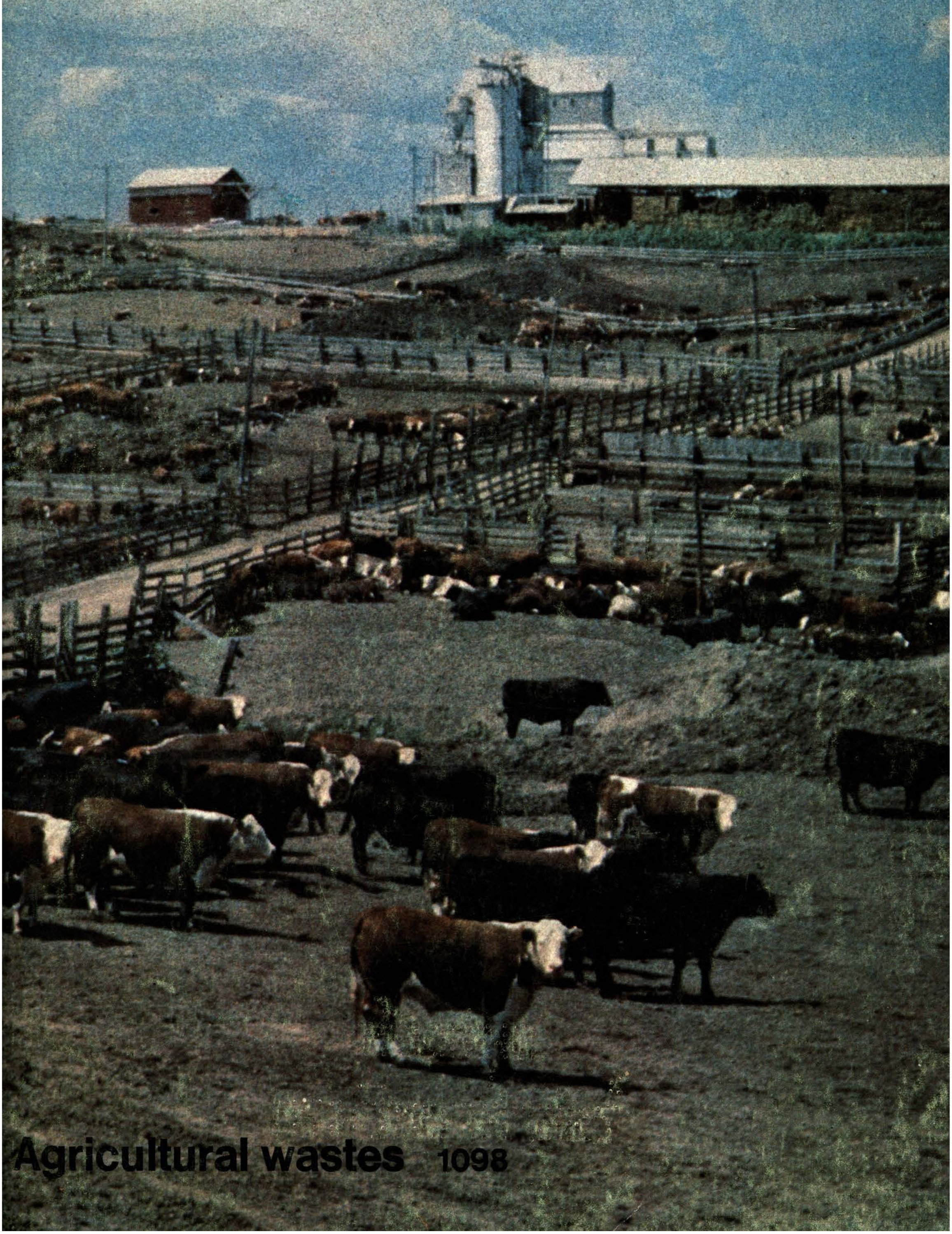
DECEMBER 1970

ENVIRONMENTAL Science & Technology



Agricultural wastes 1098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Fate of phosphorus in waste treatment processes: Enhanced removal of phosphate by activated sludge 1115

A. B. Menar and D. Jenkins

In hard water sewages, the enhanced phosphate removal by activated sludge can be rationally explained by calcium phosphate precipitation followed by trapping of the precipitate by the activated sludge floc. Phosphate removal from 20 to 30% were achieved for influent containing 10 mg P per liter. The pH in the activated sludge aeration tank is the controlling factor; operational parameters—organic loading, mixed liquor, suspended solids, and dissolved oxygen—had no effect on the removal enhancement.

Nitrogen fixation by nonsymbiotic microorganisms in some California soils 1122

P. L. Steyn and C. C. Delwiche

The rate of nitrogen fixation in different soils can be measured by two methods—direct isotopic observation of fixation rates and a more laborious acetylene ethylene method. The isotopic method was used under conditions simulated in the field; data from the two methods agree reasonably well, with some variability.

Turbulence promoters for hyperfiltration with dynamic membranes 1129

D. G. Thomas, P. H. Hayes, W. R. Mixon, J. D. Sheppard, W. L. Griffith, and R. M. Keller

Desalination of water by hyperfiltration with dynamic membranes is pollution control where removal of organic contaminants and reduction of inorganic salt concentration are the principal objectives. Detached turbulence promoters can now be fabricated which do not block the membrane surface nor provide stagnant regions where solids can accumulate or where the concentration of rejected salts can build up. Use of the promoters can result in a 50% reduction in inlet velocity, a 35% reduction in inlet pressure, and a 65% reduction in tube length.

The monitoring of hydrogen, methane, and hydrocarbons in the atmosphere 1136

W. H. King, Jr.

Atmospheric hydrocarbons, one group of pollutants which are now controlled by federal law, can be monitored by two new methods. The first method measures hydrogen, methane, reactive hydrocarbons, and unreactive hydrocarbons; it uses a selective combustor and a water sorption detector. The second method measures methane and methane plus all other hydrocarbons; it uses the selective combustor techniques with a flame-ionization detector. Although methane accounts for 60 to 90% of atmospheric hydrocarbons, it is photochemically inert.

Singlet oxygen in the environmental sciences. Possible production of $^1O_2$ by energy transfer following oxygen-enhanced absorptions 1141

J. W. Coomber, D. M. Hebert, W. A. Kummer, D. G. Marsh, and J. N. Pitts, Jr.

A mechanism for the production of singlet molecular oxygen, a reactive species in photochemical smog, has been suggested. The oxygen-enhanced absorption of light by organic pollutant molecules is a possible significant source of this material in polluted urban atmospheres. In a study with polyvinyl chloride, the species was formed by the oxygen-enhanced absorption of the polyene. Whether oxygen-enhanced absorptions have any bearing on the degradation of polyene compounds in biological systems must await further study.

Communication

Sludge dewatering by high-rate freezing at small temperature differences 1145

C. Y. Cheng, D. M. Updegraff, and L. W. Ross

Sludge has been dewatered by freezing in the past, but now by use of a film-freezing technique and the addition of at least 20 ppm of aluminum as aluminum sulfate, efficient dewatering has been achieved. The dewatering is accomplished in short times and with small change in temperature (delta T), making the process economically attractive and deserving of renewed attention. The ice film conducts heat sufficiently rapidly so that the external heat transfer mechanism controls the process.

Correspondence

Hartley photolysis of ozone as a source of singlet oxygen in polluted atmospheres 1147

W. J. Hamming

Reply by R. H. Kummler, M. H. Bortner, and T. Bauer

The importance of singlet oxygen from ozone photodissociation cannot compete with that of atomic oxygen in the photochemical smog process, especially during the morning hours when the photochemical reactions are really just getting started, and neither ozone nor singlet oxygen are present in measurable quantities. Earlier authors reported that singlet oxygen was a more important oxidizing agent in photochemical smog formation than atomic oxygen. They note that final decision on the importance of singlet oxygen awaits further evaluation of data.

Correction

Spectrophotometric determination of atmospheric fluorides 1150

P. W. West, G. R. Lyles, and J. L. Miller

This article appeared originally in ES&T, June 1970, page 487.

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letters

Missouri water quality standard

DEAR SIR:

In the Environmental Currents section of the September 1970 issue of ES&T (page 717), you report that the compromise language for the dissolved oxygen criterion for the Missouri River was not included in the approved standards.

On July 30, 1970, the Department of Interior approved the action taken by the Board, and that did include the statement on low dissolved oxygen. The dissolved oxygen standard for the Missouri River reads in full:

> The dissolved oxygen concentration shall be maintained at a minimum 5.0 mg/liter or greater. It is recognized that this standard is violated at frequent intervals for periods of two to three weeks during rising river stages or flooding in the basin. The specific sources which cause such depressions include major contributions from surface runoff (urban areas, farms, and associated activities) which have not been clearly identified. We recognize the need for a coordinated effort on the part of the tributary states and federal government to inventory these waste sources so that implementation plans can be developed to remedy the dissolved oxygen deficiency.

Peggy J. Keilholz
Missouri Water Pollution Board
Jefferson City, Mo. 65101

Scientists lose credibility

DEAR SIR:

Your editorial in the September issue ("Crying wolf once too often") made some excellent points. However, I should like to suggest that if the public is beginning to grow indifferent to cries of havoc, it must surely be cynically yawning over the many times scientists and governmental regulating agencies fail to act when they *do* know the effects of a pollutant.

We may rightfully deplore the mass media's penchant for attention-getting cataclysms, but we must also deplore their general lack of interest in exposing the temporizing of scientific bodies when confronted with clear evidence of environmental damage.

More study and research are certainly needed, but perhaps faster and better action may be forthcoming if less importance is attached to economics when applying cost-benefit analysis to the results of the research.

It would seem the most frightening prospect is for the scientist to lose his credibility to a public that watches him introduce ever more destructive elements into the ecosystem, and then display hesitancy and incompetence in allaying the damage they cause.

