

In developing countries, the result generally is starvation. In advanced countries, an increasing population and a marked trend toward urbanization are causing grievous environmental problems. It does not take genius to see that continued population growth will exacerbate all the problems. The projected U.S. population of 338 million in the year 2000 will require more water supplies, more roads, more power stations, more oil refineries, and more of all the trappings of civilization. Yet, there is already, in 1969, so much opposition to new dam, road, and power station construction, that many projects have been indefinitely shelved. Concern for the quality of life eventually may supersede the traditional American goal of expansion, but, surely, it will be a hard fight. Part of the trouble is that business is—or feels itself to be—dependent for its success on an ever greater population. Some seriously doubt that this country's industry and government would know how to manage an economy geared to a populace whose birthrate and death rate were in balance. Yet, that balance has to come, if we are not to be subject to what experts euphemistically refer to as "involuntary self-limitation" (warfare seems the most probable way).

We recognize that the editors of ES&T are hardly likely to be regarded as experts on population control or as the right people to pass judgment on current social, political, and religious mores, most of which pose solid barriers to the attainment of stable world population. But I do believe that some effective way to check the birthrate is a necessity. Otherwise, we are merely playing a game when we try to keep 90% of our sulfur oxides out of the air and all of our raw sewage out of the rivers. If this country—which, after all, is dedicated to the idea of the pursuit of happiness as an inalienable right of all its people—cannot take the lead in halting the suicidal indulgence to human reproductive capacities, then who can?

D. H. Michael Bowen

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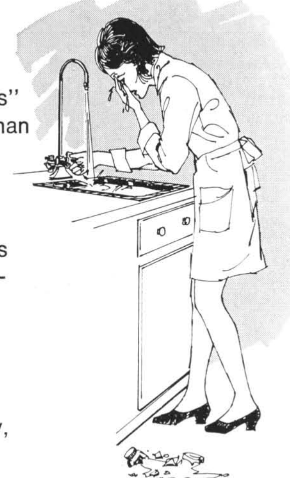

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environmental currents

WASHINGTON

White House pays attention to environmental matters

A White House report, "The Universities and Environmental Quality—Commitment to Problem Focused Education," suggests a shortage of broadly trained professionals to deal with environmental problems, and indicates the possible expansion of educational programs from 10-100 times present efforts. Also, the White house announced immediate cancellation, after a 30 day waiting period, of all garden and household use of DDT in the U.S. and publication of intent to cancel all other DDT uses in the U.S. with a request for comment within 90 days. This action was taken based on the findings of the HEW pesticides commission (ES&T, July 1969, page 613), headed by Emil M. Mrak, whose report noted that the 30 p.p.m. of DDT in certain fish was nearly one fourth the amount that causes liver and lung tumors in mice.

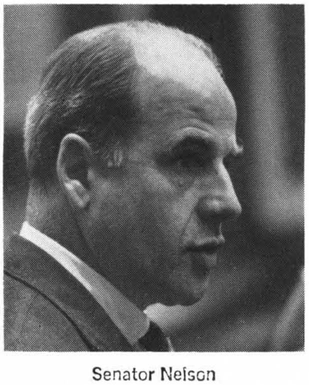
Government auditors find water pollution control ineffective

Regardless of the fact that $5.4 billion has been expended since 1957 for waste treatment facilities, little or no cleanup has been achieved for the nation's waterways, according to a recent report of the General Accounting Office (GAO). Although the federal government contributed $1.2 billion, cleanup efforts simply are overwhelmed by increasing industrial waste discharges and poor planning in the choice of Federal Water Pollution Control Administration's (FWPCA) 9400 projects, GAO reports. Last month, the Senate voted the full $1 billion authorization for fiscal year 1970 for the construction of waste treatment facilities. The final appropriation for fiscal 1970 is up to Senate-House conferees who probably will agree on a figure of approximately $750 million.

Congressmen propose low emission motor vehicle bill

The federal low emission vehicle procurement act hopefully would stimulate the development, production, and distribution of such vehicles; S. 3072 and companion bill H.R. 14534 would create a legislatively guaranteed market for innovative developers of these vehicles. In practice, the developer would make application to a five member certification board, and any vehicle certified by the board would be eligible for purchase if its procurement and maintenance costs are no more than 125% of such costs of the vehicle it can replace.

Volunteer citizens' group gains congressional attention



Senator Nelson

The Fund for New Priorities in America, along with congressional participants, recently sponsored a two day conference on the environment (Washington, D.C.). A nationwide teach-in on all U.S. campuses has been proposed for next spring by Sen. Gaylord Nelson (D.-Wis.). The senator feels that the young people of the country are more concerned and more interested in such problems than the people of the so-called establishment. The recently established Center for the Study of Responsive Laws (CSRL) last summer evaluated several federal environmental programs, including those involving air pollution, water pollution, occupational health, and food poisoning. Gary Sellers, CSRL's legal counsel, notes that the organization will study the effectiveness of some of the federal organizations charged with pollution responsibilities; CSRL's report is due by the end of Dec.

STATES

Iowa water standards to be set by federal government

Interior Secretary Walter J. Hickel has ordered Iowa to provide secondary treatment for its sewage which enters the Mississippi and Missouri Rivers and 25 smaller interstate streams by Dec. 31, 1973. Regarded as the first action of this kind taken under the Water Quality Act of 1965, Hickel's order also noted that the proposed federal standard—to be published in the *Federal Register*—contains language stating that dilution shall not be considered a substitute for proper waste treatment at any time. Industrial wastes amenable to biological treatment must be given secondary treatment by that date, while other types of waste are to receive the best practical treatment. "Before taking the step of publishing standards for Iowa, we exhausted all our other remedies under the law," says assistant secretary Carl L. Klein.

Philadelphia strengthens its air pollution code

Mayor James H. J. Tate recently signed a new air management code for Philadelphia, susperseding its 15 year old air pollution code. The new code specifies the following fines: • $25-300 for a first offense and/or 90 days imprisonment. • $100-300 for a second offense and/or 90 days. • $300 for each subsequent offense. The rules also require the use of low sulfur oil in commercial industrial fuel and retain the permits provision for construction of new installations. In addition, the new code: • Requires operating licenses which must be renewed annually and which can be revoked. • Allows drivers of vehicles which emit smoky exhaust to be halted and given an immediate summons by either the police or Health Department inspectors.

Coastal states must face up to waste disposal

Oceanic disposal of solid wastes and industrial sludge in 1968

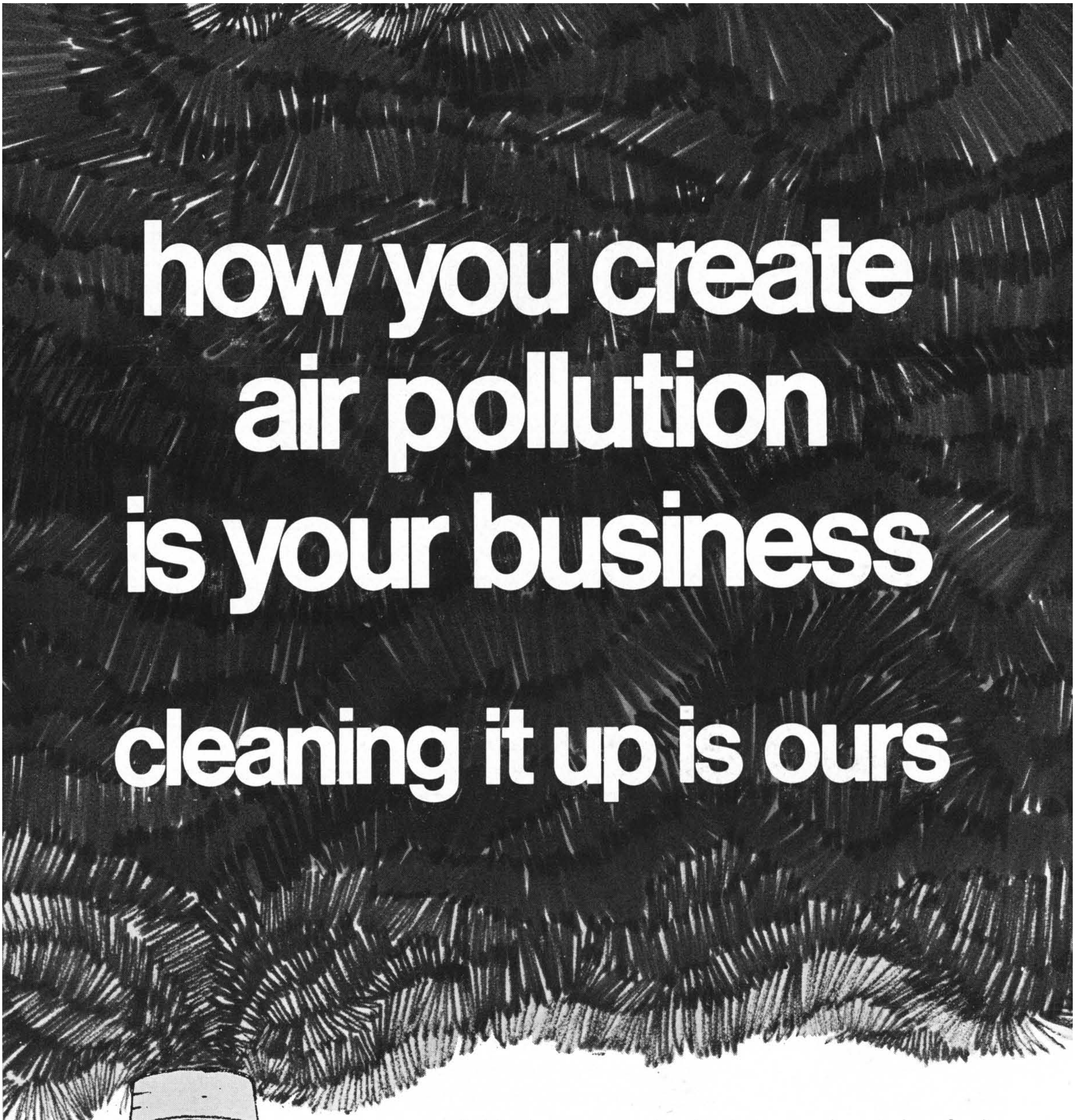
	(millions of tons)
Pacific Coast	8.3
Atlantic Coast	23.8
Gulf Coast	15.9
Total	48.0

Source: Dillingham Corp.

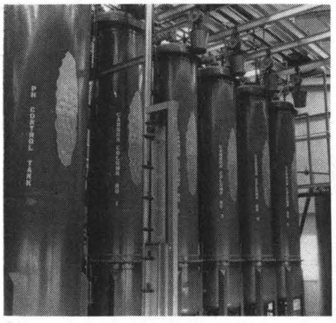
Oceanic disposal of solid wastes has become the operating rule of the day in high density metropolitan areas where there is no land left for landfill operations. The civilian sector of U.S. coastal cities disposed of 48 million tons of this material by barging in 1968 at a cost of $29 million, according to David D. Smith, director of the applied oceanography division of Dillingham Corp. (La Jolla, Calif.). In its recent report, "An Appraisal of Oceanic Disposal of Solid Wastes and Industrial Sludge from U.S. Coastal Cities," Dillingham notes that, excluding dredgings, the tonnage of material disposed to the oceans in 1968 was 9.8 million tons at a cost of $13.5 million.

San Francisco Bay area is first for urban study

Beginning next month, a regional scale demonstration project will be underway in the San Francisco area to test the usefulness of environmental resource data in improving comprehensive urban planning and decision-making. Sponsored jointly by the Departments of the Interior and Housing and Urban Development (HUD), the $311 million study will coordinate the efforts of geologists, geophysicists, seismologists, cartographers, hydrologists, and engineers with the urban planner to achieve the comprehensive picture. The final products of the three year study are expected to be maps, reports, a guide manual, and other material presenting, interpreting, and evaluating the various elements of physical resource data for the region. The first of seven pilot studies, the Bay area region study is headed by George O. Gates, Geological Survey Field Center (Menlo Park, Calif.), and Arthur Zeizel, HUD headquarters (Washington, D.C.).


how you create
air pollution
is your business
cleaning it up is ours

TECHNOLOGY



Carbon columns

Blue Plains to pilot nonbiological treatment

FWPCA has awarded a $743,761 contract to the District of Columbia for demonstration of nonbiological waste water treatment at D.C.'s Blue Plains (Md.) plant. The process to be piloted, euphemistically described as physical-chemical treatment, involves several steps that are not new in themselves, but have been under investigation for tertiary treatment for some time at Blue Plains (ES&T, October 1968, page 750): Lime addition for solids and phosphate removal, ammonia stripping, mixed media sand and coal filtration, and activated carbon adsorption. But the pilot project will be the first time these steps have been used together for treatment of raw sewage. Plans call for treatment at the 100,000 gallon per day level, with results to be compared with the biological process around which the Blue Plains plant was originally conceived.

Power company funds study of thermal enrichment

Maine Yankee Atomic Power Company will fund a $200,000, five year study of the use of warm water discharges from power plants for cultivation of commercial shellfish. The study team will be headed by R. L. Dow, research director of Maine's State Fisheries Department, and will include work on such species as native and European oysters, hard clams, marine worms, and blue mussels. Of these, only oysters are an important cash crop in Maine, and the areas available for their culture are limited by pollution. Maine Yankee has previously funded studies at the University of Maine on the broad ecological effects of power plant discharges. In announcing the new grant, president W. H. Dunham expressed his confidence that Maine Yankee's atomic facilities will have no adverse affects on the environment.

Glass in the streets?

Discarded glass containers may be a source of cheap paving material. In the first large-scale test of such a concept, Owens-Illinois has paved a stretch of road at its research center (Toledo, Ohio) with a mixture of glass and asphalt; initial test results indicate it performs as well as other paving materials. The glass, crushed to prevent tire cuts, substitutes for sand, gravel, or stone in conventional asphalt mixtures, and success of the project hinges on whether cost of processing waste glass is less than having to pay for disposal and then buying sand or stone for paving. The idea originated in a ceramic engineering class at the University of Missouri, which researched the project under a Bureau of Solid Waste Management grant.

Garbage yields possible hydrocarbon source

Research chemists at the Bureau of Mines' Coal Research Center (Pittsburgh, Pa.) have demonstrated experimentally the conversion of garbage and waste paper into a derivative which might yield commercially valuable materials. Tests so far have been limited to laboratory scale runs in which the wet, ground, materials are treated with carbon monoxide and steam at 700° F. for 20 minutes in an airtight chamber. About 90% of the organic material is converted into a petroleum-like substance; minor amounts of gas and ash also are produced. If full-scale conversion plants prove practical, each ton of feed material would yield more than a barrel of crude distiliate, from which fuels and other valuable hydrocarbons could be refined.

INDUSTRY

Steel pickling line maker moves into pollution control

Wean Industries, Inc. (Warren, Ohio), one of the world's largest designers and builders of continuous steel strip pickling lines, has added pollution control capability to its manufacturing know-how by a recent agreement with KSF Chemical Processes, Ltd. (Toronto, Ont.). Under the agreement, KSF will serve as the engineering and manufacturing arm of a new Wean division. KSF has specialized in pollution control systems based on recovery and reuse of chemicals, and the Wean-KSF agreement allows Wean to offer KSF sulfuric acid pickle line pollution control technology to its customers in the steel industry. Previous agreements between Wean, Du Pont, Interlake Steel Corp., and Ionics, Inc., have resulted in pollution control technology for pickling lines using hydrochloric acid. The new Wean-KSF technology features recovery of sulfuric acid and ferrous sulfate.

ASSOCIATIONS

Virus disease transmission needs study, says AWWA

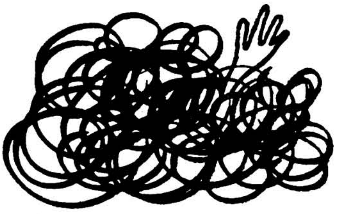
There is considerable room for research into the ways in which virus diseases can be transmitted by water supplies, according to the findings of a special study committee appointed by the American Water Works Association (AWWA). The committee recommends that a study be made to ascertain whether a problem of virus disease transmission does in fact exist—this has always been assumed in good water treatment practice whose object is the complete destruction of all pathogenic organisms. Other recommendations of the AWWA committee: • Determination if the coliform index is an adequate index of water quality. • Improvement of techniques for measuring viruses in water. • Development of methods for detecting small numbers of viruses in large volumes of water and for detecting infectious hepatitis viruses.

New York study shows deaths attributable to SO_2

The number of excess deaths in New York City can be confidently stated to be in the range of 10-20 when the mean sulfur dioxide concentration in the air is between 0.2-0.4 p.p.m., revealed Leonard Greenburg and Marvin Glasser of New York's Albert Einstein College of Medicine at a meeting of the American Public Health Assoc. (Philadelphia). This is believed to be the first time that American data have been considered statistically sound enough for such a claim to be made.

Junked autos could all be reclaimed, say scrap processors

There is no doubt whatsoever that the scrap industry has the equipment and the technology to turn every junked auto in the U.S. into high grade scrap that steel makers can use in the manufacture of high quality steel, says the Institute of Scrap Iron and Steel, Inc. (ISIS), in an official policy statement. The scrap processors concede, however, that new steel making technology and rising labor, freight, and processing costs have put scrap at a considerable disadvantage compared to foreign iron ore. ISIS specifically recommends: • Financial aid for local governments to help defray the cost of moving scrap to the processor. • Government cooperation in changing auto titling laws to speed processing of abandoned cars. • Government and industry cooperation in providing expanded markets for processed scrap.



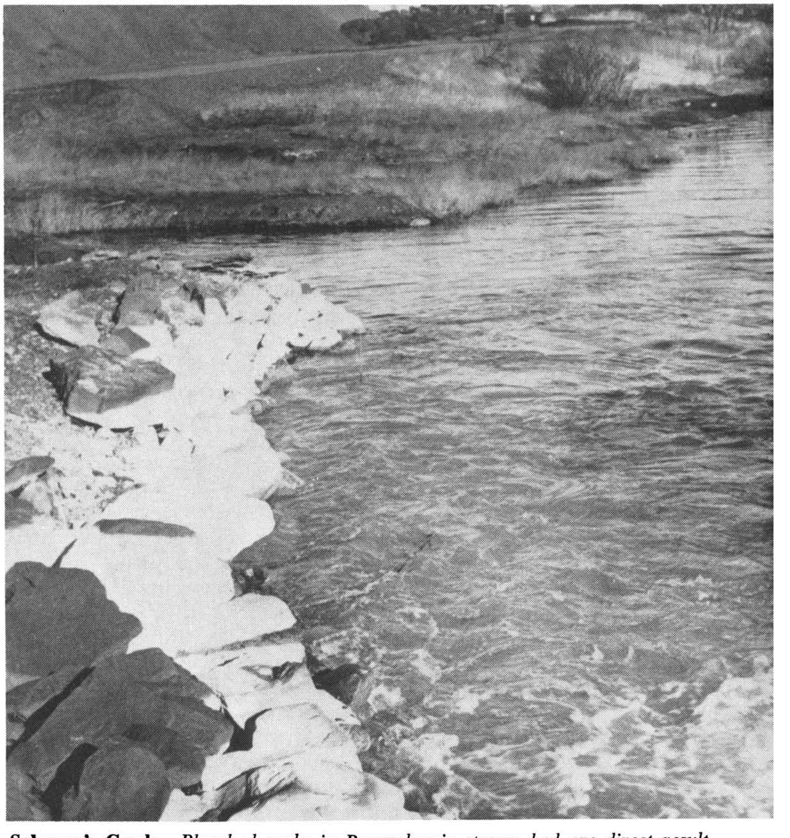
States make headway on mine drainage

Of the nation's major industrial water pollution problems, perhaps none is as complex as acid mine drainage. Certainly, it will be one of the most costly to remedy. The Federal Water Pollution Control Administration (FWPCA)—which, two years ago, placed a $3 billion price tag on nationwide control programs—bases this figure on 80% reduction of acid pollution from active and inactive mines. Now, however, FWPCA feels that to meet most of the water quality objectives being proposed, 95% treatment will be necessary, and total costs of control programs may run as high as $7 billion.

Few water pollution problems have effects as insidious as mine drainage. The chemical pollution and sedimentation it produces pose a severe threat to municipal and industrial water supplies in affected areas; streams that receive untreated mine drainage waters generally are rendered useless for recreational activities. In 1967, more than a million fish were killed by mine drainage, ranking this type of pollution as one of the primary causes of fish kills in the U.S.

About 75% of the mine drainage problem occurs in the Appalachia area alone, where it degrades over 10,000 miles of surface streams. This means that the major burden of the control costs—which ultimately must be met at local levels—will fall on a handful of states. Several of these states are gearing up control programs for enforcement of pollution abatement from active and operating mines, but these constitute less than half the problem. Fully 60% of acid drainage in the U.S. is from abandoned surface and deep shaft mines. Clearly, new legislative machinery will be necessary to cope with this problem; many states have taken the approach that control of drainage from abandoned mines by public funds is the only feasible alternative. Pennsylvania, for example, has estimated that its long-range plan for coping with abandoned mines may run as high as $1 billion.

All types of mineral mining present some version of a drainage problem, but the most serious, because of its severity and magnitude, is from coal mining. Unneutralized acidity in mine drainage from both active and inactive coal mines amounts to about four million tons per year in the U.S. Actually, over twice this amount of acidity occurs, but more than half is neutralized by the natural alkalinity of receiving streams.

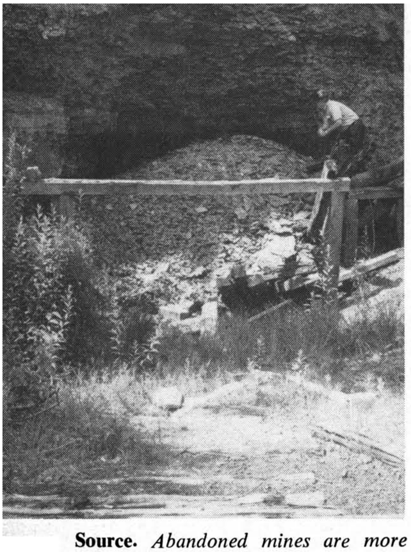


Solomon's Creek. *Bleached rocks in Pennsylvania stream bed are direct result of untreated mine drainage. Effects on water quality are even more severe*

Acid and sediment

The primary pollutants found in coal mine drainage are chemical contaminants—acids and iron and other metals—and sediment. Acid formation and some sedimentation occur when natural drainage patterns bring water into contact with sulfur bearing minerals in mines or refuse piles. Exposure of pyritic materials (iron sulfides which usually occur in conjunction with coal deposits) to air or oxygen dissolved in the water results in oxidation of these materials. Leaching by the drainage water then results in high concentrations of sulfuric acid and acid salts. Most of the sedimentation occurs when the water erodes soil and minerals and carries them along into streams and ponds.

But only the gross mechanism of acid drainage formation is known; the basic reactions involved are, at best, incompletely understood. There is some question about the precise course of the various reactions and their products. For example, there is a great difference in reactivity among the various pyritic materials, which



Source. *Abandoned mines are more than half the problem in most states*

might be explained by the surface texture or size of crystals comprising the agglomerates. Finding the slowest, or rate-determining step in the kinetic mechanism might be an important clue to control methods, such as by inhibiting the controlling step in such acid formation with such materials as carbonates or phosphates. Treatment of drainage by phosphate rich sewage plant effluents is an attractive possibility.

Oddly enough, bacteria have been implicated in the formation of acid mine drainage. It has been found that the rate of pyrite oxidation increases greatly in the presence of certain bacteria, such as ferrobacillus ferroxidans, and bacteria have been claimed responsible for production of significant proportions of highly acid mine drainage. Some current research is based on the premise that the relative importance of bacterial process is determined, and might be controlled, by the ferric/ferrous ion ratio. Another hope is the development of counterorganisms to inhibit the acid producing bacteria.

Control programs

Despite the tentative knowledge of the precise mechanisms involved, enough is known to make a start on coming to grips with the problem. Indeed, several programs already are underway, and are making some progress. An important part of these programs is prevention of the problem at its source. Sound water and soil management practices in mining areas can be effective in reducing the mine drainage problem. In surface mines, covering the mining cuts as soon as possible after mining operations are completed effectively reduces the availability of oxygen, a key link in acid formation process. In depleted shaft mines, oxygen availability is reduced by flooding the mine shaft, after sealing mine portals, bore holes, and other cracks or openings to the mine. Another effective measure is wholesale diversion of natural watercourses away from active or inactive mine sites.

But, despite such preventive measures, a certain amount of drainage is inevitable from active mines, and some form of treatment of the drainage waters is necessary. A number of advanced waste treatment concepts, among them reverse osmosis, electrodialysis, ion exchange, distillation, and crystallization, are under study for application to mine drainage. The only method as yet widely used is straightforward neutralization of the acidity, followed by flocculation and settling to separate the sludge and sediment.

Sludge problems

Neutralization of acid mine drainage usually is accomplished by the addition of lime or limestone, although sodium hydroxide has been used. After neutralization, the sludge mass is aerated mechanically, either by diffused air or step aerators, and flocculated by slow mixing.

Sludge handling and disposal is the most troublesome aspect of treatment by neutralization. One alternative is to leave the sludge in place in the settling ponds, where the sludge dewaters by evaporation and percolation. Another possibility is disposal of the sludge, after dewatering, in abandoned strip mines. In either case, consideration of groundwater flows is a necessity for determining safe disposal areas, and, in some cases, this may be a limiting factor in the treatment step.

Another practice becoming more common is discharge of the sludge to abandoned deep mines or inactive portions of producing mines. The sludge can be easily trucked or piped to boreholes for discharge, and, if properly controlled, this method is very effective. The alkaline sludge appears to essentially remain in the solid form with little resuspension of dissolved solids.

Implementation of control programs at the state levels generally will follow from implementation of proposed water quality standards. Most of the standards that have been submitted contain limits on acidity and mineral content of effluent discharges, and, in most cases, would be effective even though no specific mention is made of mine drainages. But a major stumbling block in the state programs is the problem of abandoned mines, where control techniques have not as yet been fully developed and where responsibility for control costs have not been fixed by existing legislation.

West Virginia, for example, has a plan that requires a permit for operation of active mines, which cannot be issued until the state is assured that discharge water will not pollute receiving streams. However, the state has taken the stand that an effective program for abandoned mines cannot be implemented until completion of sufficient research on control and construction costs. Indiana's implementation plan deals with mine drainage on a basin-by-basin basis; in general, the program requires that all industries, including mining, provide treatment equivalent to that required by municipalities in the same basin. In certain instances, additional treatment will be required by mining firms by the end of 1972. As in West Virginia, Indiana's abandoned mine problem has not yet been dealt with.

Pennsylvania generally is regarded as having the most comprehensive state program for the control of mine drainage pollution. This should not be surprising, in view of the fact that the state is the leading producer of anthracite coal and one of the leaders in bituminous coal mining. One state official has singled out coal mining as the largest source of pollution in Pennsylvania and the Ohio River basin.

Pennsylvania's mine drainage control program is built around a 1965 amendment to its Clean Streams Act. The basic law, originally enacted in 1937, was the state's first attempt at industrial water pollution control, but the original version specifically excluded mine drainage from its provisions. A 1945 amendment did include mine drainage, but as implemented, was aimed at preserving the quality of nonpolluted streams. Discharges to waters already polluted was allowed, and, where treatment was required, the only criterion spelled out was acidity.

The currently operative amendment of 1965 has a strongly worded nondegradation clause, which says the law's objective is "not only to prevent future pollution of the waters of the Commonwealth, but also to reclaim and restore to a clean, unpolluted con-

Monitoring. *Priorities for control programs must be based on assessment of problems.* FWPCA *is conducting nationwide inventory of sources, and industries and universities are studying mechanisms of acid formation and control methods*

dition every stream in Pennsylvania that is presently polluted." Basically, the amendment requires that all present and proposed mining operations be subject to permits obtained from the state's Sanitary Water Board. Applications for permits must be supported by technical data on pollution abatement programs both during operation of the mining and upon completion of mining activities; for strip mines, the act calls for complete backfilling and replanting of the mine sites. In implementing the act, the board has established discharge limitations on mine effluents; for active mines, the requirement is that all discharges be alkaline and the iron content must be less than 7.0 mg./l.

Pennsylvania officials are enthusiastic about the success of the 1965 regulations. Walter Heine, head of the division of mine drainage control of the Department of Health, points out that "in the three years since the amendment, the board has issued over 600 permits for deep mines, of which 200 required some form of treatment of discharges. Of these, well over half are already in operation." Heine is quick to acknowledge cooperation from the coal industry: "They have done commendable work in design and construction of treatment facilities and in treatment research." In fact, Heine estimates that, since the law was enacted, the industry has progressed farther in control technology than all federal, state, and industry efforts undertaken prior to its enactment. W. A. Lyon, director of Pennsylvania's Bureau of Sanitary Engineering, calls this effort the "fastest industrial response to any water pollution legislation."

The Pennsylvania Clean Streams Act does not contain specific provisions for control from abandoned mines, but the state is moving in on this problem by other means. Most of these problem areas have been inventoried through a $750,000 effort, in cooperation with FWPCA, and abatement plans are being formulated. Funding for this problem also is available through a 1967 state bond issue that earmarked $150 million for abandoned mine drainage control over a 10 year period. Under this program, expenditures for 1968 and 1969 were $13 million and $17 million.

Future programs

Much of the optimism about the control of mine drainage pollution stems from the broad range of programs underway at all levels of concern. Backing up the legislative efforts in the coal mining areas are extensive research programs at local state universities. The University of West Virginia, Ohio State, Penn State, and the University of Kentucky all have major projects devoted to the problem. Most coal mining firms also are active in control technology. Bethlehem Steel, for instance, which conducts extensive mining operations in western Pennsylvania, recently announced pilot plant testing of a new process for mine drainage treatment. The company has not released many details, but does say the new process can quickly neutralize the acid waters and that the precipitated solids are formed in such a way that, without prolonged settling, a clear effluent and a concentrated sludge result.

On the regional level, the Ohio River Valley Water Sanitation Commission (ORSANCO) is becoming increasingly active in the mine drainage problem. Last fall, ORSANCO's engineering committee heard testimony from member states, most of which have heavy concentrations of coal mining operations, on their control programs, with a view towards setting up a basin-wide control criteria. ORSANCO is also a principal sponsor of a series of symposia on mine drainage control, the third of which will be held at the Mellon Institute (May 19–20, 1970).

Also, on the regional level, the Appalachian Regional Council has asked the National Research Council to assist in the development of recommendations for a public program for dealing with the problem. The commission is preparing a report to Congress on research, development and engineering aspects of mine drainage control in Appalachia.

At the federal level, FWPCA shows every sign of continuing efforts on the problem, both through inventories of pollution sources and funding of research and demonstration control projects. More than $6 million has been allocated for such projects through just three sponsors—the coal industry, FWPCA, and the State of Pennsylvania —and more funds appear to be on the way. S. 7, the administration water quality bill now close to ratification by Congress, would provide $15 million in new funds for such programs.

Executives join clean water fight

Industrial representatives meet federal officials, setting precedent for U.S. water pollution abatement efforts

The National Executives' Conference on Water Pollution Abatement, a recent meeting (Washington, D.C.) of U.S. business leaders and federal officials, featured an illustrious group of international corporate executives, many of whom are listed in the "World Who's Who in Commerce and Industry." Executives from the chemical, paper, electric utility, steel, and oil industries in the U.S., Europe, and Canada discussed the practical economic aspects of water pollution abatement in their respective countries. International speakers included: Wilfrid Baumgartner, Rhone Poulenc; Harrison F. Dunning, Scott Paper; Rein Henriksen, A/S Borregaard; Neil Iliff, Chemical Industries Assoc. (London); Charles F. Luce, Consolidated Edison of New York; Brooks McCormick, International Harvester Co.; Charles B. McCoy, E. I. du Pont de Nemours; Robert M. Schmon, Ontario Paper; Edgar B. Speer, U.S. Steel; John E. Swearingen, Standard Oil of Indiana; Giorgio Valerio, Montecatini; and Casmir Prinz Wittgenstein, Metallgesellschaft A.G.

Federal representatives included: Walter J. Hickel, Secretary of the Interior; Russell E. Train, Undersecretary of the Interior; Carl L. Klein, Interior's assistant secretary for water quality and research; David D. Dominick, Federal Water Pollution Control Administration; and Lee A. DuBridge, presidential science adviser.

All conference participants recognize the importance of the fight for clean water, and look forward to a better business environment in which they and other business leaders can continue abatement efforts. One fact made clear early in the meeting was that the Nixon administration feels a commitment to satisfy the will of the electorate in this area. "The public wants a clean environment, and they are going to have it," says Interior's Klein. He notes that clean air, clean water, and unspoiled countryside are more easily attained through preventive rather than restorative methods.

International Harvester's McCormick

"Within the limits of technical and economic feasibility, our company intends to prevent pollution of water and air by its facilities."

U.S. Steel's Speer

"The problem reduces itself to one of cost effectiveness—selecting those tasks which will do the most good."

Corporate viewpoints

Without exception, business leaders at the conference acknowledge the fact that water conservation is the cost of doing business, and progress or lack of it usually boils down to the question of economics.

Referring to International Harvester's industrial category as automotive metalworking, Brooks McCormick concedes that his company's policy on industrial pollution can be summed up in 21 words: Within the limits of technical and economic feasibility, our company intends to prevent pollution of water and air by its facilities. "This is fully as much a description of past practices as a declaration of intentions," McCormick asserts. Yes, the company recognizes its social responsibility for environmental quality protection, yet, in the present decade, International Harvester's net income has averaged about 3.6% of sales dollars.

Within industries, recycle and reuse is practiced. Over a period of 25 years, International Harvester's Wisconsin Steel has reduced by 50% its demand for input water. The cost was $11.5 million at this one location, and company plans call for expenditures of an additional several million dollars. "We anticipate that our mill will be one of the first in the Chicago area to return no water whatever to the Calumet River," McCormick says.

Steel's view

Looking at the steel industry in the U.S., Edgar B. Speer states that the critical factor is water quality, not quantity, since the steel mill returns at least 90% of its water to the source. "Water treatment in the steel industry is basically a holding action in which adequate space and time must be provided to hold process water while gravity, chemical coagulation, filtration, and centrifugal force remove the pollutants picked up in the manufacture of steel."

If the money is available, cleanup will proceed, according to steel's spokesman. "Anyone is entitled to any degree of pollution abatement that he wants, but can he or the public afford it?" Speer questions. There is no problem with new plants; it's the old ones that give the industry a headache. "We just aren't earning enough money to install all the controls that, ideally, might be desirable, everywhere, all at once, just as it is manifestly impossible for the government to finance the simultaneous solution for all the major problems it faces," Speer continues. "The problem reduces itself to one of cost effectiveness—selecting those tasks which will do the most good."

The 7% investment tax credit for pollution control facilities again is in jeopardy and under serious Congressional consideration. "Whatever relief provisions are adopted, they should recognize that such expenditures are not a productive investment," says U.S. Steel's president. "I am confident that the incorporation of these provisions in the federal tax code will be needed to permit the steel industry to continue its present rate of pollution control progress," Speer concludes.

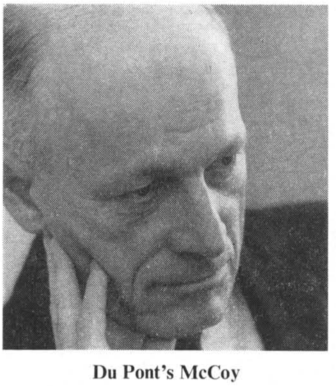
Chemical industry

Revealing an European viewpoint on the chemical industry, Neil Iliff notes that the industry has a right to its own views as to what pollution controls are adequate and what are unreasonable. "The chemical industry in Britain is expanding at twice the national average growth rate, and the industry recognizes that conservation problems are a normal part of the expansion. Hence, the increasing importance of a serious study of pollution in a wide context," Iliff says.

Iliff also notes that a study on the use and reuse of water by the chemical and allied industries is being conducted by the Society of the Chemical Industry in Britain. The findings will be available next April or May.

England's Iliff

"....The industry recognizes that conservation problems are a normal part of expansion."



Du Pont's McCoy

"We must pay more attention to the cost-benefit equation.... Most (efforts) have failed because of the economics involved."

But water pollution is just one form of environmental pollution. Du Pont's Charles B. McCoy notes that, if an effective national policy is to be created, it must be based on the pollution problem as a whole, and not just its separate parts. "We must pay more attention to the cost-benefit equation," he asserts. "To be sure, the chemical industry has been trying to find ways to retrieve useful materials from liquid outfalls and stack gases. A few of these efforts have succeeded. But most have failed because of the economics involved."

"In France, industry uses 7.4 billion gallons of water per day, of a total supply of 124 billion gallons, says Rhone Poulenc's Baumgartner. But the chemical industry's share is quite small, considering electric utility, mining, and steel industry use of water." He also notes that nine French ministries are involved in water pollution control, and the problem has been subjected to legislation.

"The total cost of water pollution eradication should represent about 14% of the annual French budget—including about 4.5% for treatment," Baumgartner says. "It is quite obvious that such expenditures will have to be spread over a period of time, currently estimated at 20 years." But he notes that the chemical industry is far from being behind, since, already, it has attained 35% of the investments necessary in the initial stage for cleanup, whereas public communities have not yet attained 15%.

Other approaches

A U.S. oil executive expresses the message of cost effectiveness in similar terms. "The central question is not whether we should have cleaner water, but how clean, at what cost, and how long to take to do the job," says Standard Oil's Swearingen. "Our challenge is to identify the complex sources of pollution and keep them within socially and economically tolerable limits."

From the viewpoint of the pulp and paper industry in Europe, "The choice is between a bigger or smaller improvement in the water situation, connected with a bigger or smaller increase in prices for pulp and paper," comments Borregaard's Henriksen.

Attended by almost 1000 industrial and business leaders, this conference is just a beginning; a second is planned for next year. Worldwide water pollution abatement is the goal.

Rx for ailing lakes—a low phosphate diet

Boundary Commission study sees detergent reformulation and tertiary treatment as only hope for lower Great Lakes

At first glance, the technical report issued last month to the U.S.-Canadian International Joint Commission on the pollution of Lakes Erie and Ontario and the St. Lawrence River contains few surprises: Yes, these waters are already in an advanced state of eutrophication, and deteriorating rapidly; yes, phosphates are a key link in the deterioration process; and yes, municipal waste effluents are the major culprit, although industrial effluents are also a threat. But the significance of the report is that it goes well beyond confirming what is already known about the lakes. Specifically, the report:

• Contains perhaps the most comprehensive inventory yet of pollution sources to these waters, and includes estimates of costs of control.