John F. Wilson
Wisconsin Ecological Society
Green Bay, Wis. 54305

Two for the price of one

DEAR SIR:

I am writing in regard to your coverage of Biocide 233, no. 73 in the New Products department of the September issue of ES&T. You have inadvertently combined descriptions of Biocide 233 and Biocide 284.

Biocide 233 is a water soluble, nonmetallic organic compound used as a preservative for water-containing systems such as latex and resin emulsions, adhesives, paper coatings, and cutting fluids. Biocide 284, 10% methylene bisthiocyanate, controls bacteria, yeasts, fungi, and most other organisms in industrial systems, and has been especially formulated for use as a slimicide in paper mills and cooling towers.

You combined the characteristics of both of these chemicals as those pertaining to Biocide 233.

Donald Kent
Spiegel & Laddin, Inc.
New York, N.Y. 01016

Sophistication in air monitoring

DEAR SIR:

Your Outlook story, "Air monitoring: how much is enough?" (ES&T, September 1970, page 723) described a growing feeling of suspicion of the need for sophisticated monitoring systems. Now, a backlash against sophistication by some is predictable; there's an understandable drive to appear ultrapractical. But *all* the evidence must be weighed, not just that which supports a convenient point of view.

For instance, response time *and* data reduction cost must be included in weighing the level of sophistication suited to a particular air monitoring system. Anyone who has had to reduce yard after yard of strip-chart data, day after day, or who has been responsible for employing people to do it, is aware that if bright enough technicians can be hired, they will be bright enough to tire of the onerous job quickly. This leads to file-cabinets full of strip charts which are much less likely to be used than computer memories with the same data.

Solving this problem doesn't always require telemetry—there are several intermediate levels of sophistication available in bridging the gap between sensor and computer, such as on-site, machine-readable recording. But, when data reduction costs are honestly weighed with response capability (and other considerations), telemetry will *always* prove cost-beneficial for large systems. This can be readily demonstrated.

To limit the collection of data to legal constraints ("if no control action can be taken, the data are useless") is equally myopic. In the first place, not much data, if any, would have been collected in the past if this had always been a ground rule. Second, there are several kinds of desirable "actions." Most local meteorological data involve little control action, but advisories are used by nearly everyone. Third, usefulness is not restricted to immediate actions; historical data are of immense use in local air quality programs. Historical data on strip charts in file cabinets are seldom disinterred.

Finally, because of the lead time required for designing, installing, and debugging adequate systems, cities with no real action plans now, but with mahogany atmospheres, should think of real-time public demands during future certain episodes. Again, it has been shown that telemetry and computerized data reduction are always the cheapest way to go if the system is large and the problem is real.

Daniel L. Esau
Litton Systems Inc.
Camarillo, Calif. 93010

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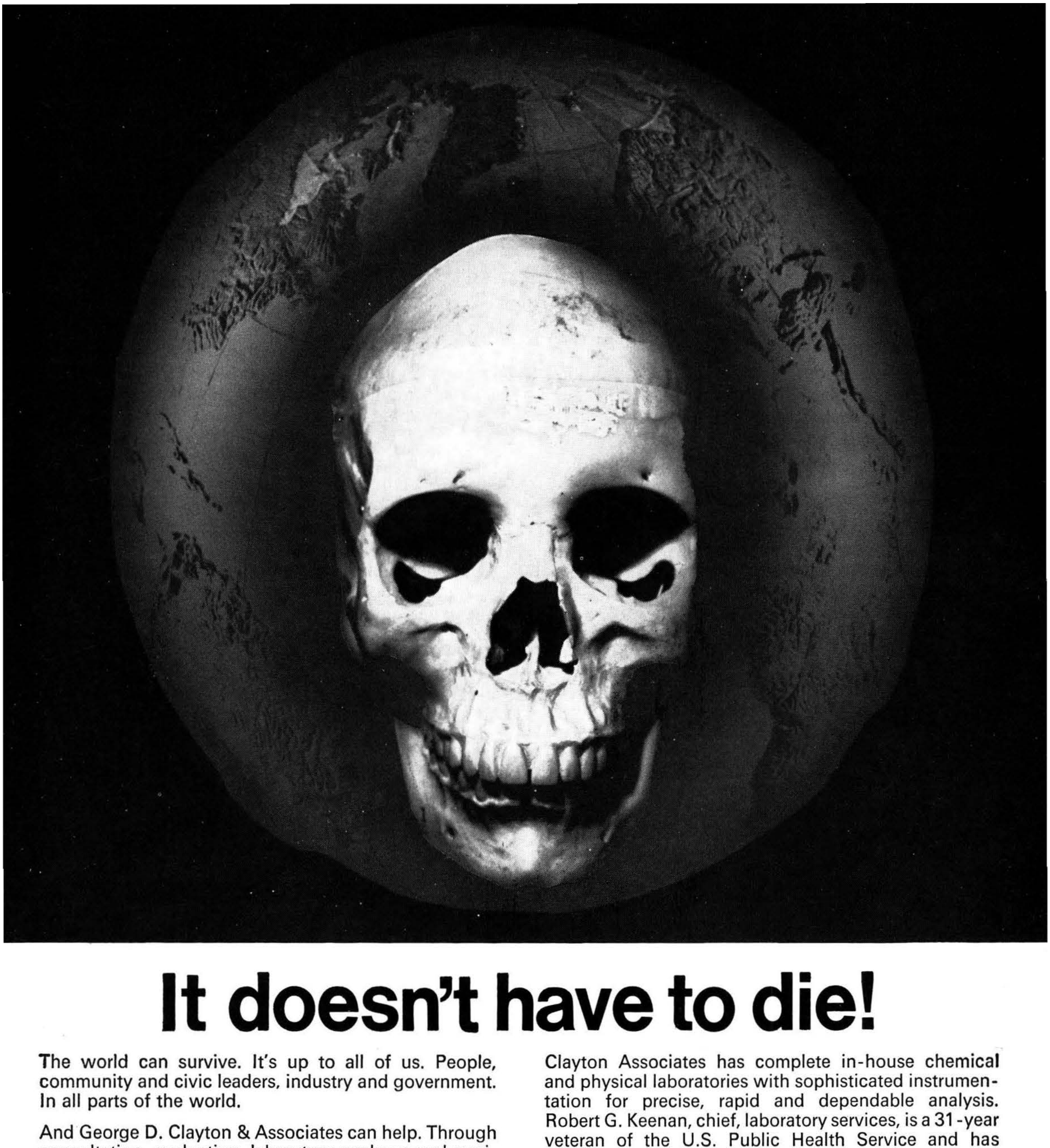

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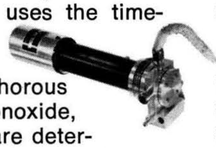

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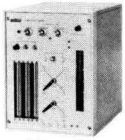

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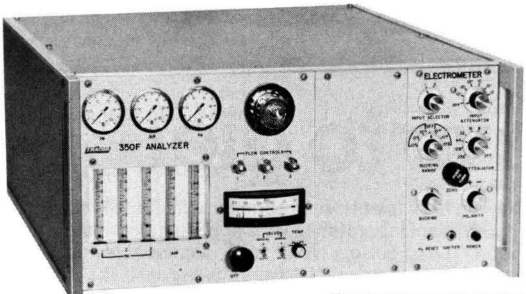

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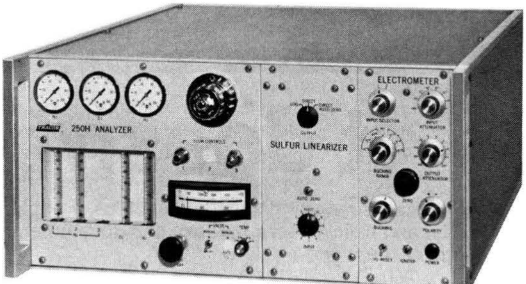
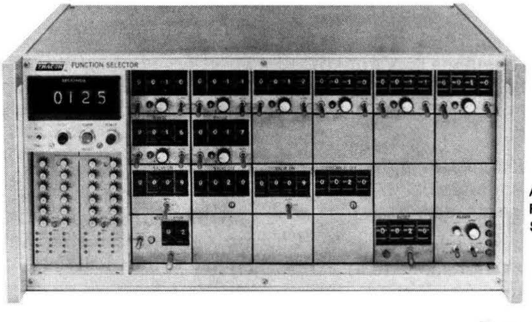


250H ANALYZER FOR
SULFUR AND PHOSPHORUS



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ES&T to carry classified job advertising

We aim to bring together employers and employees in the fast-growing but diffuse environmental field

As Perry Como used to sing on his television show, "We get letters." Unlike those sent to Mr. Como, letters to ES&T can rarely be categorized as fan mail, of course, but they are invariably interesting and sometimes instructive. Many come from students, and their sentiments can be typified by the following extract from a letter written by an electrical engineering student at an eastern university: "Within the last two or three years I have become increasingly concerned with the state of man's environment. I believe that I am sincere in my desire to try to direct the efforts of my career in the area of the environment. I am not just trying to jump on the bandwagon." This particular student was worried that his chosen major—electrical engineering—was not a good entree to an environmental job; he wished in retrospect that he had taken biology. We advised him that biology was not the only discipline needed to ameliorate the state of man's environment, and encouraged him to continue with electrical engineering. The only trouble was that we could not specifically tell him about jobs for electrical engineers that would involve environmental matters as a major component.

We don't just receive letters from students, of course. We also get them from experienced technical men and women who seek, like the student, to "do something about the environment." Again, we cannot help too much. Although we know that jobs are available, we just do not know where, exactly, they are. Occasionally, an employer will write us, asking if we know of someone with specific capabilities in the environmental field. Sometimes we do, but more often we do not. So, much as we have wanted to bring potential employer and potential employee together, we have until now had no means of doing so.

There seems little doubt that there is a crying need for manpower to carry on the fight against environmental ills. In fact, the shortage has been described by some as critical. The National Air Pollution Control Administration (NAPCA) has estimated that state and local air pollution control agencies need to increase, immediately, their personnel from 2840 to 8000 to carry out responsibilities called for by federal law. In the private sector, NAPCA estimates that 20,000 man-years are currently assigned to air pollution activities in industries; this number needs to be increased to 35,000 man-years by 1974. Undoubtedly, similar shortages, or worse, exist in the water pollution control field and in other environmental control areas.

Naturally, there is a great need for people who are trained in some aspect of environmental science or technology. Since environment is essentially an interdisciplinary subject, few schools have had programs in the area, although that situation is rapidly changing. (One area that ES&T will attempt to cover during 1971 is opportunity for education—both at the basic and graduate levels—in environmental subjects.)

But there is little use in educating people if there are no jobs for them, as American education has discovered in its sorrow during the recent financial squeeze. Consequently, ES&T has decided that the most logical and efficient way to match potential employers with potential employees is to publish a classified job advertising section each month. Readers may already have noticed several fairly large advertisements by employers in the pages of recent issues. Employers will still be able to place such ads, of course, but they will be supplemented, starting in 1971, by lower-cost advertising that is standardized in typeface and format, much in the style of *Chemical & Engineering News*. The service will be offered for both positions wanted and positions open. Details will be handled by our advertising management, Century Communications Corp., 142 East Ave., Norwalk, Conn. 06851. Those who are seeking employment as well as those seeking employees in the environmental field are urged to contact Century for full particulars.

D. H. Michael Bowen

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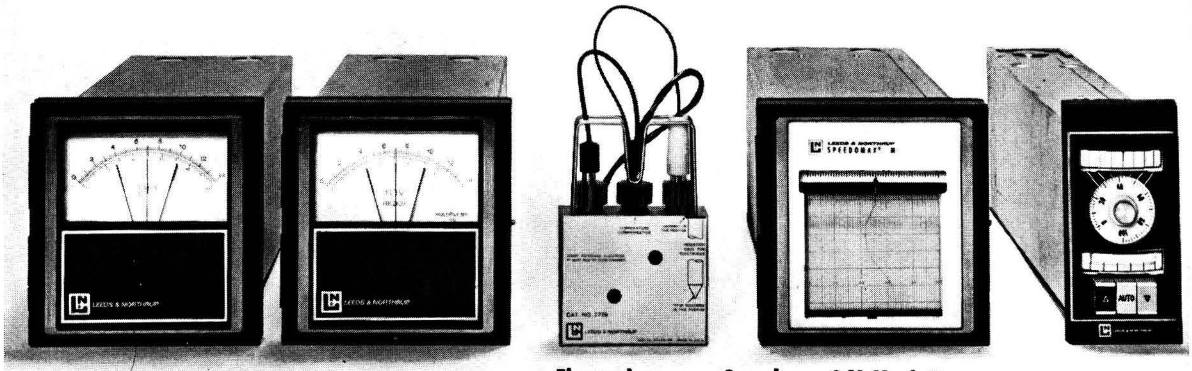

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Richard J. Sullivan
Commissioner, New Jersey Department of Environmental Protection

Pollution problems—in spades

I'm not so presumptuous as to tell the world how to resolve its environmental crises. But I am grateful for the invitation to discuss New Jersey's pollution-fighting activities briefly, in the hope that our experiences may help others.

In proportion to its size, New Jersey is the nation's most densely populated state as well as having the highest vehicular density of any state. Because of its concentration of population, industry, traffic, and agriculture, there is scarcely any pollution problem which New Jersey doesn't have—in spades.

No wonder that the state has been a pioneer in pollution control. New Jersey passed water pollution control laws as far back as 1899. It enacted the nation's first statewide air pollution control law—one year ahead of the first federal act. The updated State Air Pollution Control Law empowers the Department of Environmental Protection to promulgate regulatory codes implementing state air pollution control laws. These codes are very stringent and rigidly enforced. In this, the courts of the state have been our firm allies, upholding the department's stand in every instance in which enforcement procedure has led to court action. Since 1967, New Jersey has prosecuted and won some 200 antipollution cases of all kinds, and has collected about $250,000 in penalties. This amount includes a $20,000 fine, the largest air pollution penalty ever levied.

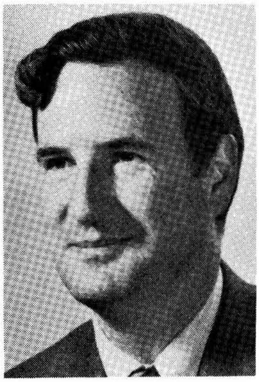
Vital as rigorous enforcement action is, it is only one aspect of New Jersey's tripartite thrust. The state employs positive measures of incentive and prevention, as well as policing and sometimes punitive enforcement measures. Recognizing that pollution control techniques and devices are costly ($10 billion a year is said to be spent nationally on pollution control), New Jersey offers the incentive of tax exemption for state-improved air and water control devices. However, this exemption may be revoked by the Commissioner of the Department of Environmental Protection at any time if the industry fails to comply with pollution control requirements.

To prevent as much pollution as possible from happening in the first place, regulations require an industry to submit specifications for examination before the state issues the requisite permit to install or alter, and a certificate to operate, equipment either causing or controlling air pollution. The state also requires an industry to file plans showing that its waste disposal techniques will not create water pollution, before the industry is granted a construction license.

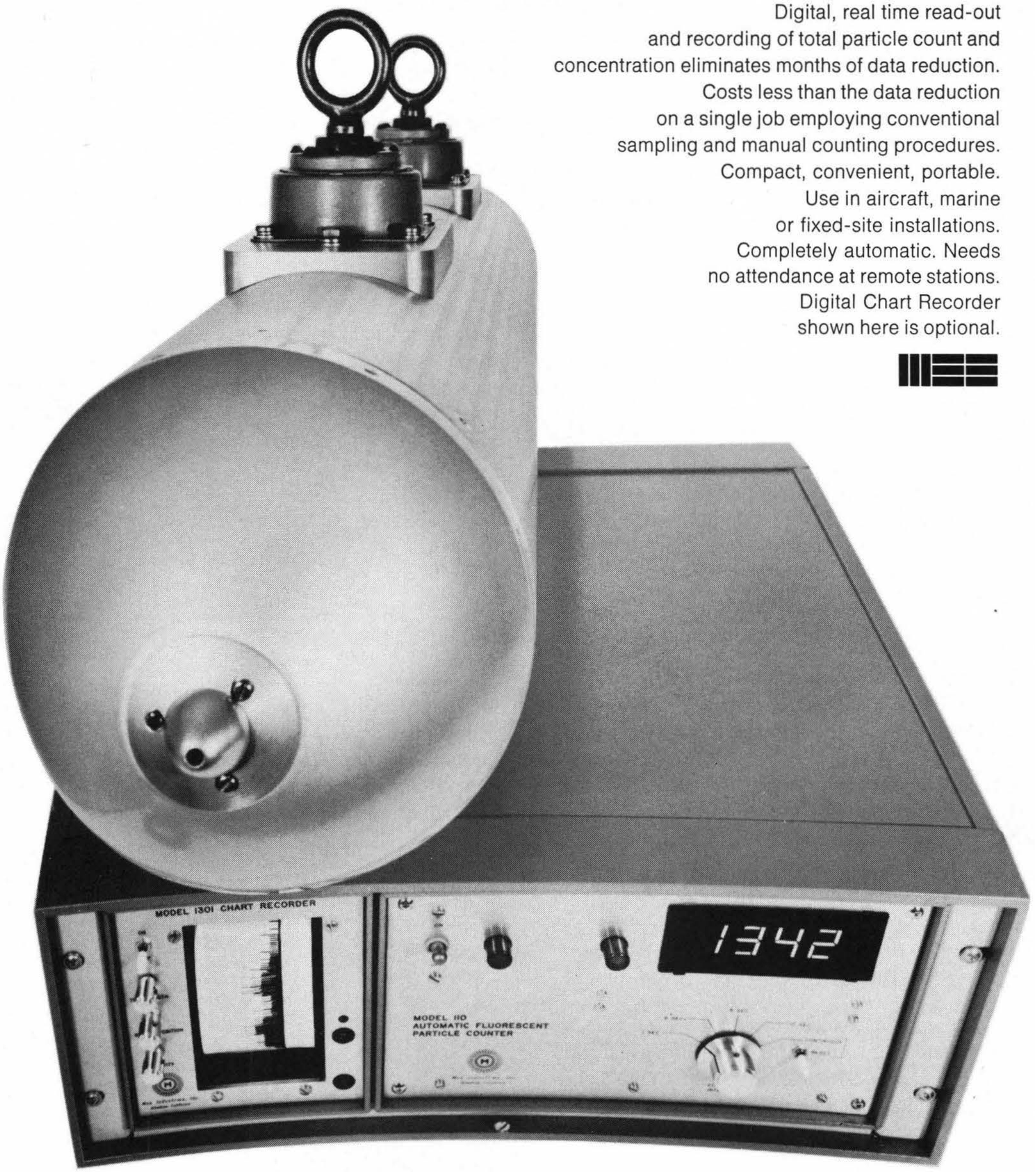
Though we have made some notable strides, our environment is still sick, and it may get sicker before it gets well. But we are determined that it *shall* get well, and we have documented evidence that the patient is showing signs of responding to treatment.

The season for making resolutions is approaching. Let us who have a personal commitment to environmental protection resolve to help develop in others, by every possible means, an acute sense of environmental wisdom. In too many cases, the frontier mentality is still with us. We think we can do what we please with our natural resources because they will always be around. We must disabuse ourselves of this illusion.