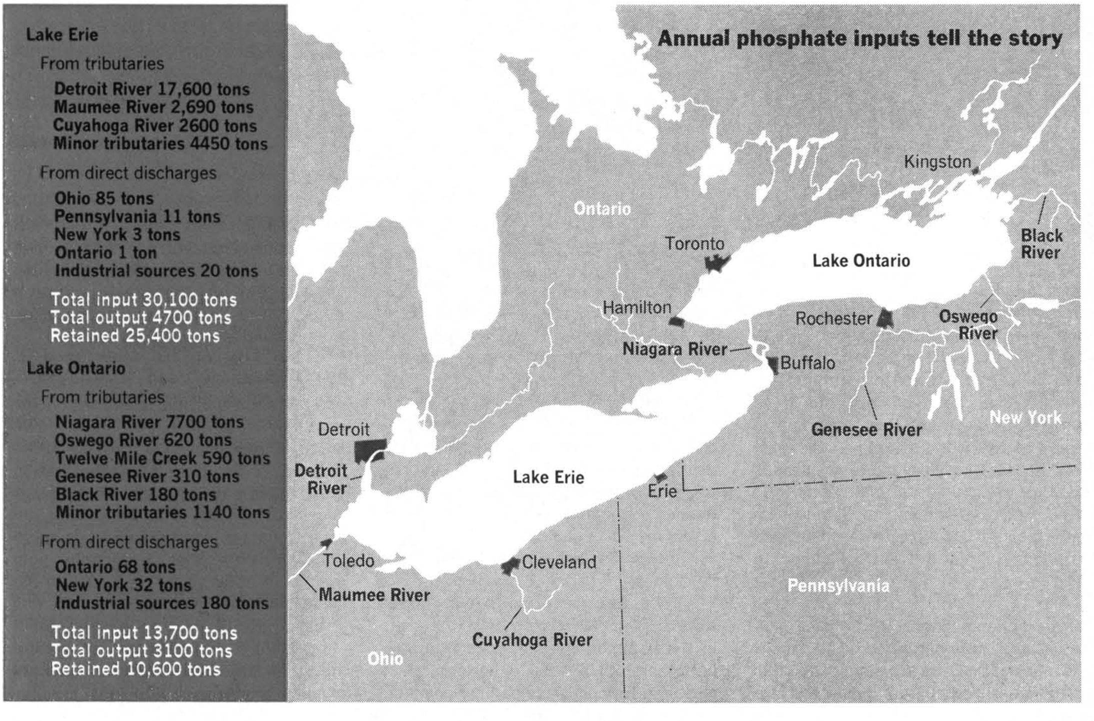
• Sets up water quality objectives appropriate to the area and recommends accelerated programs to meet these goals.

• Makes a vigorous argument that control of phosphate inputs would significantly curb eutrophication of the lakes, even in the absence of similar controls on nitrates.

• Firmly endorses elimination of phosphates from household detergents. The report maintains that partial replacement now is possible, and that complete replacement might be possible in a few years.

The report asks for continued and expanded cooperation between the U.S. and Canada on the whole range of lake pollution problems, through an appropriate board appointed to coordinate the effort. The commission plans to conduct public hearings on the report early in 1970, after which it will determine what recommendations to make to the U.S. and Canadian governments. The report's programs, if duly implemented, would result in the most thorough international pollution control compact ever enacted.

Such close cooperation could provide a formal mechanism for supplementing the Federal Water Pollution Control Administration's efforts on restoring the Great Lakes through pollution abatement enforcement conferences. A minor point of contention often broached at these conferences is the efficacy of unilateral control measures on such problems as oil spills, exploratory drilling for oil and gas, and disposal of harbor dredging spoils, that are taken without implementation on both sides of the lakes. At last year's Lake Erie conference (Cleveland, Ohio), Representative Thomas L. Ashley (D.-Ohio) contended that, for many years, both

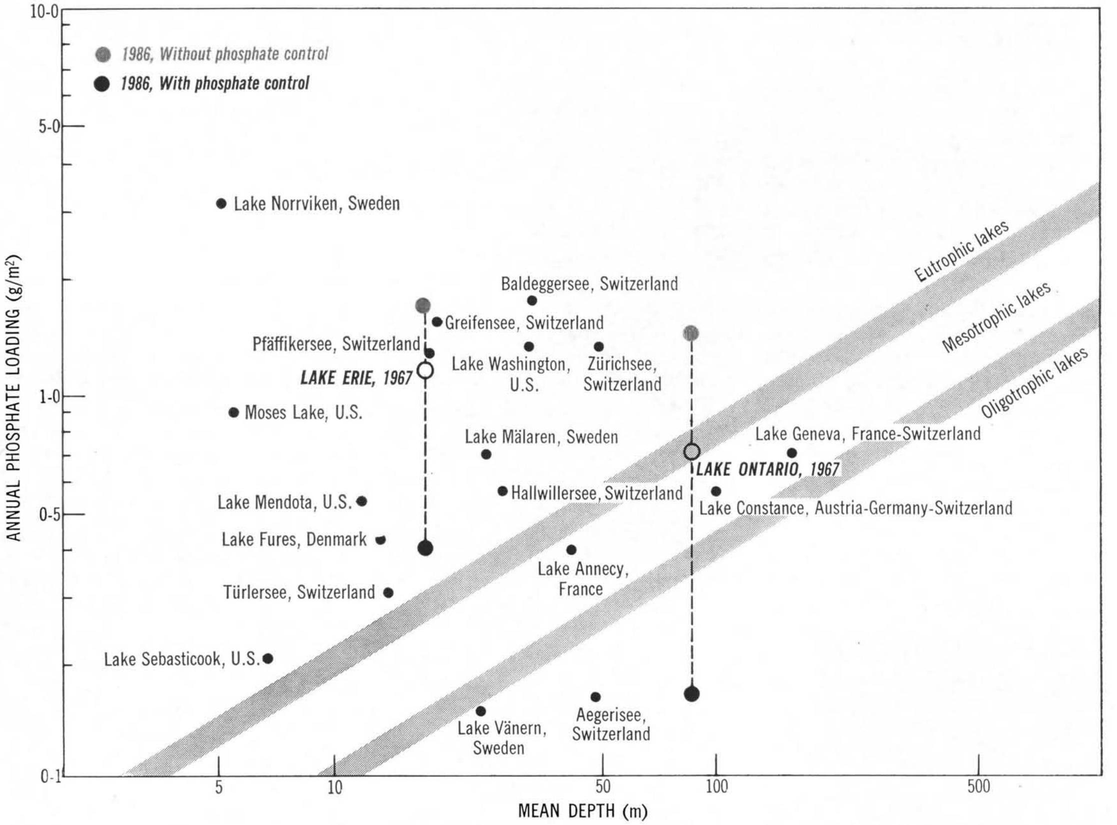


the U.S. and Canada have been in violation of the 1909 boundary treaty; one article of that treaty specifically provides that "boundary waters shall not be polluted on either side to the injury of health or property on the other."

Earlier studies

The international implications of pollution of Lakes Erie and Ontario certainly was not news to the commission, whose earliest look at the problem dates back to 1918 with issuance of a report on investigations conducted from 1913-16; another report in 1950 covered studies undertaken from 1946-48. The 1918 report was concerned with bacterial pollution from domestic sewage; it concluded that open sections of the lake were free of it, but localized contamination in nearshore areas was a direct threat to municipal water supplies.

The 1950 report indicated that many of the municipalities in the lake basins had constructed sewage treatment works and water filtration plants, but extensions of sewer services had not kept pace with population growth. Industrial pollution, not significant in 1918, was recognized as a growing problem in 1950, as was the fact that



Lower Great Lakes not beyond repair, report says

Is man-made eutrophication irreversible? The current report to the International Joint Commission proceeds from the premise that it is not: "The similarity of the eutrophication resulting from man's activities . . . to natural eutrophication is often overemphasized . . . . The extent of enrichment and eutrophication which has occurred in many of the world's lakes in the past few decades would require thousands of years under natural conditions. Indeed, such enrichment might never be possible naturally. It is unfortunate, and misleading, that the eutrophication in lakes affected by man is so often referred to as a mere acceleration of a natural phenomenon. This analogy often gives the impression that [such] eutrophication is irreversible. That this is not true has been demonstrated in a number of cases . . . ."

As to the present status of and future outlook for Lakes Erie and Ontario, the report draws on the work of R. A. Vollenweider of the Canada Centre for Inland Waters, and a contributor to the report. Vollenweider has obtained, from data on 20 lakes throughout the world, a general correlation between annual phosphate loading and mean lake depth on the one hand, and degree of enrichment—defined as oligotrophy, mesotrophy, and eutrophy, in increasing order of severity—on the other. The report then concludes:

• **Lake Ontario presently is mesotrophic.** Vollenweider's analysis puts it in the upper range nearer to eutrophy, but other criteria, such as bottom fauna, phyto- and zooplankton populations, and physicochemical characteristics, indicate that it is more oligotrophic than this. Effective phosphate controls would return Lake Ontario to an oligotrophic condition, as indicated.

• **Lake Erie, on the other hand, is highly eutrophic,** and Vollenweider's parameters would put it still within the eutrophic range, even with implementation of phosphate controls, by 1986. But, as in the case of Lake Ontario, other criteria suggest that Lake Erie is considerably less eutrophic than indicated on the chart. If so, it is more than probable that phosphate control would bring Lake Erie back into the mesotrophic range. But Lake Erie was a mesotrophic lake before the rapid enrichment of recent years, and control measures probably would not alter its condition below mesotrophy.

much of the industrial, municipal, and agricultural development was occurring without regard to the effects of multiple releases of wastes to the lakes.

The current study was initiated in 1964 when the International Joint Commission, in response to requests from the U.S. and Canada, set up advisory groups on the status of pollution in the two lakes and the international segments of the St. Lawrence River. The report of these groups disposes of the problem of cross-boundary pollution by frankly admitting that it probably exists: "While difficult to state that a given concentration of pollutant on one side of the lakes is tied to a particular source on the other, it is clear that inputs from both sides have transboundary effects."

Instead, the report devotes much of its effort to recommending technical and legislative machinery for control measures. Phosphate enrichment is singled out for special emphasis, and is the subject of the report's most sweeping recommendations. Phosphate content of detergents should be reduced immediately to minimum practical levels, with complete replacement of phosphorus in detergents with less innocuous substances as soon as possible, but not later than 1972. Furthermore, 80% removal of phosphates from all effluents should be provided, by 1972 in the Lake Erie basin and by 1975 in Lake Ontario. Treatment of waste effluents for phosphate removal must be in addition to, and not a substitute for, detergent reformulation.

Controlling nutrients

The rationale for the necessity of both measures is somewhat intricate. Phosphorus and nitrogen are, of course, widely recognized as the most important nutrients responsible for eutrophication, but some debate still occurs about whether phosphorus or nitrogen is controlling. The report states that there is every reason to believe that phosphate is the controlling factor in the enrichment of the lower Great Lakes. As evidence, the report cites the work of J. R. Vallentyne of the Fisheries Research Board of Canada's Freshwater Institute (Manitoba). In his studies, Vallentyne showed that algae blooms could be produced in lake water samples by the addition of 2% raw sewage, or even 2% effluent from secondary treatment plants. Addition of effluent treated to remove phosphorus, but not nitrogen, showed no algae bloom, but subsequent addition of phosphate alone to these samples did.

One other reason for the control of phosphorus in the absence of nitrate controls is that the phosphate loadings can be controlled more effectively. The report notes that 57-70% of the phosphorus loadings is from municipal and industrial waste effluents, as opposed to 30-40% for nitrogen. Furthermore, efficient and relatively inexpensive methods are available for 80-95% removal of phosphorus during sewage treatment, whereas comparable elimination of nitrogen compounds is not yet feasible.

Removal costs

Given this evidence of the desirability of phosphorus control, the argument for both detergent reformulation and removal at the treatment plants is largely one of economics. The report estimates that treatment costs for phosphate removal at the treatment plant would be reduced by a half to two thirds with replacement of phosphate detergent builders. Detergent sources account for 70% of the phosphorus in municipal waste, and 50% in Canada. The current average phosphate content of sewage is about 10 mg./l.; if the detergent contribution were eliminated, an 80% removal process would reduce the typical concentration to 0.6 mg./1. To achieve the same effluent concentration without replacement of detergent phosphates would require 95% removal at the treatment plant, at two to three times the cost, largely due to the additional chemicals needed and the solid waste produced.

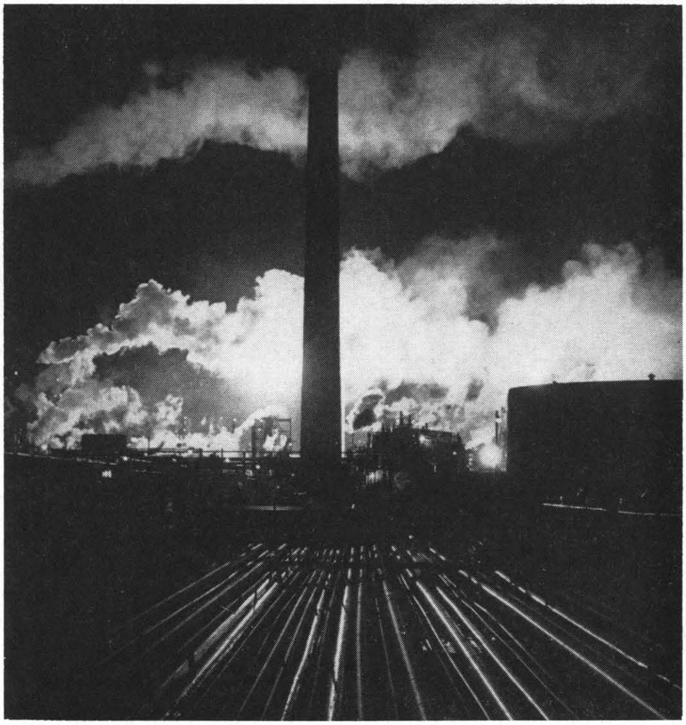
The total cost of meeting the report's water quality objectives is put at about $1.4 billion in the U.S. and $212 million (Canadian dollars), in Canada. These figures include capital costs for phosphate removal of $265 million in the U.S. and $40 million in Canada. Although detergent reformulation probably would have little effect on capital costs for phosphate removal, the report states that the operating costs for the treatment plants would be greatly reduced. For example, in the Lake Erie-Detroit-St. Clair River system, the cost of 95% phosphate removal from a 10 mg./1. effluent would involve a total annual cost for chemicals of $17.6 million dollars. The same results could be obtained at a cost of $5.3 million by 80% treatment of a 3 mg./1. effluent which would result from phosphate-free detergents. Scaling up these figures to the entire Lake Erie-Lake Ontario-St. Lawrence River basin, the total annual savings for each country would be $478 million in the U.S. and $26 million in Canada.

Water quality objectives for lower Great Lakes

Parameter	Limits	Remarks
COLIFORMS	Less than 1000 total and 200 fecal coliforms per 100 ml.	International waters will be protected if local conditions meet these standards
DISSOLVED OXYGEN	Not less than 6.0 mg./l. in epilimnion	Established to support fish and associated biota
DISSOLVED SOLIDS	No more than 200 mg./l.	Water supplies affected at 500 mg./l.
TEMPERATURE	No change which affects beneficial use	Lack of data on effect of changes precludes absolute limits
TASTE AND ODOR	Virtually none	Phenols not to exceed a monthly average of 1.0 μg./l.
pH	No change from present	Present pH within desirable level limits
IRON	Not to exceed 0.3 mg./l.	Conforms to USPHS and Canadian drinking water standards
PHOSPHORUS	Limited to extent necessary to prevent nuisance growth of algae	Algae blooms can be expected phosphorus and nitrogen exceed 10 and 300 μg./l.
RADIOACTIVITY	Gross beta less than 1000 pCi/l., radium-226 3 pCi/l., and strontium-90 10 pCi/l.	Meets USPHS drinking water standards.

Firms pool anti-pollution efforts

Pioneer venture shows how companies benefit from concerted action on environment



Pipelines. *Refinery products are feedstocks for neighboring chemical plants*

According to the local chamber of commerce, it is "fascinating by day, a fairyland of lights by night . . . an awe inspiring sight." And, while it is perhaps no great rival to Disneyland, there is no doubt that the concentration of refineries and chemical plants stretching for 20 miles along the east bank of the St. Clair River in southwestern Ontario is an impressive sight indeed. Refinery flare stacks give off a fiery glow that can be seen at night for miles around.

There's no great secret about the attractiveness of the area to the chemical industry. First, there is the St. Clair River—a fast running stream that, for much of its length, is a full half mile wide—which is both a source of water and a vital part of the St. Lawrence Seaway linking the upper Great Lakes with the Atlantic Ocean. Second, and probably even more important, the first oil in North America was discovered just 20 miles from Sarnia, the chemical valley's biggest city. Imperial Oil Co. (now 70% owned by Standard Oil of New Jersey) built a refinery here in 1897, and, from small beginnings, the area has grown into Canada's biggest concentration of chemical industry. As elsewhere, chemical plants were built to utilize the petroleum based feedstocks a big refinery can provide. There are three refineries near Sarnia now.

Active cooperation

The overall appearance of the area is, of course, very much like that of other areas where chemical and petroleum companies have moved in a big way. This might be a strip along the Ohio River in West Virginia or the Delaware River in Pennsylvania and Delaware. What is different about the chemical industry along the St. Clair River in Lambton County, Ontario, is its ability to speak with one voice to citizens and government, even though more than a dozen different firms are located there. This situation was made possible by the establishment of an industrywide cooperative group known as the Lambton Industrial Society (LIS).

LIS originated in embryo in 1952 when the Ontario Research Council (a now defunct group set up by the provincial government) suggested to the area's three largest chemical concerns—Imperial Oil, Dow, and Polymer Corp.—that they undertake studies of air, water, and soil pollution in the St. Clair River region. The three companies set up the St. Clair River Research Committee and, in that same year, initiated an air monitoring survey of the area that has continued in constantly expanding form. As time passed, other firms joined the committee until, today, there are 12 members. The 12 include all of the major chemical firms located along the river for 20 miles south of Sarnia. In 1967, the name of the committee was changed to the Lambton Industrial Society, and LIS was incorporated as a nonprofit association.

Organization

Broad policy decisions for LIS are made by the society's board of directors, which is composed of 12 men, one from each member company. A director usually is the senior man at his company's plant (works manager, for instance), but some directors are corporate vice presidents of companies that have corporate headquarters as well as plants in the region. Five of the directors comprise the executive committee of president, vice president, secretary, treasurer, and member at large. The executive committee runs LIS within the framework of its board's policy guidelines. Assisting the executive committee is one of LIS' two paid, full-time employees—the society's manager (the other is the manager's secretary). In many ways, establishment of the position of manager in 1967 was a very smart move for LIS to make. Two years of experience have shown that manager H. Mason Jones has been able to make substantial contributions to the smooth running of the society and, equally important, to act as an informal communications channel between the various member firms.

Two committees serve the detailed information and planning needs of

Members of the Lambton Industrial Society

Allied Chemical Canada

Cabot Carbon of Canada

Canadian Industries

Chinook Chemicals Corporation

Dow Chemical of Canada

Du Pont of Canada

Ethyl Corporation of Canada

Fiberglas Canada

Imperial Oil Enterprises

Polymer Corp.

Shell Canada

Sun Oil Co.

LIS' board of directors—one is a technical committee and the other covers public relations. The 12 members of the technical committee—again, one from each company—generally are their companies' plant pollution control administrators. This year's chairman, Herbert S. Wilson, is environmental control coordinator at Imperial Oil's refinery. The public relations committee is composed of just five or six public relations men; not all member firms have P.R. men in the Sarnia region. A big task for the P.R. committee is the arranging of the once a year briefing LIS gives for the benefit of local government, civic, and news media officials.

Programs

The general objective of LIS was spelled out in 1967 as: "To promote joint and individual effort by member industries in fields of education and research to achieve control of industrial pollution of air, soil, and water consistent with government regulations and good corporate citizenship." LIS programs in education are centered around the need to let the public know what the companies are doing about their pollution problems. To this end, LIS has held three annual briefings for press and radio, with generally good reception being afforded the industry representatives. Manager Mason Jones feels that press relations now are excellent, after an early unfortunate incident in which newspapers used LIS' own air quality data to browbeat its members.

Each member company performs its own in-house research on pollution control techniques; such research is not performed under the auspices of LIS. LIS research programs are based on the need for information on air and water quality in the region. The laws in Ontario are strict by U.S. standards and the province's air pollution legislation specifies air quality criteria in terms of several parameters (oxides of nitrogen, hydrocarbons, and hydrogen sulfide, among others) that are only now being talked about in the U.S. New construction or plant modification will not be granted a permit by Ontario's Department of Energy and Resources Management unless certain design standards, based on these criteria, are complied with. The same department requires compliance with water pollution standards, although these are by no means so well specified as the ones for air quality. Nevertheless, there are, in effect, effluent criteria with respect to pH, oxygen demand, oil, phenolic materials, etc., imposed on plant waste waters.

The air monitoring program which the St. Clair River Research Committee started in 1952 has expanded to encompass five main monitoring stations around the county. The stations continuously measure atmospheric conditions such as temperature and wind speed, and concentrations of sulfur oxides, nitrogen oxides, aerosols, particulates (dustfall and suspended), and hydrocarbons. LIS itself does not take the measurements; instead, it retains the Ontario Research Foundation (ORF) on a contract basis. ORF employs three men full time in Sarnia to run the monitoring network, which costs LIS about $100,000 a year to support. Results of the ORF surveys, together with air quality information gathered by the individual companies themselves, is shared with the Ontario government and made public from time to time.

At present, LIS has no water quality monitoring program of the magnitude of its air quality efforts, although setting up such a program is under discussion. However, every few years, LIS has commissioned a biological specialist to conduct a complete biological survey of the bottom of the St. Clair River from Lake Huron to Lake St. Clair. These surveys have the purpose of taking an inventory of pollution sensitive organisms from natural bottom life.

Advantages for members

What advantages do LIS members enjoy as a result of membership?

- **First,** there is an opportunity to share in a responsible program to inform the public of what it and other companies are doing to combat pollution. The public tends to see industry as a single entity, and membership by all the firms in the area permits companies to respond to criticism in a unified way.
- **Second,** joint support of air quality data gathering and pooling of in-house data, especially when these data are made public (whether or not favorable to industry), lends considerable credibility to the sincerity of member companies' intentions.
- **Third,** and somewhat more intangible, there is the benefit to be derived from close contact with the people responsible for pollution control in other companies. Although technical information and even technical aid is given on occasion, a major benefit is that the society's manager can and does exert pressure on any member firm that is guilty of poor practice which might bring approbation on all area industry from an aroused public.

Outlook

The success of the Lambton Industrial Society should make the cooperative idea worthy of emulation elsewhere. Mason Jones is aware only of one other similar cooperative effort in North America—that of the Laval Industrial Association in Quebec. But, if the arrangement works in Ontario, there seems no reason why it would not work in any of the other heavily industrialized regions on this or any other continent.

Nixon administration: Its first environmental step

Created by Executive Order on May 29, the Environmental Quality Council is gearing up for an assault on environmental problems

Like an iceberg whose visible portion is a mere fraction of its total mass, the activities of the Nixon administration's Environmental Quality Council (EQC) that have surfaced seem small in comparison with EQC's inner working and planning activities that still lie deep beneath the waters of federal bureaucracy. Nevertheless, considerable activity is being coordinated at various interdepartmental and interagency meetings, in committee assignments, and on federal agencies' environmental quality programs.

"One main objective of EQC is to get the federal government to march as much in the same direction on policies that affect the environment as seems reasonable to do," says John L. Buckley, technical assistant at the office of Science and Technology (OST). Buckley, key coordinator for EQC activities, offers some insight to the Nixon administration's council.

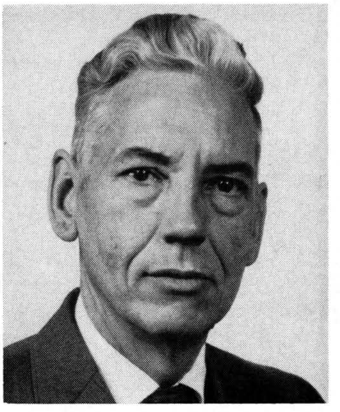
Activities

Organizationally, EQC members are President Richard M. Nixon, Vice President Spiro T. Agnew, and secretaries of six federal departments—Agriculture; Commerce; Health, Education, and Welfare (HEW); Housing and Urban Development (HUD); Interior; and Transportation. The President's science adviser, Lee A. DuBridge, serves as EQC's executive secretary. But, within each department, there is a rotating group of federal personnel who attend EQC meetings and with whom OST's technical assistant maintains close contact. Buckley also is concerned with the direction that the federal government will take on environmental matters.

To date, three EQC meetings have been held; all secretaries attended the second meeting. A number of other federal departmental officials have attended and participated in EQC meetings as well as a number of other less formal interagency and interdepartmental meetings. In addition, observers from the Bureau of the Budget (BOB), the Council of Economic Advisers (CEA), and other federal departments and agencies—such as the Department of State, Department of Defense, and the Atomic Energy Commission (AEC)—participate in both types of meetings, Buckley explains.

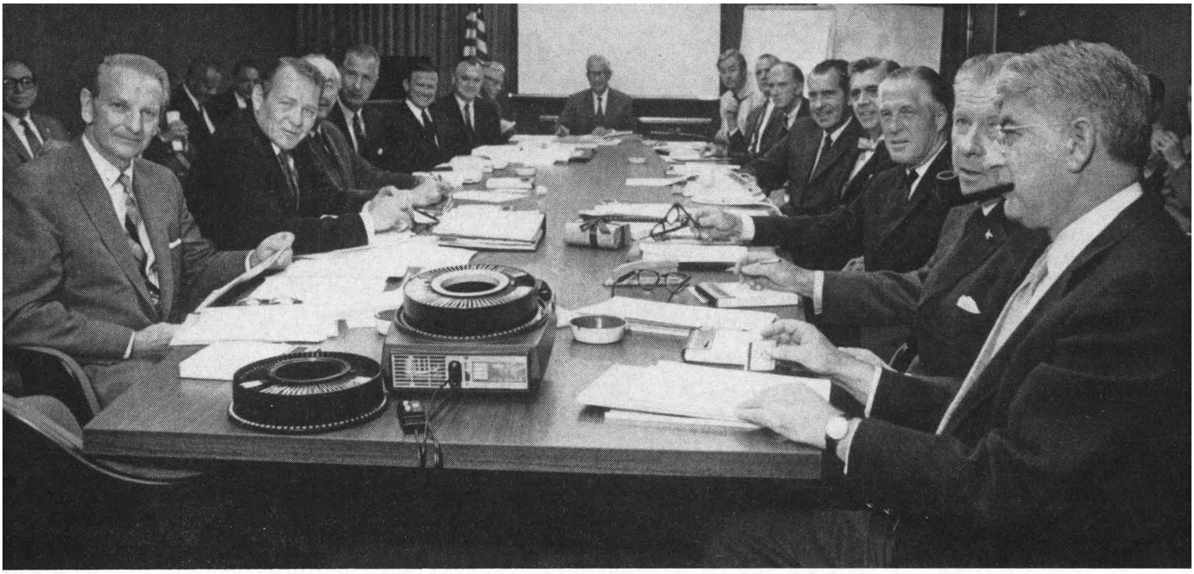
Within EQC, seven committees have been established with chairmanships and memberships spread over the six departments. Each cabinet member chairs one or more of the committees. Agriculture Secretary Clifford M. Hardin chairs the newly-formed pesticides committee. Transportation Secretary John A. Volpe and Interior Secretary Walter J. Hickel each head two committees. The automotive air pollution committee and the handling and transportation of toxic and hazardous materials committee are headed by Volpe, while Hickel chairs the outdoor recreation committee and a water pollution committee. HEW Secretary Robert H. Finch chairs an air pollution committee; George Romney, Secretary of HUD, chairs one for solid wastes; Secretary of Commerce Maurice H. Stans' noise committee rounds out the existing seven. There is now a specific committee assigned to pesticide problems (previously, the activities on pesticides that occurred in Agriculture, HEW, and Interior apparently were to be pulled together by DuBridge's staff). "If necessary, further studies would be sponsored by OST," Buckley explains.

"Many EQC activities are not as formal as its three earlier meetings,"



John L. Buckley

". . . Environmental Quality Council is using the talents of the federal government to focus on environmental problems. . . . Very often, the inputs on any one environmental problem are broad due to the background of the various council members. This leads to a further understanding of a particular problem and, often, departs from any parochial view of any one department or agency."



Environmental Quality Council

Membership and committees

Committees	Agriculture Clifford M. Hardin	Commerce Maurice H. Stans	HEW Robert H. Finch	HUD George Romney	Interior Walter J. Hickel	Transportation John A. Volpe	Other federal participants
Automotive air pollution							
Solid waste							
Handling and transportation of toxic and hazardous materials							Defense AEC State
Outdoor recreation							
Noise							Labor
Water pollution							BOB CEA
Air pollution							

Denotes membership Denotes chairmanship

Buckley notes. "Many things are going on even though some of the committees have not yet met formally. In fact, much of the committee activity is being performed by staff personnel within the departments . . . . EQC is more than a mere discussion forum," Buckley continues. "Very often, the inputs on any one environmental problem are broad due to the background of the various council members. This leads to a further understanding of a particular problem and, often, departs from any parochial view of any one department or agency. Ultimately, a decision at the highest level for best national interest will be reached."

For example, based on his earlier experience as director of a major U.S. manufacturer of automobiles, HUD's Romney can make considerable impact on the automotive air pollution committee. "In this way, EQC is using the talents of the federal government to focus on environmental problems," the OST spokesman says. "There is a whole range of environmental matters in which the federal government can play a major role." EQC consideration will be given to how the council can help make the day-to-day activities and procedures of the federal government more responsive to the needs of the environment.

"The federal government exercises fairly strong leverage simply by being a major purchaser of materials," Buckley explains. Federal muscle could be used in purchase specifications which would then provide incentive to the public and private sectors to improve environmental quality. For example, the purchase of low pollution automobiles by the federal government would tend to set a precedent for the rest of the nation to follow. The requirement of degradable packaging materials in specifications would be another way that the federal government could bring environmental quality considerations to bear on the activities of the public and private sectors. But the direction that this country ultimately will take rests on the President's decision on the environment, Buckley believes.

Committee insights

Automotive air pollution occupied a large part of the business at EQC's second meeting (San Clemente, Calif.). Here, Transportation Secretary Volpe urged that EQC undertake some kind of a program to speed progress in this area, but the program details are not yet public. A prime goal is rapid improvement of the environmental situation with respect to the automobile.

Held prior to the hearings on extension of the Solid Waste Disposal Act of 1965, Secretary Romney's recent committee meeting focused attention on the posture of the federal government with regard to solid waste. Committee consensus was amply emphasized by administration officials as they testified before Senator Muskie's air and water pollution subcommittee (ES&T, November 1969, page 1160).

"Interior's Bureau of Outdoor Recreation has statutory authority for coordination of outdoor recreation across the U.S. as a whole," Buckley explains. There are many state and local agencies having public lands that are managed by the federal government. So, this committee's first concern will be the question of consistency of policies with regard to public use. For example, the U.S. Army Corps of Engineers has a large number of visitors each year to its reservoirs, and the public's use of these waters for recreational purposes needs to be considered, along with use of other public areas such as National Parks and Forests.

Agency comments

James D. Braman, Transportation's assistant secretary for urban systems and the environment, points out that the various EQC committee chairmen ultimately will be reporting their findings and suggesting policies to the council. (In fact, several chairmen presented reports at its third meeting held last month.) These reports will indicate some steps that the chairmen hope to follow to bring environmental problems under control.

Braman, formerly mayor of Seattle, was a wise choice for the newly established post of urban systems and environment. He brings considerable experience and knowledge of urban systems to his new assignment. As mayor, he participated extensively in the activities of the National League of Cities and the U.S. Conference of Mayors, and served as head of each group's transportation committee.

The assistant secretary noted that Transportation's involvement is confined at this time to the impact of transportation on the total environment. The Department of Transportation has nothing to do with the broad field of poisons in the air, soil, water, etc. "These are important concerns of other federal agencies," Braman says. "But the department is concerned with the kinds of programs that will be more productive of progress in the field of automotive air pollution in the near future."

Progress on automotive air pollution, the largest item on the San Clemente meeting schedule, might have bogged down over jurisdictional disputes were it not for EQC. The cleanup program for the present gasoline engine might well be the responsibility of HEW, according to Braman. HEW has developed an organization that is familiar with the problem, knows what progress has been made and the goals for the next few years. "So, Transportation concerns itself with future transportation systems with accompanying low level of pollutants," Braman notes. "This is our goal."

Within Agriculture, Secretary Hardin's memorandum #1664, dated Oct. 3, established an environmental quality executive committee. The primary purpose of this standing committee will be to coordinate the department's interests and responsibilities in the nation's effort to assure a quality environment for all people. Theodore C. Byerly, chairman of the committee, points out that pollution is only one aspect of Agriculture's involvement with environmental quality programs and EQC. "Pollution programs are not synonymous with environmental quality programs . . . . Actually, they are only a minor part."

Discussing pollution, Byerly noted that sediment is the main pollutant, tonnage wise; animal wastes come next based on volume considerations; and forestry and crop residues are the next main pollution concerns. Moving to Agriculture's environmental quality interests—which Byerly admits are a bit harder to pin down—he notes that the number one priority perhaps is a national pattern of land use. Here, main concern must be devoted to the use of land for its highest productive capacity. Byerly observes that statistics reveal that 50 million acres less croplands are cultivated now than 50 years ago. In addition, there are 80 million acres less for livestock grazing than 50 years ago.

So, multiple use land concepts also must be applied in the agricultural field. Agriculture's Forest Service, for example, might assess the economic tradeoffs for the development of land used for food and fiber, water, wildlife, and recreation.

Commerce's role

James R. Hibbs, adviser on environmental quality in Commerce, says that the department's interest in noise is not limited to aircraft noise, but includes industrial, traffic, and residential noises. Hibbs noted that Secretary Maurice H. Stans chairs a committee on noise. A draft policy is being formulated, and will be considered by the council at a later time.

Another area in which Commerce is involved is solid waste, Hibbs continues. The department has prepared reports on:

- Steel industry scrap problems.
- Auto abandonment.
- Auto wrecking industry.

Similar to the inner organizational activity within Agriculture, Commerce's staff participates in committee staff work and develops background information to meet continuing department policy responsibilities in the environmental area.

What federal direction will grow out of EQC activities only time can tell. Probably, only after the committees report back to the council, and after President Nixon announces his order of priorities will the public become aware of the continuing federal attention to environmental matters.

In any event, the comments on environment in Nixon's first State of the Union message next month and the attention for environmental funds in the budget request of the U.S. Government for fiscal year 1971 certainly will be followed by the growing number of environment watchers.

Man and nature at odds in the delta

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One who knows the Mississippi will promptly aver—not aloud but to himself—that ten thousand River Commissions, with the minds of the world at their back, cannot tame that lawless stream, cannot curb it or confine it, cannot say to it, 'Go here,' or 'Go there,' and make it obey; cannot save a shore which it has sentenced; cannot bar its path with an obstruction which it will not tear down, dance over and laugh at . . . . But a discreet man will not put these things into spoken words; for the West Point engineers have not their superiors anywhere; they know all that can be known of their abstruse science; and so, since they conceive that they can fetter and handcuff that river and boss him, it is but wisdom for the unscientific man to keep still, lie low, and wait till they do it."

Mark Twain
"Life on the Mississippi"

And do it, they have. The accomplishments of the Corps of Engineers have been remarkable and far reaching. The question arises, however: Have the consequences ranged beyond their expectations?

In any region, man's environment is a complex and interrelated system. Modifications to any element of the system, whether beneficial or harmful, can cause changes to other elements which may have similar or dissimilar effects. Today, the emphasis is on harmful environmental changes. However, man has been engineering and introducing changes to improve his environment for many centuries. Modern technology has, of course, accelerated this process. Man has never, except in the course of warfare, deliberately set out to degrade his environment; however, it is a fact that the harmful changes caused by man generally have resulted from his introduction of major improvements.

The use of the automobile—which has been greatly accelerated by development of today's highway system —has resulted in a major source of air pollution. Intensive use of groundwater has, in many instances, resulted in degradation of the aquifers by saltwater encroachment. Insecticides and fertilizers have polluted surface waters; and so on. Weather modification, which promises much help to arid regions as well as those often beset by hurricanes, also carries the threat of undesired side effects—even disasters.

It has become increasingly apparent that the physical and biological framework of our environment is an intricately interwoven system. The input from man—either intentional or otherwise—has an effect which ultimately is controlled by the system itself.

These complexities vary considerably in detail from region to region. Mark Twain's alluvial valley and delta provide an excellent example of the strong effect of regional complexities. The Mississippi's assets include its navigable channel and the rich natural levee deposits that bound it, while its tendency to flood and to migrate by meandering are deficits. The U.S. Army Corps of Engineers has endeavored to enhance navigability and to protect the natural levees by controlling floods and stabilizing banks. In so doing, however, they have eliminated the river's ability to construct new natural levees through deposition at the time of overflow. Meanwhile, inability to completely stabilize banks has resulted in the loss of previously existing natural levees. Other complex aspects of the lower Mississippi alluvial valley and its delta include population distribution, agricultural pattern, and natural resource and industrial development.

The alluvial valley of the Mississippi River and its delta constitute approximately half of southeast Louisiana. A distinctive pattern of land use exists, with the natural levees of the present and ancient channels originally providing the only land suitable for rural and urban habitation and development. Generally, this still is true today. The remainder of this area consists of swamps, marshes, and myriad interconnected streams. With the exception of the Mississippi and Atchafalaya Rivers, the streams are very sluggish and drainage is poor. The Mississippi River, in particular, dominantly influences the region. It drains nearly half of the continental U.S. and, together with its major distributary, the Atchafalaya River, now carries approximately 1,700,000 tons of sediment daily to the Gulf of Mexico.

The Mississippi also provides fresh water and navigable facilities to scores of industries and cities which line its banks. An expensive system of levees and floodways has been constructed to protect the land use of its alluvial valley. The lower alluvial valley is confined by terraced uplands which progressively decrease in elevation southward. In an area 25 miles southeast of Baton Rouge on the east side, and in the vicinity of New Iberia on the west side, this older surface slopes beneath the present fan shaped deltaic plain.

The climate of the region is distinctive. Large masses of moisture-laden air, blown inland from the Gulf of Mexico, have blessed the area with abundant rainfall. A high runoff from the streams and at least partial recharge of groundwater aquifers is thus assured. Furthermore, because of the wind pattern, the development of atmospheric inversions conducive to extreme air pollution conditions is uncommon. While these are plus factors, the same set of climatic conditions is responsible for occasional hurricanes. The devastation caused from these frightful storms is accentuated by the low relief of the coastal areas.