The next generation of Americans must be inculcated with the values of environmental sensitivity. They must be made to realize their place in the ecological system, and that abuse of the environment is, in effect, self-destruction. We must replace the right-of-exploitation concept with the responsibility-of-stewardship concept. We must learn that it is in our own interest to observe the rights of others. If this were learned universally, not only would we have a cleaner physical environment, but we might also develop the mental climate ultimately enabling us to achieve peace on earth as well.



Richard J. Sullivan, a mechanical engineer by training, has been employed by the State of New Jersey since 1950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WASHINGTON

Nixon picks Ruckelshaus as EPA administrator

William D. Ruckelshaus

Prior to his appointment as administrator of the Environmental Protection Agency (EPA) last month, William D. Ruckelshaus was assistant attorney general of the civil division in the Department of Justice. Ruckelshaus is no Johnny-come-lately to environmental matters. His former posts include majority leader of the Indiana legislature (1966–69) and assistant attorney general for the state of Indiana, where he prosecuted water polluters and other violators of state health and environmental control laws and regulations. What's more, he wrote the Indiana air pollution control law in 1963.

FWQA focus: industrial inventory and enforcement

The Federal Water Quality Administration (FWQA) started its inventory of industrial wastes last month by mailing FWQA Forms 120 to 250 companies. Interior Secretary Walter J. Hickel indicated his displeasure recently with the 1977 timetable agreed to by conferees in the Potomac River enforcement conference, which was first convened in 1957. Hickel wants the date moved to 1974; by the end of this month conferees are to report on the feasibility of moving the date for expansion of the Blue Plains Plant (Washington, D.C.) to 309 mgd from 240 mgd at a cost of $366 million.

NAPCA finalizes controls for '72 to '74 cars

The National Air Pollution Control Administration's (NAPCA) revised regulations and test procedures for '72 to '74 vehicles became effective last month. The new regulations and standards will reduce hydrocarbons (HC) emissions 80% and carbon monoxide (CO) emissions 69% of pre-1968 cars without exhaust controls. Although current standards were intended to achieve this level of control, the 1970 cars only showed 73% control of HC and 62% control of CO. Thus, the 1972 emissions standards have been set slightly higher than those proposed earlier (ES&T, August 1970, page 627).

Second national contract let for operator training

The Departments of Labor and Interior's FWQA completed a second 18-month contract for the training of 1000 waste treatment plant operators in 27 states. The training is aimed at paraprofessionals—underskilled, unemployed, or underemployed disadvantaged workers. The $1.26 million contract includes $689,900 for on-the-job training under the Manpower Development and Training Act, and $570,000 from the Department of Health, Education, and Welfare supplemental funds. The first national contact (NC) provided for the training of 940 trainees in 20 states (ES&T, November 1969, page 1156).

Peace Corps finds new role in the environmental decade

The Peace Corps (PC) and Smithsonian Institution (SI) recently joined forces for sending environmental advisers to developing countries. Under the new program, which was announced by PC director Joseph Blatchford and SI secretary S. Dillon Ripley, volunteers would be sent abroad to deal with water pollution, resource management, and score of other environmental problems. "Many of the volunteers are expected to come from post-graduate schools in the biological sciences and natural resource management," Ripley says. In the 60's decade, PC mainly sent educational advisers abroad.

STATES

Voters across U.S. pass water bond issues

State bond issues for water pollution control have been on ballots throughout the U.S. Illinois recently passed a $750 million grant for pollution control; $650 million is allotted for water pollution control, with the remainder for land pollution regulation. In California, a $250 million bond issue provides funds for construction of waste treatment facilities and enables California to receive federal assistance. Maine's voters approved a $4 million bond issue to aid in cleaning up oil spills. Floridians recently passed a constitutional amendment allotting $100 million per year for loan to municipalities for sewage facility construction or improvement.

Wigwam burners on the way out in Oregon

New emissions standards adopted for 1971 by the Lane County (Ore.) Regional Air Pollution Authority will have the effect of outlawing wigwam burners, which are commonly used to dispose of wood refuse in the lumber industry. Because of the expense involved in upgrading wigwams to standards required by the new regulations, it is likely that wood refuse will henceforth be burned elsewhere. Fortunately, low water levels in the dams serving northwest hydroelectric plants have produced a power shortage, and Oregon utilities have needed to use wood refuse and other wastes in conventional steam-raising plant to augment electricity supplies.

Sen. Edmund S. Muskie

Muskie views Machiasport oil dilemma

In reference to the Senate hearings called to explore oil and coastal environment situation in Machiasport, Me., Sen. E. S. Muskie (D.-Me.) said these hearings show that "no methods presently exist which would either effectively foreclose the possibility of massive oil spills or sufficiently clean them up if they were to occur." Muskie believes that the oil industry must abide by the terms that Maine decrees (including environmental respect) or not come to Machiasport at all.

Iowa begins survey of pesticide levels

The State Hygenic Laboratory and the State Conservation Commission are conducting a statewide survey of pesticide levels in fish. Research at the University of Iowa is currently in progress to determine whether reverse osmosis can be used to remove small pesticide molecules and other trace organic substances from water. These programs are part of a broad-based University of Iowa Research effort dealing with problems of pesticides in the environment.

Pennsylvania, OSW study water desalting

The Office of Saline Water (OSW) and the state of Pennsylvania are exploring the potential of desalting processes to treat acid mine drainage and provide supplemental supplies of freshwater for municipalties and industry. Secretary of the Interior Walter J. Hickel and the Pennsylvania Department of Mines and Minerals Industries announced the two-year agreement which calls for: • Information exchange related to research on desalting; • Research in the desalting processes for acid mine drainage and other saline waters; • Development of a specific desalting plant.

environmental currents

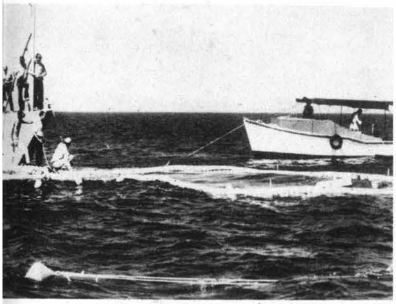
TECHNOLOGY

Clean fuel development efforts speeded up

The quest for low-sulfur fuels is moving into high gear on many fronts. Along with a stepped-up effort on coal pyrite removal (see page 1104), other fuel upgrading plans have been announced: In October, the Institute of Gas Technology unveiled a coal conversion pilot plant for making low-sulfur pipeline gas. The unit will be in full operation by March, and plans call for a commercial process by 1977. Earlier this year, Panhandle Eastern Pipe Line Co. and Peabody Coal undertook joint development of a mine-mouth, 300 ft^3/day coal gasification process, with hopes for commercialization by 1980. Esso Research & Engineering has just been issued a patent on fuel oil desulfurization; an Esso affiliate is already using this process at a new Venezuelan plant that supplies residual fuel oil to the eastern U.S.

New auto exhaust catalyst curbs NO_x by 90%

Esso Research & Engineering says a unique nickel-copper catalyst, "the most promising" yet uncovered, can reduce NO_x emissions from 1970 model cars by 90%. A 90% reduction capability would meet proposed post-1975 emission standards, but Esso says the catalyst is not yet ready for commercial use. At present stage of development, the catalyst would need replacement every 8000 to 15,000 miles with unleaded gas, and more frequently with leaded gas. The company says it will present further technical details in a paper scheduled for presentation in a few months. But in its announcement, Esso hints at a dual-catalyst system for complete control that might include the new catalyst for nitrogen oxides control plus a second one to control hydrocarbons and carbon monoxide emissions.



Oil containment

Oil containment method slated for full testing

The U.S. Coast Guard has awarded a $1 million contract to Johns-Manville Corp. for further development of an oil containment system for offshore oil spills. The J-M containment method was one of four, selected from 40 designs originally submitted, chosen by the Coast Guard for small-scale development. A one-quarter scale model was built and tested in May and successfully demonstrated 99% recovery of a test soybean oil slick in the Gulf of Mexico. The new development contract calls for building a full-scale prototype that can be air dropped and tested in rough sea conditions: 5-ft waves, 20-mph winds, and two-knot currents. J-M will serve as prime contractor and develop the prototype barrier; three other firms are involved and will develop the deployment systems.

New plastic bottle incinerates without noxious emissions

An acrylonitrile-based plastic, suitable for beverage and food containers that can be safely incinerated, has been developed by Vistron Corp., a subsidiary of Standard Oil Co. (Ohio). At a recent meeting of the Society of Plastics Engineers, Vistron's J. D. Idol gave results of tests on the resin conducted at Midwest Research Institute and New York University: Levels of up to 80% in incinerated refuse did not change emissions significantly. Nitrogen oxides were released in amounts typical of gas-fired appliances, and nitrogen containing hydrocarbons were affected more by incinerator operation than by the presence of the plastic. Total hydrocarbon emissions were not affected. Bottles made from the resin have been successfully test-marketed, and Vistron is already making semicommercial quantities of the resin.

When it comes to H_2S analysis... The Air Monitor IIA now has the answers.

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The Air Monitor IIA is based upon those features that have made continuous flow analysis the most reliable method for automated wet chemical analysis. It features a built-in recorder and range expander, manifold, and colorimeter, plus fitted containers capable of supplying the IIA with reagents for one week of unattended operation.

The internationally accepted West-Gaeke procedure is used for SO_2 analysis, the Saltzman procedure for NO_2 determinations and the Methylene Blue procedure for detection of H_2S. For additional information, please write:

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A Division of Technicon Instruments Corporation
Tarrytown, New York 10591

environmental currents

INDUSTRY

Firm will survey pollution control market

The New York City management services firm of **Dun & Bradstreet, Inc.** is undertaking a research program to determine which parts of industry will provide pollution control companies with their best prospects. D&B interviewers will query executives in a random sample of 2000 U.S. plants to discover their current usage of control products and services and their pollution abatement spending plans through 1975. According to William B. Schlefer, Director of Research Sales, D&B can also perform exclusive interviewing for any client with special information needs, this information to be kept confidential to the particular client. The project is scheduled to start in January 1971, and to be completed by May.

Packaging industry worried by degradable materials

The basic function of packaging—to protect products—may be seriously impaired by an emphasis on development of self-destructing, but structurally weak, materials according to an expert in the design of packaging systems. Joseph M. Murtha, president of **Sandgren & Murta, Inc.,** told a Chicago symposium that he also believes products such as edible films, uv-sensitive plastics, and soluble glass containers may actually lead to an increase in the number of consumer complaints. What needs to be discovered, in Murtha's view, is the real extent of consumer interest in pollution and disposability, relative to convenience and cost. Murtha suggested that a greater effort toward recycling packaging products would be a better solution to problems of litter and disposability than development of self-destructing products.

Dow aims for total recycle of plant water streams

Harold Bosscher, manager of the Midland Division of **Dow Chemical Co.,** told attendees at a special press visit to the Midland, Mich., chemical manufacturing facilities that the division's goal is to "get out of the river." The river in question is the Tittabawassee, which Dow uses as a source of process and cooling water. The company is building 28 new cooling towers and its immediate aim is to reuse 50% of all cooling water. Superintendents in the manufacturing areas have also been put on notice that Dow's extensive waste treatment plant will not be expanded in size and that there will be building-by-building accountability for pollution control. All new manufacturing units will be designed so that they produce no wastes; the process design assignment has been handed to the company's new Environmental Research Laboratory.

Warning system spots pollution in Dutch industrial area

The heavily industrialized port city of Rotterdam, Holland, has installed automatic air pollution warning systems consisting of sulfur dioxide monitors tied into a central computer. Dubbed "sniffing poles" by the Dutchman in the street, 31 detector masts measure SO_2 concentration and wind direction and velocity. The poles are located so that, no matter which way the wind blows, at least eight are downwind of the principal pollution sources. Abnormally high levels of pollution in one particular area can be traced to the source within a minute. If atmospheric conditions result in an overall high pollution level, an alert goes out to all area industries which then (voluntarily) restrict emissions for the duration of the episode. The system was designed by **Philips Gloeilampenfabrieken.**

Dutch "sniffing pole"

← Circle No. 10 on Readers' Service Card

Agriculture poses waste problems

A small business grows and expands until it and its production reach corporate size, and then it becomes a major polluter—a story heard all over the country. This situation now exists in the agricultural industry. In days gone by, farming wastes—from poultry, livestock, and the like—could be scattered over the countryside and forgotten or just neglected. With the present massive agricultural production, however, the farmer is hard pressed to find adequate means for waste disposal. Commercial poultry, beef, and pork operations are all faced with the problem of wastes that contaminate air, water, and land.

Increasing concentration and intensity of agricultural activities, necessary to the development and prosperity of the economy, are responsible for many new environmental issues. The agricultural waste problem was discussed both at the New Jersey Agricultural Waste in an Urban Environment conference in September, and the Agricultural Research Institute's (ARI) annual meeting in October. Primary sources of pollution resulting from agricultural practices can be grouped as:

- Animal wastes.
- Wastes from processing of raw agricultural products.
- Rural domestic wastes.
- Sediment from land.
- Plant nutrients from fertilizers.
- Inorganic salts and minerals resulting from irrigation.
- Pesticides.
- Aeroallergens and infectious agents.
- Particulate and gaseous substances derived from the combustion of wastes.
- Natural plant emissions.

The agricultural industry definitely contributes to the contamination of the atmospheric environment, says Leonard H. Weinstein of Boyce Thompson Institute for Plant Research. "Agriculture is both the recipient of and contributor to water pollution," P. C. Kearny, a research chemist with the U.S. Department of Agriculture (USDA), told the ARI group. "The productivity and stability of soils depend on proper conservation and management of water," reported William P. Martin, head of the Department of Soil Science, University of Minnesota. Conversely, the amount and quality of water depend very much on the effective management of the land over and through which the water must flow. Since soil pollutants can become water pollutants and vice versa, the contaminant must be combated from both sides.

Animal wastes

"Livestock and poultry wastes are of considerable concern because of the huge amounts produced and the concentration of animals at central production points," says L. B. Nelson, Tennessee Valley Authority (TVA). In the U.S., animal wastes amount to about 2.0 billion tons annually, a third of which is liquid, which is equivalent to waste production from a human population of about 2 billion.

The main problem is encountered in the practice of confined production; for example, a feedlot would often have populations of 10,000 to 50,000 animals; poultry operations range up to 250,000 birds; milk cows number up to 200; and swine populations range 1500 or more. J. W. Claybaugh, management consultant, Dekalb AgResearch Inc., told the New Jersey meeting, "It is not the quantity; it is the concentration. Instead of a few hundred hens on every farm, we now have . . . a few farms with specialized production consisting of many thousands of birds and often with insufficient land for proper application as fertilizer."

Narrow-profit margins and high-overhead costs necessitate low-cost methods of waste management. Furthermore, these wastes have limited agricultural value, in contrast to chemical fertilizers. However, animal refuse can be a serious water pollutant because of its high biological oxygen demand (BOD) and the nutrients and pathogens contained within the material itself.

Animal wastes also create odor problems. Cattle numbering 10,000 on one feedlot will produce 260 tons of manure each day. Claybaugh points out that the movement of urbanites to the country has resulted in much debate concerning the rights of the farmer and the people who live near his odoriferous farm. A poultry operation with 270,000 hens creates 35 to 40 tons of manure daily. With little or no utilization of this material, odor will, of course, be more and more staggering as the manure accumulates. The story is much the same for dairy cattle and swine operations. So, waste disposal has become a major problem to the modern farmer.

Large-scale animal operations and their present means for massive, solid waste disposal, do put a strain on the soil. How much of this waste can be applied to the land without doing damage? Says Thomas J. Army, the Great Western Sugar Co., "Because of economic restrictions in transporting manure great distances, we can expect selected soils and sites to receive inordinately heavy doses of animal wastes." Dealing with wastes in this manner leads to water pollution as well as an odor problem.

Agricultural processing

Agricultural processing industries include pulp and paper, meat slaughtering and packing, cotton processing, canning, dairy products, sugar refining, frozen fruits and vegetables, poultry, hides and leather, and wool scouring. Each has listed waste control as its main problem. Liquid wastes from these industries are characterized by a high BOD, large amounts of suspended solids, various inorganic constituents, including nitrates and phosphates, and the involvement of substantial amounts of water.

Domestic pollutants

Rural domestic wastes consist of human wastes and other by-products of the household. Of the 17 million homes in rural areas, a surprising num-

Today's high-intensity farming methods are producing more and more pollutants

ber do not have piped water and lack adequate disposal of these domestic wastes into lakes and streams.

Sediment from land

About half of the total sediment load in waterways originates from crop land, says Nelson. One to 2 billion tons of sediment reach major streams annually. "Excessive plant nutrients in water," derived from soil erosion, stated Kearny, "give rise to eutrophication of lakes and streams, and a high level of nitrate in potable water."

Natural and man-made dusts contribute more than 30 million tons of particulate matter to the atmosphere annually. Causes of airborne dust include devegetation of land through poor conservation practices, increase in the acreage under cultivation, fallowing, or drought.

Fertilizers

Thus far, there is no positive evidence that the use of chemical fertilizers causes water pollution, Nelson pointed out. However, streams that flow through agricultural areas contain significant amounts of nitrates and phosphates, and use of nitrogen and phosphate fertilizers has greatly increased in the last decade—from 1 million tons of nitrogen in 1950 to 7 million in 1969; from 2 million tons of phosphate in 1950 to 4.7 million in 1969.

The use of fertilizers may result in excess nitrogen and phosphorus in the soil. The buildup of elements in the soil may result in injury to vegetation, but more likely, it becomes a contaminant of waterways. "The immense quantities of fertilizers applied to the land, as well as manure spread in the field, surely lead to enrichment of many nearby or underlying waters," adds Martin Alexander, Department of Agronomy, Cornell University.

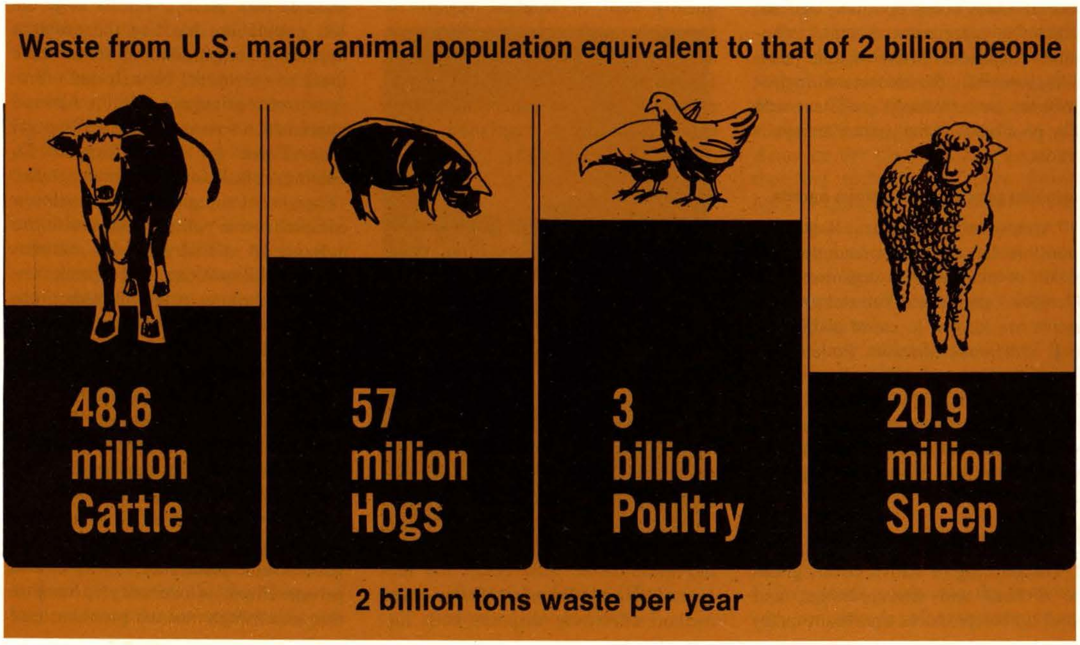
Irrigation problems

Mainly in the arid western states, irrigation drainage waters are laden with soluble salts which may modify the quality of water for use further downstream. Of the 30 million acres of irrigated lands in 17 western states, about half have salinization problems.