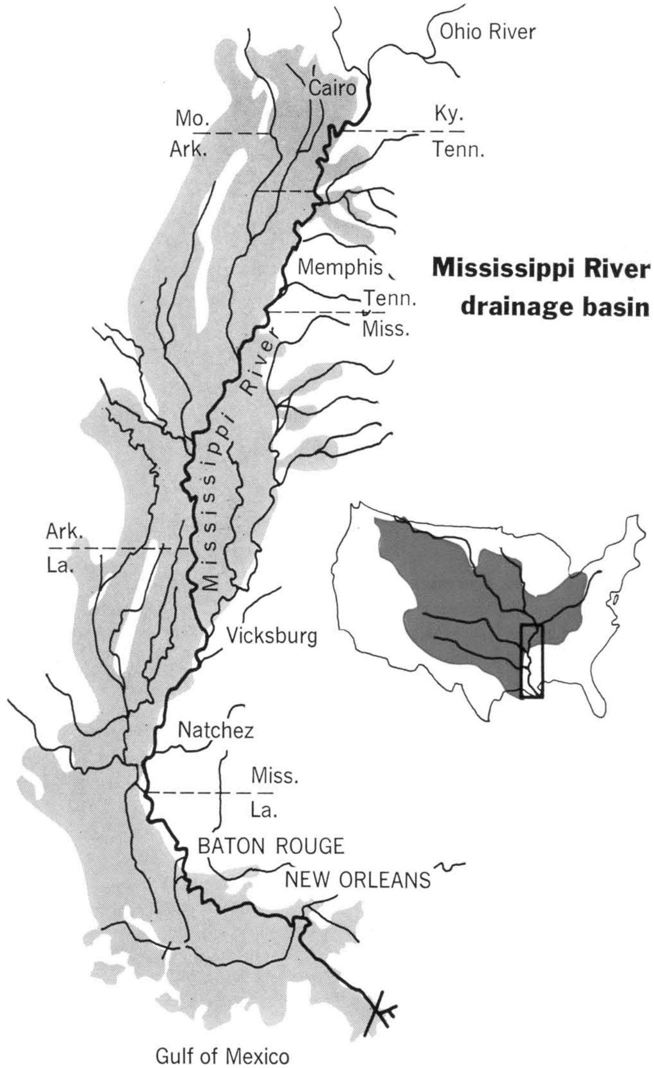
Industrial development

Vast underground mineral resources constitute a major regional factor in the pattern of environmental development. In 1967, petroleum production in Louisiana amounted to more than $3.5 billion; sulfur, more than $140 million; and salt, nearly $50 million. A major part of this mineral wealth was produced from the southeast part of the state. In Twain's day, the agricultural potential was well developed (and is tremendously more so today), but the enormous possibilities of the mineral resources were undreamed of; the gold that Cortez and the conquistadors sought was, figuratively, buried in the Gulf Coast. The presence of these natural resources has been a major factor in attracting a great chemical complex to the area.

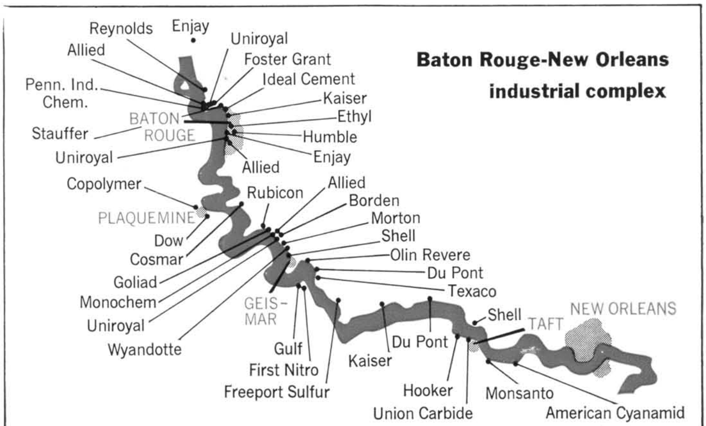
A major part of this industrial growth has occurred along the banks of the Mississippi. The river serves as both a superb waterway and a source of the large quantities of water required by the modern chemical industry. The stretch of the river from Baton Rouge to New Orleans has been compared to the Ruhr valley in Germany. Certainly, the character of the region has been rapidly and markedly changed; however, the blessings of this development have not been obtained without a price. The usual air, water, and thermal pollution and noise associated with large chemical plants now threaten the tranquility and health of the populace.

Somewhat less appreciated is the disappearance of the unique culture that once graced the banks of the Mississippi and was described so eloquently by Mark Twain.

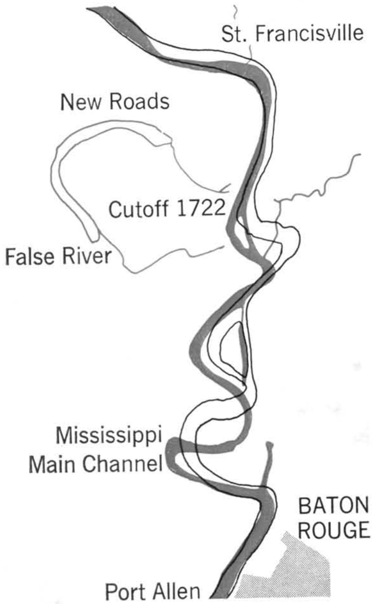
The Mississippi River, its alluvial valley, its delta, and the associated natural and artificial processes, must be understood for proper environmental planning in southeast Louisiana. This is especially true with regard to major changes in the surficial environment. However, these physical characteristics also are a very important set of basic parameters to consider in planning concerned with air, water, thermal, and noise pollution.



Mississippi River drainage basin



Baton Rouge-New Orleans industrial complex



Meander. *False River (above) was formed by natural short circuit in main channel of the Mississippi River*

Alluvial and deltaic processes

The especially unique environmental aspects of the Mississippi's alluvial valley and delta—more than 30,000 square miles of it—are its relative youth, the changeable nature of its surficial features, and its susceptibility to large-scale alteration by man. Generally, other types of physiographic regions can be modified only to a more limited degree. Major control of geologic processes elsewhere usually consists of changes to the groundwater regime.

Since the close of the last continental glaciation more than 15,000 years ago—which was followed by a rise in sea level of several hundred feet—the Mississippi has meandered back and forth across the valley, filling it with deposits of sand, silt, and clay. During this period of time, a series of deltas has been built and abandoned on the continental shelf, culminating in the modern bird's foot delta.

A complicating factor is the regional subsidence of the deltaic plain, particularly along the coastal margin. In the area where sedimentation is concentrated locally, the effect of subsidence is counteracted and the delta is extended gulfward, thus lengthening the channel and eventually resulting in abandonment of the channel for a new and shorter course. The abandoned sub-delta eventually sinks beneath gulf level and is destroyed by coastal waves and currents.

H. N. Fisk traced the development of these ancient channels and deltas. The two remarkable things about this changing pattern of the river are its relatively rapid tempo of movement and the apparent delicate balance of its temporary positions of equilibrium. Of the early channels of the lower Mississippi, Old River now is a large oxbow lake created by the Raccourci cutoff of 1848, and False River was formed in 1722 by abandonment of a former meander loop. The farthest downstream point where rapid changes occurred is in the Solitude Point-Thomas Point area just northwest of Baton Rouge. A little farther north, the town of Port Hudson (a Civil War battle site) has been abandoned because the river meandered away from it. Channel changes between Baton Rouge and the Gulf during historic time have been relatively minor because this part of the channel is cut into silt and clay rather than sand.

Artificial changes

The works of man have had some effect on these channel and deltaic changes. This effect has become increasingly important with time. Considered broadly, these man-made changes have been effected in two ways:

• **As a result of deliberate attempts to control the river.** For example, the Bonnet Carre Spillway was built just west of New Orleans to divert flood waters at critical times from the channel to Lake Pontchartrain. This spillway, used only three times (1937, 1945, and 1950) has not resulted in any permanent major changes other than some filling of the spillway itself. There is a contrasting pattern of land use on either side of the spillway—the old, typical agricultural development of the natural levee, and, opposite, a modern petrochemical plant. The West Atchafalaya, Morganza, and Atchafalaya Basin Floodways have had profound environmental effects. The streams, lakes, swamps, and wildlife within and without this system have been drastically altered in order to provide a second major outlet of floodwaters to the sea. Related to this vast project has been the design of control structures to regulate the flow of the Atchafalaya River—the most important and northernmost distributary of the Mississippi River. An increase in the flow of the Atchafalaya River, observed as early as 1880, continued at a rapid rate during the 1930's and 1940's. The possibility of modern abandonment of the Mississippi's channel from the head of the Atchafalaya River to the Gulf in favor of the shorter route by way of the Atchafalaya alarmed the Corps of Engineers, prompting the corps to commission a study by Fisk, Kolb, and Wilbert to investigate the likelihood of this occurrence. As a result of this study, it was decided to build a control-gate structure at the origin of the Atchafalaya to limit its flow and prevent diversion of the Mississippi. This represented a major environmental control by man.

This great river, one of the largest in the world, has—for the moment—been tamed. Its channel has been shortened, part of its flow is diverted by floodways, and it is contained by levees for much of its length and throughout the region under discussion. It remains to be seen whether such control can be maintained effectively.

• **Large-scale developments in the alluvial valley and the delta that have resulted in unplanned changes.** In this category, the exploitation of petroleum resources can be considered a major influence. In order to reach critical areas in the swamps of the valley and marshes of the coast and delta, many miles of canals were constructed to tie in with the complex interconnected system of bayous and rivers. These canals have altered water distribution and wildlife patterns. And the very fact that they have made an extremely remote area readily accessible also has affected wildlife distribution.

The most striking changes have occurred in the delta. Comparisons of aerial photographs taken in 1950 and 1968 show that a large section of marshland in the delta has become open water. The effect of this major physiographic and environmental change on wildlife is, as yet, unknown.

A few examples have been given of large-scale man-made changes in the regional environment that have had unexpected and unintended results. An assessment of their ultimate worth is difficult to make and any conclusions will have to be based on highly subjective considerations.

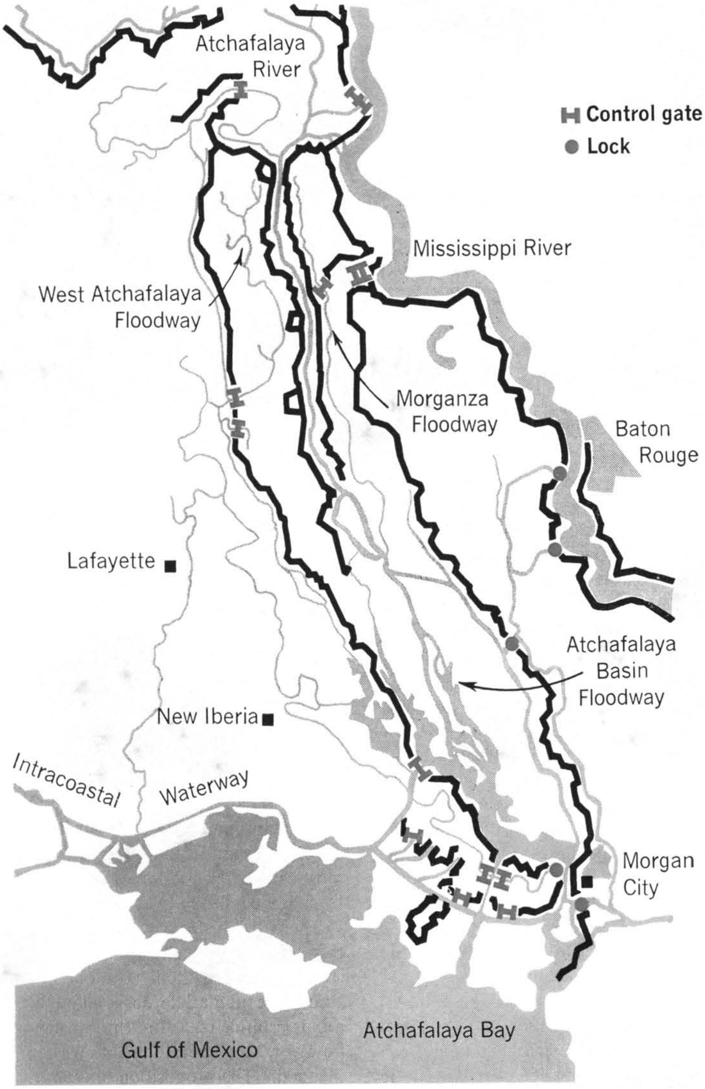
Future possibilities

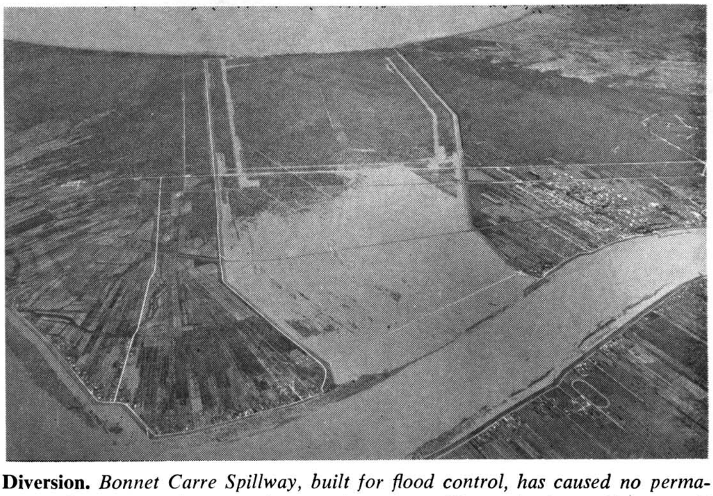
Many opportunities for further environmental changes still exist. The ease of major physical changes in the environment, with attendant biological alterations, results from the relatively high rate of the geological processes in operation here. The natural processes operable in this alluvial and coastal environment proceed at a much higher rate than do most other geologic processes.

Three examples of such engineered changes include one dealing with the modern channel of the Mississippi, another with the delta, and the third with Lake Pontchartrain.

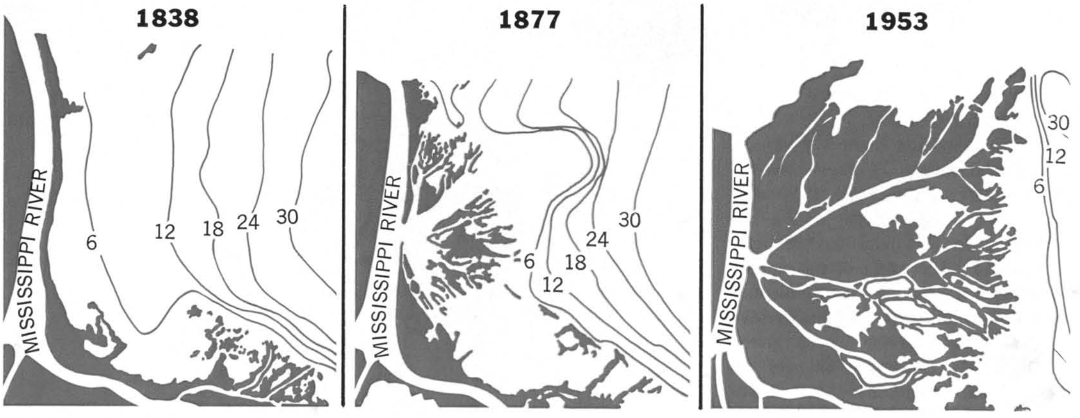
One of the prime large recreational bodies of water nearest Baton Rouge is False River, an abandoned channel of the Mississippi. However, it is about 20 miles from the city, which is undergoing rapid growth as an urban and industrial center. Fortunately, the natural pattern of the Mississippi River and the plans for its control by the Corps of Engineers present the opportunity for creating a lake similar to False River within five miles of Baton Rouge.

A large constricted meander loop occurs in the Mississippi River between Baton Rouge and Plaquemine, just northeast of Plaquemine. The point of land enclosed by this loop is known as Manchac or Australia Point. The Corps of Engineers has built a levee across this point so that a cutoff could be made across the point in times of exceptional flooding. This option has never been implemented, but it remains an active possibility. It is suggested that a new





Diversion. *Bonnet Carre Spillway, built for flood control, has caused no permanent changes in drainage basin other than filling of the spillway itself*



Marsh growth. *Ditch cut across dike in 1862 inadvertently caused slow formation of sub-delta (water depth in feet)*

channel (for the river) be constructed across the neck of the point. The construction of two dams across the present channel then could create a large lake similar to False River. One of these dams would be located across the north arm of the meander downstream from the beginning of the new cutoff, the other at the bendway just north of Manchac Landing, where a proposed waterway would connect the Mississippi to Lake Pontchartrain and points east.

The portion of the old channel thus closed off would serve as a large, deep recreational lake of great beauty. The dam at Manchac Landing would ensure that the southern arm of the bend would remain open to serve as a deep water port to industries that may build along its banks.

A more ambitious proposal envisions the transformation of Lake Pontchartrain from a brackish to a fresh water lake. This change would be effected by constructing a dam and lock system in the Rigolets, which connects Lake Pontchartrain with Lake Borgne and, through it, with the Gulf of Mexico. After the brackish water is flushed out, the new, fresh water character of Lake Pontchartrain would be maintained principally by the Tangipahoa, Tchefuncte, and Amite Rivers which flow into Lake Maurepas which outlets into Lake Pontchartrain through Pass Manchac. If the flow of these three rivers proves insufficient to reduce and maintain the salinity of the lake at an acceptably low level, it might prove feasible to divert the flow of Pearl River into the lake. (This proposal probably will meet with serious objections from the fishermen who operate in the lake.) Careful consideration will have to be given to the advantages and disadvantages which would follow from this development.

A third proposal—the formation of a new sub-delta for the Mississippi River—would involve significant physical and ecological changes for the region. It has already been pointed out that major changes have occurred in the present delta with attendant loss of marshland because of man's activities. The forced development of a new sub-delta would replace all or part of the marshland that has been invaded by marine waters. However, adverse effects would occur, with almost certain destruction of oyster beds by subsequent salinity changes.

There is historical precedent for this action by man. In 1862, construction of a ditch (Cubitts Gap) across the natural levee resulted in a minor sub-delta. In this instance, however, the development was unplanned. The proposition offered here is novel, since the idea advanced is to deliberately form a man-made delta. Similar suggestions probably have been made in the past but have not been formally presented in the literature.

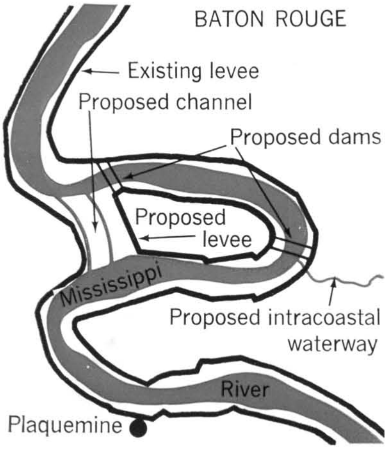
All of the three proposals described represent major alterations in the geomorphology of the region, with consequent effects on the biological community—including man. This is particularly true for the last two ideas. Serious consideration of all consequences would have to be given before any implementation of these ideas could be undertaken. In fact, we want to stress the interactions which follow single purpose acts designed to change conditions in this kind of region and to emphasize the need for early study and thought of unfavorable feedback.

Conclusions

A general principle to consider in modifying, regulating, or controlling large-scale geologic features or processes is to use the natural forces, so far as possible, to create a desired effect. For example: It is a natural tendency for a river like the Mississippi to meander. Attempts to rigidly maintain the position of its channel by the use of such controls as levees and revetments pit the engineer against the natural forces of the river. Cutoffs, spillways, newly constructed distributaries, and other similar works are compatible with natural morphological changes, however, and use the natural forces to advantage. It is not intended to imply that levees and revetments should not be used as control structures, but it is suggested that their basic artificial nature should be recognized in planning their use.

The complexities of the interaction between the total environmental system (land, water, and air) are well known. We call attention to the unique nature of these relationships for a specific kind of regional environment represented by a low lying coastal area. Southeast Louisiana does have special sets of conditions. However, many parallels can be drawn with other coastal environments.

The significant point is the need for special consideration of regional factors in environmental planning and management. These regional factors go far beyond the set of physical parameters which have been discussed here. They also include such things as sociological and political characteristics and influences. These conclusions suggest the advisability of nationwide training of environmental planners,



Recreation. *Proposed Manchac cutoff would create a large artificial lake*

Delta. *Aerial photographs taken in 1950 (top) and 1968 (bottom) show that large areas of marshland have become open water. Long-term effects are unknown*

engineers, and scientists. Certainly, such programs should not be provincial. However, there will be a real need for environmentalists with a special knowledge of the regions in which they will work.

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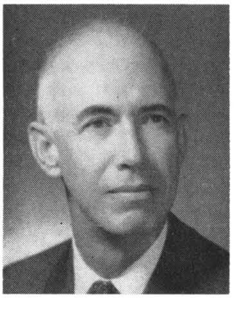

Clarence O. Durham, Jr., *is director, School of Geology, and professor of geology, Louisiana State University. Previously, he was chairman of the geology department, and director of research for the Louisiana Geology Survey. He received his B.S. from the University of Texas (1942) and his Ph.D. from Columbia University (1957). Durham has served as consultant to oil and mineral companies, and directed a study of the geological aspects of the Baton Rouge groundwater survey. He is a member of the American Association of Petroleum Geologists, American Geophysical Union, AAAS, Sigma Gamma Epsilon, and Sigma Xi.*

Designing for air conservation

Applying sound criteria to potential emission sources should be first step in design and development

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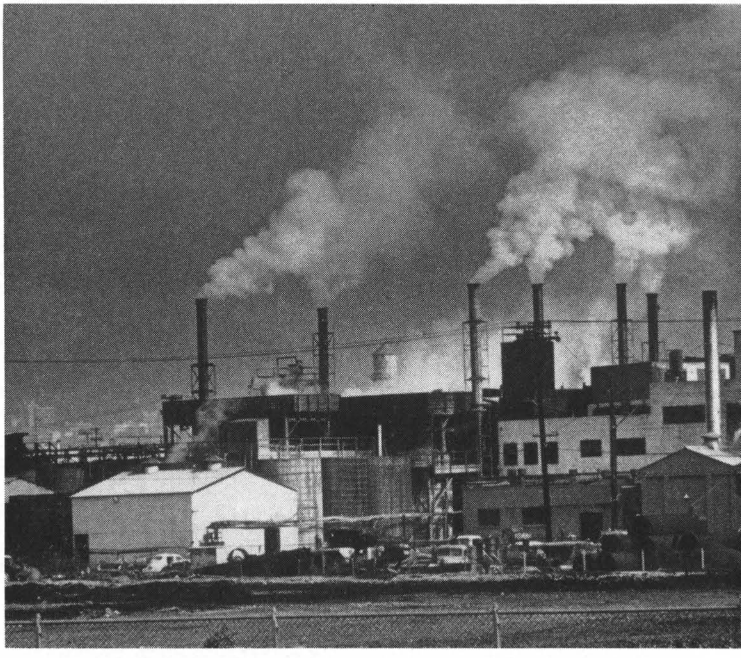

Conservation of air is a matter of major and growing concern. As the Air Conservation Commission of the American Association for the Advancement of Science recently stated, "The commission has been impressed by the need not only to control pollution, but also to develop programs to conserve the air." The application of a basic concept of industrial air conservation programs to process design and product development, we feel, requires additional emphasis in the overall air pollution control problem.

The concept of air conservation can be related directly to the dictionary definition of conservation: "deliberate, planned or thoughtful preserving; . . . preservation." In other words, air conservation is the preservation of air as a natural resource. As applied to industrial activity, it means the prevention of emission of undesirable materials to the air by thoughtful planning at the process design and product development stages, and should be the first step in any air pollution control program.

Foresight

Air conservation should be distinguished from other basic methods for correcting air pollution problems, such as removing the pollutant material from an effluent just prior to the final exhaust stage. This normally is accomplished by the addition of control equipment at the point of exhaust; the equipment often is added after a production facility has been designed and put in operation. In most cases, air pollution control is actually an afterthought, without proper consideration given to this problem prior to plant construction.

Another control technique—atmospheric assimilation—has been utilized to dilute pollutants after they are emitted. However, the environment—especially on a local or regional basis—has a limited assimilation capacity, and these limits must be understood at the early stages in the design and development of source operations.

A successful industrial air conservation program begins with increased communications between research and development personnel, pilot plant operators, and engineers within a company. By creating an awareness of the problem, new criteria can be applied to process design and product development. Awareness of the potential air pollution problem is initiated by asking some basic questions: Will the process or product have an effluent? Will it create an effluent in its operation, use, or disposal? Does the effluent have potential air pollution capability?

Process design

Air conservation can be applied to process design in each of four different phases of a manufacturing operation—raw materials, process reactions, process equipment, and operating procedures.

• **Raw material substitution.** It is possible that a nonessential ingredient in the raw material may cause an air pollution potential. In this case, removal of the nonessential ingredient before the raw material is introduced into the process should be explored. If the raw material itself presents the air pollution potential, use of an alternate material should be studied.

An example of the removal of an unwanted raw material ingredient to prevent air contamination is the substitution of low sulfur fuel oil and coal in boiler operations to reduce sulfur dioxide emissions. Regulations requiring use of low sulfur fuels are in effect in most of the areas on the East Coast, and fuel desulfurization methods are being developed by the coal and petroleum industries. The selection of raw materials—in this case, the boiler fuel—represents an application of air conservation to new boilers as well as boilers in existing plants.

Another example of substitution of an alternate raw material to prevent air pollution is the use of nonreactive solvents in process operations in areas where photochemical smog is a problem and solvents are evaporated to the atmosphere. Regulations requiring this substitution are in effect in several regions of the West Coast. In this case, the solvent itself may be reformulated. Promulgation of hydrocarbon solvent regulations to control photochemical smog has created a new demand for aqueous solvent systems for many process operations.

• **Process modification.** Modification of a process to correct a potential air pollution problem requires examination of the reactions and unit operations involved. Some unit operations may be added to conform with the objectives of air conservation. These ideas can be applied to a wide range of process sizes and types.

The use of thermonuclear energy to replace fossil fuel in electrical power generation is process modification on a large scale. The unit operation, in this case, is changed from fuel combustion to nuclear fission, and one criterion for making this change is a reduction in air pollution potential.

Another process modification for correcting an air pollution potential is utilization of electric battery or fuel cell power to replace the internal combustion engine for motor vehicles, or the use of the cleaner burning turbine engine to replace the piston engine. Here again, one of the incentives for making this change in unit operation is the air pollution problem created by the internal combustion engine now used in automobiles.

The addition of a unit operation to a process can present an opportunity for byproduct recovery. For example, in the petroleum industry, waste hydrogen sulfide gases that used to be burned in flares now are reacted by the Claus process to yield elemental sulfur. This process modification produces one and a quarter million tons of sulfur per year in the refinery industry in addition to preventing an air pollution problem.

Byproducts need not always be recovered; they can be used in other ways. For instance, in hydrocarbon solvent drying operations, the solvent in the exhaust gases can be either collected for reuse, or used as a source of heat for the drying process. The addition of a catalytic or direct flame combustion unit and a heat exchanger to the process can make this heat available. The use of such closed loop processes that recycle either waste solvents or heat from the solvents is gaining increased attention as a process technique.

• **Equipment alteration.** Another approach to air conservation takes the form of either alteration of the basic equipment or replacement of one type of equipment with another. This obvious approach to correcting the air pollution potential of a process often may be overlooked because of time honored methods of equipment purchase and use.

Equipment alteration ranges from the use of floating roof storage tanks in place of vapor vented tanks in refineries and solvent plants to the use of reverberatory furnaces in place of cupolas in iron foundries. More well-known examples are alterations to the internal combustion engine to reduce automotive emissions. The positive crankcase breather valve system now used to return crankcase vapors to the carburetor is one result of applying air conservation criteria; others include such engine changes as carburetor leaning, spark retardation, and so on.

In industrial applications, whether to make equipment alterations often can be decided by evaluating the arrangement and the ventilation requirements for process operations. This may reveal that some operations are over ventilated and create increased evaporation or entrainment of material. The replacement of open vat cooking kettles or open air operations under a hood with a closed reactor may significantly reduce air pollution. In some cases, the hood over an open vat cooking operation can be redesigned to reduce the overall exhaust volume and reduce the size and cost of any control equipment required.

• **Procedural changes.** Changing operating procedures, although not as well documented as other approaches to air conservation, is, nevertheless, a basic method that often can be applied where atmospheric assimilation is relied upon to disperse contaminants.

This can be illustrated by the Tennessee Valley Authority power plant at which sulfur dioxide emissions are reduced during adverse meteorological conditions by changing to a low sulfur fuel. It is also common practice in boiler operations to employ special procedures for starting, cleaning, and stoking fires.

An example of procedural changes for air conservation that occurred at 3M Co. recently involved addition of reactants to ventilated batch operations. Some reactants with strong odors were being evaporated in large amounts when the operators made manual additions to the batch process. These peak concentrations in the exhaust caused odors downwind from the plant. Instead of adding a wet scrubber or other air pollution control equipment to control the exhaust, the operating procedures were changed to feed reactants at a controlled rate to the process; evaporation of material was reduced to a minimum. This not only corrected the odor problem, but allowed a reduction in the total amount of reactant required for the process.

Procedural changes are most useful where manual operations can be replaced by automatic control. The continuous development of operating procedures and good housekeeping practices that are consistent with air conservation principles is an important part of maintaining an effective industrial air pollution control program.

Many other examples of application of these four approaches to air conservation in process operations can be cited. In some cases, a combination of approaches can be used; however, this is most useful at an early stage of process design.

Product development

For purposes of applying air conservation to product development, it is possible to consider a product at three stages: Manufacture, use, and disposal. The manufacturing process has already been discussed; here we shall consider criteria involving a product's use and its ultimate disposal.

• **Product use.** Safety and hygiene have long been considerations for product use; now it is becoming necessary to add one more consideration, air conservation, to both consumer products and intermediate products for industrial use.

The photochemical solvent regulations represent one example of applying product use considerations. Some of the regulations impose on the seller restrictions or responsibilities for product composition For example, the sale or use of hydrocarbon solvent containing material of photochemically reactive composition in one quart containers or larger is prohibited. In addition, the use of a photochemically reactive solvent for architectural coatings is restricted to emissions of one gallon per day. These restrictions point up the necessity of considering air conservation criteria where product use will be a factor in air pollution.

An example of an intermediate product that is subjected to similar requirements is fuel oil. As previously mentioned, the sulfur content of fuel oils is subject to restrictions in some areas on the East Coast, and the refinery producing this product must apply air conservation criteria to the product as well as to the refinery process.

On a larger scale, the automobile is a product that is now subject to air conservation needs in its future development. This sequence of events, where the requirements which were once regional and are now nationwide, has set the pattern for other products now faced with regional restrictions. The two factors accelerating this trend are the interstate nature of most markets and the economy of producing a uniform product throughout all areas of the country.

• **Product disposal.** In general, not all ingredients of a product are completely consumed in its use. The residual material must be disposed of. Due to the tightening of air, water, and land pollution regulations at various government levels, air conservation considerations should be applied to the product residue itself, including those times contaminated by the product, such as containers. This is becoming increasingly important to a society which stresses disposable consumer products and no deposit-no return containers. Landfill has been a common practice for final disposal, but is not satisfactory when the residual products are nondegradable or may contaminate the soil or groundwater.

Disposal of product residues by incineration is likely to be the future trend, and will require evaluation of both the degree of combustion that can be achieved and the products of combustion. This is particularly important in combustion of halogenated byproducts and hydrocarbon materials which produce combustion products such as phosgene and oils.

Applying these conservation considerations during process design and product development not only can aid in correcting an air pollution potential but also can determine true profitability and marketability. It is important that this be done at the research and development and pilot plant levels—before any new process or product reaches its final stage.

The air conservation program in any business organization should start with strong management support and be implemented through intracompany coordination and information exchange. In large industries, this can be done through a central staff with defined responsibilities for pollution control and awareness. One of the most useful methods for creating the required awareness is the use of seminars for key personnel in design and development. Efficient distribution of pertinent literature and updating of regulatory requirements also are helpful.

This is especially important in a multiproduct company. The 3M Co., for instance, markets more than 40 major product lines and has 100 manufacturing plants in the U.S. and abroad. The importance of applying air conservation at the design and development levels is borne out by the fact that 25% of the products presently marketed by 3M were developed in the last five years.

The concept of air conservation represents prevention of pollution before the fact by close scrutiny at the process design and product development stages. In the long run, this could result in a considerable saving in the total cost of an industrial air pollution control program. Air conservation or air pollution prevention will receive increasing emphasis in industrial pollution control programs.

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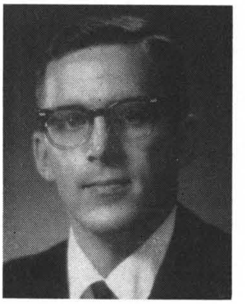

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Pesticides in Drinking Water

Waters from the Mississippi and Missouri Rivers

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■ Over 500 grab samples of finished drinking water and related raw water were assayed for 10 organochlorine pesticides, their metabolites, and related compounds. The samples were collected between March 1964 and June 1967 from 10 selected municipal finished water supplies whose source was either the Mississippi or the Missouri River. Both 100-ml. and 1-gallon sample sizes were assayed. Included is a statistical evaluation of the one-step extraction method using 1-gallon samples to which known amounts of the 14 compounds were added at levels ranging from 0.06 to 5.0 p.p.b. Over 40% of the finished water samples contained detectable dieldrin and more than 30% contained detectable endrin, *p,p'*-DDT, and *p,p'*-DDE. Twenty per cent of the 63 samples assayed for chlordan contained detectable concentrations; five of these were in excess of 0.25 p.p.b. Aldrin, HCE, and heptachlor were found only occasionally. No toxaphene nor methoxychlor was detected.

In the early 1940's, a synthetic organic compound was used for the first time for pesticidal control. The effectiveness of this organic compound, commonly called DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane], stimulated the synthesis of many organic compounds with varying degrees of pesticidal, herbicidal, and fungicidal activity. Today a large number of these synthetic compounds are being used routinely as pesticides in agricultural programs. One type, the organochlorine compounds, including dieldrin (1,2,3,4,10,10-hexachloro - 6,7 - epoxy - 1,4,4*a*,5,6,7,8,8*a* - octahydro - 1,4-*endo,exo*-5,8-dimethanonaphthalene), endrin (1,2,3,4,10,10-hexachloro - 6,7 - epoxy - 1,4,4*a*,5,6,7,8,8*a* - octahydro - 1,4-*endo,endo*-5,8-dimethanonaphthalene), and aldrin (1,2,3,4,-10,10 - hexachloro - 1,4,4*a*,5,8,8*a* - hexahydro - 1,4 - *endo,exo*-5,8-dimethanonaphthalene), is not readily degraded under normal conditions. Although extremely small concentrations of these compounds are required for pesticidal control, the effect on public health of their gradual increase in our environment is under close scrutiny.

Realizing that river water was becoming contaminated with these organochlorine compounds from runoff after permissible spraying procedures and possibly from careless handling of these compounds during manufacture or application, the Public Health Service has monitored major river basins in the United States for organochlorine pesticidal compounds since 1957. Breidenbach, Gunnerson, *et al.* (1967) report that the presence of DDT and related compounds has been fairly common during the entire period and that dieldrin has dominated the pesticide occurrences in all river basins since 1958.

The observation that the massive fish kills in the Mississippi River in 1963 were produced by one of these, endrin, caused concern about the efficiency of water treatment plants in removing these compounds from finished drinking water where river water is the source. Many of these pesticides, such as DDT, may occur in the water with no observable effect on odor or taste.

To monitor the river water, the pesticides from several thousand gallons of water were concentrated by adsorption on carbon. Assays were then made of the chloroform extracts of the carbon. The results from this method indicate general trends of contamination. To detect the high concentration that might occur in a spill of pesticides into water, grab samples must be assayed. When this surveillance study was started, no suitable methods were available to detect pesticides in the part per billion (p.p.b.) concentration range in small samples of water. Now, with the gas chromatographs equipped with electron-capture detectors, a 1-gallon sample can be quantitatively assayed for organochlorine compounds in this concentration range. Also, there were no suggested limits for these pesticidal compounds in finished waters. Concentrations in the part per trillion (p.p.t.) range were being reported for river water.

In 1964, a concentration level of 0.1 p.p.b. was used as the lower limit for the quantitative assays for endrin, dieldrin, *p,p'*-DDT, and related compounds in the grab samples of finished water. Concentrations less than this were reported as "detectable." In 1965, maximum permissible levels were assigned to each of the organochlorine compounds based on the "maximal acceptable concentrations" suggested on July 9, 1965, by the Subcommittee on Toxicology to the Public Health Service Advisory Committee on Drinking Water Standards. These concentrations ranged from 0.001 p.p.m. for endrin to 0.078 p.p.m. for heptachlor. In 1967, the "maximum reasonable stream allowances" suggested by Ettinger and Mount (1967) were accepted as guidelines. These ranged from 0.1 p.p.b. for endrin to 20 p.p.b. for methoxychlor.

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With the use of gas chromatographs equipped with electron-capture detectors, a precision of ±0.01 ng. per 5 μl. is easily attainable for solutions of the commonly used organochlorine pesticides in concentration ranges from 0.1 to 1 ng. per 5 μl. (20 to 200 ng. per ml. or p.p.b.). Residues of these compounds are extracted from the environment into organic solvents. For increased sensitivity the solvents may be concentrated before portions are chromatographed. The vapor pressure of these compounds is such that the error due to loss during the concentration step is minimal if the final volume is at least 1 ml. With smaller final volumes, considerable skill is required for quantitative analysis. If the pesticide analyst has an unlimited supply of the environmental media available for assay, purification steps can be included, so that it is possible to observe these residues when they are present in a part per trillion range.

Two methods were used in this surveillance study. One required a 100-ml. sample and the other a 1-gallon sample. During 1964, 100-ml. samples were collected for assay. Studies to evaluate the precision and accuracy of this method, employing the recovery of endrin added to the water at a level of 0.1 p.p.b. were run parallel with the surveillance samples. In 1965, the method using 1-gallon samples was developed, and both 100-ml. and 1-gallon samples were collected for assay. In 1966–67, only the statistically evaluated method, using 1-gallon samples, was used.

The number of pesticides looked for in the water samples was gradually increased from the initial three compounds, endrin, dieldrin, and DDT, to a total of 14 compounds including 10 pesticides, their metabolites, and related compounds.

Experimental Procedures and Materials

Sampling Sites. Grab samples were collected from municipal finished-water treatment plants in Carville, La.; Algiers Treatment Plant, New Orleans, La.; Carrolton Treatment Plant, New Orleans, La.; Vicksburg, Miss.; Cape Girardeau, Mo.; Burlington, Iowa; St. Louis, Mo.; Jefferson City, Mo.; Kansas City, Mo.; and Omaha, Neb.

Sample Preparation. MATERIALS. Gallon jugs with flat bottoms and narrow mouths, capped with Teflon-covered cork-lined plastic caps, were calibrated at the 3.5-liter volume level. Glass-stoppered, 125-ml. reagent bottles were calibrated at the 100-ml. volume level.