Pesticides

Pesticides are usually classified according to the organism they control and include insecticides, herbicides, fungicides, nematicides, plus a few others. These chemicals enter the water through suspended soil particles and organic matter contaminated with pesticides that dissolve in runoff and irrigation tail waters, gravitational fallout from air and washout by rain, accidental sprayings of water surfaces and wind drift, and inadequate disposal of pesticide containers and unused materials. Once in the water, these chemicals may kill aquatic organisms or enter the food chain, magnifying their concentrations with each member in the chain.

In addition to affecting water quality, pesticides can alter the air ecosystem. According to Weinstein, the use of pesticides for agricultural production, land improvement, and vec-



Chemical fertilization. *Increasing fertilizer use is linked with nearby stream pollution. In 1969, 4.7 million tons of* P_2O_5 *and 7 million tons of* NO_3 *were used*

tor control can result in atmospheric problems by evaporation or volatilization from treated areas, the spread of soil particles to which the pesticides have become attached, or by drift following application of dust and sprays by aerial or land rig methods. Warren C. Shaw, Assistant to the Director, Crops Research Division, USDA, emphasized, "While there has been considerable discussion of the harmful effects caused by pesticides on nontarget organisms, few, if any, reliable data exist to document the annual losses caused by airborne agricultural chemicals."

"Yesterday's desirable pesticide may become today's soil pollutant and tomorrow's water contaminant," continues Alexander. Many organic pesticides, especially the chlorinated hydrocarbons, are extremely persistent and may pose hazards for years after application.

Aeroallergens and infectious agents

"Atmospheric transport is largely responsible for the widespread dissemination of plant disease organisms and allergens," continues Weinstein. These agents are known to cause plant, animal, and human diseases. Pollens and toxins that cause human allergies account for 10.5 million lost work days each year. Aerial distribution of spores has caused epidemic outbreaks of stem rust of wheat and late blight of tomato.

Waste-combustion pollutants

The burning of native cover, grasses, orchard and vine prunings, and slash timber produces significant quantities of particulate pollutants, photochemically reactive gases, and toxic contaminants. Burning is commonly used to eliminate reservoirs where insects, bacteria, and odors originate. For each ton of residue from burned grasses, the composition consists of 15.6 lb of particulate pollutants, 101 lb of carbon monoxide, and 12.3 lb of hydrocarbons.

Natural plant emissions

Terpenes and other organic vapors that evolve from growing plants may contribute to the formation of toxic air pollutants by photooxidation with nitrogen oxides. The haze that is frequently seen in forested regions is formed by such a reaction. Weinstein added that vegetation is responsible for the emission of 0.107 ton of terpenes per day per square mile (Air pollution damage to vegetation, ES&T, August 1970, page 635).

Solutions

Solutions for various pollutants of air, water, and land are often intertwined; a single control may take care of several pollution problems. One large poultry operation in Pennsylvania (Cloisterdale Farms, Inc.) is converting to a manure drying process which reduces odor, weight, and bulk. This approach is also being used on livestock and swine operations. Shredding and composting are also employed to utilize wastes.

Another technique is the subsod injector, which deposits a band of liquid waste 28-in. wide below the surface of the soil. The plow-furrow-cover method effectively disposes both liquid and solid wastes. The manure is placed in a furrow which is immediately covered. One disadvantage of these methods is their impracticality when the ground is frozen.

In the agricultural processing industries, treatment plants are often built to take care of the wastes produced. Seabrook Farms, Inc., N.J., has a waste disposal system which handles an average daily flow of 4.5 million gallons of water, with peak flow of 12 million gallons daily.

Erosion control practices and soil conservation programs could effectively reduce air, water, and soil pollution. Reduction of nutrient losses from fertilizers is a problem that requires much research. If the conditions are determined under which there are heavy nutrient losses, then agriculture can begin to develop corrective measures. Until these conditions are controlled, the rates and times of applications, regulating incorporation into the soil, and controlled irrigation can reduce losses.

Government action

States are initiating programs to investigate agricultural waste problems as population grows and spreads into rural areas. For instance, the small state of New Jersey, with its large urban population, has had the problem appearing sooner than in some other areas. As a result, New Jersey's Secretary of Agriculture, Phillip Alampi, appointed an Animal Waste Disposal Task Force in 1967. Richard D. Chumney, task force chairman, states, "The aim of the group is to develop a comprehensive policy to cope with the nuisance of animal waste, its accumulation and disposition, and to seek continuing solutions to the ultimate problems such waste poses to our citizens."

Alampi adds, "Agriculture is not of concern to farmers alone. Its complexities carry right on through to the marketplace and municipalities. For instance, it affects food processors, since they have wastes to dispose of. Sewage systems, stream systems, water tables, even the soil itself in some areas may be affected." The cooperation of government researcher, farmer, and private citizen is necessary to combat this increasingly serious problem. CEK

What's the U.S. Army doing in water pollution control?

For the first time ever, the Corps of Engineers is issuing permits for all discharges

Gone are the days when the Corps of Engineers, in their issuance of permits, are concerned only with the impact a proposed project may have on navigation. The Corps' new regulatory role in pollution control extends their permit-granting authority to include all discharges or deposits into the navigable waters of the U.S. Initially, the Corps will concentrate on major sources of industrial pollution. Although the Corps' announcement of its expanded permit-granting authority came on July 30, official word from Washington has not yet gone out to the Corps' 37 district offices located around the country.

"We expect to issue instructions to the field offices around the first of next year," says Robert E. Jordan III, General Counsel and Special Assistant to the Secretary of the Army for Civil Functions. "The Corps has been issuing permits for structures in the navigable waters for a long time (essentially since the 1899 act). Since 1966, we have had a requirement that applicants seeking permits must consider esthetics, fish, and wildlife effects, water quality, and the like. In general, our long-term permits are reviewed every five years."

Jurisdiction

Authority for the Corps' expanded program stems from a combination of the Refuse Act of 1899 and the National Environmental Policy Act of 1969 (P.L. 91-190) (ES&T, February 1970, page 103). The latter requires that all federal agencies interpret their authority with environmental impact in mind. Authority for the Corps of Engineers to take action on water pollution is contained in the 1899 Refuse Act. "In our review of the Refuse Act, we realized that here was the authority that should be used," Jordan explains.

Coupled with the Refuse Act, P.L. 91-190 requires federal agencies to step up the government's widespread program on water pollution abatement.

A draft of a proposed interagency agreement between the U.S. Army's Corps of Engineers and the Federal Water Quality Administration (FWQA) identifies the manner in which the two agencies will cooperate to enforce the 1899 Refuse Act. Although the agreement has been discussed with other interested agencies, including the Department of Justice and the Council on Environmental Quality, the agreement has been delayed, as have other pending environmental matters, in the executive reorganization creating the Environmental Protection Agency (EPA). The recipient of one of this year's Arthur S. Fleming awards for the 10 top men in the federal government, Jordan personally piloted the agreement through the federal establishment. It perhaps will be finalized early next year.

Robert E. Jordan III
Army's General Counsel

Although the Corps' emphasis to date has been on new constructions in or on the navigable waters, the present federal consensus is that the Refuse Act will be used in the general interest of the public, and the forthcoming Refuse Act permit program attests to this.

For example, actions can be brought under the Refuse Act where the defendant has not met the following conditions: "The defendant does not have a permit from the Secretary of the Army or the Corps of Engineers authorizing such deposit." The Refuse Act (33 U.S.C. 407) can be interpreted to include industrial discharges; the only type of refuse exempted under the act is "refuse flowing from streets and sewers and passing therefrom in a liquid state."

The furor raised by the Corps' July 30 announcement has not subsided yet. The fact that the Corps would be looking at all discharges, including industrial discharges, poses a real concern to industry. Myriad inquiries to local Corps district officials attest to that concern.

Rationale

"We aren't going into the program with an attitude of arrogance or of heavy handedness," Jordan explains. "But the Corps and the Federal Water Quality Administration are going to have to work together to come up with sensible solutions to problems.

"The Corps' permit program must be carried out with balance and good sense," he continues. "As the program begins to impact on particular industries, there is going to be some unhappiness on the part of the community to which those industries are important.

"Most of the industries want to do the right thing," Jordan believes. As he testified before the Senate Commerce Subcommittee this July, "You obviously overnight cannot apply the Refuse Act around the country. If you did, you would shut down industry throughout the U.S., and we all recognize that this results in an intolerable economic situation, so we all must exercise good judgment and common sense."

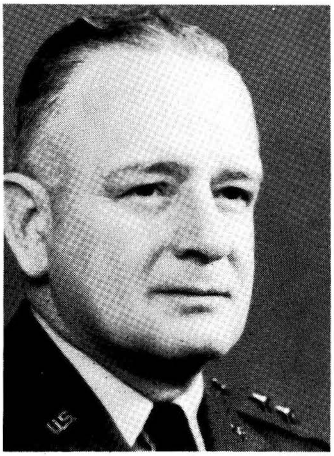
What this recent interpretation of the Corps' role means to industry is that any structure or outfall line leading into navigable waters must be covered by a permit from the Corps, that any discharge from the structure or outfall line must meet all water quality standards applicable to receiving waters, and that state certification must also be included as required by section 21(b) of the Water Quality Improvement Act of 1970, P.L. 91-224 (ES&T, May 1970, page 379). "It's a complicated business," Jordan concedes.