COLLECTION OF SAMPLES. After the jugs and bottles were cleaned and calibrated, they were shipped in insulated containers to the sampling stations. Water samples were collected directly in the jugs or bottles. A 10-ml. volume of pesticide quality hexane was added immediately to each sample, and the jug or bottle was closed tightly, and shipped in the insulated container to the laboratory in Cincinnati, Ohio, by air parcel post.

EXTRACTION. In both the 1-gallon and the 100-ml. methods, the pesticides were extracted from the water phase into the hexane phase without a transfer step. For this, the 100-ml. water samples, each containing 10 ml. of hexane, were shaken for 4 minutes. For the 3.5-liter samples, each containing 10 ml. of hexane, the gallon jug was placed on a stir jack somewhat off-center from the stirring motor. When the stirring apparatus was started, the hexane was drawn down through the vortex formed in the water by the rotating stirring bar and circulated in the form of small droplets into the water. These droplets rose through the water to the top of the jug and recirculated through the vortex. Placing the jug off-center on the stir jack caused the bottom of the vortex to be slightly off-center from the center of the rotating stirring bar. In this position, the stirring bar tended to "cut off" the lower portion of the hexane vortex and resulted in greater displacement of hexane and in more uniform droplets of hexane. The stirrer kept the water in motion, so that the circulating hexane was relatively evenly distributed throughout the water sample during the extraction.

After extraction, sufficient water of known quality was added to both sized samples so that the hexane layer was localized in the neck of the bottle. A portion of the hexane layer was transferred to a conical 15-ml. centrifuge tube with the use of a suitable device such as a pipet and pipet bulb or dropper. Quantitative removal of hexane was not required, since calculations were based on the original volume of hexane added. The extracts were then transferred to dry, conical, 15-ml. glass-stoppered centrifuge tubes and held until assayed. The intermediate transfer step was useful in obtaining a hexane sample free of the water phase. Occasionally there was an emulsion at the interface of the two phases; if so, it was broken during the intermediate step. Five-microliter portions of the hexane extracts from the gallon sample, representing extractives from 1.75 ml. of water, were chromatographed. The hexane extracts were concentrated by placing each centrifuge tube in a beaker of water on a steam bath for the statistical evaluation of the method for chlordan, toxaphene, and endrin, and for the routine assays of the drinking water samples.

For the 100-ml. samples, the hexane extract was chromatographed after a fourfold concentration (from 8 to 2 ml., where 5 μl. of extract represented extractives from 0.2 ml. of H_2O) and again after an additional 20-fold concentration, where 5 μl. represented extractives from 4 ml. of H_2O. This 20-fold concentration step was sensitive to small deviations in handling and was the source of the low precision observed with this method as compared with the method employing a 3.5-liter sample.

Assays. All assays were run on gas chromatographs equipped with electron-capture detectors. The following instruments were used: Beckman Model 2 modified by the addition of electron-capture detector, Jarrell-Ash Models 26700 and 28-730, and MicroTek Model 220.

The Beckman and Jarrell-Ash units were equipped with parallel plate electron-capture detectors with a tritium source. These detectors were held at 210° C. for 24 hours a day, 7 days a week. The MicroTek unit was equipped with an electron-capture detector of the pin cup design with a Ni_{63} source. This detector was held at 275° C. for 24 hours a day, 7 days a week. For all detectors, the potential across the electrodes was optimized when necessary to produce about 80% of the maximum current. Tritium foils were replaced when the maximum current dropped below 2×10^{-9} ampere. In routine work, this replacement was required about every 12 months. In the 2 years that the Ni_{63} detector was in use on this project, the maximum current did not drop below 4.0×10^{-9} ampere.

Either prepurified or extra-dry nitrogen was used as the moving phase. A precolumn consisting of a 4-foot, $^1/_4$-inch o.d. copper column packed with Molecular Sieve 5A, 60- to 80-mesh, was used on all of the instruments. The precolumns were activated just before use by heating to 500° C. for 2 hours. They were replaced when necessary; the lifetime was usually measured in months. Suitable flow control was maintained on the Beckman and Jarrell-Ash units with the second stage of the two-stage cylinder regulator. Flow rates, as measured by the soap bubble technique at the detector exit, of 30 to 100 ml. per minute were used. They varied with the column

Table I. Column Characteristics

Column	Length, Feet	Diameter, I.D., In.	Composition	Stationary Phase	Inert Phase	Mesh	Oper. Temp., ° C.	N_2 Flow, Ml./Min.	Av. Life of Column, Months	Special Characteristics
1	6	1/8	Glass	5% DC-200	Gas-Chrom Q	80/100	200	30	<3	No on-column decomp.
2	4 1/2	1/4	Aluminum	3% OV-17	Gas-Chrom Q	60/80	190	70	over 12	No on-column decomp.
3	6	1/4	Aluminum	4% QF-1 2% Epon 1001	Anakrom ABS	50/60	200	60	6–12	Epon added to increase endrin sensitivity
4	5	1/4	Aluminum	3% XE-60	Gas-Chrom Q	100/120	175–200	100	6–12	
5	6	1/4	Aluminum	1% Apiezon L 2% Epon 1001	Anakrom ABS	50/60	202	130	12–18	Shift in rel. ret. of DDE and dieldrin
6	6	1/4	Aluminum	4% Reoplex 400 2% Epon 1001	Anakrom ABS	50/60	192	100	12–14	

diameter and length, the stationary phase, and the mesh size of the inert support.

The stationary phases used in these studies included:

Silicone gum.	GE-XE-60, cyanoethyl methyl and dimethyl type
Silicone fluids.	DC QF-1, trifluoro propyl methyl type
	DC 200, methyl type
	OV-17, methyl phenyl type (50-50)
Polyester.	Reoplex 400
Hydrocarbon.	Apiezon L
Polymer.	Epon 1001 (epoxy resin)

The inert supports, either Gas-Chrom Q or Anakrom ABS, were used. The column characteristics are described in Table I. For the statistical evaluation of the preferred method, column 1 was used for series A and column 2 for series B and C. Columns 2, 3, and 4 were used for assaying finished-water samples, and columns 5 and 6 for verifying the identity of peaks observed on the other columns. The relative retention times for 12 organochlorine compounds on the six columns are listed in Table II. Electron-capture detectors with a tritium source were used with columns 3, 4, 5, and 6. For these four units, 1 to 2 ml. of hexane were injected at the end of each working day. This routine that retards the gradual decrease in efficiency and sensitivity of the system was not required for column 2, which was attached to a detector with a Ni_{63} source. Two sets of data were obtained on column 2 for evaluation of the precision and accuracy of the one-step extraction method. The first set was collected on the column just after it was built; the second set, 7 months later. During this 6-month interval, over 300 finished-water samples were assayed on this unit. The higher detector temperature is believed to be a major contributing factor in the stability of this unit over such a long period of time. During 1964, assays were run on columns containing Dow 11 and Epon 1001 coated on Fluoropak 80. These columns lacked the efficiency of those described above and were discontinued as more efficient stationary phases became available. Column 2, used on the

Table II. Relative Retention Times of Pesticide in Columns[a]

Pesticides	Liquid phase / Column No.	DC 200 1	OV-17 2	QF 1 + Epon 3	XE 60 4	Apiezon L + Epon 5	Reoplex 400 + Epon 6
α-BHC		0.23	0.18	0.21	0.33	0.10	0.15
Heptachlor		0.41	0.32	0.34	0.40	0.27	0.24
Lindane		0.19	0.25	0.39	0.42	0.23	0.37
Aldrin		0.52	0.40	0.41	0.38	0.27	0.34
δ-BHC		0.27	0.36	0.67	0.20	0.29	0.26
β-BHC		0.23	0.31	0.62	0.23	0.36	0.93
HCE		0.65	0.62	0.81	0.77	0.53	0.62
p,p'-DDE		1.0	1.0	1.0	1.0	1.0	1.0
Dieldrin		1.0	0.98	1.4	1.2	0.90	1.1
Endrin		1.1	1.2	1.7	1.4	1.1	1.5
p,p'-DDT		1.7	1.9	2.0	2.1	1.7	2.8
Methoxychlor		2.6	4.0	2.3	2.4	3.4	2.7

[a] Ratio of retention time for each compound, measured in cm., to retention time for *p,p'*-DDE.

Table III. Pesticides Used As Standards

Pesticide	Source	Purity as Described by Supplier, %
Aldrin	Shell Chemical Co.	99 ±
Chlordan	Panta Industries, Inc.	60
γ-Chlordan	Velsicol Corp.	99.8
Dieldrin	Shell Chemical Co.	99.1 ± 0.3
p,p'-DDT	Recrystallized in lab.	MP 106–107
DDE	Geigy Agricultural Chemicals	[a]
Endrin	Shell Chemical Co.	99 + W
Heptachlor	Panta Industries, Inc.	99 +
HCE	Velsicol Chemical Corp.	99
Lindane	DHEW, Food and Drug Adm.	—
α-BHC	DHEW, Food and Drug Adm.	—
β-BHC	DHEW, Food and Drug Adm.	—
δ-BHC	DHEW, Food and Drug Adm.	—
Methoxychlor	E. I. du Pont de Nemours and Co., Inc.	99 +
Toxaphene	Panta Industries, Inc.	100

[a] No data available.

MicroTek 220 gas chromatograph equipped with the Ni_{63} electron-capture detector, was the most efficient unit for assaying organochlorine compounds. It had a theoretical plate number of 1500 and a HETP of 0.09 cm. for dieldrin. The retention time for dieldrin was 19 minutes.

Identification of Compounds. In gas chromatography, compounds are identified by comparison of the retention time or retention volume with that for known compounds. The source and purity of the compounds used for identification in this surveillance project are listed in Table III. In 1964, only three of these standards, *p,p'*-DDT (and *p,p'*-DDE), dieldrin, and endrin, were used in examining the chromatograms from the surveillance project. By December 1966, standard solutions of all of the 15 compounds listed in Table III were used for identification of compounds in the water samples. Either pesticide quality hexane or spectroquality ethyl acetate was used to prepare concentrated standard solutions of 1.00 mg. per ml. for each of the 15 compounds. With the use of pesticide quality hexane, suitable dilutions of each standard were prepared to attain three or more concentration levels on the linear portion of the calibration curves. A concentration range of 0.1 to 0.6 ng. produced linear calibration curves for most of the compounds used in these studies.

Quantitative Analysis. Since symmetrical peaks were produced, peak heights were used as a measure of concentration. To measure the peak height, the base line was extended under the peak to form the peak base. Then a perpendicular was dropped from the peak maximum to the peak base. The peak height was this perpendicular measured in centimeters. Calibration curves were prepared by plotting peak height in centimeters against the concentration in nanograms.

Recovery Studies. For statistical evaluation of the efficiency of the preferred method, the 10 pesticides were added to finished water, each at a concentration level equal to or less than the maximum reasonable stream allowance suggested by Ettinger and Mount (1967). The one isomer of chlordan that was available and the three isomers of lindane, α-, β-, and δ-BHC, that occur with lindane in pesticide mixtures were also included in the evaluation of the precision and accuracy of the method.

The concentrations of each pesticide actually used were chosen so that a 5-μl. injection of the hexane extract (before any concentration step) produced a peak height of 2 to 10 cm. and appeared on the linear portion of the calibration curve for each compound. These concentrations were less than the maximum reasonable stream allowances that Ettinger and Mount (1967) suggested for all of the pesticides, except endrin, chlordan, and toxaphene. For these three compounds, a second series of data was then collected after a fourfold concentration of the hexane extract.

Mixtures of the standard solutions were prepared for the recovery studies by diluting known volumes of the concentrated solutions so that a 50-μl. portion could be added to each 4-liter sample of water for the recovery studies—for example, an 8 to 1000 dilution of the concentrated standard solution produced a solution containing 400 ng. of contaminant per 50 μl. This 50-μl. portion, when added to 4 liters of water, produced a sample containing 0.1 p.p.b. Each mixture of standard solutions contained from one to six of the pesticidal compounds. Combinations were chosen to give well-resolved peaks on the gas chromatograph. Each compound except toxaphene, chlordan, and the chlordan isomer was assayed in at least two different combinations under each of the three instrumental conditions. To prepare the theoretical amounts in the known solution, 50-μl. portions of the mixture of standard solutions were diluted to 10 ml. with "distilled-in-glass" hexane. A 5-μl. portion of the solutions containing theoretical concentrations was injected into the gas chromatograph before and after each injection.

Three sets of data, series A, B, and C, were compiled for estimating the precision and accuracy of the one-step extraction method. Since there was a variation in the sensitivity of the instruments at the time each series was run, the concentration of each compound was not held constant for the three sets of data. The actual concentrations used are shown in Table IV.

For the recovery studies, 1-gallon portions of water of known quality (Cincinnati tap water put through an activated carbon filter) were placed in each of several gallon jugs for replicate assays. A stirring bar was added to each. A 100-μl. Hamilton syringe was used to add a 50-μl. portion of the mixture of standard solutions to each jug; a precaution observed was having the needle of the syringe below the surface of the water when each sample was discharged. After the cap to the jug was screwed on tightly, the sample was allowed to mix for 1 hour with the magnetic stirrer on low speed. Then it was left undisturbed until extracted. This period between contamination and extraction varied from 12 to 64 hours. The 10-ml. volume of hexane was added immediately before extraction.

Under the conditions described above, the samples were extracted and assayed. A theoretical solution was prepared with each set of replicate samples by diluting a 50-μl. portion of the mixture of standard solutions to 10 ml. with hexane. This technique in preparing the theoretical solutions was used to cancel volumetric calibration errors. Five-microliter portions of the theoretical solutions were chromatographed before and after each of the replicate samples.

Table IV. Estimates of Mean Recoveries and 99% Confidence Intervals for 14 Pesticides

	Concentration Range, P.P.B.	Series	Std. Deviation, S	Degrees of Freedom, ν	$\bar{X} \pm \frac{St_{(\nu,\, 1-\alpha/2)}}{\sqrt{n}}$
Endrin	0.2 to 0.3	A, BC	6.4	28	104.4[b] ± 3.1
	0.06[a]	C	10.9	11	88.4 ± 9.8
α-BHC	0.06 to 0.1	A, BC	5.6	32	89.2 ± 2.5
Dieldrin	0.1 to 0.3	A	6.1	33	94.1 ± 5.3
		BC			102.6 ± 3.2
			5.4	29	
Aldrin	0.06 to 0.1	A			90.6 ± 4.7
		BC			97.4 ± 3.0
Methoxychlor	2.5 to 4.6	A	6.0	9	85.0 ± 6.2
		BC	5.1	20	101.3 ± 3.0
Chlordan		A	NR		NR
isomer	0.12	C	6.6	14	95.6 ± 4.9
Lindane	0.06 to 0.1	A	2.2	9	85.3 ± 2.3
		BC	4.8	20	89.7 ± 2.8
Heptachlor	0.1	A	2.5	9	63.3 ± 2.6
		B			71.6 ± 2.7
		C	3.8	19	85.6 ± 4.4
HCE	0.1 to 0.3	A	2.8	9	101.7 ± 2.9
		B	4.5	25	105.0 ± 2.7
		C_1			94.3 ± 4.4
		C_2			
p,p'-DDT	0.5 to 1.1	A	11.7	9	71.1 ± 13.1
		B	5.6	20	88.0 ± 4.0
		C			102.4 ± 6.0
δ-BHC	0.06 to 0.5	A	5.1	9	54.8 ± 5.2
		B	5.8	4	52.2 ± 7.2
		C_1	1.0	7	54.0 ± 0.8
		C_2	6.0	7	58.1 ± 4.7
β-BHC	0.2 to 1.3	A	2.0	9	46.1 ± 2.1
		B			48.5 ± 3.6
		C_1	2.8	18	42.0 ± 2.8
		C_2			45.6 ± 2.8
Chlordan,	1.3	A	6.0	9	85.0 ± 6.2
60%	0.25[a,c]	C[d]	...	...	...
Toxaphene	2.5	A	11.2	9	94.7 ± 11.5
	2.5[a,c]	C[d]	...	...	...

[a] Fourfold concentration of hexane extract before it was chromatographed.
[b] True mean (μ) is expected to lie between $\bar{X} - \frac{St_{(\nu,\, 1-\alpha/2)}}{\sqrt{n}}$ and $\bar{X} + \frac{St_{(\nu,\, 1-\alpha/2)}}{\sqrt{n}}$ 99% of time when $\alpha = 0.01$.
[c] When adjusted for 60% purity, concentrations become 0.75 and 0.15 p.p.b.
[d] Only qualitative studies.

Results and Discussion

Statistical Evaluation. To obtain estimated proportion recoveries, the sample peak height for each compound in each replicate sample was divided by the standard peak height preceding it on the chromatograph. Because toxaphene and chlordan are mixtures of compounds, they produced multiple peaks with all the columns. Areas under the multiple peaks for these two pesticides were plotted against the concentration for the data in the series A recovery study. For the C series, run on column 2, quantitative results were not possible for these compounds. Quantitative recovery data, however, were collected for one isomer of the chlordan mixture on column 2.

The standard deviation (S), the mean per cent recovery ($\bar{X}$), and the 99% confidence intervals were used to evaluate the recovery efficiencies (Table IV).

For these statistical evaluations, endrin, at a concentration level <0.1 p.p.b., toxaphene, and chlordan were treated separately and data from series B and C were combined. This combination series, BC, consisted of 38 sets of data, each set consisting of five to eight replicate recovery assays for each compound. Series A consisted of 11 sets of data with each set made up of 10 replicate assays for each compound.

All statistical tests were performed with a prechosen significance level of $\alpha = 0.01$. The assumption that the per cent recoveries were independent observations obtained from a normal population was tested with the use of two techniques: a test for nonnormality (Pearson and Hartley, 1962) and a graphical test (Dixon and Massey, 1957).

The mean recoveries and standard deviations were computed for the 14 compounds. Estimates were calculated for each of the runs within each of the three series for each compound. Homogeneity of variance tests as shown by Dixon and Massey (1957) was computed, and variances were pooled

Table V. Pesticides in 1-Gallon Samples of Water[a]

Location	Date	Lindane	BHC's	Aldrin	*p,p'*-DDE	*p,p'*-DDT	Dieldrin	Endrin	Heptachlor	HCE	Chlordan
					Finished Drinking Water						
Algiers	03/31/65 08/25/65			0/7	1/12	1/12	10/12	4/12			
Carrolton	03/31/65 08/25/65			0/6	0/12	0/12	6/12	3/12			
Carville	03/29/65 12/14/67	1/1	1/1	1/19	1/19	1/19	9/19	1/19	1/10	1/10	
Vicksburg	03/29/65 05/25/67	4/6	5/6	3/45	23/45	23/45	21/45	7/45	1/24	6/37	0/6
Cape Girardeau	04/19/65 06/07/67	6/6	6/6	9/39	7/39	6/39	18/39	3/39	0/13	0/13	0/6
Omaha	05/04/65 05/23/67	3/5	4/5	2/19	1/19	1/19	4/19	1/19	0/19	0/19	0/6
St. Louis	12/11/66 05/25/67	6/7	6/7	2/7	1/7	0/7	5/7	1/7	0/7	0/7	1/6[b]
Burlington	03/24/65 06/06/67	5/6	5/6	2/11	4/11	3/11	3/11	0/11	0/6	1/6	0/5
Jefferson City	05/30/66 05/26/67	4/7	5/7	2/15	5/15	4/15	5/15	0/15	0/15	0/15	1/6
Kansas City	03/19/65 05/23/67	5/9	5/9	16/52	10/54	10/54	24/54	4/54	1/33	13/54	12/28[c]
Total		34/47	37/47	37/220	53/233	49/233	105/233	24/233	3/127	21/161	14/63
					Raw Water						
Carville	12/14/66 01/05/67	2/2	2/2[b]	0/2	1/2	1/2	0/2	0/2	0/2	0/2	0/1
Vicksburg	02/27/67 05/25/67	4/4	4/4	1/4	2/4	2/4	2/4	1/4	1/4	0/4	1/4
Cape Girardeau	03/29/65 06/07/67	4/8	5/8	4/8	3/8	2/8	5/8	2/8	0/8	0/8	0/6
Jefferson City	05/30/66 05/26/67	4/7	6/7	5/15	3/15	4/15	8/15	0/15	0/15	1/15	1/7
Kansas City	05/04/66 05/23/67	7/7	7/7	12/22	3/22	3/22[b]	10/22	1/22	1/22	4/22	9/22[d]
Omaha	04/20/66 05/23/67	4/6	5/6	4/16	3/16	3/16	4/16	1/16	0/16	0/16	0/6
Total		25/34	29/34	26/67	15/67	15/67	29/67	5/67	2/67	5/67	11/46

[a] Ratio of number of samples with detectable concentrations to total number of samples.
[b] One sample assayed at 0.5 p.p.b.
[c] Four samples assayed from 8 to 0.25 p.p.b.
[d] Two samples assayed from 0.5 to 0.3 p.p.b.

where insufficient evidence existed to reject the null hypothesis that they were equal. Standard analysis of variance tests were performed to examine a similar hypothesis that the mean recoveries for a given pesticide were equal. The significant results were separated into groups of means by Duncan's test (1955). For example, the variances from all runs were pooled for dieldrin and aldrin, but, for each compound, the mean recovery for series A was lower than the mean recovery for BC (see Table IV). Only two compounds were found, endrin, at 0.2 to 0.3 p.p.b., and α-BHC, where a single estimate could be reported for both mean recovery and variance. δ-BHC was the compound showing the widest differences in precision, and none of the runs could be pooled.

There is no explanation to date for the mean recovery values greater than 100% that were observed for endrin, at 0.2 to 0.3 p.p.b., dieldrin, methoxychlor, HCE, and DDT. The water used in these studies did not contain detectable concentrations of these pesticides. The proportional amount of the hexane in the vapor phase was held at a minimum during the extraction step.

For some of these pesticides the actual concentrations used in these recovery studies is significantly lower than the maximum stream allowances suggested by Mount and Ettinger (see Table VII). The safety factors range from 50 times for lindane and 10 times for heptachlor to 2 to 5 times for aldrin, HCE, and methoxychlor. Dieldrin and DDT were studied at the same concentration as the suggested allowance. None of the columns used in these studies had sufficient sensitivity for endrin and chlordan for them to be detected at the suggested levels without concentrating the hexane extract. To look for synergistic effects, endrin was included in mixtures with the other 10 compounds at a level that could be measured quantitatively. An additional recovery study was then done for endrin at a lower concentration. For this the water was

Table VI. Pesticides in 100-Ml. Samples of Water[a]

Location	Date	Aldrin	p,p'-DDE	p,p'-DDT	Dieldrin	Endrin
		FINISHED DRINKING WATER				
Algiers	03/03/64 12/17/64	0/2	5/19[b]	5/19[b]	2/19	14/19[b]
Carrolton	03/03/64 12/17/64		3/20	3/20	7/20	14/20[c]
Carville	04/16/64 06/08/66	4/26[b]	13/39[c]	12/39[b]	14/39	24/39[d]
Vicksburg	03/31/64 06/30/66	4/41	29/41[e]	28/41[e]	23/41[d]	34/41[f]
Cape Girardeau	06/02/64 03/14/66	2/25	13/25[b]	14/25[b]	13/25[c]	11/25[d]
Burlington	06/30/64 03/22/66	0/10	2/10	2/10	2/10	4/10[b]
St. Louis	06/11/64 06/16/66	3/32	14/32[b]	14/32[b]	17/32[b]	10/32[b]
Jefferson City	06/04/64 07/16/64	1/7	3/7	3/7	7/7	6/7
Kansas City	06/11/64 05/23/66	3/10	1/10	1/10	0/10	5/12[d]
Omaha	06/01/64 03/07/66	4/20	7/20	6/20	6/20	10/20[d]
Total		21/173	90/223	88/223	91/223	132/225
		RAW WATER				
Carville	06/17/64 03/10/66	0/3	5/10	5/10	6/10	3/10[b]
Cape Girardeau	06/02/64 03/14/66	1/12	2/12	2/12	4/12	4/12[d]
Kansas City	04/27/66 05/23/66	0/2	0/2	0/2	0/2	0/2
Total		1/17	7/24	7/24	10/24	7/24

[a] Ratio of number of samples with detectable concentrations to total number of samples.
[b] One sample assayed >0.1 p.p.b.
[c] Two samples assayed >0.1 p.p.b.
[d] Three samples assayed >0.1 p.p.b.
[e] Four samples assayed >0.1 p.p.b.
[f] Six samples assayed >0.1 p.p.b.

contaminated with endrin at a 0.06-p.p.b. concentration level and extracted according to the usual procedure. Then the hexane extract was concentrated fourfold before being chromatographed. The resultant mean recovery was 88.4%, with a standard deviation of 10.9. Because of the difference in sensitivity of columns 1 and 2 for toxaphene, recovery data were obtained at the suggested level of 2.5 p.p.b. for the unconcentrated hexane extract on column 1 and for an extract concentrated fourfold on column 2. Chlordan was assayed on column 1 at a level 5 times higher than the suggested allowance of 0.25 p.p.b. and at the 0.25-p.p.b. level on column 2 after a fourfold concentration of the hexane extract. In series A, column 1, recoveries of 85 and 95% were estimated for chlordan and toxaphene by comparing the area under the multiple peaks with those for the standards. For the series C, column 2, quantitative data were not collected for these pesticides. A mean recovery of 96%, however, was obtained for the chlordan isomer. The concentrated sample extract for toxaphene and concentrated standard produced chromatographs that could not be distinguished from each other.

Mean recovery values greater than 85% were attained in all sets of data for lindane, α-BHC, and aldrin each at levels ranging from 0.06 to 0.1 p.p.b.; for HCE and dieldrin each at levels ranging from 0.1 to 0.3 p.p.b.; for endrin at levels of 0.2 and 0.3 p.p.b.; and for methoxychlor at levels of 2.5 and 4.5 p.p.b. Mean recovery data for *p,p'*-DDT at concentration levels ranging from 0.5 to 1.1 p.p.b. ranged from 71% in series A through 88% for series C to 102% for series B. Recoveries for heptachlor at a concentration level of 0.1 p.p.b. ranged from 63% in series A through 86% in series B to 72% in series C. Low but consistent recoveries were observed for the β and δ isomers for BHC in all of the sets of data.

Surveillance Samples. Data for 300 1-gallon samples of water (233 samples of finished water and 67 samples of raw water) collected between March 1965 and May 1967 are given in Table V. These data include the samples used to compare the two methods. Data for 249 small, 100-ml. samples of water (225 samples of finished water and 24 samples of raw water) that were collected between March 1964 and June 1966 are given in Table VI. In 1964 the chromatographs of the water samples were compared with chromatographs for standard solutions of *p,p'*-DDT, *p,p'*-DDE, dieldrin, and endrin. In samples assayed after December 1966, the chromatographs for standard solutions of 15 compounds were used for identification of peaks in the sample chromatographs. For this reason, all data in Tables V and VI are given as the ratio of

Table VII. **Guidelines for Maximum Permissible Levels of Pesticides in Finished Waters**

(Parts per billion)

	1964	1965–6[a]	1967[b]
Lindane		56.0	5.0
Aldrin		32.0	0.25
Heptachlor		78.0	1.0
HCE		18.0	1.0
Dieldrin	<0.1	18.0	0.25
Endrin	<0.1	1.0	0.1
p,p'-DDT plus related compds.	<0.1	42.0	0.5
Methoxychlor		35.0	20.0
Toxaphene		5.0	2.5
Chlordan		52.0	0.25

[a] Based on "maximal acceptable concentrations" of Subcommittee on Toxicology (1965).
[b] Based on the "maximum reasonable stream allowances" of Ettinger and Mount (1967).

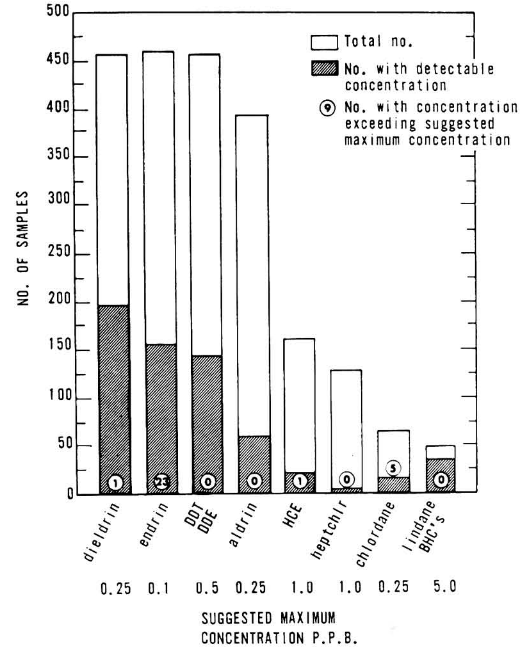

Figure 1. Pesticides in finished drinking water, 1964–67

the number of samples containing observable concentrations of the pesticide over the number of samples assayed for the pesticide. Those observable concentrations that produced peak heights less than 2 cm. were assayed qualitatively. The standard curves of peak height *vs.* concentration were used to quantitate data from the 1-gallon samples for larger concentrations. Only those quantitative data in excess of 0.1 p.p.b. are reported in the footnotes of Table V. Because of the low precision with the method using 100-ml. samples, the number of samples with assays in excess of 0.1 p.p.b. are listed in the footnotes of Table VI. Occasionally the presence of a large concentration of either an unknown compound or one of the pesticides prevented assay for the other pesticides in this group; this is reflected in the varying values for the denominator.

Table VII lists the three sets of guidelines used in this surveillance study for maximum permissible levels of pesticides. The "maximum reasonable stream allowances" of Ettinger and Mount (1967) were used as a guideline for all of the data reported in Table V on 1-gallon samples.

Lindane (γ isomer of 1,2,3,4,5,6-hexachlorocyclohexane) and the BHC's were observed in more than 80% of all assayed samples from Vicksburg, Carville, Cape Girardeau, Burlington, and St. Louis. In contrast, only 55 to 60% of water samples from the other stations contained detectable concentrations of lindane. Although a few of the samples from Burlington, Omaha, and Jefferson City contained detectable concentrations of endrin, up to 40% of the samples from stations along the lower Mississippi contained detectable concentrations of this pesticide.

The number of samples containing concentrations in excess of 0.1 p.p.b. of endrin decreased from 23 in the period 1964–65 to none in the period 1965–67. Only one sample was observed during the entire period with a concentration of dieldrin in excess of the 0.25-p.p.b. limit suggested by Ettinger and Mount. However, six samples in 1964–65 contained dieldrin in excess of 0.1 p.p.b. The 63 samples assayed after December 1966 were examined for toxaphene (essentially a mixture of isomers of octachlorocamphene), but none of these results were positive. In contrast, 14 of these samples contained chlordan (2,3,4,5,6,7,8,8 - octachloro - 2,3,3*a*,4,7,7*a* - hexahydro - 4,7-methanoindene), and in five of these samples, the level was greater than 0.25 p.p.b. Twelve of the 14 samples containing chlordan came from one location.

Results of all of the samples of finished water assayed by both methods are summarized in Figure 1. Over 40% of all samples contained detectable dieldrin; about one third of the samples contained endrin, *p,p'*-DDT plus *p,p'*-DDE, or both. Although only 47 of the samples were assayed for lindane and the BHC's, over 70% of the samples contained detectable concentrations of these pesticides. None of these samples, however, contained concentrations in excess of the suggested allowance of 5.0 p.p.b.

In the statistical evaluation of the method it became obvious that the three different sets of instrumental conditions used in these studies affected recoveries and precision data for the organochlorine pesticides. For this reason, it was not possible to treat these recovery data in the conventional way of averaging data from all runs and reporting confidence limits. For an evaluation of this method using one set of instrumental conditions, the following procedure is suggested.

The formula in Equation 1 may be used to calculate the number of samples needed to estimate the per cent recovery within certain limits.

$$\begin{matrix}\text{Upper limit}\\ \text{Lower limit}\end{matrix} = \bar{X} \pm \frac{St_{(\nu,\, 1-\alpha/2)}}{\sqrt{n}} \qquad (1)$$

where $\bar{X}$ = mean recovery = $\left(\sum_{i=1}^{n} x_i/n\right)$

$$S = \text{standard deviation} = \sqrt{\frac{\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2/n}{n-1}}$$

n = number of observations

$t_{(\nu,\, 1-\alpha/2)}$ = critical t value at prechosen α level and ν degrees of freedom

Table VIII. Confidence Limits Computed for an Example Where $S = 6.0$ and $\alpha = 0.01$

No. of Observations, n	$\bar{X} \pm St_{(\nu,\ 1-\alpha/2)}/\sqrt{n}$
3	$\bar{X} \pm 34.4$[a]
4	$\bar{X} \pm 17.5$
5	$\bar{X} \pm 12.4$
6	$\bar{X} \pm 9.9$
7	$\bar{X} \pm 8.4$
8	$\bar{X} \pm 7.4$
9	$\bar{X} \pm 6.7$
10	$\bar{X} \pm 6.2$
15	$\bar{X} \pm 4.6$
20	$\bar{X} \pm 3.8$
25	$\bar{X} \pm 3.6$

[a] ν is degrees of freedom associated with S, $n - 1$ for this situation.

The problem is to calculate n when $a = \frac{St_{(\nu,\ 1-\alpha/2)}}{\sqrt{n}}$ is fixed at some desired level and when α is specified—e.g., to estimate the recovery of the method $\bar{X} \pm 4.0$ ($a = 4.0$) when $\alpha = 0.01$. This formula also requires some idea of the S (standard deviation) value. These studies indicate that $S \cong 6.0$ for aldrin, dieldrin, endrin, and DDT. Table VIII shows the limits for various sample sizes (n) between 3 and 25. To achieve an expected value of the limit of $\bar{X} \pm 4.0$, 20 observations would be needed. The expected value of the limits are interpreted to mean that the true mean recovery will lie within the interval $\bar{X} - 4.0$ and $\bar{X} + 4.0$ in 99% of the experiments. These studies are performed in a narrow concentration range. The number of observations, n, can be selected to obtain the confidence desired in estimating the mean recovery.

A wider range of concentrations and the resulting regression problems may also be considered; estimates for the present study are in the concentration range ≤ 1 p.p.b.

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Performance of Porous Cellulose Acetate Membranes for the Reverse Osmosis Treatment of Hard and Waste Waters

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Reverse osmosis is a general separation process. Its application for saline water conversion and similar problems is being studied extensively using the Loeb-Sourirajan type porous cellulose acetate membranes (Sourirajan, 1967). This process is particularly suitable for the treatment of hard waters, polluted waters, and sewage waters (Ironside and Sourirajan, 1967). This paper gives some performance data of the CA-NRC-18 type porous cellulose acetate membranes (Sourirajan and Govindan, 1965) for such applications. These data are significant from the points of view of industrial water treatment, water renovation and re-use, and water pollution control.

Experimental Details

Reagent grade chemicals and porous cellulose acetate membranes (designated as CA-NRC-18 type films) made in the laboratory were used. The films were cast at −10° C. in accordance with the general procedure described earlier (Sourirajan and Govindan, 1965) using 68.0 weight % acetone, 17.0 weight % cellulose acetate (acetyl content 39.8%), 13.5 weight % water, and 1.5 weight % magnesium perchlorate for the film casting solution. Membranes shrunk at different temperatures were used to give different levels of membrane porosity and performance at preset operating conditions.

■ The performance of a few typical Loeb-Sourirajan type porous cellulose acetate membranes is reported for the treatment of hard, polluted, and sewage waters. The membranes used are specified in terms of pure water permeability constant and solute transport parameter for sodium chloride. Using feed waters containing 300- to 800-p.p.m. hardness (expressed as $CaCO_3$), product waters containing 2 p.p.m. or less could be obtained with 90% product recovery and an average initial flux of 38 gallons per day per sq. foot at 1000 p.s.i.g. The possibility of producing "ultrapure" waters by repeated reverse osmosis processing is indicated. The separation of common pollutants such as nitrates, borates, fluoride, alkyl benzene sulfonate (ABS), ammonia, and phosphates, and a few others usually present in plating wastes, and the applicability of the reverse osmosis process for the treatment of sewage waters and water renovation are illustrated.

The experiments were carried out at the laboratory temperature (23° to 25° C.) in the pressure range 200 to 1000 p.s.i.g., using the apparatus described by Sourirajan (1969). The reverse osmosis cell was a stainless steel pressure chamber consisting of two detachable parts. The film was mounted on a stainless steel porous plate embedded in the lower part of the cell through which the membrane-permeated product water was withdrawn at the atmospheric pressure. The upper part of the cell contained the feed solution under pressure in contact with the membrane. Two parts of the cell were clamped and sealed tight, using rubber O-rings. Compressed nitrogen gas was used to pressurize the system. About 250 cc. of feed solution were used each time. The feed solution was kept well stirred during the experiment by means of a magnetic stirrer fitted in the cell about 1/4 inch above the membrane surface. Of the feed, 25 to 90% was recovered as product, and the product concentrations given in this paper are the over-all product concentrations. The compositions of the feed and product solutions were analyzed by a Bausch & Lomb precision refractometer, by conductance measurements, or by the other standard methods of analysis indicated below.

Each membrane was subjected to a temperature (shrinkage) and then a pressure treatment before use in reverse osmosis experiments. The temperature treatment consisted of heating the film gradually under water from the laboratory temperature to the required temperature, where it was kept for 10 to 15 minutes and subsequently cooled rapidly. The shrunk membrane was mounted in the cell and subjected to a pressure treatment which consisted of permeating water under pressure through the membrane at 1200 p.s.i.g. for at least an hour. The pressure was then released, and the membrane kept in contact with water at atmospheric pressure for several hours. The membrane was then ready for use in reverse osmosis experiments. The effective area of the film in the cell was 9.6 sq. cm. In each experiment, the pure water permeability [PWP], and average product rate [PR] in grams per hour per 9.6 sq. cm. area of film, the volume fraction product recovery, and the initial feed concentration and the average product concentration were determined. In all cases, the terms "product" and "product rate" refer to the membrane-permeated product solutions, and the separation and product rate data can be reproduced within ±1 and ±5%, respectively. The variation in product rate data is due to the viscosity change of product, which is about 2.5% per degree centigrade.

Water Analysis. Calcium and magnesium ions were analyzed by titration with EDTA, biochemical oxygen demand (B.O.D.) was determined using the azide modification of the iodometric method, ABS was determined colorimetrically, and total dissolved solids were determined by evaporation, following the procedures given for each by the American Public Health Association (1965). Phosphates and nitrates were analyzed by autoanalyzers, and very low concentrations of calcium and magnesium were determined by the atomic absorption technique. Other inorganic salts were analyzed by the specific resistance measurements, using a conductivity bridge.