So, the Corps will be issuing permits for industrial discharges, even if the discharge is harmless (it does not violate a water quality standard) or the industry is on schedule in its voluntary compliance scheme established under the administrative procedures of FWQA, in some enforcement conference.

Permits

"Our permit system would be closely tied with FWQA," Jordan explains. So that industry will have only one form to fill out, the FWQA waste water profile inventory form will be used.

"Submission of the inventory profile is mandatory only in the sense that if somebody wants a permit from the Corps, then they must submit the form so that we can pass judgment on their plans," Jordan elaborates. "Nobody is going to be required to furnish the information. But if they don't, then the Corps will not issue the permit."



Maj. Gen. Frank P. Koisch
Chief, Corps' Civil Works Directorate

"In other words, how could the Corps decide whether a plant should be granted a permit for such an industrial discharge unless you know what is being discharged, both in volume and composition?"

In practice, the Corps' group that will be responsible for the permits program is the Office of Chief of Engineers, the Civil Works Directorate, which is headed by Maj. Gen. Frank P. Koisch. The people involved with day-to-day administration of the permits, of course, will be the district engineers and their operational staffs. The operational division of that function is headed by Mark Gurnee.

"The Corps has the machinery (for permits) already in being, and it may as well be used," Gen. Koisch says. "The Corps has a better geographically distributed organization (than EPA) for handling the permits," he adds. "The Corps can perform a real service to the country and materially assist the new EPA."

What is likely to happen in actual operation is that the Corps would send each application for a permit to the FWQA and ask: What do you think? Does it meet the applicable water quality standard? If not, can we grant a permit with certain conditions attached, such as timetables which would bring them into compliance by a certain date?

Then, the Corps would issue its permit conditioned upon compliance with agreements reached, including specified deadlines for compliance. State certification required under section 21(b) of P.L. 91-224 would, of course, have to be obtained before any Corps' permit could be issued.

Advice

Many federal regulatory agencies, now perhaps for the first time, are feeling the pressure from the environmentalists and have established citizen advisory boards to provide the agency with more detailed familiarity with some of their problems. One example is the Water Pollution Control Advisory Board (ES&T, June 1970, page 471).

The Corps is no exception. Its six-member advisory board was established in April and represents a broad range of environmental knowledge and experience. Chairman of the Corps' advisory board is Charles H. Stoddard, an environmental consultant from Duluth, Minn.

"I expect that it (the board) will provide not only advice on specific problems, but, perhaps more important, contribute to an enhanced mutual understanding and confidence between the Corps and both the general public and the conservation community," says Lt. Gen. F. J. Clarke, chief of the Army Corps of Engineers.

Looking ahead

Much remains to be done. Rather than set up a new permit program authority under the aegis of the EPA, the Corps' existing permit-granting authority within the federal government could perform a service in the continued war on water pollution. The Refuse Act permit program is a powerful force; there are tens of thousands of industrial plants discharging into navigable waters and 4000 new ones are being built each year. As the manpower and financial needs are met, the Corps stands ready to perform an invaluable role in the government's crackdown on water pollution. SSM

Is pollution insurable?

Only if the discharge is accidental, say insurers; even then, coverage may be unavailable

Man's social problems—inflation, prosperity, famine, depression, to name a few—are, and have been, the insurance industry's main concerns. Now the insurance business, not unlike many other industries, is deeply involved in and has taken a stand on another pertinent social problem—environmental pollution.

In April, the Insurance Company of North America (INA) formally introduced an attitude toward liability insurance coverage in pollution suits. Charles K. Cox, president of INA, announced, "INA will continue to cover pollution which results from an accidental discharge of effluents—the sort of thing that can occur when equipment breaks down. But we will no longer insure the company which knowingly dumps its wastes." Thomas Ashcraft, also of INA, has said that the primary concern of the insurance industry concerning pollution claims is the extent of its obligation to its insureds under the language of the liability policy contract.

Exclusion endorsement

After INA announced its program for dealing with environmental issues, the majority of the insurance companies in the U.S. filed similar policies in all the states plus Washington, D.C. and Puerto Rico. In effect, this statement of policy is not newly contrived. Tom O'Day, Director of Public Affairs, American Mutual Insurance Alliance (AMIA) (113-membered trade organization of mutual insurance companies) signifies that there has always been coverage for accidental pollution, and the resulting suits were paid off. However, the exclusion endorsements now make it a matter of record that the insurance companies are not going to pay for deliberate pollution. In fact, claims made against deliberate pollution were never justifiable and were not paid; but now this fact is stated in black and white.

The only new policy in this claim area concerns the release of oil or gas in water. Neither deliberate nor accidental spillage of oil or gas in water will be covered by liability insurance. The insurance companies have, in effect, said to industry that this is a sensitive matter and extra precautions must be taken. If mistakes are made, there will be no insurance protection.

Donald W. Perin, director of research, National Association of Insurance Agents, Inc., contends, "Insurance companies not only defended their clients when they were sued by third parties for bodily injury and property damage caused by pollution, but they also paid judgments up to the policy limits, provided the coverage was written on an 'occurrence' basis."

Environmental improvement

"Now the insurance industry is taking the position that it is not going to willfully help polluters of the atmosphere, waterways, or land," says O'Day, "By removing insurance coverage of environmental violators, the insurance companies are making it difficult for these offenders to continue polluting." Adds Perin, "With all the emphasis which has been placed on the necessity of reducing all forms of pollution for the health and welfare of the public, it would almost seem to be against public policy to protect a policy holder for the consequences of his quasi-illegal acts."

State approval

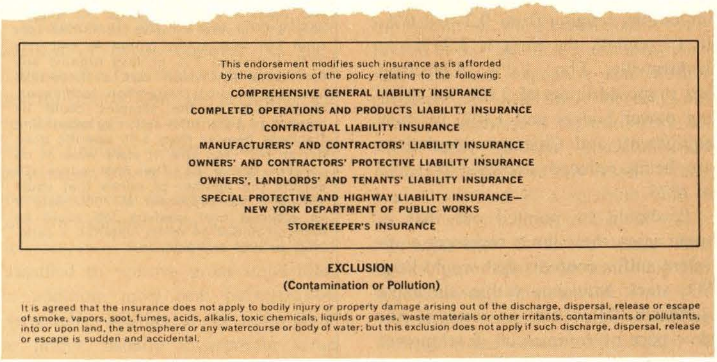
With any change or new statement of policy concerning insurance, the matter must be presented to and approved by each state. Insurance companies are regulated within each state and their policies must be approved by the insurance commissioner. At the end of October, 42 states had approved the exclusion endorsements. Louisiana, Maryland, Vermont, Tennessee, and New Hampshire disapproved; and the policy changes are pending in New Jersey, North Carolina, Pennsylvania, and Puerto Rico.

Environment, present and future

Is this exclusion endorsement an act of refusal to cooperate with industry? Not according to O'Day: "Part of the package of taking a client on is evaluating problem possibilities and suggesting solutions." Insurance company engineers are trained to assist client companies in applying pollution control techniques. For example, the Hartford Insurance Group has announced the formation of an environmental services unit that will help its industrial policyholders in pinpointing and controlling pollution exposures.

Are changes planned for the future? INA's Ashcraft surmised that insurance companies will continue to add and alter policies governing pollution liability as long as theories on pollution continue to grow.

CEK



This endorsement modifies such insurance as is afforded
by the provisions of the policy relating to the following:

COMPREHENSIVE GENERAL LIABILITY INSURANCE
COMPLETED OPERATIONS AND PRODUCTS LIABILITY INSURANCE
CONTRACTUAL LIABILITY INSURANCE
MANUFACTURERS' AND CONTRACTORS' LIABILITY INSURANCE
OWNERS' AND CONTRACTORS' PROTECTIVE LIABILITY INSURANCE
OWNERS', LANDLORDS' AND TENANTS' LIABILITY INSURANCE
SPECIAL PROTECTIVE AND HIGHWAY LIABILITY INSURANCE—
NEW YORK DEPARTMENT OF PUBLIC WORKS
STOREKEEPER'S INSURANCE

EXCLUSION
(Contamination or Pollution)

It is agreed that the insurance does not apply to bodily injury or property damage arising out of the discharge, dispersal, release or escape of smoke, vapors, soot, fumes, acids, alkalis, toxic chemicals, liquids or gases, waste materials or other irritants, contaminants or pollutants, into or upon land, the atmosphere or any watercourse or body of water; but this exclusion does not apply if such discharge, dispersal, release or escape is sudden and accidental.

Exclusion endorsement. *This clause is typical for pollution coverage policies*

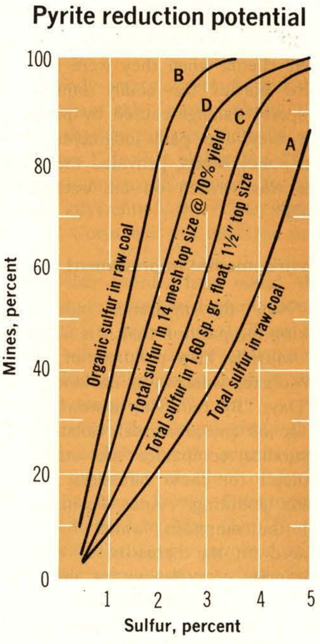
Sulfur codes pose dilemma for coal

Pyrite removal programs stepped up, but offer only partial solution

The much-touted energy crisis for which the country is headed may have consequences that transcend the likelihood of troublesome power blackouts and brownouts of electrical power that palgued power planners and consumers this past summer. Potentially more significant is that the race to keep abreast of the nation's power demands may be on a collision course with well-intentioned local air pollution control regulations that limit the sulfur content of fuels burned for power generation. Sulfur content of all fossil fuels has become an important factor in power needs planning. But since the dominant U.S. energy source is coal, and likely to remain so for some time, nowhere is the energy demand/pollution control dilemma more urgently in need of resolution than in the case of judicious use of the U.S.'s enormous coal reserves.