Results and Discussion

Basic Transport Equations. The Kimura-Sourirajan analysis (Kimura and Sourirajan, 1967) gives rise to the following basic equations relating the pure water permeability constant, A, the flux of solvent water, N_B, the solute transport parameter, $(D_{AM}/K\delta)$, and the mass transfer coefficient, k, on the high pressure side of the membrane:

$$A = \frac{[PWP]}{M_B \times 9.6 \times 3600 \times P} \quad (1)$$

$$N_B = A[P - \pi(X_{A2}) + \pi(X_{A3})] \quad (2)$$

$$= \left(\frac{D_{AM}}{K\delta}\right)\left(\frac{1 - X_{A3}}{X_{A3}}\right)(c_2X_{A2} - c_3X_{A3}) \quad (3)$$

$$= kc_1(1 - X_{A3}) \ln\left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right) \quad (4)$$

From the experimental [PWP], [PR], and feed and product concentration data, the values of A, $(D_{AM}/K\delta)$, and k can be calculated for each experiment. Both A and $(D_{AM}/K\delta)$ depend on the porous structure of the membrane surface, and hence they are different for different membranes; both are functions of operating pressure, and, in addition $(D_{AM}/K\delta)$ depends on the chemical nature of the solute. For the type of membranes used in this work $(D_{AM}/K\delta)$ is independent of feed concentration and k at a given operating pressure for solutes such as sodium chloride.

Membrane Specifications and Applicable Mass Transfer Coefficient Correlation. It has been shown (Sourirajan, 1969) that the membrane performance data given in terms of product rate and solute separation (or feed and product concentra-

Table I. Membrane Specifications[a]

Film No.	$A \times 10^6$, G. Mole H_2O / Sq. Cm. Sec. Atm.	$(D_{AM}/K\delta) \times 10^5$, Cm./Sec.
H-1	1.618	0.679
H-2	1.765	6.990
H-3	1.914	9.232
H-4	0.886	0.972
H-5	1.695	3.457

[a] Film type CA-NRC-18
System [NaCl–H_2O]
Operating pressure 1000 p.s.i.g.

Table II. Separation of Calcium and Magnesium Ions in Aqueous Solution[a]

Film No.	System	Feed Water Hardness, P.P.M. $CaCO_3$	Product Water: Hardness, p.p.m. $CaCO_3$	Product Water: Product rate, gal./(day) (sq. ft.)
H-1	$CaCl_2$–H_2O	302	2	38.6
	$CaCl_2$–H_2O	498	2	42.3
	$CaCl_2$–H_2O	782	2	41.4
	$MgCl_2$–H_2O	315	<1	41.1
	$MgCl_2$–H_2O	516	<1	37.4
	$MgCl_2$–H_2O	800	2	36.1
	$(CaCl_2 + MgCl_2)$–H_2O	300	<1	34.2
	$(CaCl_2 + MgCl_2)$–H_2O	495	<1	36.7
	$(CaCl_2 + MgCl_2)$–H_2O	807	<1	35.1
H-2	$CaCl_2$–H_2O	302	17	42.8
	$CaCl_2$–H_2O	504	21	42.8
	$CaCl_2$–H_2O	806	26	42.6
	$MgCl_2$–H_2O	315	24	49.2
	$MgCl_2$–H_2O	509	36	43.7
	$MgCl_2$–H_2O	829	45	41.5
	$(CaCl_2 + MgCl_2)$–H_2O	304	19	43.5
	$(CaCl_2 + MgCl_2)$–H_2O	504	28	43.8
	$(CaCl_2 + MgCl_2)$–H_2O	805	41	42.6
H-3	$CaCl_2$–H_2O	301	28	45.2
	$CaCl_2$–H_2O	508	42	50.4
	$CaCl_2$–H_2O	802	64	51.2
	$MgCl_2$–H_2O	302	29	51.6
	$MgCl_2$–H_2O	505	43	51.7
	$MgCl_2$–H_2O	806	60	47.3
	$(CaCl_2 + MgCl_2)$–H_2O	289	22	51.9
	$(CaCl_2 + MgCl_2)$–H_2O	498	36	50.0
	$(CaCl_2 + MgCl_2)$–H_2O	812	52	43.5

[a] Operating pressure 1000 psig.
Product recovery 90%.

tions) have firm significance only if the membrane is specified in terms of A and $(D_{AM}/K\delta)$ for a reference solute, and the appropriate mass transfer correlation applicable to the high pressure side of the membrane under the experimental conditions is given. Accordingly, the specifications of the particular membranes used in this work are given in Table I in terms of A and $(D_{AM}/K\delta)$ for sodium chloride at 1000 p.s.i.g. The A-values given are the initial ones; they usually decrease as a function of time because of membrane compaction, but the $(D_{AM}/K\delta)$ values do not change (Kimura and Sourirajan, 1968). Following the earlier work (Kimura and Sourirajan, 1967; Sourirajan and Kimura, 1967), the mass transfer coefficient correlation applicable for the experimental conditions used may be expressed as a generalized dimensionless parameter $(N_{Sh}/N_{Sc}^{0.33})$ where

$$N_{Sh} = \frac{kd}{D} \tag{5}$$

and

$$N_{Sc} = \frac{\nu}{D} \tag{6}$$

The values of the above parameter were determined in a large number of experiments using several feed solution systems ($NaCl$–H_2O, $CaCl_2$–H_2O, and $MgCl_2$–H_2O), and different concentrations of the system $NaCl$–H_2O. The average of the values obtained for the above parameter was 124, most of the values obtained being within 10% of the average value.

Reverse Osmosis for Treatment of Hard Waters. Hardness is of special concern in municipal and industrial water supply. Hard water requires much soap before a lather is formed, and hard water deposits sludges or incrustations on surfaces with which it comes into contact and in vessels and boilers in which it is heated. The responsible substances are calcium and magnesium ions, and to a lesser extent (because of their normally smaller concentrations), those of iron, manganese, strontium, and aluminum. In the operation of boilers, foaming, priming, scale formation, caustic embrittlement, and corrosion increase with operating pressures. Foaming and priming entrain moisture and solids in steam. The solids carried over may then be deposited in steam lines, turbines, and other equipment. The tolerances for hardness (expressed as p.p.m. $CaCO_3$) of water are 80, 40, 10, and 2 for boilers operating in the pressure ranges below 150, 150 to 250, 250 to 400, and over 400 p.s.i.g., respectively (Fair and Geyer, 1961b).

Therefore, the treatment of hard waters to produce boiler feed waters of acceptable quality is an important industrial problem. The application of reverse osmosis for the treatment of hard waters was hence investigated and some results are presented in Tables I to IV and Figure 1. These experimental data do not represent the limits of separation and product rate obtainable with each film. With a higher mass transfer

Table III. Separation of Iron, Manganese, Strontium, and Aluminum Ions in Aqueous Solution[a]

System	Solute Concn. in Feed, P.P.M.	Product Water: Solute concn., P.P.M.	Product Water: Product rate, gal./(day) (sq. ft.)
$FeCl_3$–H_2O	795	40	19.0
$MnSO_4$–H_2O	500	<1	25.7
$SrCl_2$–H_2O	485	17	23.7
$AlCl_3$–H_2O	503	11	26.9

[a] Film H-4. Operating pressure 1000 p.s.i.g. Product recovery 90%.

coefficient on the high pressure side of the membrane, a better solute separation and product rate can be obtained in most cases. Under the given experimental conditions, the data, however, illustrate the combination of separation and product rate obtainable for each film. Since the mass transfer correlation applicable for the high pressure side of the membrane is the same for all the experiments in this work, the above comments are applicable for all the data presented in this paper. Further, since the data presented are for high product recovery (90% in most cases), the experiments often took several hours to complete; consequently, the reported product rate data already include at least a part of the membrane compaction effect. On the basis of the known characteristics of the films used in this work (Kopeček and Sourirajan, 1969), it is reasonable to expect that product fluxes of about 70 to 80% of those reported here will be realized practically under conditions of continuous operation for long periods of time.

Table II gives the results obtained with three films. $CaCl_2$, $MgCl_2$, and 1-to-1 mixture of $CaCl_2$ and $MgCl_2$ were used as solutes. Three different initial feed concentrations (~300, 500, and 800 p.p.m. expressed as $CaCO_3$) were tested. The hardness and rates of product water obtained at volume recoveries of 25, 50, 75, and 90% were determined. Only the 90% recovery data are presented in Table II. The results show that even with 90% recovery, product water hardness of ~2 p.p.m. was obtained with film H-1 with an initial average product rate of 38 gallons per day per sq. foot at 1000 p.s.i.g. Under the same conditions the hardness of product water obtained ranged from 17 to 45 p.p.m. for film H-2 and 22 to 64 p.p.m. for film H-3, with corresponding average product rates of 43.6 and 49.2 gallons per day per sq. foot, respectively. With lower recoveries, the hardness of product water was even less, and product rate more favorable in all cases.

Table IV. Softening of Natural Hard Waters[a]

Film No.	Source of Feed Water	Feed Water Hardness, P.P.M. $CaCO_3$	Product Water: Hardness, p.p.m. $CaCO_3$	Product Water: Product rate, gal./(day)(sq. ft.)
H-1	Coalinga, Calif.	843	<1	26.5
	Webster, S.D.	610	<1	28.6
	Roswell, N.M.	641	4	29.6
	San Diego, Calif.	340	2	30.4
	Indianapolis, Ind.	247	4	30.0
H-2	Coalinga, Calif.	843	12	40.1
	Webster, S.D.	610	5	43.2
	Roswell, N.M.	641	14	42.9
	San Diego, Calif.	340	7	45.1
	Indianapolis, Ind.	247	11	45.0

[a] Operating pressure 1000 p.s.i.g. Product recovery 90%.

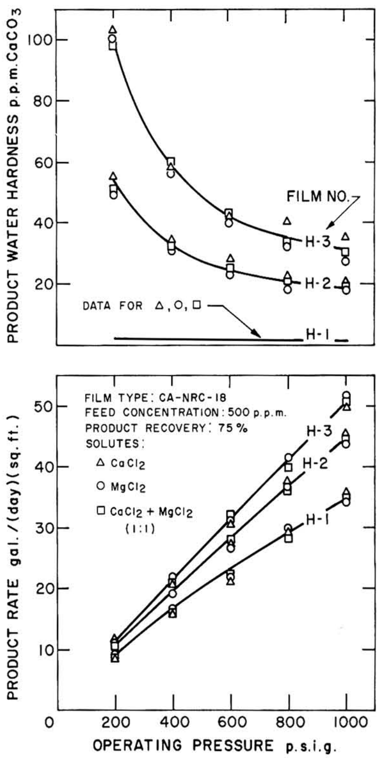

Figure 1. Effect of pressure on membrane performance for reverse osmosis water softening

Table III illustrates the performance of film H-4 for the separation of iron, manganese, strontium, and aluminum ions present in low concentrations. The data also show that the reverse osmosis technique can be successfully applied for such separations.

Figure 1 shows the effect of pressure on the quality and flux of product water with a feed whose hardness was 500 p.p.m. Since solute separation generally decreases with decrease in operating pressure, data of the type presented in Figure 1 determine the minimum operating pressure necessary for specific applications. The results show that film H-1 gives product water hardness of 2 p.p.m. or less in the entire pressure range 200 to 1000 p.s.i.g. tested.

Table IV illustrates the performance of films H-1 and H-2 for softening some natural hard waters obtained from different sources.

The high solute separations and product rates obtained with the films used in this work indicate that reverse osmosis can be successfully used for the economic treatment of industrial and natural hard waters to give product waters of

Table V. Results of Repeated Reverse Osmosis Operation[a]

System	Feed Water[b] Hardness, P.P.M. $CaCO_3$	Product Water Recovery, %	Hardness, p.p.m. $CaCO_3$	Product rate, gal./(day) (sq. ft.)
$CaCl_2$–H_2O	2.25	25	0.125	35.2
		50	0.125	35.8
		75	0.175	35.2
	2.54	90	0.225	36.6
$MgCl_2$–H_2O	2.14	25	0.120	35.2
		50	0.140	35.7
		75	0.140	35.9
	2.18	90	0.260	36.6

[a] Film H-1. Operating pressure 1000 p.s.i.g.
[b] Product obtained from once-processed hard water.

acceptable quality for domestic use as well as for high pressure boilers.

Production of Ultrapure Waters by Repeated Application of Reverse Osmosis. The development of new industries in the electronic, semiconductor, and nuclear areas, and the expansion of many old industries such as the pharmaceutical, utility, and electrochemical fields have created a demand for large quantities of "ultrapure" water. A leading contributor to the field of production of ultrapure water is the electrical power industry. The use of boilers operating at or close to supercritical pressure is on the increase. Typical specifications for feed water quality for subcritical boilers (operating at 1800 to 2400 p.s.i.g.), and supercritical boilers (operating at pressures >3200 p.s.i.g.) are, respectively, 0.5 and 0.05 p.p.m. total dissolved solids (Calmon and Kingsbury, 1966). Such ultrapure waters can be produced by repeated application of the reverse osmosis process to the available feed water. This is illustrated in Table V, where the feed used was a composite sample of the product waters obtained from the once processed hard waters (hardness = 300 to 800 p.p.m. $CaCO_3$). The product water obtained by the twice-operated reverse osmosis process (Table V) is already suitable as feed for subcritical boilers. An additional reverse osmosis processing of the above waters can give waters suitable as feed for supercritical boilers. In view of the facts that the data given in Tables I and V refer to 90% recovery, and the product rates obtained are sufficiently high (~36 gallons per day per sq. foot at 1000 p.s.i.g.), the technique of repeated operation of the reverse osmosis process might prove economical for the production of large quantities of ultrapure waters.

Table VI. Separation of Some Water Pollutants[a]

System	Solute Concn. in Feed, P.P.M.	Product Solute concn., P.P.M.	Product rate, gal./(day) (sq. ft.)
$NaNO_3$–H_2O	492	87	27.3
$Na_2B_4O_7$–H_2O[b]	524	16	26.1
NaF–H_2O	505	26	26.4
NaCl–H_2O	507	78	27.6
ABS–H_2O	95	<1	20.9
ABS–H_2O	300	<1	19.6
NH_4NO_3–H_2O	487	97	23.2
Na_3PO_4–H_2O	480	3	20.4

[a] Film H-4.
Operating pressure 1000 p.s.i.g.
Product recovery 90%
[b] pH of feed = 9.0.

Table VII. Separation of Some Salts Present in Plating Wastes[a]

System	Solute Concn. in Feed, P.P.M.	Product Solute concn., p.p.m.	Product rate, gal./(day) (sq. ft.)
$ZnSO_4$–H_2O	535	48	20.7
$Pb(CH_3COO)_2$–H_2O	504	32	20.4
$CuSO_4$–H_2O	500	8	19.2
$NiCl_2$–H_2O	500	14	19.2
CrO_3–H_2O	512	22	21.5
$SnCl_2$–H_2O	500	49	20.8
$AgNO_3$–H_2O	500	135	22.6
$Fe(SO_4)_2(NH_4)_2$–H_2O	525	19	20.1
$Ni(SO_4)_2(NH_4)_2$–H_2O	515	22	20.9
$Cr(SO_4)_3$–H_2O	500	9	22.1
$HAuCl_4$–H_2O	500	109	19.1

[a] Film H-4.
Operating pressure 1000 p.s.i.g.
Product recovery 90%.

Separation of Common Water Pollutants. Excessive amounts of nitrates, borates, fluorides, chlorides, phosphates, ABS, and ammonium ions are usually regarded as pollutants in municipal and industrial water supply. Nitrates and phosphates serve as nutrients for the growth of algae and other aquatic plants which render the water unfit for recreational and other uses; further, fish and other aquatic life are deprived of oxygen by the decomposing algae and plant life. While small concentrations of fluorides appear beneficial in reducing the prevalence of dental caries, excessive amounts of fluorides are definitely associated with the prevalence of mottled teeth in many communities. Excessive amounts of nitrates are held responsible for some infant illnesses (Fair and Geyer, 1961a), and excessive amounts of chlorides render the water unfit for drinking. The presence of ABS even in concentrations of only 1 p.p.m. will produce substantial frothing and, being nonbiodegradable, it will accumulate in water, producing very undesirable foams. The pretreatment of water for the removal of the above pollutants may be necessary in many water supply systems. Table VI shows that the above pollutants can be effectively removed by the reverse osmosis process. As pointed out earlier, the solute separations given in Table VI do not represent the limits obtainable by the reverse osmosis process. By the appropriate choice of the porosity of the preshrunk membrane, practically any degree of solute separation can be obtained. The data presented in Table VI show that the separations and product rates obtainable with the type of films used in this work are sufficiently significant for consideration for practical industrial applications.

Separation of Pollutants from Plating Wastes. The waste effluents from metal finishing plants contain numerous toxic constituents (Promisel, 1960). The toxicity limits to fish life with respect to, for example, copper, lead, zinc, and chromium are 0.02, 0.1, 0.1, and 1.0 p.p.m., respectively (Hawksley, 1967). Hence the treatment of plating wastes, especially dilute wastes, is a serious problem in the metal-finishing industry. Since profuse rinsing is a prerequisite of a sound finish, very large quantities of water are involved; and some of the waste constituents have economic value (Lancey, 1955).

Consequently, the problem of treating plating wastes is important from the points of view of water pollution control, water re-use, and waste recovery. The data presented in Table VII illustrate the possible applicability of the reverse osmosis technique for the removal of substances present in plating wastes. The data given are for 90% recovery in a single-stage reverse osmosis process using ~500 p.p.m. of solutes. The actual concentration of solutes in plating wastes is usually much less. Since the same degree of separation can be expected at lower concentrations also, more than one reverse osmosis processing may not be necessary in many situations. In any case, by repeated operation of the process with 90 to 95% recovery in each operation, product water of any desired quality can be obtained along with concentrated solutions suitable for waste recovery.

Table VIII. Reverse Osmosis for Sewage Water Treatment[a]

Solute or Equivalent	Solute Concn. in Feed, P.P.M.	Operating Pressure, P.S.I.G.	Product	
			Solute concn., p.p.m.	Product rate, gal./(day) (sq. ft.)
B.O.D.	24	1000	3	29.6
	46	1000	8	35.8
	37	1000	2	38.4
	25	1000	5	31.0
	36	1000	5	28.7
	44	500	15	14.6
	46	500	8	16.2
	24	500	5	19.6
	37	500	7	18.8
	21	500	4	18.4
NO_3^-	0.24	1000	0.1	34.2
	0.50	1000	0.25	34.0
	0.07	1000	0.03	28.7
PO_4^-	2.5	1000	0.01	34.2
	1.8	1000	0.01	34.0
	3.5	1000	0.02	29.7
ABS	0.7	1000	0.05	29.6
	0.8	1000	0.05	35.8
	0.4	1000	0.02	38.4
	1.2	1000	0.08	31.0
	1.5	1000	0.10	28.7
	1.8	500	0.20	14.6
	0.8	500	0.08	16.2
	1.2	500	0.01	19.6
	1.1	500	0.01	18.8
	1.3	500	0.01	18.4
Total dissolved solids	284	1000	32	29.6
	454	1000	9	35.8
	76	1000	0.1	38.4
	324	1000	9	31.0
	278	1000	7	28.7
	434	500	49	14.6
	385	500	19	16.2
	350	500	30	19.6
	265	500	23	18.8
	294	500	62	18.4

[a] Film No. H-5.
Feed raw sewage water.
Product recovery 90%.

Reverse Osmosis for Sewage Water Treatment. The present primary and secondary sewage treatment facilities have as their main objectives the removal of B.O.D. and suspended solids. These treatments are not designed to remove nitrates, phosphates, or the nonbiodegradable surfactants. The removal of the latter would be the objective of tertiary sewage treatment facilities which are not in extensive use today. Reverse osmosis can effectively take the place of tertiary treatment, and sometimes both secondary and tertiary treatments, and offers an effective means of upgrading sewage water to a quality practically suitable for all water uses. Some pilot plant results of sewage water treatment by reverse osmosis have been reported (Bray *et al.*, 1965; Sudak and Nusbaum, 1968). Table VIII gives the results obtained with a typical film and a number of samples of raw sewage water obtained from the Ottawa City primary sewage treatment plant. Experiments were made at two operating pressures, 1000 and 500 p.s.i.g., with particular reference to the removal of B.O.D., nitrate, phosphate, ABS, and total dissolved solids. The performance of the membrane was found to be very good with respect to the removal of all the above contaminants. The average B.O.D. removals were 85.8 and 80.8% at 1000 and 500 p.s.i.g., respectively. Under the conditions of the experiments made, the average separations of nitrates, ABS, and phosphates were 50.3, 93, and >99%, respectively. The average product rates were 32.7 and 18.3 gallons per day per sq. foot at 1000 and 500 p.s.i.g., respectively. The above results indicate that the reverse osmosis process using the type of porous cellulose acetate membranes used in this work has the potentialities of becoming an economic means of renovation of waste waters.

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Nomenclature

A	= pure water permeability constant, gram mole H_2O/sq. cm. sec. atm.
c	= molar density of solution, gram mole per cc.
d	= effective diameter of membrane surface, cm.
D	= diffusivity of solute, sq. cm. per sec.
$(D_{AM}/K\delta)$	= solute transport parameter, cm. per sec.
k	= mass transfer coefficient, cm. per sec.
M_B	= molecular weight of water
N_B	= water flux through membrane, gram moles per sq. cm. per sec.
N_{Sc}	= Schmidt number
N_{Sh}	= Sherwood number
P	= operating pressure, atm.
[PR]	= product rate, grams per hour per 9.6 sq. cm. of film area
[PWP]	= pure water permeability, grams per hour per 9.6 sq. cm. of film area
X_A	= mole fraction of solute
$\pi(X_A)$	= osmotic pressure corresponding to X_A, atm.
ν	= kinematic viscosity of feed solution, sq. cm. per sec.

SUFFIXES

1 = bulk solution on high pressure side of membrane
2 = boundary solution on high pressure side of membrane
3 = product solution

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Volumetric Calibration of Permeation Tubes

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■ Alternative means were needed for calibration of permeation tubes used to generate accurately known low concentrations of gases for use as standards. A microgasometer technique was developed employing a compensated Warburg syringe manometer with a sensitivity of 0.1 μl. The average 95% confidence interval was $\pm 1\%$ for rate measurements made over 1- to 2-hour periods on sulfur dioxide permeation tubes; agreement with gravimetric calibrations was good. The theoretical relationships are given for rate calculations with allowances for temperature, pressure, solubility, and compressibility corrections. The method is a simple, rapid, inexpensive, and broadly applicable fundamental technique.

Permeation tubes have been developed as simple, convenient, and accurate means for generating accurately known low concentrations of gaseous pollutants to serve as standards for testing and calibration. O'Keeffe and Ortman (1966) showed that liquefiable gases such as sulfur dioxide, nitrogen dioxide, various hydrocarbons, halogenated compounds, ammonia, and hydrogen sulfide, when enclosed in tubes of inert plastic such as FEP Teflon, escape by permeating the tubing walls at constant, reproducible, temperature-dependent rates. Such tubes also have been prepared for anhydrous hydrogen fluoride (Jacobson, 1967), and for phosgene and organic mercury compounds (Linch, Stalzer, *et al.*, 1968). Scaringelli, Frey, *et al.* (1967) demonstrated exact equivalence between weight losses of sulfur dioxide permeation tubes and measurements made both colorimetrically and microcoulometrically. Thomas and Amtower (1966) also reported successful tests. Sulfur dioxide permeation tubes were collaboratively tested in the Analytical Methods Evaluation Service Study No. 1 (Saltzman, 1968; Tye, O'Keeffe, *et al.*, 1968), with favorable results.

Devices such as thermal conductivity and flame ionization detectors can serve as secondary standards; however, they ordinarily determine only relative values, and must be calibrated with known quantities of the test substances. Primary standards, on the other hand, are prepared by techniques involving calibrations by weight, volume, pressure, coulometry, etc., in an accurate and preferably convenient manner.

Because permeation tubes are used as primary standards, convenient and accurate techniques are needed for their calibration. Most of such work has been done by gravimetric measurements; however, this method requires maintaining the tubes at precisely controlled temperatures for

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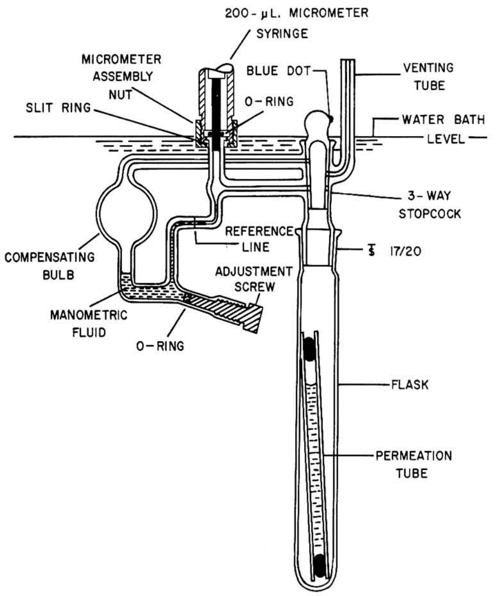

Figure 1. Schematic diagram of microgasometer assembly submerged in water bath

Apparatus, except for flask, commercially available as Gilmont Warburg compensated syringe manometer. Capacity of micrometer syringe, 200 μl., in 20 turns with 0.2-μl. divisions. Stopcock, shown in venting position, is turned 180° for operation

several weeks to get sufficient weight losses for accurate determinations. Colorimetric and coulometric techniques require special reagents or equipment. This report deals with the volumetric calibration of permeation tubes. A microgasometer technique is recommended as a simple, rapid, accurate, and broadly applicable alternative means of measuring the gas permeation rates. It is especially convenient for substances such as hydrocarbons, which otherwise could not be conveniently determined in a primary standard manner with microgram sensitivities. The work reported was conducted with sulfur dioxide permeation tubes of the type used in the collaborative study.

Apparatus

The apparatus was a Gilmont compensated Warburg syringe manometer (Figure 1). The microgasometer was completely submerged in a water bath to maintain a known constant temperature. Volumetric measurements were made with a Gilmont micrometer syringe having a capacity of 200 μl. in 0.2-μl. divisions (10 μl. per turn), and fabricated of polypropylene. The permeation tube was placed in the test tube flask shown at the lower right of the figure, connected to the syringe manometer at the ₮ 17/20 joint. During operation the vent outlet of the apparatus was closed. The measurements therefore were independent of changes in barometric pressure during a run. The closed compensating bulb connected to the manometer on the side opposite the flask prevented minute changes in bath temperature from inducing any pressure differentials.

The permeation tubes tested were constructed of FEP Teflon tubing, 5 inches long, of $^1/_4$-inch outside diameter and 0.03-inch wall thickness and were filled with liquid sulfur dioxide (at approximately 3-atm. pressure). Each end was sealed with a 1-cm. length of FEP Teflon rod and clamped with a crimped aluminum band.

In initial work a constant-temperature bath was employed. Because its intermittent heating and cooling produced excessive fluctuations of the measured volumes, later runs were made with an insulated 20-gallon plastic container filled with water. The top was covered with a piece of Plexiglas whenever adjustments were not being made. This heat sink was adequate for the purpose; for more constant temperature, one can insert a metal coil through which thermostatically controlled water is circulating.

Procedure

The apparatus was carefully cleaned, so that the manometer fluid presented a good meniscus at the reference line. The three-way stopcock was greased with fluorosilicone grease and left in the vented position (blue dot facing venting outlet). The flask joint also was greased.

The manometric fluid for this work was *n*-nonane containing a few hundredths of 1% of a nonionic surfactant (SAG-47; Union Carbide Corp.). The solubility of sulfur dioxide in this liquid was so slight that no corrections were necessary. (In later work dodecane without a surfactant was used successfully.)

The adjustment screw was removed, and 1.3 ml. of nonane were introduced from a pipet into the apparatus. The volume of fluid was adjusted so that upon replacement of the adjustment screw the meniscus in the horizontal capillary was near the reference line. The screw and capillary were examined carefully, and any bubbles were discharged at the compensating bulb. Care was taken never to allow the nonane to wet the stopcock joint, since this necessitated cleaning and regreasing the joint.

The flask containing the permeation tube was connected to the apparatus with the stopcock in the venting position, and the system was submerged in the heat sink, as shown in Figure 1. The micrometer screw was set initially to extend the plunger fully. The adjustment screw was turned so that the meniscus of the manometer fluid was close to the reference line. One hour sufficed to reach thermal equilibrium if the tube and the water bath were initially at a controlled constant temperature close to the ambient value. The stopcock was then turned 180° to the closed operating position. The micrometer screw was turned to bring the meniscus of the manometric fluid a few millimeters to the right of the reference line and the volume reading was noted. A stopwatch was started at the exact moment when the permeating sulfur dioxide pushed the meniscus past the reference line. After 10 or more minutes, the meniscus was returned to a position just to the right of the reference line by readjusting the micrometer screw, and the volume reading again was noted. At the moment when the meniscus crossed the reference line for the second time, the stopwatch reading was noted. This procedure was repeated without stopping the watch for a number of additional intervals up to a total time of about 2 hours.

Results

Early runs were made with water as a manometer fluid, but constant permeation rates could not be obtained because of the solubility of the sulfur dioxide in this liquid. Good results were then obtained with nonane.

Figure 2 is a plot of volume *vs.* time for seven runs conducted on four permeation tubes. Very close adherence to a linear relationship was observed for volumes up to 200 μl. The slopes of the lines, which represent the permeation rates in microliters per minute, were determined by fitting straight

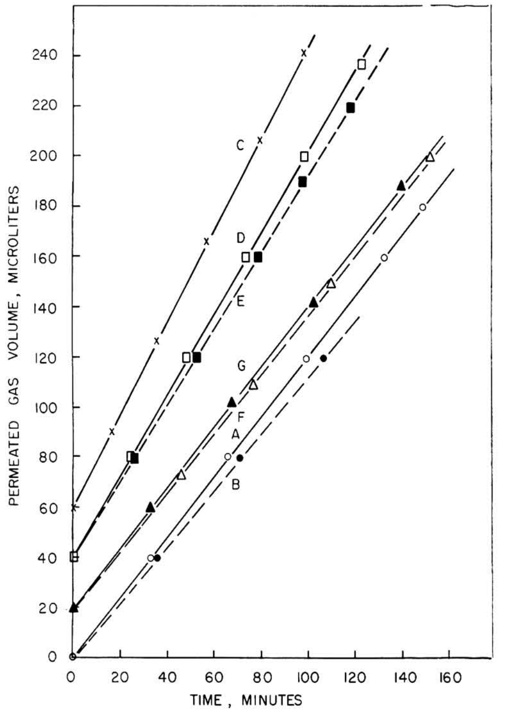

Figure 2. Volumetric calibrations of four sulfur dioxide permeation tubes

Letters refer to run designations, at different temperatures listed in Table I. Lines displaced vertically for easier visibility

○, ● Tube 1
X Tube 2
□, ■ Tube 3
△, ▲ Tube 4

lines to the points by the method of least squares. In this calculation the volume reading at zero time was taken as one point of equal statistical weight with the other measurements. The fitted lines thus did not necessarily pass through these initial readings; the intercepts differed from the latter by amounts ranging from −0.8 to +0.5 μl. The average difference was +0.07 μl. The slopes obtained from these calculations are given in the eighth column of Table I. The 95% confidence interval of each slope, expressed in per cent, is indicated in the ninth column. This averaged about 1%, which is very satisfactory considering the microvolumes that were measured in the short times. Accurate results can be obtained with measurements over intervals of even less than an hour.

The validity of these measurements was determined by comparing them with earlier gravimetric calibrations of the same tubes (Table II). After the weighings were completed, the volumetric measurements were conducted at various times over a period of a month and a half. Thus there were intervals of several weeks between the two sets of measurements.

Calculations

Because of the high temperature coefficient of the permeation rate, it was necessary to correct all measurements to a standard temperature, taken as 25°C., for comparisons.

The calculations for converting the slope, S, of the volumetric measurements to the gravimetric rate at 25°C. were made by means of Equation 1. A correction of about 4 Torr was required for the vapor pressure of the nonane. Assumedly, as the volume expanded, additional nonane evaporated to maintain this vapor pressure. (This correction was negligible for dodecane used in later work; at 25°C. its vapor pressure is only 0.13 Torr.)

$$G_o = S \frac{298.16}{(t + 273.16)} \frac{(P - p)}{760} \frac{W}{24.47} B \qquad (1)$$

where G_o = gravimetric rate, μg. per minute, corrected to 25°C.
S = experimental volumetric rate, μl. per minute
t = temperature, °C.
P = barometric pressure, Torr, at the moment the microgasometer vent was closed
p = vapor pressure of manometer fluid, Torr, at t°C.
W = molecular weight of test gas (=64.066 for SO_2)
B = gravimetric temperature correction factor, G_o/G
24.47 = gram molecular volume, liters, at 25°C., 760 Torr

Several investigators (O'Keeffe and Ortman, 1966; Scaringelli, Frey, *et al.*, 1967) have shown that the variation of the gravimetric permeation rate with temperature follows the quantitative relationship in Equation 2, which is similar to that for a chemical reaction. The activation energy was 14,540 cal. per gram mole. Only about a third of this was accounted for by the heat of vaporization of liquid sulfur dioxide. The remainder was required for the activated diffusion process. The molecules of sulfur dioxide rupture the weak intermolecular bonds of the Teflon as they move through the walls of the tube in a series of discontinuous jumps. The energy of bond recombination behind them is dissipated and lost.

Since the gravimetric corrections were applied over a relatively small temperature range, a few degrees centigrade, the calculations were simplified. The approximation in Equation 3 leads to the final relationship shown in Equation 4. This latter equation gave results within 2 parts per thousand of the exact Equation 2 for this work.

$$\ln\left(\frac{G}{G_o}\right) = -\frac{E}{R}\left[\frac{1}{T} - \frac{1}{T_o}\right] \qquad (2)$$

$$\frac{1}{T} - \frac{1}{T_o} = \frac{1}{T_m^2}(T_o - T) \qquad (3)$$

$$\log_{10}\left(\frac{G_o}{G}\right) = \log_{10} B = K(25 - t) \qquad (4)$$

where G = gravimetric rate, μg. per minute
E = activation energy, cal. per gram mole
R = gas constant, 1.986 cal. per gram mole
T = absolute temperature, °K. (=t + 273.16)
T_o = standard temperature, 298.16°K. (=25°C.)
T_m = mean temperature, $(T_o + T)/2$
K = empirical constant determined for each type of permeation tube (=0.03637 for these tubes in range 20° to 25°C.)

Final results of these temperature correction calculations for the volumetric calibration data are shown in the last column of Table I, and for the gravimetric calibrations in the fourth column of Table II. The ratios of the corrected rates determined by the two techniques are indicated in the sixth column of Table II. The rates from the volumetric measurements averaged about 3% higher than those from the gravimetric measurements. In view of the long time interval be-

Table I. Volumetric Calibration Data

Tube No.	Run	Mean Temp., °C.	Temp. Range, °C.	Initial Press., Torr	No. of Run, Min.	No. of Points	Calcd. Slope, μl./Min.[a]	95% Confidence Interval of Slope, %	Calcd. Grav. Rate at 25°C., μg./Min.
1	A	22.19	0.06[b]	744.9	149	6	1.209	0.48	3.943
	B	21.61	0.04	750.2	106	4	1.128	0.76	3.900
2	C	24.18	0.22	753.9	98	6	1.839	0.34	5.101
3	D	23.56	0.11	752.5	122	6	1.618	1.08	4.731
	E	23.01	0.15	751.1	118	6	1.528	0.80	4.679
4	F	22.44	0.10	745.0	152	5	1.187	2.10	3.787
	G	22.16	0.43	744.5	140	5	1.205	1.72	4.297

[a] Straight line fitted to experimental points by method of least squares.
[b] Constant temperature bath utilized; all other runs with heat sink water bath.

tween the two sets of measurements and the different techniques involved, this agreement is good.

Corrections for Gas Solubility

To outline the theoretical limitations for general applications of this method, calculations were made to determine the corrections for the solubility of the test gas in the manometer fluid. The total volume of permeated gas is equal to the sum of the gas present in the air space and that dissolved in the manometer fluid. The volume of dissolved gas is proportional to the volume of liquid and to the mole fraction of test gas in the air space; it is corrected from 0°C. (the usual standard gas temperature for published values of solubility coefficient, α) to t°C. The correction for solubility is given by the last term on the right of Equation 5:

$$V = (V_2 - V_1) + \alpha v \frac{(V_2 - V_1)}{V_2} \frac{(t + 273.16)}{273.16}$$

or

$$V = (V_2 - V_1)\left[1 + \frac{\alpha v}{V_2} \frac{(t + 273.16)}{273.16}\right] \quad (5)$$

where V = total volume of permeated gas, ml. [t°C., $(P - p)$ Torr]
V_2 = final gas volume, ml
V_1 = initial gas volume, ml.
v = volume of manometer fluid, ml.
α = solubility coefficient of test gas in manometer fluid at temperature t, ml. of gas (0°C., 760 Torr) per ml. of liquid

For the present work with sulfur dioxide and nonane, the value of α was estimated to be 0.03, about the same as for O_2 in water at 25°C. (α for CO_2 is 0.76). Since v is 1.3 ml. and V_2 about 50 ml. for the flask and apparatus, the fraction $\alpha v/V_2 = 0.03 \times 1.3/50 = 0.0008$. The temperature correction factor at 25°C. is 1.0915. The product of these numbers is negligible compared with the value of unity in the preceding term.

In an extreme case, for a very low permeation rate and a soluble test gas, a little test gas could leak into the compensating bulb. With proper choice of manometer fluid, these corrections can be made negligible.

Corrections for Gas Compressibility

The foregoing calculations were made on the basis of ideal gas volumes. For some gases, however, deviations from the perfect gas law occur within ambient pressures and temperatures. Estimates of these errors for common applications were therefore developed.

These deviations are usually expressed as the compressibility factor, z, defined as the ratio of the actual to ideal gas volume. If compressibility data for a specific gas are not available, a generalized plot may be employed. This expresses the relationships among compressibility, reduced pressure (ratio of actual to critical pressure for the substance), and reduced temperature (ratio of actual absolute temperature to critical absolute temperature). Such calculations were made assuming 25°C. temperature and 1-atm. partial pressure for acetylene, ammonia, butane, hexane, hydrogen sulfide, pentane, propane, and sulfur dioxide. Reduced temperatures ranged from 0.63 to 0.97, and reduced pressures from 0.01 to 0.03. A generalized plot extending to these low reduced pressures (Saltzman, 1958) indicated compressibility factors ranging from 0.99 to 0.95. However, if the gas partial pressures were taken as 0.1 atm., in all cases the compressibility factors were between 0.99 and 1.00. A single run can be made with less than 500 μl. of permeated gas, including

Table II. Comparison with Gravimetric Calibration Data

Tube No.	Weight Loss, G.[a]	Grav. Rate, μg./Min[a]	Calcd. Grav. Rate at 25°C., μg./Min. From gravimetric data	Calcd. Grav. Rate at 25°C., μg./Min. From volumetric data	Ratio Vol. to Grav. Rate	Deviation from Mean Ratio, %
1	0.0644	2.984	3.759	3.922[b]	1.043	+1.2
2	0.0839	3.888	4.898	5.101	1.042	+1.0
3	0.0812	3.763	4.740	4.705[b]	0.993	−3.9
4	0.0661	3.063	3.858	4.042[b]	1.048	+1.6
				Mean	1.031	

[a] Weight loss during 21,580-minute interval (approx. 15 days), at mean temperature of 22.24°C., temperature range 0.05°C.
[b] Mean of two runs.

equilibration time in the vented position. Assuming a total flask and apparatus volume of 50 ml., the test gas partial pressure easily could be kept below 0.01 atm., and the compressibility correction can thus be kept negligible.

In the case of nitrogen dioxide, however, corrections are appreciable because of the equilibrium between the monomer and the dimer:

$$2\ NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$$

Some calculations showed that the effective compressibility factors (on a monomer basis) decreased in an approximately linear manner from 1.00 to 0.94 as the partial pressure of $NO_2 + N_2O_4$ increased from 0 to 0.01 atm.

The correction is calculated as follows:

$$V' = \frac{(V_2 - V_o)}{z_2} - \frac{(V_1 - V_o)}{z_1} \quad (6)$$

where V' = corrected ideal volume of permeated gas, ml. [t°C., $(P - p)$ Torr]

$(V_2 - V_o)$ = total permeated gas volume in apparatus at end of run

$(V_1 - V_o)$ = total permeated gas volume in apparatus at beginning of run

z_2 = compressibility factor at end of run

z_1 = compressibility factor at beginning of run

Application of this exact equation is difficult, because only $(V_2 - V_1)$ is experimentally measured during the run. A close approximation is more convenient:

$$V' = \frac{(V_2 - V_1)}{{z_m}^2}$$

where z_m = mean of compressibility factors at beginning and end of the volume measurement.

The mean compressibility factor is that for the mean partial pressure of gas. This may be calculated from the time interval beginning at the moment when the permeation tube is placed in the flask and connected to the apparatus, until the middle of the measuring run. It may be assumed that the vented gas is essentially only air.

Available nitrogen dioxide permeation tubes have a relatively short life. Calibration by the rapid volumetric method thus would be more advantageous than by the slower gravimetric method.

In the case of hydrogen fluoride, the following reactions occur:

$$n\ HF\ (g) \rightleftharpoons (HF)_n\ (g)$$

At ordinary temperatures, the vapor is a mixture of the monomer and polymers up to $n = 8$; of the polymers, the trimer and tetramer are most abundant. The fraction of polymers increases with partial pressures of the gas and of water vapor as well as with decreasing temperature. At low pressures the gas is essentially the monomer. Thus volumes may require a polymerization correction, but such data are not now available. The compressibility corrections on the basis of the critical pressure and temperature were found to be negligible by means of the generalized plot. This calibration, of course, could not be carried out in a glass apparatus because of chemical reaction.

Discussion

Mathematical correction equations have been presented for effects of gas solubility and compressibility. One other effect that should be considered is the reduction of permeation rate because of gas partial pressure in the apparatus. The driving force for the permeation process is the difference in gas pressure inside and outside the tube. An appreciable percentage change in this difference as the gas accumulates outside the tube will occur only for substances having vapor pressures of about 1 atm. or less at ordinary temperatures, such as hexane, pentane, hydrogen fluoride, and nitrogen dioxide. With proper choice of manometer fluid and with short runs, all these corrections can be kept at a negligible level.

The volumetric calibration technique should be broadly applicable to all types of permeation tubes. For gases such as hydrocarbons, the use of manometer fluids such as water and stopcock lubricants based on glycerol would be more appropriate. The technique has been demonstrated to be simple, rapid, and accurate, and requires relatively inexpensive apparatus. It is recommended as a useful means of calibrating permeation tubes.

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Size-Separating Precipitation of Aerosols in a Spinning Spiral Duct

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■ A new instrument is described, facilitating particle size spectrometry and size distribution analysis of aerosols in terms of aerodynamic diameters. The aerosol particles are precipitated according to their aerodynamic size along a strip foil about 180 cm. in length. This foil forms the outer wall of a spiral duct, which is cut into a plane disk mounted on the rotor of a special centrifuge. Aerosol flow rates of up to 3 liters per minute can be fed into the centrifuge rotor at the center of rotation, where the aerosol is entrained into a laminar flow of clean air passing by the aerosol inlet and traveling through the spiral duct to the perimeter of the rotor. Total flow rate, aerosol intake, and rotor speed can be varied independently. This provides various operating conditions to be set for optimum performance with regard to deposition range, sampling rate, and size resolution. During a single test run, the instrument precipitates aerosol particles that differ in size by about two orders of magnitude. Best results are obtained at a rotor speed of 3000 r.p.m., where the centrifuge precipitates aerosol particles of sizes between 5×10^{-4} cm. and at least 8×10^{-6} cm. in diameter with a reasonably high degree of size resolution in different locations along the strip foil. For sizes above 3×10^{-5} cm., an excellent size resolution is obtained which facilitates the determination of aerodynamic diameters of aggregates of uniform spheres which differ only by their geometrical configuration. Calibration curves as obtained with latex spheres under different operating conditions are given to demonstrate the performance of the instrument. The influence of secondary flow patterns in the spiral duct is investigated, and an estimate of the entrance losses of the aerosol is given.

In 1950, five years after May (1945) had introduced the principle of cascade impaction for the size separation of airborne particles, Sawyer and Walton (1950) built the first centrifugal device capable of separating aerosols into a continuous spectrum of sizes. The instrument, called a conifuge, deposited the particles according to their aerodynamic size along the outside wall of a conical annular duct. In spite of the promising aspects of this design, the cascade impactor remained for a long time the only precipitator for size-selective sampling of airborne particles. In later years, another principle of centrifugal precipitation of airborne particles was introduced (Goetz, Stevenson, *et al.*, 1960; Kast, 1961) which partially abandoned the desired size separation in favor of a higher sampling rate. These instruments had curved quadrangular ducts and achieved merely a quasi-cumulative size distribution of the precipitate. Due to the complexity of the deposition patterns, however, great difficulties were encountered in attempts to devise a mathematical method for an accurate size distribution analysis (Stöber and Zessack, 1964). This and other drawbacks put serious restrictions on the general applicability of such cumulative centrifugal devices. It is surprising that during that period of quest for a real aerosol-size spectrometer, the size-separating conifuge principle of Sawyer and Walton has not been utilized again, except for one aerosol size distribution study on cigarette smoke (Keith and Derrick, 1960).

In recent years, however, with the growing interest in small, respirable airborne particles in the micron and submicron size range, attempts were revived to improve size-separating precipitation by centrifugal devices. A number of publications appeared in the literature describing instruments which all made use of the conifuge principle (Berner, 1968; Hauck and Schedling, 1968; Stöber, 1967; Tillery, 1967). In all of these designs, the aerosol is fed into a spinning annular duct with a coaxial flow of clean air, which is traversed by the aerosol particles according to their aerodynamic diameter. Stöber and Flachsbart (1969) critically reviewed these efforts. Although the sampling rate can be improved considerably in comparison to the original design of Sawyer and Walton, it became apparent that within the dimensions of a feasible design of this kind, an acceptable resolution of sizes is confined to a size range of, at best, one order of magnitude. For a desirable extension of this range, it seems to be necessary to abandon the conifuge principle and develop an instrument which provides an extended path length along which the particles can be separated.

This paper describes a new design which uses a spiral duct of rectangular cross section cut into a special centrifuge rotor. The instrument is a true aerosol-size spectrometer and facilitates excellent size resolution over a size range of almost two orders of magnitude, while the aerosol sampling rate is of the order of 1 liter per minute.

Design of the Spiral Centrifuge

The essential part of the new device is a spiral duct cut into the disk-shaped rotor of a centrifuge. Figure 1 shows a photograph of the top of the rotor disk. The arrow indicates the direction of rotation. The disk has a diameter of 26.2 cm. The spiral duct consists of six semicircles of different radii. It has a straight, almost radial, extension beyond the center of the rotor. The height of the duct parallel to the axis of the rotor is 3.30 cm. The width is 1.73 cm. at the center of the rotor and narrows down to 1.00 cm. at the outer end of the first semicircle. From there on, the rest of the spiral duct is of constant width. Along the outer wall of the spiral section of the duct a small groove is cut into the bottom. It holds in place a chromium-plated brass foil of 0.015-cm. thickness and 179.5-cm. length. The foil is 3.35 cm. wide and forms a strip which covers the entire curved section of the outer wall.

While the rotor is spinning, clean air enters the duct through

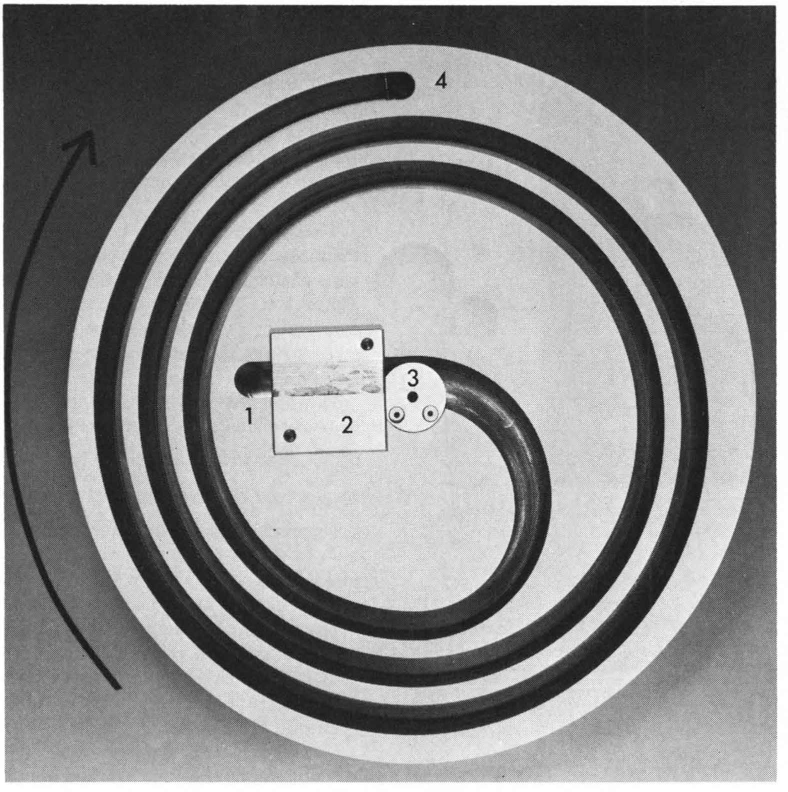


Figure 1. View of centrifuge rotor and spiral duct

the off-center air inlet, 1 (Figure 1), and flows to the inserted laminator, 2. In Figure 2 the laminator is removed from the rotor to show the five thin brass foils mounted parallel to the vertical walls of the rectangular duct. In this section, the clean air is quickly stabilized and emerges as a laminar flow from the downstream end. It then approaches an exchangeable aerosol inlet section, 3, at the center of the rotor. The aerosol enters the inlet section through the center bore and is released into the duct as an air sheath parallel to the inner wall of the duct, where it will be entrained into the laminar flow. Figure 3 shows an aerosol inlet section which was used in experiments with high aerosol flow rates. This particular design releases the aerosol through a set of short capillaries. For high-resolution tests, however, where reduced aerosol flow rates are required, another design was employed which had a narrow slit adjacent to the inner wall.

When leaving the center of rotation, the aerosol particles are subjected to the centrifugal forces of the spinning rotor and start moving in a radial direction across the laminar air stream. Their trajectories are determined by the operating conditions of the centrifuge and the aerodynamic size of the particles. Thus, while the air is flowing down the duct to the outlet, 4, the particles are settling, according to their size, in different locations on the strip foil along the outer wall. For analysis of the deposit, the strip can easily be removed from the rotor.

Figure 4 is a schematic vertical section of the rotor assembly.

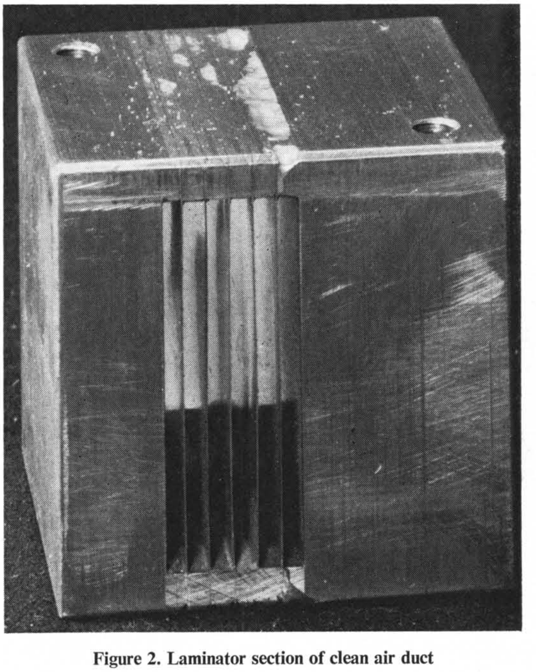


Figure 2. Laminator section of clean air duct

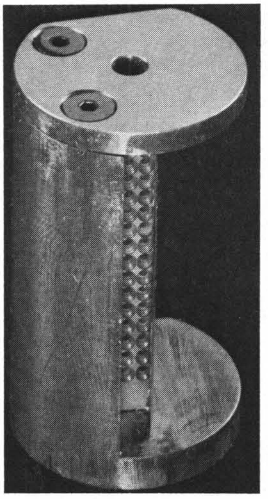


Figure 3. Aerosol inlet section (for relatively high aerosol flow rates)

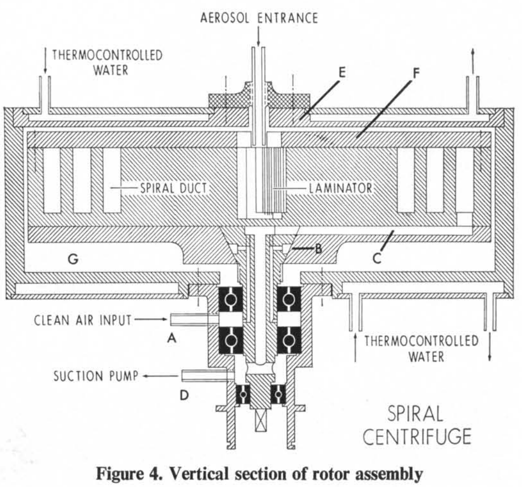


Figure 4. Vertical section of rotor assembly

It shows the housing and the technical arrangements for the air flow. Clean air under constant pressure is supplied to the air inlet, A (Figure 4), where it enters a chamber formed by the bushing of the rotor housing and two sealed ball bearings. Then, the air passes through six capillaries (only two of which are visible in Figure 4) parallel to the axis of the shaft and enters an annulus, B, from where a duct (invisible in Figure 4) leads to the air inlet of the spiral channel. When properly adjusted, the air pressure will be down to atmospheric level just before the flow reaches the center of the rotor. From there on, a subpressure supplied by a suction pump will maintain the flow through the rest of the conduit. After passing the spiral, the air enters a radial duct, C, at the perimeter of the rotor. This duct connects to a coaxial bore in the shaft, which opens into the exit chamber between the lower pair of sealed bearings. From here the air is finally removed by the suction line, D, which is operated at constant subpressure.

By varying and adjusting the pressure of the clean air supply and the subpressure of the suction line, a wide variety of flow rates can be established, independent of any selected rotor speed. A controlled excess suction at the outlet, D, generates a slight subpressure at the aerosol inlet section and, thus, controls the aerosol flow through the nonrotating aerosol duct of the housing lid, E, into the rotor.

The housing lid, E, is inserted into the cylindrical housing wall. By removing it and unscrewing the rotor lid, F, the spiral duct and the foil strip are accessible for inspection and analysis.

The housing of the rotor is made of copper to provide good thermal conductivity for the coolant ducts, which are integral parts of all outside walls (not all ducts are shown in Figure 4). The coolant is supplied by a thermostat and facilitates the temperature control of the instrument. The temperature is measured by means of thermoelements extending into the free space, G.

The rotor assembly is fitted to the drive unit of a commercial high-speed laboratory centrifuge (Sorvall, SS-3) and permits speeds up to 12,000 r.p.m.

Theoretical Considerations

None of the aerosol centrifuges with spinning curved ducts built in the past used the principle of entraining the aerosol into a flow of clean air, nor were they designed to give a real particle size spectrum. The new instrument, however, works as an actual size spectrometer. It is, in principle, the centrifugal version of a type of gravitational dust separator with a horizontal duct which has been used successfully for the size spectrometry of airborne particles of diameters above 10^{-4} cm. (Timbrell, 1954; Boose, 1962).

Since the new centrifuge provides complete size separation, it permits a simple empirical calibration with test aerosols and does not necessitate a mathematical method of size distribution analysis that depends upon theoretical models of the pattern of deposit concentrations. In view of this, the technical details of the instrument were chosen with little regard to the requirements of a feasible theoretical approach for a calculation of particle trajectories, location of deposition, or deposit concentrations under specific operating conditions of the centrifuge. Instead, priority was given to practical aspects, as long as a laminar flow in the duct was maintained and turbulent mixing of the aerosol with the clean air was avoided.

The spiral duct is composed of semicircles which are alternately eccentric and concentric with respect to the center of the rotor. In spite of the fact that this causes a rather odd relationship between the radius vector and the length of the outer wall, the semicircular arrangement was chosen because, for a given rotor diameter, it permits a greater length for the curved duct than in the case of an Archimedean spiral with continuously increasing radius vector.

The cylindrical coordinates of the spiral pattern of the outer wall of the duct and the length of the wall depending upon the radius vector are given by

$$0 \leq \phi \leq \pi \text{ (first semicircle)}$$

$$r = \sqrt{r_0^2 - a^2 \sin^2 \phi} - a \cos \phi \tag{1a}$$

$$l = r_0 \operatorname{arc\,cos} \frac{r_0^2 + a^2 - r^2}{2ar_0} + l_a \tag{2a}$$

$$\pi \leq \phi \leq 2\pi \text{ (second semicircle)}$$

$$r = r_0 + a \tag{1b}$$

$$l = (r_0 + a)(\phi - \pi) + \pi r_0 + l_a \tag{2b}$$

$$2\pi \leq \phi \leq 3\pi \quad \text{(third semicircle)}$$

$$r = \sqrt{(r_0 + a + k)^2 - k^2 \sin^2 \phi} - k \cos \phi \qquad (1c)$$

$$l = (r_0 + a + k) \text{ arc cos} \times \frac{(r_0 + a + k)^2 + k^2 - r^2}{2k(r_0 + a + k)} + \pi(2r_0 + a) + l_a \qquad (2c)$$

$3\pi \leq \phi \leq 4\pi$ (fourth semicircle)

$$r = r_0 + a + 2k \qquad (1d)$$

$$l = (r_0 + a + 2k)(\phi - 3\pi) + \pi(3r_0 + 2a + k) + l_a \qquad (2d)$$

$4\pi \leq \phi \leq 5\pi$ (fifth semicircle)

$$r = \sqrt{(r_0 + a + 3k)^2 - k^2 \sin^2 \phi} - k \cos \phi \qquad (1e)$$

$$l = (r_0 + a + 3k) \text{ arc cos } \frac{(r_0 + a + 3k)^2 + k^2 - r^2}{2k(r_0 + a + 3k)} + \pi(4r_0 + 3a + 3k) + l_a \qquad (2e)$$

$5\pi \leq \phi \leq 6\pi$ (sixth semicircle)

$$r = r_0 + a + 4k \qquad (1f)$$

$$l = (r_0 + a + 4k)(\phi - 5\pi) + \pi(5r_0 + 4a + 6k) + l_a \qquad (2f)$$

A graphical plot of the foil length, l, *vs.* the radius vector, r, is shown in Figure 5.

For the desired total flow rates of up to 20 liters per minute, laminar flow conditions were provided by selecting suitable dimensions for the cross section of the spiral duct. A conservative interpretation of existing experimental data (Cornish, 1928) shows that the critical Reynolds number for stable laminar flow in rectangular ducts is certainly not less than 1300 if we define

$$\text{Re} = \frac{\bar{v}}{\nu} \frac{4Q}{U} = \frac{2F}{(B_0 + H_0)\nu} \leq \text{Re}_{\text{crit}} \qquad (3)$$

From the design data of the instrument, we obtain

$$\text{Re} = 3.25F \leq \text{Re}_{\text{crit}} \qquad (4)$$

as a maximum value of the Reynolds number in the spiral duct. Accordingly, we may expect a stable laminar flow of up to 24 liters per minute.

If, in a first approximation, we disregard the curvature of the duct, we may make use of a general analytical solution for the stationary laminar flow in a straight rectangular duct (Cornish, 1928). The corresponding velocity profile is close to a superposition of two parabolic functions along the wall coordinates (Stöber and Zessack, 1964). For the spinning spiral duct, however, there will be a certain stationary deformation of such laminar flow. This effect is, in part, due to a special field of centrifugal forces which is caused by the curvature of the flow. It tends to move the air toward the outer wall of the duct. In addition, with the direction of rotation as shown in Figure 1, the eccentric semicircles generate Coriolis forces which result from the radial flow components and act toward the outer wall. Since the viscous flow of air along the streamlines is moving faster in the center of the duct than close to the walls, the correlated transversal forces are finally effecting a double vortex of secondary flow in the cross-sectional plane of the duct, as schematically shown in Figure 6.

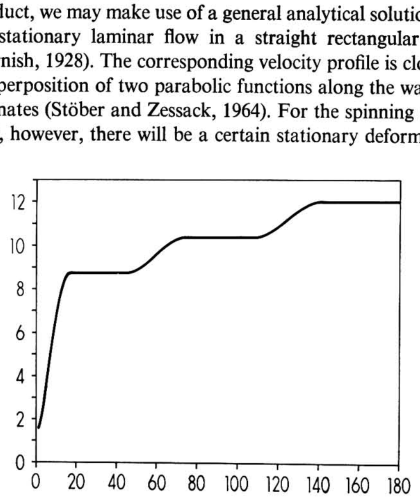


Figure 5. Relationship between radius vector r and distance l along the sampling foil

(abscissa: l in cm., ordinate: r in cm.)

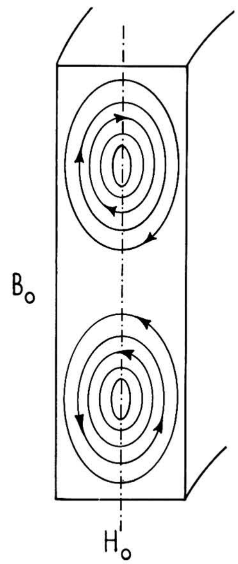


Figure 6. Schematic diagram of secondary flow in the cross-sectional plane of the air duct

The double vortex causes the laminar streamlines to form a pair of counter-rotating helices along the path of the duct. These helices will limit the effectiveness of the instrument. As long as the outward velocity components in the center of the duct are small compared to the radial particle velocities created by the centrifugal field of the spinning rotor, the vortex may be disregarded. This will be the case for sufficiently large aerosol particles. If, however, the outward velocity components of the vortex are comparable or even greater than the particle velocities, as in the case of sufficiently small aerosol particles, the properties of the vortex become increasingly predominant; the actual size resolution of the instrument will decrease, and finally disappear.

For an optimum performance of the instrument, operating conditions must be found so that the helices will not turn more than a fraction of one revolution along the total length of the spiral duct. Although this has to be done experimentally by trial and error, a computation of the forces normal to the outer wall of the duct as depending upon total flow and rotor speed is very useful for this purpose, because these forces are responsible for the vortical motion, and they may serve as an indicator of the degree of the flow deformations.

Neglecting the actual width of the duct, the centrifugal forces caused by the curved flow and acting upon a volume element of air are approximately described by

$$dK_{fl} = \rho_{air} b_{fl} dh \; db \; dl \qquad (5)$$

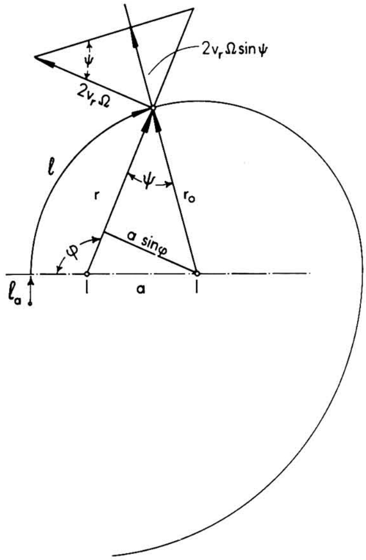


Figure 7. Diagram of Coriolis forces in the air duct

with the acceleration

$$b_{fl} = \frac{v^2}{R} \quad (6)$$

where R is the local radius of the curvature of the duct and v depends upon the cross-sectional coordinates b,h.

In addition to the centrifugal effect of the curved flow, there are Coriolis forces occurring in the eccentric semicircles of the duct. They cause a tangential acceleration

$$b_{cor} = 2v_r\Omega \quad (7)$$

which contributes to the acceleration normal to the wall of the duct. The components of these forces can be derived from geometrical relations, as shown for the first semicircle, where $R_0 \simeq r_0$, in Figure 7. We obtain from the graph

$$(b_{cor})_{norm} = 2v_r\Omega\sin\psi \quad (8)$$

where

$$\sin\psi = \frac{a\ \sin\phi}{r_0} \quad (9)$$

With the simple relation

$$v_r = \frac{dr}{dl}\,v \quad (10)$$

and, from Equation 2a,

$$\frac{dr}{dl} = \frac{a\ \sin\phi}{r_0} \quad (11)$$

the total acceleration normal to the outside wall is obtained by combining Equations 6 to 11. We find for

$0 \leq \phi \leq \pi$ (first semicircle)

$$b_{norm} = 2a^2\Omega\sin^2\phi \cdot \frac{v}{{r_0}^2} + \frac{v^2}{r_0} \quad (12a)$$

In a similar way, we obtain for

$\pi \leq \phi \leq 2\pi$ (second semicircle)

$$b_{norm} = \frac{v^2}{r_0 + a} \quad (13a)$$

$2\pi \leq \phi \leq 3\pi$ (third semicircle)

$$b_{norm} = 2k^2\frac{v\Omega\sin^2\phi}{(r_0 + a + k)^2} + \frac{v^2}{r_0 + a + k} \quad (12b)$$

$3\pi \leq \phi \leq 4\pi$ (fourth semicircle)

$$b_{norm} = \frac{v^2}{r_0 + a + 2k} \quad (13b)$$

$4\pi \leq \phi \leq 5\pi$ (fifth semicircle)

$$b_{norm} = 2k^2\frac{v\Omega\sin^2\phi}{(r_0 + a + 3k)^2} + \frac{v^2}{r_0 + a + 3k} \quad (12c)$$

$5\pi \leq \phi \leq 6\pi$ (sixth semicircle)

$$b_{norm} = \frac{v^2}{r_0 + a + 4k} \quad (13c)$$

With the numerical values of the design data, these equations indicate that the largest transversal forces occur in the first semicircle. The strong initial acceleration is due to the Coriolis forces which, in this section, exceed by far the forces caused by the curvature of the flow.

For the regular direction of rotation (Figure 1), the transversal forces generate a displacement, ΔH, which causes the effective width

$$H_{eff} \simeq H_0 - \Delta H \quad (14)$$

in the center of the duct to be smaller than the geometrical width, H_0. This will extend the lower size limit of precipitation in the center of the duct to smaller particles, but, at the same time, it reduces the quality of the size separation. This adverse effect becomes predominant when the displacement, ΔH, approaches values comparable with the width, H_0. Under this condition, the vortical motion parallel to the height, B_0, is no longer negligible, because it carries successively a significant amount of air from the sides into the center of the duct and, thus, increases the foil area accessible for a given aerodynamic size. As a result, overlapping of deposits of distinct particle size occurs more readily—*i.e.*, the actual size resolution is reduced.

Spinning the rotor in the opposite direction will cause the double vortex to reverse its rotation in the first semicircle, because the reversed Coriolis forces dominate this section. Since the displacement, ΔH, in the center of the duct changes directions accordingly, the effective width, H_{eff}, in the center of the duct will actually be larger than the geometrical dimension, H_0. This effect reduces the range of particle sizes collectable on the foil, so that the lower limit of complete precipitation occurs at coarser sizes. At the same time, an increase of size resolution for moderate values $|\Delta H| < H_0$ may occur. This improvement, however, will be impaired by the vortical motion which, as before, becomes of significant influence when $|\Delta H|$ approaches or exceeds H_0.

Calibration of Size-Separation Patterns

No attempts were made to derive a theoretical expression for the particle trajectories in the duct, because the design of the instrument facilitates a simple calibration with quasi-monodisperse aerosols of known size.

A few representative operating conditions were selected for

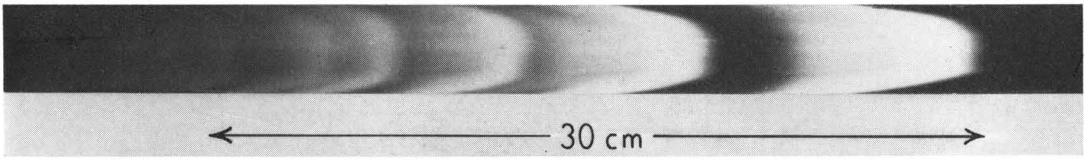


Figure 8. Deposit of latex aerosol (5×10^{-5} cm. spheres) collected at an aerosol flow rate of 1.6 liters per minute

Operating conditions: 3000 r.p.m.; total flow rate, 19 liters per minute; slit width, ca. 0.3 mm.

a number of test series with commercially available latex-spheres (Dow Chemical Co., Midland, Mich.) of uniform sizes between 8.8×10^{-6} and 3.5×10^{-4} cm. in diameter.

The uniform latex spheres in the form of aqu eous suspen sions were fed into an air blast nebulizer. The latex concentrations of the suspensions were increased with increasing particle size up to 10 mg. per ml. The nebulization rate was about 0.15 ml. per minute. The aerosol output of 8 liters per minute was fed into an open-ended vertical duct. Dry air at a flow rate of 2 liters per minute was added to the duct to facilitate easy evaporation of the original water droplets of the nebulizer. With properly adjusted concentrations in the aqueous suspension, this arrangement produced aerosols of latex spheres which consisted of a mixture of single airborne spheres and aggregates of two and more spheres. The aerosols were sampled under isobaric conditions from the lower end of the duct. To obtain heavy visible deposits on the foil, the samples were taken over extended periods of time, varying between 10 minutes for coarse latex particles and several hours for latex spheres smaller than 10^{-5} cm. in diameter.

For the performance tests and calibrations, rotor speeds between 1500 and 6000 r.p.m. were employed, and the total flow rate was varied between 5 and 19 liters per minute. Depending upon the particular aerosol inlet section used in the test, the aerosol flow rate was adjusted somewhere between 0.6 and 15% of the total flow rate.

Under most of the selected operating conditions, the test runs indicated a very good size resolution for the first half of the foil length. In this section, all tests produced a sequence of deposits of different degrees of aggregation. The deposits could be discriminated visibly. They all had quasi-parabolic contours at the leading edge and were almost symmetrical to the center line of the foil. Figure 8 gives a typical example for high flow rates.

Because of the great regularity and similarity of the deposit patterns, it was not necessary to check the correlation between the deposit position in the pattern and the degree of aggregation for all latex sizes used in the tests. However, for a few selected sizes, the aggregates of the different deposits were identified by regular and scanning electron microscopy.

To obtain regular electron micrographs, a number of carrier grids were placed along the center line of the foil strip and covered with large sheets of formvar foils, thus holding the grids in place. Prior to the tests, the coated strips received a thin chromium layer to avoid possible charging effects from the deposited particles. After the test, the grids were removed by cutting the formvar around the edges of the grids. The grids with the deposits were shadowed with chromium under vacuum and then investigated in the electron microscope.

For studying the deposits in the scanning electron microscope, the sections of the strip foil carrying deposits were cut into small pieces (ca. 0.5 by 0.5 cm.) which were vacuum-shadowed with gold and then directly inspected with the scanning electron microscope.

The results indicated that in each major deposit, as discriminated visibly, the aggregates were all alike, and each con-

Table I. Relative Aerodynamic Diameter, f_n, of Aggregates of n Uniform Spheres

		f_3	f_4	f_5	f_6	f_7	f_8	f_9	f_{10}	f_{11}	f_{12}
As Used for Calibration											
	1.18	1.33	1.46	1.54	1.65	1.73	1.81	1.88	1.91	1.97	
As Obtained by Using the Calibration Curves											
Latex sizes $>10^{-5}$ cm.	1.189	1.343	1.471	1.568	1.676	1.748	1.812	1.887	1.936	1.996	2.043
Number of tests	66	57	40	30	26	23	20	15	13	11	9
Standard deviation	0.025	0.031	0.027	0.040	0.027	0.030	0.033	0.040	0.051	0.053	0.036
Mean error	0.25%	0.31%	0.29%	0.46%	0.32%	0.36%	0.41%	0.57%	0.72%	0.80%	0.58%
Latex size 3.57×10^{-5} cm.	1.179	1.322	1.457	1.549	1.664	1.735	1.801	1.867	1.919	1.981	2.035
Number of tests	16	16	13	12	12	12	11	10	10	9	8
Standard deviation	0.017	0.021	0.018	0.024	0.025	0.027	0.031	0.025	0.033	0.032	0.026
Mean error	0.36%	0.40%	0.34%	0.45%	0.44%	0.45%	0.55%	0.43%	0.55%	0.53%	0.45%
	f_{13}	f_{14}	f_{15}	f_{16}	f_{17}	f_{18}	f_{19}	f_{20}	f_{21}	f_{22}	f_{23}
Latex size 3.57×10^{-5} cm.	2.11	2.17	2.22	2.25	2.30	2.33	2.36	2.43	2.51	2.56	2.57
Number of tests	2	2	2	2	2	2	2	2	2	2	2

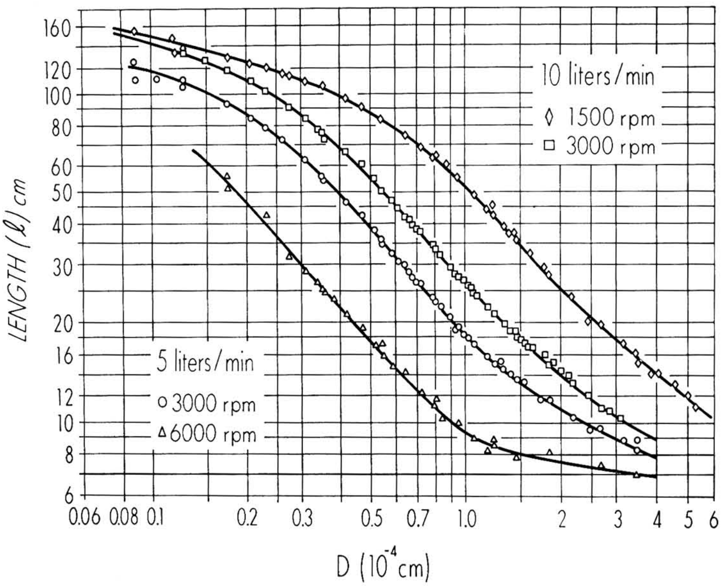


Figure 9. Calibration curve for the size separation under various operating conditions

tained one more sphere than the aggregates of the adjacent deposit at greater foil length, l. The leading deposit was always made up of single spheres. In most cases, five to seven aggregates besides the deposit of single spheres were easily discernible. The size resolution was substantially increased by using aerosol inlet sections with narrower slits at reduced aerosol flow rate. By applying the results of a recent investigation (Stöber, Berner, *et al.*, 1969) on aerodynamic diameters of aggregates of uniform spheres, all discernible deposits could be utilized for calibration purposes. Table I gives the numerical values of the relative aerodynamic diameters used for the calibrations.

Taking the maximum length of each deposit at the center line of the foil, a number of calibration curves were established. Some of them, as obtained at various rotor speeds, are plotted on logarithmic scales in Figure 9. These curves cover a size range of almost two orders of magnitude. At a flow rate of 5 liters per minute, the lower size limit apparently extends well below 8.8×10^{-6} cm., the smallest latex size available for calibration tests.

The deposition of this size at rotor speeds as low as 1500 r.p.m. had not been expected. In fact, the deposition occurring along the upper inflection of the curves stretching over the latter half of the length of the strip must be predominantly controlled by the secondary flow pattern in the air duct. This can be concluded from a simple theoretical estimate.

The centrifugal force pushing the particles to the outer wall of the duct is at a maximum in the sixth semicircle of the duct. In analogy to earlier calculations (Stöber and Flachsbart, 1969; Stöber and Zessack, 1964), we obtain in this section of the duct

$$\frac{dr}{dt} = \frac{D^2\Omega^2(r_0 + a + 4k)}{18\eta}\left(1 + \frac{2\beta}{D}\right) \tag{15}$$

and by applying this expression to the whole duct, we overestimate

$$\Delta r \leq \int_{l_a}^{l_1} \frac{dr}{dt}\frac{dl}{\bar{v}} = \frac{D^2\Omega^2 H_0 B_0(r_0 + a + 4k)\,(l_1 - l_a)}{18\eta\, F}\left(1 + \frac{2\beta}{D}\right) \tag{16}$$

at the foil length, l_1.

On the upper curve of Figure 9, we find $l_1 = 110$ cm. for a particle size of 3×10^{-5} cm. Thus, at 1500 r.p.m. and 10 liters per minute, Equation 16 gives $\Delta r \leq 0.27H_0$. This indicates that more than 73% of the radial motion of the particle toward the outer wall was provided by a secondary flow in the air duct. The effective width was less than 27%: $H_{eff} \leq 0.27H_0$. Accordingly, the size resolution at this point is smaller than along the steeper section of the calibration curve. At 1500 r.p.m. and 10 liters per minute, the deposit of single latex spheres of 3.57×10^{-5} cm. at $l_1 = 104$ cm. covers a section of the foil which is more than 8.5 cm. long. Under the same operating conditions, the deposit area of spheres of 2.64×10^{-5} cm. at $l_1 = 114$ cm. overlaps with the doublet deposit of the same spheres at and below $l_1 = 108$ cm., in such a way that the two deposits are barely discernible.

Reducing the aerosol flow at 1500 r.p.m. improved the resolution to some degree. However, if good resolution was desired for sizes at and below 3×10^{-5} cm., it was more effective to increase the rotor speed to 3000 r.p.m., thus shifting the deposits to smaller l values.

At 3000 r.p.m. and a total flow of 10 liters per minute, the resolution for spheres of 3.57×10^{-5} cm. at $l_1 = 76$ cm. is still excellent. Under this operating condition, overlapping does not occur for test spheres bigger than 1.5×10^{-5} cm., for which $l_1 \simeq 120$ cm.

An increase of the rotor speed to 6000 r.p.m. did not further improve size resolution for the smaller particles. At this speed, distortions of the flow in the duct caused overlapping of the deposits of spheres of 1.76×10^{-5} cm. and their aggregates at $l_1 < 55$ cm., although the total flow rate was reduced to 5

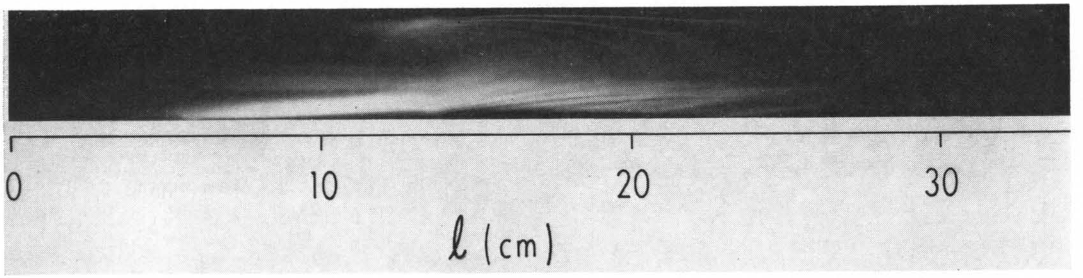


Figure 10. Irregular deposition of latex aerosol (3.57 × 10^{-5} cm. spheres) at an aerosol flow rate of 0.2 liters per minute

Operating conditions: 6000 r.p.m.; total flow rate, 5 liters per minute; slit width, ca. 0.3 mm.

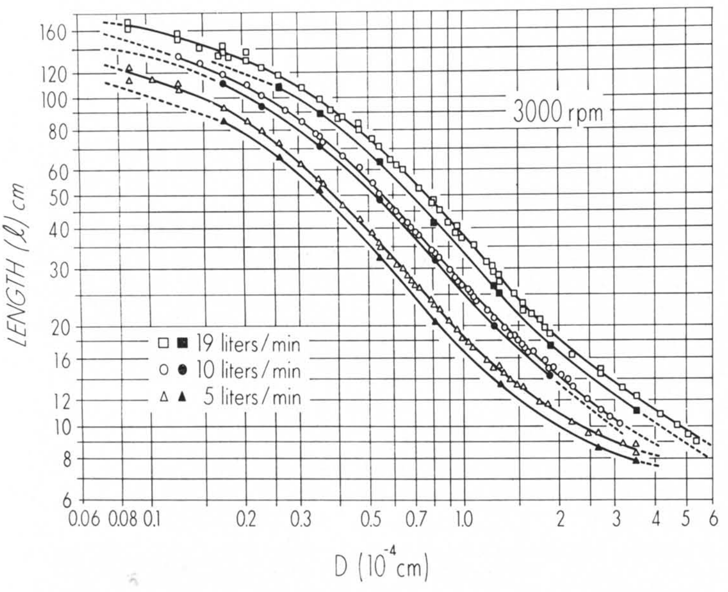


Figure 11. Calibration curves for the size separation at 3000 r.p.m. and different total flow rates

liters per minute. There were also highly irregular deposition patterns at short distances $l_1 < 20$ cm., as shown in Figure 10.

In view of these difficulties, the rotor speed of 3000 r.p.m. was selected as standard speed for routine measurements. The calibration curves for three different total flow rates at this speed are given in Figure 11. The band width of each curve along l indicates the area on the foil as covered by deposits of single latex spheres at an aerosol flow rate of 4% of the total flow. The band width along D is then related to the actual size resolution. In fact, the resolution is better than indicated on the graph, because the latex spheres are not precisely monodisperse, so that part of the extended area of a deposit of single spheres can be attributed to the size distribution of the latex spheres.

Experimental Effects of the Secondary Flow in the Spiral Duct

Although it could be estimated from the calibration curves that the deposition of small particles ($\simeq 10^{-5}$ cm.) must strongly be influenced by the secondary flow pattern, the deposit areas in these tests, except for high rotor speeds of 6000 r.p.m. or high total flow rate (19 liters per minute) at low rotor speed (1500 r.p.m.) appeared to be surprisingly regular. The leading edges seemed to be patterned after a parabolic velocity profile of the air flow in the duct, and the drawn-out shape at greater distances from the aerosol entrance could qualitatively be attributed to the image projection of the aerosol entrance slit, which must increase the length, Δl, of a deposit with increasing distance, l. Accordingly, the deposit length can be reduced to some degree by reducing the slit width of the aerosol entrance. Because of all this rather regular behavior, the influence of the double vortex does not readily show up in the deposition patterns. It can be revealed only by quantitative considerations, because, as long as in Equation 14 $\Delta H < H_0$, the double vortex merely modifies the projection of the flow velocity profile, as illustrated in Figure 12b.

The situation changes drastically when the direction of rotation of the rotor is reversed. The predominant Coriolis forces in the first semicircle of the duct will, then, reverse the rotation of the double vortex, and the deposit area for uniform latex particles should degenerate into a shape as illustrated by Figure 12c. Actual deposition patterns obtained with latex at various rotor speeds confirm and exceed this expectation. Figure 13 gives some photographs of typical examples. The

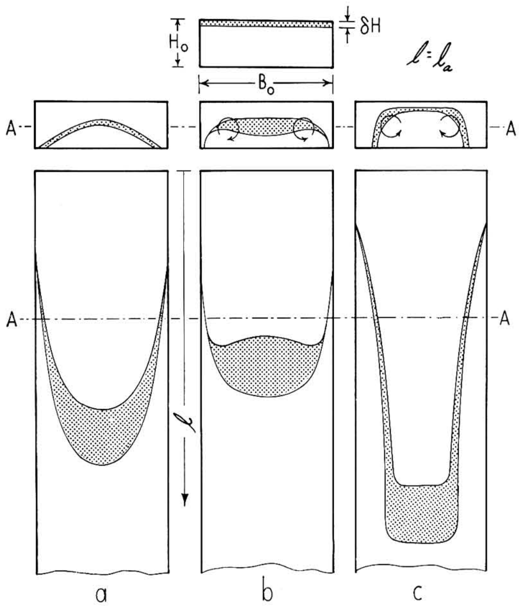


Figure 12. Schematic diagrams of the distribution of monodisperse aerosol over the cross-section of the duct and along the foil strip

a. For a straight duct
b. For a spiral duct with regular direction of rotation
c. For a spiral duct with reversed direction of rotation

influence of the double vortex on the deposition pattern is now quite apparent. Along the edges of the foil there are aerosol deposits in streaks consisting of several lines with well-defined borders. These streaks taper out into narrow deposits more or less parallel to the center line of the foil. Finally, there appear some deposits across the foil between the streaks.

Electron micrographs reveal that the line structure of the streaks is due to size separation. Where the lines are no longer twisted, the inner border lines represent deposits of single spheres, whereas the sequence of lines closer to the edge of the foil is composed of latex clusters of increasing degree of aggregation. The deposits occurring in the center of the foil correspond to the regular precipitates under normal operating conditions. Thus, the leading deposit in the center consists of single spheres and the following precipitates are made up by doublets, triplets, and bigger aggregates, respectively.

In the streaks, the length of the deposit line of a given aggregate extends to some degree beyond the area of the corresponding deposit in the center of the foil. These distinct lines of deposition mark the projected location of the centers of the double vortex. Thus, from the photographs, we can conclude that the centers move closer toward the edges of the foil when the rotor speed is increased. Changing the total flow rate has a less significant influence, if any, on the vortex centers.

The deposits at 1500 and 3000 r.p.m. have some similarities. Aerosol particles deposited near the edge of the foil are found only at the beginning of the deposit close to the aerosol entrance. This indicates that the vortical velocities at these rotor speeds are not big enough to carry substantial amounts of aerosol from the center over to the edge of the foil. At 3000 r.p.m., the size-separated deposits appear eventually in the center of the foil. At 1500 r.p.m., where the centrifugal forces are substantially reduced, the vortical motion delays the centrifugal precipitation of the utilized latex particles to the extent that no center deposit is formed within the length of the spiral duct.

At 6000 r.p.m., Figure 13 indicates strong distortions similar to those shown for regular operating conditions in Figure 10. Undoubtedly, the vortices become quite prominent at this rotor speed. The twisted deposition patterns along the edges of the foil reveal clearly that each vortex completes a full revolution at a distance $l \simeq 25$ cm. The center lines of the double vortex are close to the edges of the foil and, since the rotor speed creates great centrifugal forces on the particles used in these particular tests, there occurs still a size-separated deposition in the center of the foil, which is quite pronounced at the total flow rate of 5 liters per minute.

The observed increase of the space between the center lines of the double vortex with increasing rotor speed has some bearing on the relation between the transversal forces and the displacement, ΔH. With the observed changes of the geometrical pattern of the secondary flow, a potential increase of the displacement, ΔH, by increased transversal forces may be counteracted by the widening distance between the center lines of the double vortex. It is reasonable to assume that the improvement of the size resolution for fine aerosol particles as obtained at regular operating conditions by increasing the rotor speed from 1500 to 3000 r.p.m. is partly due to this influence.

An estimate of the minimum displacement, ΔH, involved in the deposition process under routine operating conditions, where $\Delta H < H_0$ is maintained, can be obtained experimentally by comparing test results obtained for both directions of rotation under otherwise identical operating conditions. Figure 14 shows the photograph of such tests.

Using number indices for discriminating the two experiments at opposite directions of rotation of the centrifuge, we can write for the regular case

$$ {}_1H_{\mathrm{eff}} = H_0 - \Delta H_1 \tag{14a} $$

and for the reversed direction of rotation

$$ {}_2H_{\mathrm{eff}} = H_0 + \Delta H_2 \tag{14b} $$

For the purpose of an estimate, let us further assume

$$ \Delta H_1 \simeq \Delta H_2 = \Delta H \tag{17} $$

We can, then, find a value γ so that

$$ {}_2H_{\mathrm{eff}} = \gamma l_2 \tag{18} $$

and, since the duct is a spiral with increasing centrifugal forces,

$$ {}_1H_{\mathrm{eff}} < \gamma l_1 \tag{19} $$

This gives

$$ \frac{{}_1H_{\mathrm{eff}}}{{}_2H_{\mathrm{eff}}} = \frac{H_0 - \Delta H}{H_0 + \Delta H} < \frac{l_1}{l_2} \tag{20} $$

or

$$ \Delta H \geq \frac{(l_2 - l_1)H_0}{l_1 + l_2} \tag{21} $$

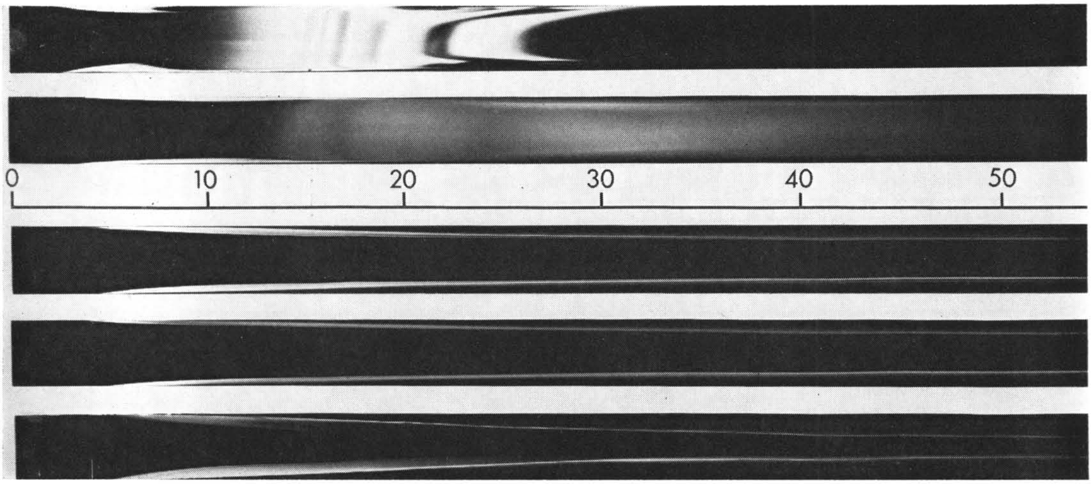
where the equality is appropriate for $l_2 - l_1 \ll l_1 + l_2$.

From the results at 3000 r.p.m., as shown in Figure 14, we obtain for the deposits of single spheres the actual values of $l_1 = 47.5$ cm. and $l_2 = 87.5$ cm. Thus, the displacement is

$$ \Delta H > 0.30\ H_0 $$

At shorter distances, the doublet and triplet deposits give $\Delta H > 0.24\ H_0$ and $\Delta H > 0.18$, respectively.

For a comparison, Equation 16 can be employed. Utilizing



From top to bottom:

1. 6000 r.p.m.; total flow, 5 liters per minute; aerosol flow, 0.1 liter per minute; latex size, 3.57×10^{-5} cm.
2. 6000 r.p.m.; total flow, 10 liters per minute; aerosol flow, 0.1 liter per minute; latex size, 3.57×10^{-5} cm.
3. 3000 r.p.m.; total flow, 10 liters per minute; aerosol flow, 0.1 liter per minute; latex size, 5.48×10^{-5} cm.
4. 3000 r.p.m.; total flow, 19 liters per minute; aerosol flow, 0.2 liter per minute; latex size, 8.10×10^{-5} cm.
5. 1500 r.p.m.; total flow, 10 liters per minute; aerosol flow, 0.2 liter per minute; latex size, 8.10×10^{-5} cm.

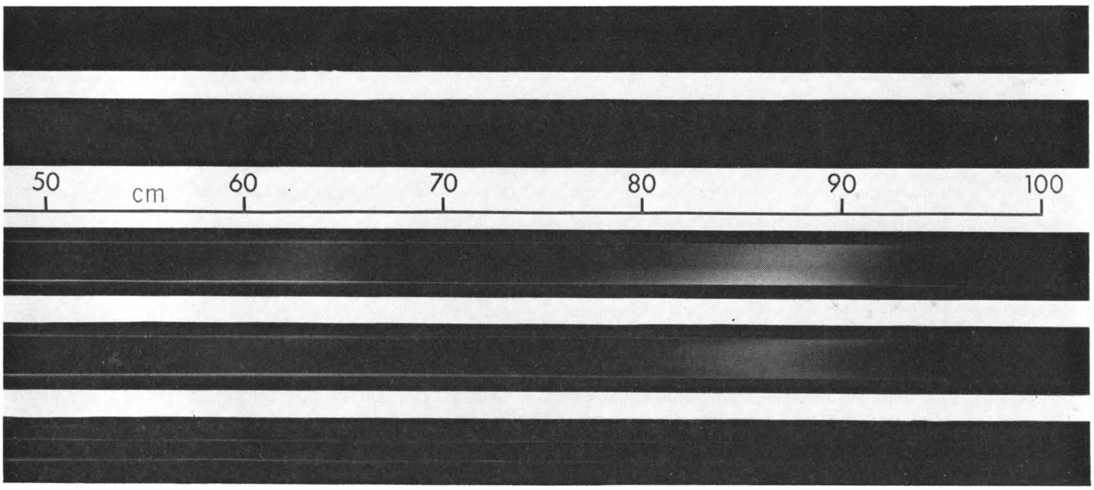


Figure 13. Foil deposits under various operating conditions with reversed direction of rotation of the centrifuge

the radius vector r of the location of the deposit of single spheres at $l_1 = 47.5$ cm., we obtain a value of $\Delta r < 0.80\ H_0$. In view of Figure 5, we can conclude that, for values $l_1 \gtrsim 40$ cm., Equation 16 does not overestimate the radial particle displacement Δr by more than 25%, if the radius vector r at l_1 is employed. Thus, we obtain

$$0.64\ H_0 < \Delta r < 0.80\ H_0$$

which corresponds to

$$0.20\ H_0 < \Delta H < 0.36\ H_0$$

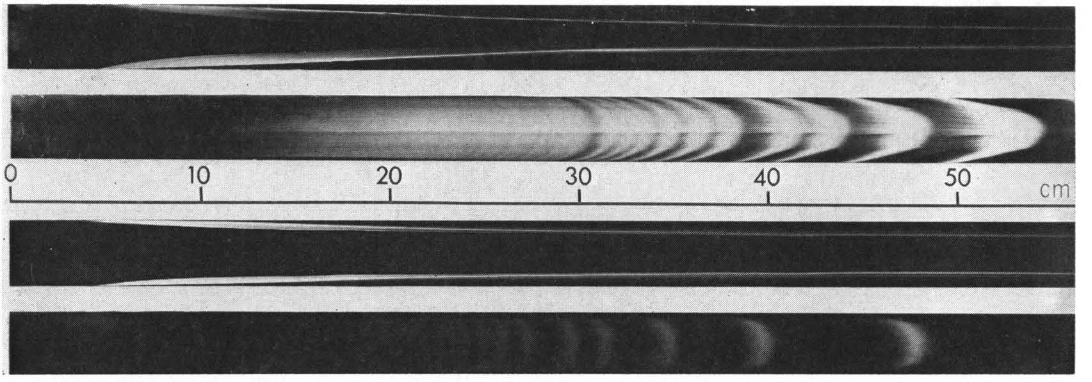
Considering the approximate nature of these calculations, the results seem to be in reasonable agreement and compatible with the experiments.

Experiments at Very High Size Resolution

In many of the calibration tests, the size resolution was equal to the best results so far reported (Berner, 1968). In view of these easily obtained results, an attempt was made to further increase the size resolution by reducing the aerosol flow rate below 1% of the total flow and using a special aerosol entrance section with a 0.1-cm. center bore and a very narrow slit. Figure 15 gives a photograph of the foil of one of the successful tests under such conditions.

In these experiments, more than 20 distinct deposits can be discriminated on the foils. A weak additional deposit appears between the familiar dense deposits of doublet and triplet aggregates, and a similar additional precipitate can be discriminated in front of the dense quadruplet deposit. Electron micrographs made in these two areas showed that in the first case the deposit consisted of chain-like triplet aggregates (Figure 16, upper right), whereas in the latter case the aggregates were quadruplets in the form of branched chains (Figure 17, upper right).

A systematic electron microscopic survey of all the deposits of the high-resolution tests revealed further details about some



From top to bottom:

1. Reversed direction

2. Regular direction at 1500 r.p.m.; total flow, 10 liters per minute; aerosol flow, 0.2 liter per minute; latex size, 8.10 × 10^{-5} cm.

3. Reversed direction

4. Regular direction at 3000 r.p.m.; total flow, 10 liters per minute; aerosol flow 0.1 liter per minute; latex size, 5.48 × 10^{-5} cm.

Figure 14. Comparison of foil deposits obtained under opposite directions of rotation of the centrifuge

special types of aggregates. A series of regular electron micrographs is shown in Figures 16–21. The relative aerodynamic size, f, as indicated for each micrograph, is derived from the size values taken from the calibration curves. In general, all aggregates in each major deposit have almost the same configuration. They tend toward optimum sphericity. In the size range smaller than the octahedral sextuplets (Figure 19, lower right), however, there occur also small concentrations of chain-like aggregates, which are either superimposed upon the major deposits or are found in the spaces between them. Figures 16 to 19 show a variety of straight and branched chain configurations. Average values of the relative aerodynamic size, f, for some configurations are given in Table II, together with values calculated from results by Kunkel (1948).

Chain aggregates of more than eight spheres were observed with latex spheres of 3.57 × 10^{-5} cm., but they were very rare. Deposits of sizes beyond f = 1.75 generally consisted of aggregates of rather spherical shape. Figures 20 and 21 give typical examples. Up to the seventeenth major deposit, the regular size increase of the aggregates by one sphere from deposit to deposit could be verified by counting the spheres of the aggregates on micrographs taken under high-energy electron transmission, which made the latex spheres translucent. For larger aggregates, it was difficult to avoid counting errors,

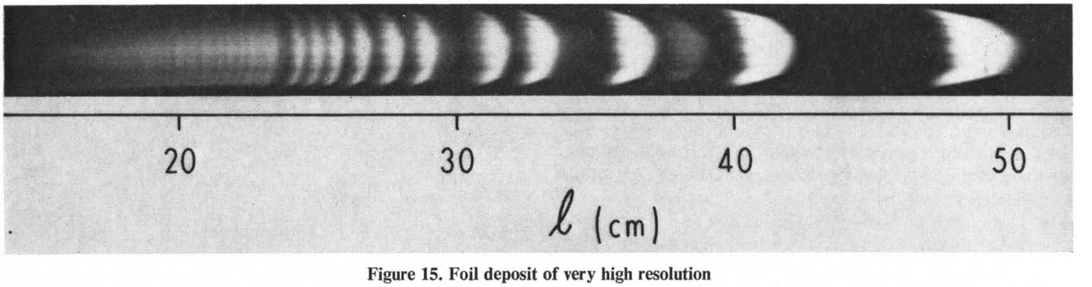


Figure 15. Foil deposit of very high resolution

Operating conditions: 2000 r.p.m.; total flow, 10 liters per minute; aerosol flow, 0.1 liter per minute; latex size, 7.14 × 10^{-5} cm.

TABLE 2

RELATIVE AERODYNAMIC DIAMETERS, f, OF AGGREGATES OF n UNIFORM SPHERES OF DIFFERENT CONFIGURATION

n	configuration	as observed: f	as observed: number of tests	reference: Kunkel (16)
2	oo	1.19	66	1.17
3	ooo	1.28	10	1.25
3	∴	1.34	57	1.28
4	oooo	1.38	3	1.30
4	o∴	1.42	5	
5	ooooo	1.42	2	
6	oooooo	1.45	1	
4	⁘	1.47	40	
7	ooooooo	1.48	1	
5	oo∴	1.50	2	
6	ooo∴	1.52	1	
8	oooooooo	1.52	1	1.37
8	ooo8oo	1.56	1	
5	88	1.57	30	
8	ooooo∴	1.60	1	
6	⠿	1.68	26	1.54

and there was reason to believe that some size increases involved more than one sphere at a time. An evaluation of the relative aerodynamic size of 23 successive major deposits obtained with latex spheres of 3.57×10^{-5} cm. in diameter is given in Table I. The first 11 values may be compared with the listed average values obtained by re-evaluating all latex measurements of sizes between 1.26×10^{-5} and 3.49×10^{-4} cm. by means of the established empirical calibration curves. The agreement among these data and with other results (Stöber, Berner, *et al.*, 1969; Hochrainer and Brown, 1969) is very good. The micrograph of the quintuplet aggregates (Figure 22, lower right) indicates a random deposition, rather than the "parachute" effect observed in the cylindrical conifuge (Stöber, Berner, *et al.*, 1969). This may be due to the more complex air flow pattern in the spiral duct, which could prevent the orientation of the quintuplets.

Aspects of Aerodynamic Size Distribution Analysis

The most desirable application of the new centrifuge is, of course, the analysis of the aerodynamic size distribution of aerosol particles. For this purpose, an additional calibration is necessary, relating the deposit concentration or the total amount of deposited particles of a given size interval to the airborne concentration prior to sampling. This can be done entirely in an empirical way either by utilizing the whole width of the strip foil or, for experiments at high resolution, by selecting a narrow strip along the center line of the foil for the correlation to the airborne concentration.

The only requirement for the feasibility of such approaches is that a significant proportion of the airborne particles will pass through the aerosol inlet section without being trapped. In other words, the entrance losses should not exceed some 10% of the total amount of the size interval under consideration. A simple estimate for the two types of aerosol inlet sections used in the tests will show that this condition is reasonably fulfilled.

We overestimate the initial losses of the coaxial aerosol flow by considering the flow as coming from a round impactor jet. For aerosol flow rates up to 3 liters per minute, an inlet section with a center bore of 0.4 cm. in diameter was used. Aerosol flow rates of 0.2 liter per minute or less were employed in connection with an inlet section having a 0.1-cm. center bore. In both cases, the average linear velocity of the coaxial aerosol flow is about 400 cm. per second. Using these data for calculating a maximum impaction efficiency according to theoretical results reported in the literature (Ranz and Wong, 1952), we find that no impaction occurs for particle diameters up to 4×10^{-4} or 2×10^{-4} cm. with the 0.4-cm. or the 0.1-cm. center bore inlet, respectively. For a standard procedure at an aerosol flow of 1 liter per minute through the 0.4-cm. center bore inlet, Table III gives the theoretical values of impaction losses. This indicates that, within the size range of interest, impaction losses in the aerosol inlet system are rather negligible.

Table III. Maximum Impaction Losses in the Aerosol Inlet Section with 0.4-Cm. Center Bore at an Aerosol Flow Rate of 1 Liter per Minute

D (10^{-4} Cm.)	$\sqrt{\Psi}$	Loss, %
5	0.16	0
6	0.19	0
7	0.23	0
8	0.25	0
9	0.29	25
10	0.32	35
12	0.38	80

Of greater significance are the losses which occur in the radial extension of the aerosol inlet, as formed between the inner wall of the duct and a thin brass sheath defining the slit width, s. Figure 22 shows a cross section of the actual arrangement parallel to the rotor plane. Assuming an aerosol duct with parallel walls along the sheath length, l_s, at a distance, s, we overestimate the precipitation of particles during their radial passage toward the slit. The precipitation is caused by the Coriolis acceleration, as given by Equation 7. The residence time, t_s, inside the narrow duct is

$$t_s = \frac{l_s}{v_r} \tag{22}$$

and by Stokes' law we obtain

$$\frac{\Delta s}{t_s} = \frac{\rho D^2}{18\eta} \times 2v_r\Omega \tag{23}$$

or, after combining Equations 22 and 23,

$$\Delta s = \frac{\rho D^2 \Omega l_s}{9\eta} \tag{24}$$

This is the thickness of a layer from which all particles are removed and deposited on the brass sheath. For a standard slit width $s = 0.1$ cm. and the regular length of the sheath $l_s = 0.8$ cm., the maximum losses by Coriolis acceleration are listed in Table IV. These results indicate that practically all losses in the aerosol entrance section are due to the angular acceleration of the aerosol flow. The losses can be reduced by widening the slit width, s, and reducing the sheath length, l_s. Under the specified conditions of the inlet, the losses may exceed 50% for particle sizes of 6×10^{-4} cm. and more. Thus, the calibration of deposit concentrations in this size range becomes dependent upon the slit width. For particles smaller than 2×10^{-4} cm., however, such influence is rather insignificant.

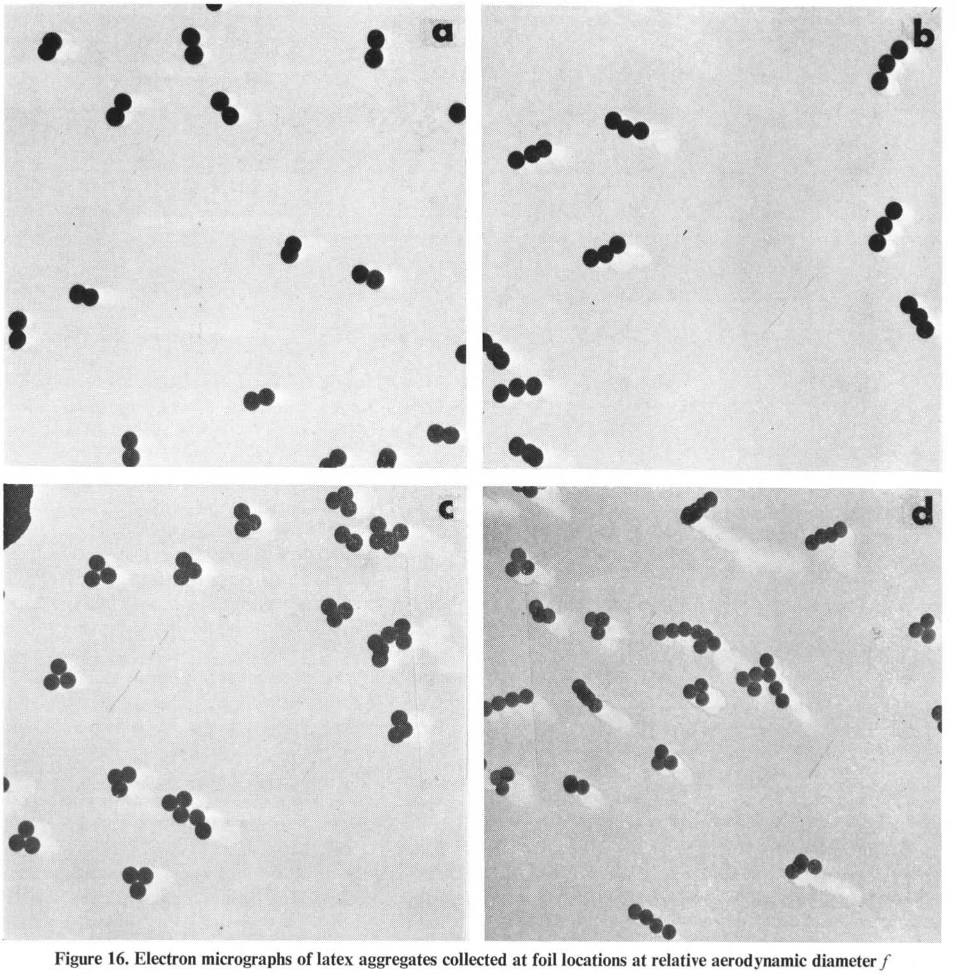


Figure 16. Electron micrographs of latex aggregates collected at foil locations at relative aerodynamic diameter *f*

a. Sphere size, 7.14 × 10^{-5} cm.; f = 1.19
b. Sphere size, 7.14 × 10^{-5} cm.; f = 1.28
c. Sphere size, 7.14 × 10^{-5} cm.; f = 1.33
d. Sphere size, 3.57 × 10^{-5} cm.; f = 1.37

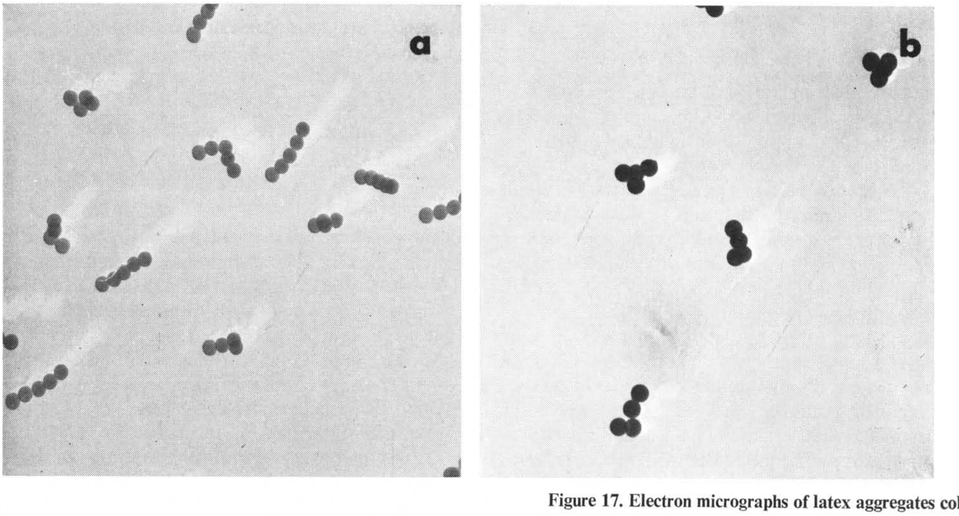


Figure 17. Electron micrographs of latex aggregates collected

a. Sphere size, 3.57 × 10^{-5} cm.; f = 1.42 b. Sphere size, 7.14 × 10^{-5} cm.; f = 1.43

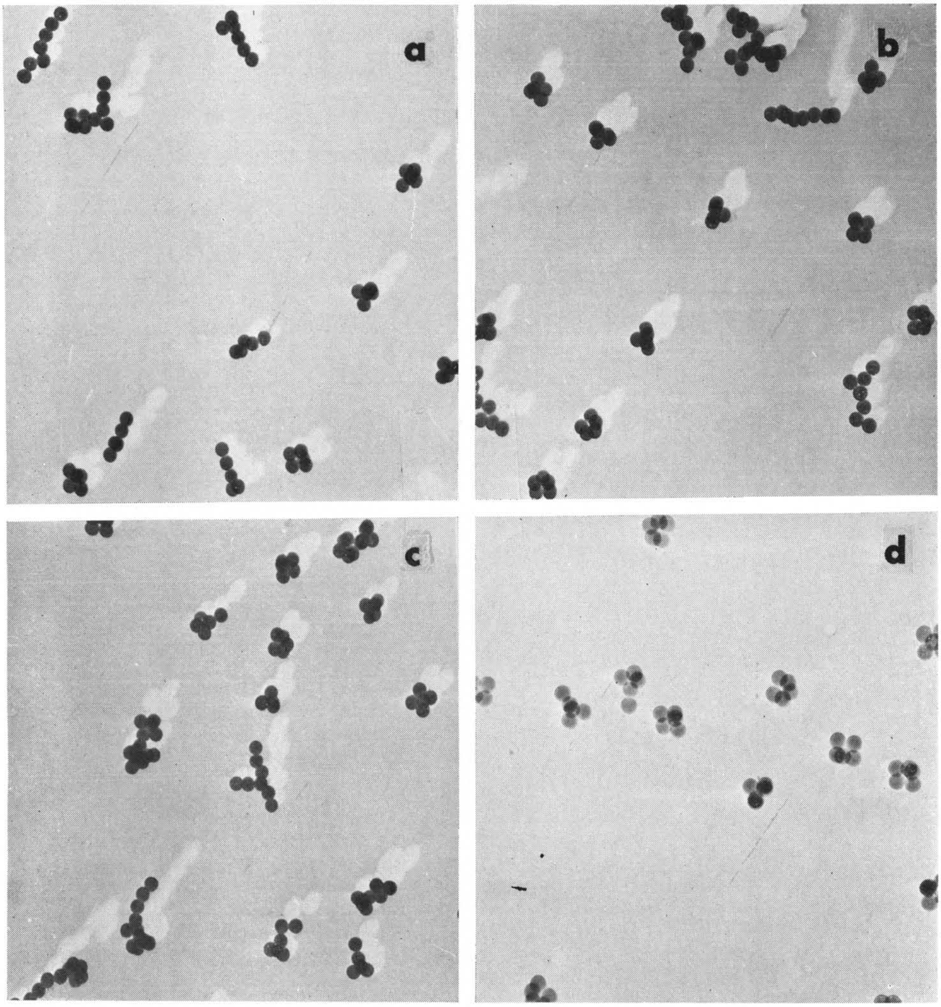
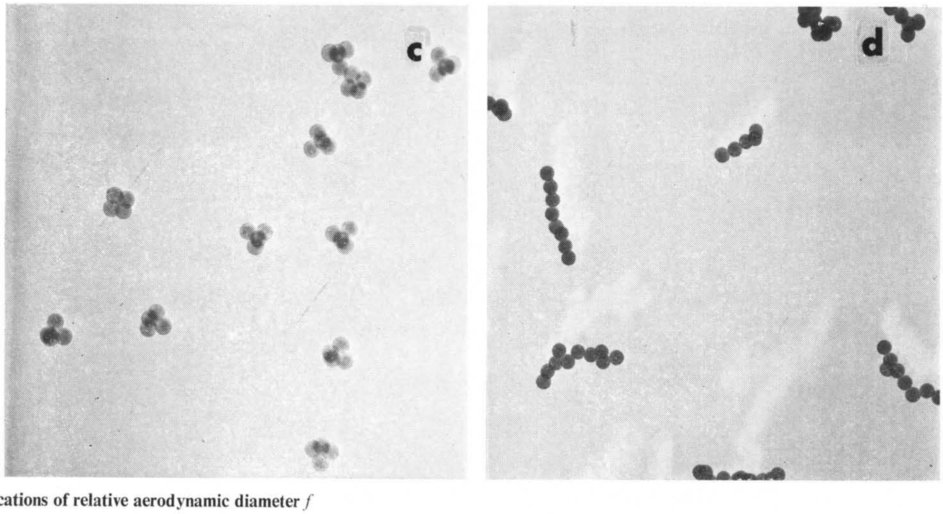


Figure 18. Electron micrographs of latex aggregates collected at foil locations of relative aerodynamic diameter f

a. Sphere size, 3.57×10^{-5} cm.; $f = 1.53$
b. Sphere size, 3.57×10^{-5} cm.; $f = 1.55$
c. Sphere size, 3.57×10^{-5} cm.; $f = 1.55$
d. Sphere size, 7.14×10^{-5} cm.; $f = 1.56$



at foil locations of relative aerodynamic diameter f

c. Sphere size, 7.14×10^{-5} cm.; $f = 1.47$ d. Sphere size, 3.57×10^{-5} cm.; $f = 1.52$

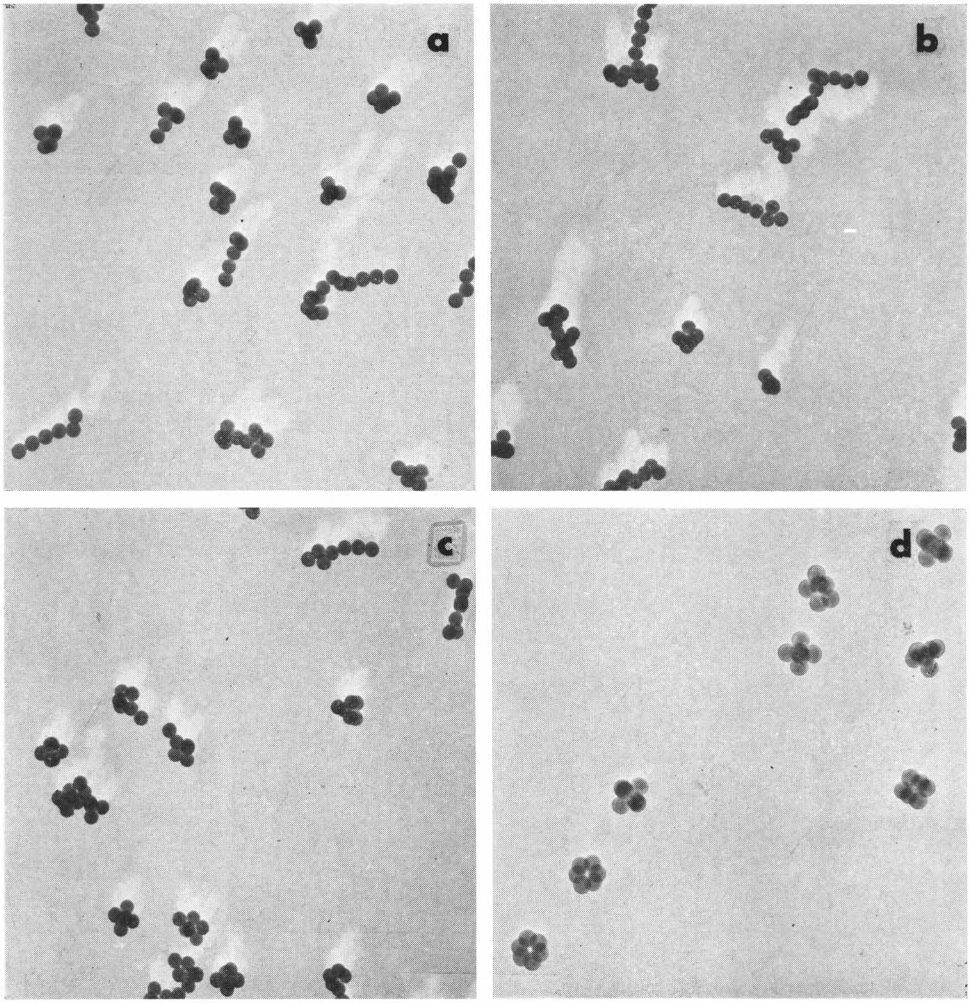


Figure 19. Electron micrographs of latex aggregates collected at foil locations of relative aerodynamic diameter f

a. Sphere size, 3.57×10^{-5} cm.; $f = 1.57$
b. Sphere size, 3.57×10^{-5} cm.; $f = 1.63$
c. Sphere size, 3.57×10^{-5} cm.; $f = 1.64$
d. Sphere size, 7.14×10^{-5} cm.; $f = 1.67$

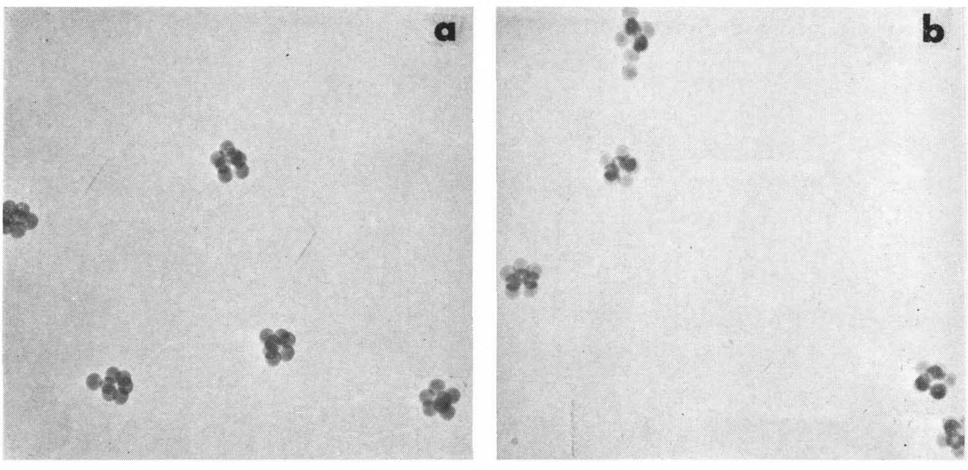


Figure 20. Electron micrographs of latex aggregates collected

a. Sphere size, 7.14×10^{-5} cm.; $f = 1.74$ b. Sphere size, 7.14×10^{-5} cm.; $f = 1.82$

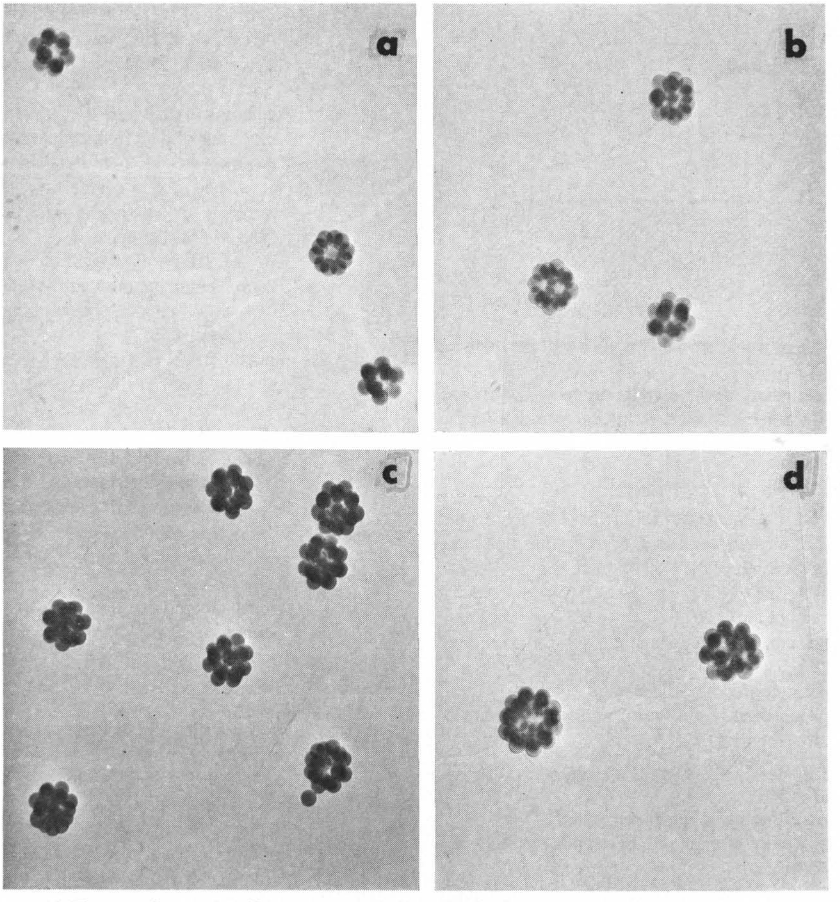
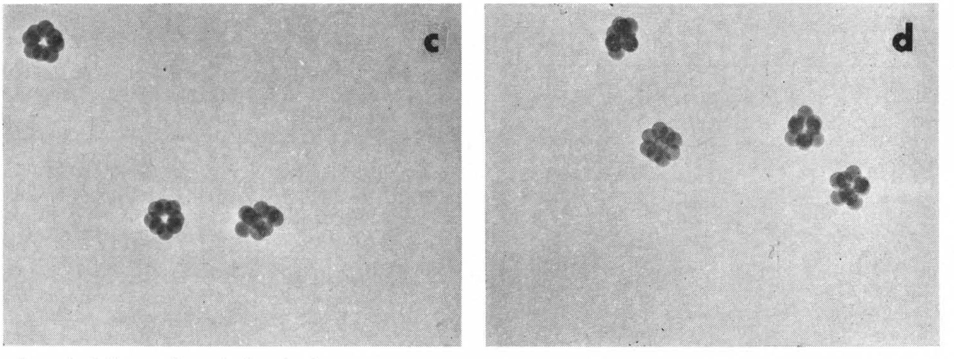


Figure 21. Electron micrographs of latex aggregates collected at foil locations of relative aerodynamic diameter f

a. Sphere size, 7.14×10^{-5} cm.; $f = 2.00$
b. Sphere size, 7.14×10^{-5} cm.; $f = 2.17$
c. Sphere size, 7.14×10^{-5} cm.; $f = 2.30$
d. Sphere size, 7.14×10^{-5} cm.; $f = 2.48$



at foil locations of relative aerodynamic diameter f

c. Sphere size, 7.14×10^{-5} cm.; $f = 1.85$ d. Sphere size, 7.14×10^{-5} cm.; $f = 1.89$

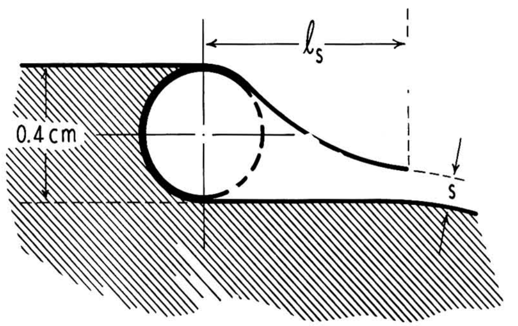


Figure 22. Cross-section of aerosol inlet at center of rotation

An experimental study of the correlation between airborne concentration of the aerosol and deposit concentration on the strip foil is presently in progress.

Nomenclature

β = 8.2×10^{-6} cm., empirical factor as related to the Cunningham correction at mean free molecular path length of 6.53×10^{-6} cm.
η = 1.84×10^{-4} gram cm.$^{-1}$sec.$^{-1}$, viscosity coefficient of air at 20° C.
ν = 0.143 cm.^{2}sec.$^{-1}$, kinematic viscosity coefficient of air at 20° C.
ϕ = angular coordinate at center of rotor
ψ = angle between radius vector and vector of curvature (Figure 7)
Ψ = $\frac{\bar{v}}{18\eta D_c}(D^2 + 2\beta D)$ (Ranz and Wong, 1952)
ρ = particle density F, gram cm.$^{-3}$
ρ_{air} = 1.29×10^{-3} gram cm.$^{-3}$, density of air at 20° C.
Ω = $2\pi N$, angular velocity of rotor, sec.$^{-1}$
a = 3.60 cm., eccentricity of first semicircle (Figure 7)
b = coordinate along height of spiral duct, cm.
b_{cor} = Coriolis acceleration, cm. sec.$^{-2}$
$(b_{cor})_{norm}$ = component of Coriolis acceleration perpendicular to wall of duct, cm. sec.$^{-2}$
b_{fl} = centrifugal acceleration in curved flow, cm. sec.$^{-2}$
b_{norm} = effective acceleration perpendicular to wall of duct, cm. sec.$^{-2}$
B_0 = 3.30 cm., height of spiral duct
D = aerodynamic diameter of aerosol particle, cm.
D_c = diameter of center bore of aerosol inlet section, cm.
f = relative aerodynamic diameter of aggregate of uniform spheres
F = rate of total volume flow through spiral duct, cm.^{3} sec.$^{-1}$
h = coordinate along width of spiral duct, cm.
H_0 = 1.00 cm., width of spiral duct
H_{eff} = effective width of duct for particle size separation, cm.
ΔH = displacement of volume element of air along h in center of duct by secondary flow, cm.
k = 0.84 cm., eccentricity of third and fifth semicircle
K_{fl} = centrifugal force in curved flow, gram cm. sec.$^{-2}$
l = coordinate of length along the strip foil (outer wall of duct), cm.
l_a = 1.02 cm., length of straight section of strip foil
l_s = 0.8 cm., length of slit sheath
Δl = length of foil deposit area of monodisperse aerosol particles, cm.
n = number of particles in an aggregate
N = rotor speed of centrifuge, sec.$^{-1}$
Q = cross section of spiral duct, cm.^{2}
r = radius vector from center of rotor, cm.
r_0 = 5.12 cm., actual radius of curvature of outer wall of first semicircle (Figure 7)
Δr = radial or transversal displacement of particles relative to air flow, cm.
R = radius of curvature, cm.
Re = Reynolds number
Re_{crit} = critical Reynolds number for laminar flow conditions
s = width of aerosol entrance slit, cm.
Δs = transversal displacement of particles before leaving entrance slit, cm.
t_s = residence time of particles in the entrance slit, sec.
U = perimeter of spiral duct, cm.
v = local linear flow velocity in spiral duct, cm. sec.$^{-1}$
$\bar{v}$ = average linear flow velocity in spiral duct, cm. sec.$^{-1}$
v_r = radial linear velocity component, cm. sec.$^{-1}$

Table IV. Aerosol Losses in the Entrance Slit
Slit Width s = 0.1 Cm.

D (10^{-4} Cm.)	Δs	$\frac{\Delta s}{s}$, %
1	0.0015	1.5
2	0.0061	6
3	0.0136	14
4	0.0243	24
5	0.0380	38
6	0.0547	55
7	0.0745	75
8	0.0973	97

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Microelectrode Determination of Oxygen Profiles in Microbial Slime Systems

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■ Dissolved oxygen profiles were measured above and within a bacterial slime mass under a continuous flow of nutrient. The microprobe tip was 1.5 μ in diameter and its location, with respect to the slime-water interface, was known to ± 2 μ. With dilute media, the respiration was substrate limited and high concentrations of oxygen were found throughout the slime mass. More concentrated media increased utilization so that oxygen concentrations approached zero in the depth of the slime.

The microelectrode described by Whalen *et al.* (1967) was of the polarographic type and consisted of a glass capillary tube drawn out to a long, tapering point 1.5 μ in diameter. The tube was filled, to within 10–20 μ of the tip, with a metal alloy. A layer of gold was electroplated on the alloy, and the remainder of the recess was filled with collodion. A pure silver wire coated with silver chloride served as a separate anode. A voltage of 0.6–1.1 was impressed across the electrodes, and changes in current were recorded with a picoammeter-servo recorder combination. Current flow between the electrodes is linear with the oxygen activity, and is relatively insensitive to stirring.

The slime film was developed in a small, continuous-culture growth chamber, with the bacteria growing attached on an especially prepared microscope slide. To protect the delicate cathode tip when probing near the lower or attaching layer of cells, predrilled holes in the Plexiglass slide were filled with 2% Difco agar.

The growth chamber was seeded with heterotrophic bacteria, including at least 18 species obtained from a polluted stream (Sanders, 1966), and sealed for 24 hours. At the end of this attachment period, a flow of 280 ml. per minute of 20 parts per million nutrient broth (*BBL*) was initiated and maintained for eight days. The substrate velocity along the slide was 1.5 feet per second and the temperature was 27° C.

Then the top of the chamber was removed and the bottom containing the slime was clamped onto the stage of a Leitz Panphot microscope. The chamber was connected to an inlet manifold so that substrates containing 20 and 500 parts per million nutrient broth, with either high or low concentrations of dissolved oxygen, could be selected for flow through the chamber. The flow rates were adjustable, and the mean depth of flowing substrate over the slime was about 3.3 mm.

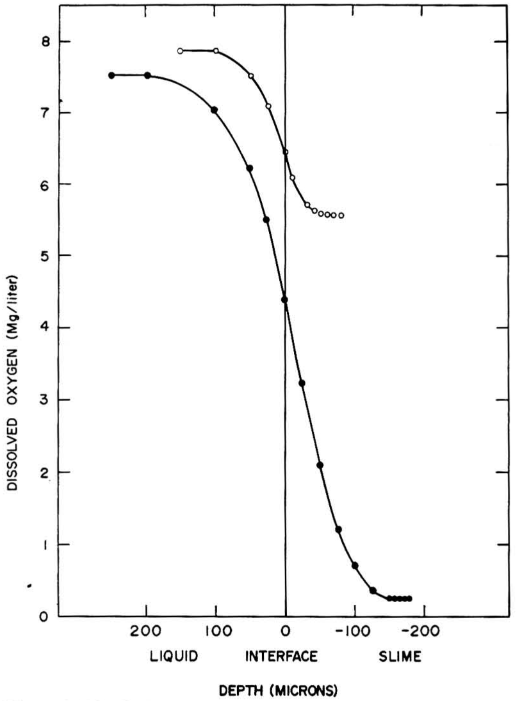

Figure 1. Dissolved oxygen profiles for bacterial slime in a continuous-flow system determined with microelectrode. Nutrient flow was 1.5 feet per second and temperature 27° C. With nutrient broth 20 mg. per liter (○—○), the oxygen in the slime stabilized at 5.5 parts per million below 75 μ in depth. With 500 mg. per liter nutrient broth (●—●), the profile reached 150 μ before stabilizing at 0.25 parts per million

The slime film was examined optically with a 75X water immersion objective and had an average population density of 15 cells per 100 μ^2, and ranged in depth from 150 to 200 μ.

During the probing operation, the microscope objective was replaced by the microelectrode held in the objective mount. Thus, the probe tip was positioned in the same areas as the visual observations, and the location of the probe was determined directly from the precalibrated micrometer scale on the microscope.

The slime surface was located optically with the substrate flowing, and electrically when the chamber was drained and the probe lowered until it made contact with the slime mass. Repeated probings indicated that the surface was determined within 2 μ.

After locating the surface, the microprobe was raised into the flowing liquid until the oxygen gradient stabilized. The probe was then lowered and readings taken at 25-μ increments at 30-sec. intervals, until the tip had penetrated the slime mass to a depth where the oxygen gradient stabilized.

The oxygen profile determined for the slime with air-saturated, 20-parts per million substrate flowing at 1.5 feet per second (Figure 1) shows that the oxygen concentration in the liquid and the film decreased with depth until a constant 5.5 parts per million was reached at a depth of 50 μ below the slime-nutrient interface. Thus the diffusion rate for oxygen into the slime film was higher than the respiration rate for that particular substrate concentration. These test conditions closely duplicated the growth conditions maintained during the eight days' culture period. When the substrate concentration was increased to 500 parts per million and the probe moved to an adjacent location (within 1 mm.), the new oxygen profile was much steeper, starting 200 μ above the slime-nutrient interface and extending down to a depth of 150 μ. The oxygen concentration at this level was 0.24 parts per million, and the total slime thickness was 175 μ. Other experiments using nutrient with a lower initial oxygen concentration showed an oxygen profile approaching zero in the lower layers of the slime.

These experiments demonstrate the applicability of the microelectrode dissolved oxygen system for the direct measurement of oxygen concentrations and gradients in liquids and in microbial slime films. This should lead to direct determinations of oxygen and nutrient diffusivity coefficients for slime systems, and provides a method for studying the respiration of aquatic organisms with respect to their microenvironments.

Acknowledgment

The authors thank the Ecological Engineering staff of the Southeast Water Laboratory, Federal Water Pollution Control Administration, for their assistance in culturing the microorganisms, and the Division of Research, St. Vincent Charity Hospital, for making and supplying the microelectrodes.

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Whalen, W. J., Riley, J., Nair, P., *J. Appl. Physiol.* **23** (5), 798–801 (1967).

Received for review April 16, 1969. Accepted August 14, 1969. Mention of products and manufacturers is for identification only and does not imply endorsement by the Federal Water Pollution Control Administration or U.S. Department of the Interior.

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Environmental Pollution Instrumentation. Edited by Robert L. Chapman. 190 pages. Instrument Society of America, 530 William Penn Place, Pittsburgh, Pa. 15219. 1969. $7.00, members, $9.00, nonmembers; paper.

This monograph consists of symposia papers covering the state of the art and latest developments in air, water, and noise pollution. Monitoring air pollutants, vehicle exhaust data processing, chemical analysis by remote sensing, and the future of instrumentation in water pollution control are among topics discussed.

Principles and Practices of Incineration. Richard C. Corey. ix + 297 pages. Wiley-Interscience, 605 Third Avenue, New York, N.Y. 10016. 1969. $14.95, hard cover. ■

The Biological Aspects of Water Pollution. Charles G. Wilbur. vii + 296 pages. Charles C. Thomas, Publisher, 301-327 E. Lawrence Ave., Springfield, Ill. 1969. $23.75, hard cover. ■

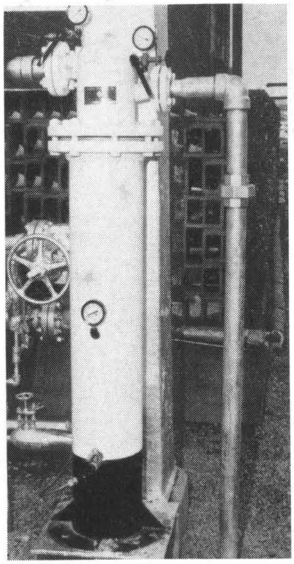
Garbage As You Like It: A Plan to Stop Pollution by Using Our Nation's Wastes. Jerome Goldstein. 243 pages. Rodale Books, Inc., 33 E. Minor St., Emmaus, Pa. 18049. 1969. $4.95, hard cover. ■

Progress in Oceanography: Volume 5 Edited by Mary Sears. xi + 191 pages. Permagon Press, Inc., Maxwell House, Fairview Park, Elmsford, N.Y. 10523. 1969. $11.00, hard cover. ■

Natural Resource Information for Economic Development. Orris C. Herfindahl. A Resources for the Future Publication. ix + 212 pages. Johns Hopkins Press, Baltimore, Md. 21218. 1969. $7.00, hard cover. ■

An Oceanic Quest: The International Decade of Ocean Exploration. Publication 1709. Prepared under the auspices of the Committee on Oceanography, National Research Council, and Committee on Ocean Engineering, National Academy of Engineering. 115 pages. National Academy of Sciences, 2101 Constitution Ave., N.W., Washington, D.C. 20418. 1969. $3.75, paper. ■

new products digest



Cyclone separator

The company claims that the Cor-Clone is ideal for removing suspended solids—mud, silt, sand, dead algae—from process cooling water in recirculating and once-through cooling systems. The continuous operating cyclone separator achieves separation by vertical inertia controlled within specific ranges. Containing no moving parts, the device is easy to maintain, and is available in light models having separator capacities of 5-300 g.p.m. which will control suspended solids of system capacities from 500-500,000 gallons. Vulcan Lab. **61**

Automatic stack monitor

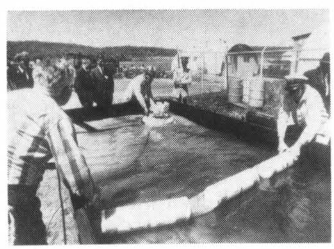
The AISI Stack Monitor—an automatic mass effluent monitoring system which can be applied as a process control device or air pollution monitor to stacks discharging particulate matter—is available. The device has specific application in such steelmaking processes as basic oxygen furnace, blast furnace, and open hearth, as well as in power generation, paper mills, cement plants, and chemical and petroleum industries, the company says. Research Appliance Co. **62**

Slime and algae suppressant

A new water treatment agent is designed to control slime deposits in recirculating cooling water systems. The company claims that dispersants contained in Nalco 209—a dry pulverized chlorine-release compound—help to remove existing deposits and prevent fouling due to buildup of new microbial or chemical deposits. Nalco Chemical Co. **63**

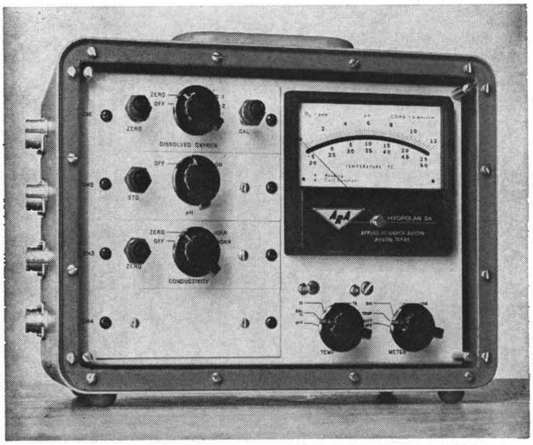
Refuse compactor

A small, low investment refuse compactor for use in high-rise buildings is available. The PowerMite is a hydraulic stationary packer which crushes refuse inside an attached container. When the container is full, it is detached, hauled away by a truck handling unit, emptied, and returned to the PowerMite. The company says the unit can be used with any size container system—ranging from 3 cubic yards-42 cubic yards. Dempster Brothers, Inc. **64**



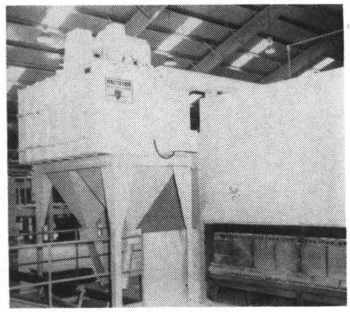
Sweeping up oil spills

The Sunshine Chemical Oil Recovery Broom (SCORB)—or Seabroom—works with Slickbar (a weighted plastic curtain which surrounds an oil spill) to clean up oil spills in the sea. Seabroom, which floats on the water, has vacuumed up 170 gallons of fuel oil in minutes, according to the company. In addition, after the spill is sucked up, water settles out of the recovered mixture, and the oil can be reused. Sunshine Chemical Corp. **65**



Atmospheric particle counter

Accurate long-term monitoring of particulate air pollution is possible with a new analytical particle counter, according to the company. The device counts particles in the atmosphere at concentrations up to 10 million particles per cubic foot, analyzing one cubic foot of air per minute, optically detecting and registering particles as small as 0.3 μ in one of four digital counter channels. Particles detected over a one minute period are summed up in the counters and automatically printed out by an integral digital printer. Particle Technology, Inc. **66**



Dust filter

The Pactecon Dust Collector recovers dust and sand from kiln processed brick cleaned by sand blowing as the cooled brick passes through the sand blowing operation. Continuous operation and intermittent models handle volumes of 300-3000 c.f.m. at temperatures to 250° F. with 99.9% collection of particles over 1-2 micron in size, the company says. W. W. Sly Manufacturing Co. **67**

Continuous level measurement

A continuous level measuring instrument, providing uninterrupted level readings under loading, unloading, and storage conditions of virtually all liquids and dry materials, is available. The Uni-Sonic-100 gage operates on sonic echo ranging principles accomplishing accurate and instant level gaging over a 0-200 foot range, regardless of container type, size, and location, according to the manufacturer. The instrument is designed to gage all liquids, including slurries and highly viscous substances, and can measure dry bulk materials used in mining, paper, cement, plastics, ceramic, food, and chemical industries. Inventron Industries, Inc. **68**

new literature digest

Waste water treatment. Two publications discuss possible applications and advantages of activated carbon to waste water treatment. Bulletin D-110, "Activated Carbon for Waste Water Treatment" covers such topics as when to consider activated carbon for solving pollution problems, which carbon process is best, how much is required, and expected costs. "Evaluation of Granular Carbon for Waste Water Treatment (D-111) describes powdered carbon tests, laboratory column tests, and pilot carbon tests. Both publications feature flow sketches and diagrams. Atlas Chemical Industries, Inc. **91**

Water pollution control. Case histories of successful application of the Mixmeter systems in treatment of industrial waste water are included in a 4 page bulletin. The continuously electronic controlled, portable, semipermanent and permanent installations have wide application in mills, mines, water and sewage works, as well as in chemical, food, and paper processing industries, according to the manufacturer. Shirley Machine Co. **92**

Deodorant insecticide. A technical report describes the effectiveness of Deodorant Insectex Granules (DIG) in eliminating odors and destroying insects. The company claims that DIG ". . . releases a vapor blanket which kills flies, gnats, roaches, termites . . . and other flying and crawling insects attracted by wastes and garbage, while it inhibits the spread of odors." Eagle Chemical Co. **93**

Air pollution instrumentation. The company's line of instruments with application in air pollution detection and control are listed in a new catalog. Combustible gas detectors, combustion analyzers, temperature and humidity recorders, and various test devices are included. Bacharach Instrument Co. **94**

Notes about littering. A 19 page brochure presents basic facts about littering—what it is, who does it, why, and how it can be stopped. Illustrated with whimsical drawings, "The Litter Fact Book" aims to provide the

general public with some information on a serious contemporary problem. Glass Containers Manufacturers Institute, Inc. **95**

Evaporative losses. "Activated Carbon for Effective Control of Evaporative Losses" is the title of a new 10 page publication. Bulletin 690086 considers the physical properties of activated carbon that affect its ability to store and then release gasoline vapors. Selection of activated carbon, adsorptive life of the carbon, and factors affecting system design are among topics covered. The bulletin also features graphic material and a list of references. Calgon Corp. **96**

Solving waste problems. A 12 page illustrated brochure (Bulletin 69 WWT01-A) discusses how waste treatment systems can be designed to solve various domestic, commercial, and industrial waste problems. Secondary treatment systems, based on the Aero-pack modified activated sludge plant, are described, and combination secondary-tertiary treatment systems are detailed. Dravo Corp. **97**

Wet scrubbers. The Flooded Disc wet scrubbers for dust and mist collection are detailed in Bulletin RC-975. The 12 page publication describes operating principle, features, and applications, and includes tables of dimensions. The company says the scrubber, which has no nozzles, requires no high water pressure, has a turn down ratio of more than 20:1, and is used for in process gas cleaning, product recovery, plant environmental control, and removal of gaseous pollutants. Research-Cottrell, Inc. **98**

Films

The National Medical Audiovisual Center has announced the availability of three films concerning the air pollution problem:

"Beware the Wind" (M-1707-X) is a 16 mm, 22 minute, color and sound presentation, narrated by Robert Preston. The film shows the origin and evolution of dirty air in American and European cities, stressing the threat of worldwide pollution. Principal air pollution sources, effects of air pollution on animals, people, and property, and ways of technologically cleaning the air also are illustrated.

"On a Clear Day You Can Almost See Terminal Tower" (M-1712-X) is a 16 mm, 22 minute, color and sound film produced by a Cleveland (Ohio) TV station. In addition to presenting the principal sources of the city's air pollution and their impact on city life, the film stresses the need for taking preventive action, and contrasts the level of air pollution in Cleveland with that of Cleveland, Tenn.

"Beware of Ill Winds" (F-1745-X) is a 35 mm, 39 frame filmstrip with accompanying manual, which describes the regional approach to air pollution control under provisions of the Air Quality Act. The role of public hearings prior to state adoption of federal standards is discussed.

Films are available for free, short-term loan. Order by title and number from: National Medical Audiovisual Center (Annex), Station K, Atlanta, Ga. 30324 (Write direct).

meeting guide

December 15–17
American Petroleum Institute and Federal Water Pollution Control Administration

Joint Conference on the Prevention and Control of Oil Spillage

Americana Hotel, New York City

Included in the 3 day session are a review of recent major oil spill incidents; discussion of the federal government's plan for dealing with such incidents; and industry's plan to deal with oil spills. In addition, such topics as harvesting techniques and fate and behavior of oil in water will be covered. For information: W. A. Burhouse, American Petroleum Institute, 1271 Avenue of the Americas, New York, N. Y. 10020

December 26–31
American Association for the Advancement of Science

136th Annual Meeting

Boston, Mass.

Featured at this year's meeting will be a 1 day symposium, Power Generation and Environmental Change: Reconciling man's desire for power with the needs of his environment. Another 1 day session will be devoted to a symposium on undergraduate education in environmental science. Information available through AAAS, 1515 Massachusetts Ave. NW, Washington, D.C. 20005

January 15–16
TAPPI, Michigan Division of the Paper Industry, and Western Michigan University

14th Annual Pulp and Paper Conference

Western Michigan University Student Center, Kalamazoo

Chemical additives—application, theory, and control is the theme of the conference. Papers and discussion will treat such topics as wet strength, sizing, retention aids, and the effects of such chemicals on effluent abatement control. For information, contact: Department of Paper Technology, Western Michigan University, Kalamazoo, Mich. 49001

January 25–30
Engineering Foundation

Research Conference on Waste Water Engineering in the Food Industry

Asilomar Conference Grounds, Pacific Grove, Calif.

Purpose of the conference is to investigate the management of waste water in the food industry, pollution abatement, treatment procedures, and cost reduction as related to the food industry. Topics to be discussed include pollution abatement, planning with people; economics of managing waste water; solids handling from waste water treatment; and FWPCA demonstration grants.

February 2–5
Weed Science Society of America

Annual Meeting

Queen Elizabeth Hotel, Montreal, Canada

Weed science and food—Canada, Britain, and the U.S. is the theme of the meeting. Leading authorities from government and industry will present papers dealing with various aspects of weed science and vegetation control.

February 11–12
Illinois Department of Public Health, and Department of Civil Engineering, University of Illinois

12th Sanitary Engineering Conference

Urbana, Ill.

The conference is aimed toward engineers and scientists in government, industry, or private practice, as well as water works managers and operators. Sessions will include papers and discussion topics under the general theme: Nitrate and water supply: source and control.

March 18–19
U.S. Bureau of Mines and IIT Research Institute

2nd Mineral Waste Utilization Symposium

Chicago, Ill.

This year's symposium will be divided into four sections, covering utilization of mining wastes; industrial wastes; municipal refuse; and scrap. Papers will be presented by investigators representing research centers, resources centers, and contractors. For information: Murray A. Schwartz, IIT Research Institute, 10 W. 35th St., Chicago, Ill. 60616

March 24–26
University of Houston and Environmental Control Administration

National Industrial Solid Wastes Management Conference

University of Houston, Tex.

Papers will be presented on such topics as research and development on organic and mineral industrial wastes characterizations; collection, handling, processing, conversion, or utilization; byproduct production processes from wastes; secondary material processes; economics; and resource recovery techniques from urban and industrial solid wastes. For further information: H. Nugent Myrick, Cullen College of Engineering, University of Houston, 3801 Cullen Blvd., Houston, Tex. 77004

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March 31–April 3
International Association for Great Lakes Research

13th Conference on Great Lakes Research

Statler Hotel, Buffalo, N.Y.

The program consists of five half day sessions of technical papers and a half day general session including a symposium of contributed papers on Great Lakes of the World. Purpose of the meeting is the promotion of all aspects of research and dissemination of research information on the Great Lakes and their basins.

April 19–22
American Association for Contamination Control

9th Annual Technical Meeting and Exhibit

Convention Center, Anaheim, Calif.

Technical sessions will feature presentation of papers on new work or developments for contamination control in industrial manufacturing or processing related to products and environment, or related to biological, pharmaceutical, hospital, or other applications in the life sciences. Subject areas include standards, control of environment, quality control, and packaging. For further information, contact: William T. Mahoney, AACC, Six Beacon St., Boston, Mass. 02108

Call for papers

December 31 deadline
American Society of Civil Engineers, and Department of Civil Engineering and the Water Resources Research Center, University of Massachusetts

3rd National Symposium on Sanitary Engineering Research

Abstracts may be submitted for a Specialty Conference on Disinfection, to be held July 13-15, 1970, at the University of Massachusetts, Amherst. Topics to be covered in the symposium are mode of biocidal action by disinfectants and other agents; kinetics of disinfection; water disinfection; effect of waste water disinfection on natural streams. Further details available from: Tsuan H. Feng or Lawrence N. Kuzminski, Department of Civil Engineering, University of Massachusetts, Amherst 01002

January 31 deadline
International Union of Air Pollution Prevention Associations

2nd International Air Pollution Conference

Proposals to present papers may be filed with the sponsors of the meeting, to be held Dec. 6-11, 1970, Washington, D.C. Six concurrent sessions will include air pollution chemistry and physics; air pollution meteorology; air pollution medicine and biology; air pollution engineering; air pollution control administration; air pollution surveys. Proposals may be submitted in the language of the author. For information: Arthur C. Stern, Department of Environmental Sciences and Engineering, University of North Carolina, P.O. Box 630, Chapel Hill, N.C. 27514

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All authors' names and all names appearing in articles are indexed, except for those names appearing in meeting programs, feature articles, research papers, bibliographies, book reviews, and the Pollution Control Directory portion of the October issue.

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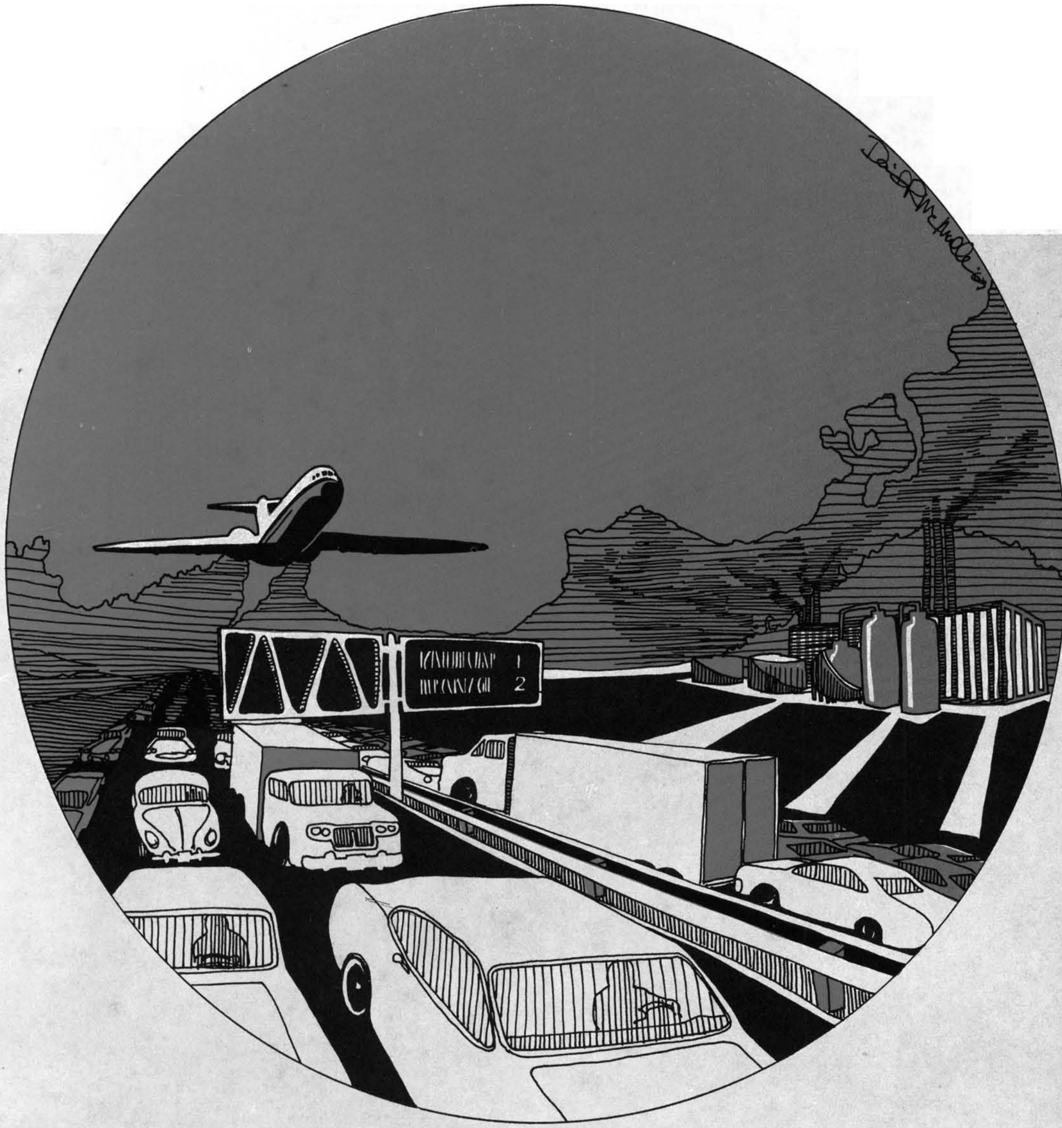

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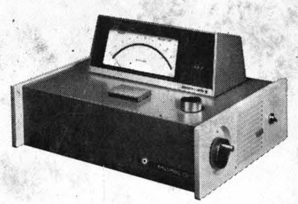

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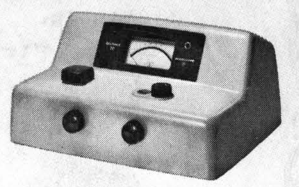

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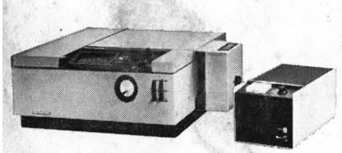

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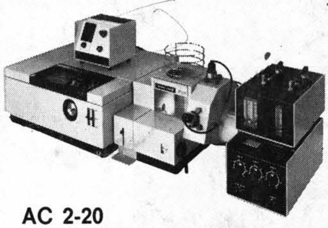

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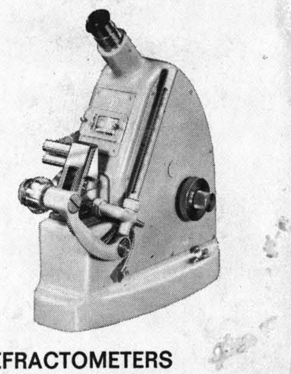

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