A quick look at some of the fuel sulfur limits applicable to coal that have been passed by control agencies sketches the picture: In the East, the cities of New York, Philadelphia, and Washington, D.C., and the states of Maryland and New Jersey already have limitations ranging from 0.2 to 1.0%. In Cincinnati, the limit is 1.25%; in Jacksonville, Fla., 1.0%; Cleveland has proposed limits of 2.0% for existing power boilers and 1.0% for new equipment; and Chicago's regulations are being reduced stepwise to 1.5% in 1973.

It should be pointed out that in some cases, these limits represent equivalent sulfur contents that would keep SO_2 stack emissions within allowable standards. However, in view of the slow pace of commercial development of stack gas cleaning devices (ES&T, June 1970, page 474), the regulations in effect translate into an unprecedented demand for low-sulfur fuels. For example, the National Research Council–National Academy of Sciences, in its guidelines to federal facilities for compliance with air pollution control regulations, recommends stack gas cleanup only as a last resort, and suggests that federal agencies should tailor fuel procurement policy to a 1% less sulfur content. Federal installations account for only a small portion of the U.S. power demand, but this policy is probably similar to that adopted by most public and private power agencies, at least for the short term.

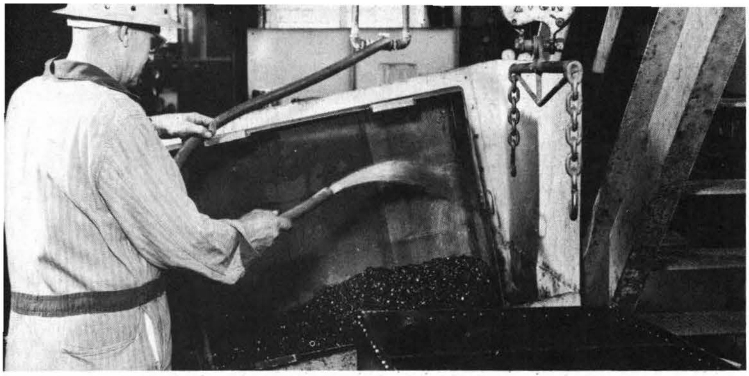


This graph depicts the levels of total and organic sulfur in samples of raw coal collected by the Bureau of Mines from 200 Eastern U.S. coal beds. As shown, only 6% of the samples contained less than 1% total sulfur (curve A) and only 35% contained 1% or less organic sulfur (curve B), which sets a theoretical limit for physical separation techniques. About 12% of the samples could be cleaned to 1.0% total sulfur by separating fractions heavier than 1.60 specific gravity, at 1½" top size, if yield were of no concern (curve C). The final curve (D) depicts the number of mines that could provide a 1.0% product at 70% yield if an efficient coal washing job could be done on minus 14 mesh material, a capability not yet available

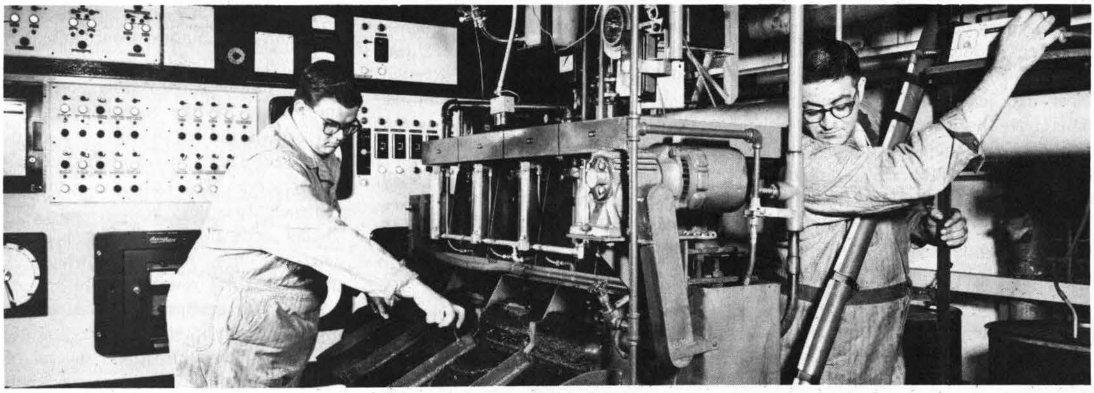
Coal reserves

It is easy to understand the reliance on coal as our prime energy source. It is the only major fuel which could, by itself, meet the cumulative energy demands of the country for the remainder of the century and beyond. Recoverable reserves—those mineable at or below present costs—equal about 220 billion tons, enough at present production rates to last for about 400 years. Bituminous coal, the most important type for steam generation, accounts for about 45% of the total. This would provide a comfortable cushion for satisfying energy needs for some time, were it not for the fact that its sulfur content varies widely, ranging from 0.5 to 5.0%, and even higher in some areas. Thus, the demand for naturally occurring low-sulfur coal is already severely stressing supply and sparking an increased emphasis on coal desulfurization technology.

Some of the required technology is available and could offer partial (but not total) relief from the SO_2 emissions problem. Programs are underway



Testing. *"Float-sink" methods (left) are used to study effect of staged crushing on pyrite liberation; froth flotation (below) is a promising separation technique*



aimed at incorporating coal-desulfurization steps into commercial coal preparation schemes, but whether this can be done in time to allow sulfur-in-fuel codes to survive intact, in the absence of broad advances in flue gas cleaning technology, remains to be seen.

Sulfur sources

Just how much can be accomplished by present coal desulfurization technology is largely limited by the natural distribution of sulfur within coal, where it occurs in two forms. Organically bound sulfur arises from the original sulfur content of the vegetable matter from which the coal seam was formed, and is evenly distributed throughout the coal deposit. Inorganic sulfur, in the form of pyrite (FeS_2), is that which has leached into the coal seam after its has formed, and is deposited in discrete lumps distributed more or less randomly through the coal deposit. Though it is difficult to generalize, pyrites usually represent 40 to 60% of a given coal's sulfur content, and are the only form of sulfur accessible to practical coal desulfurization techniques. Organic sulfur, of course, would be readily removed through coal gasification processes, but this technology is at least 10 years from commercial development, according to most estimates.

A current Bureau of Mines survey of representative coal samples from 200 mines east of the Mississippi is one way of putting the potential of pyrite removal in perspective. Initial results of this survey, which is a major part of the Bureau's coal desulfurization program, show that less than 10% of sampled mines had 1% or less total sulfur content; more importantly, only about 35% of the samples could be cleaned to a sulfur content of below 1.0%, even with near-quantitative removal of pyrite.

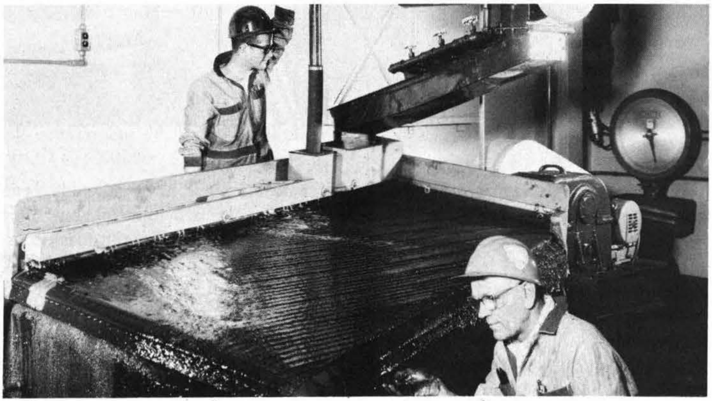
Existing technology

Whatever its limitations, the attractiveness of pyrite removal lies partially in the fact that some degree of desulfurization can be accomplished by adaptation or extension of existing technology. Most modern coal preparation plants include steps taken to upgrade coal in terms of Btu content; for example, prior to crushing for delivery, most run-of-mine coal is hand classified to remove gross impurities. In addition, most coal pulverization operations, whether at the mine plant or utility, usually incorporate some type of air classification for further upgrading of the product. Most of these preparation steps have generally been geared toward ash removal, but some reduction in sulfur content does occur.

In addition, there are several coal washing techniques in use or being developed for application to desulfurization. Most involve grinding coal to desired size ranges, and classifying the coal on the basis of particle size and specific gravity. Since all noncoal impurities, including pyrites, have a heavier specific gravity, the density of a coal particle is a direct measure of its purity.

A common method of coal cleaning is the Baum coal washing jig, in which a pulsating fluid stratifies pulverized coal in increasing density from top to bottom; the cleaned coal is overflowed at the top. This is the most popular and least expensive coal washer commercially available, but may not effect as accurate a separation as desired. More accurate separations are made in dense medium vessels. Here, coal is slurried in a medium with a specific gravity close to that at which the separation is to be made. The lighter, purer coal floats to the top and is continuously skimmed off.

Another common coal washing method is the concentrating table, or Diester table. A mixture of pulverized raw coal and water is floated over a series of parallel ridges, or riffles, mounted on a flat surface which is slightly skewed from the horizontal. As the table is jigged in a reciprocating motion, the lighter, smaller coal particles are preferentially wafted over the riffles to the bottom side of the tables, while heavier, larger, and more impure particles trend along the riffles to the sides. The coal discharged along the two edges of the table constitute a continuum of material of increasing quality, and by drawing off selective fractions, any desirable range of purity may be obtained. Commercial tables commonly have a rated capacity of about 10 tons per hour. Although most data available for commercial units have been concerned with ash removal efficiency, it is quite possible that Diester tables will be able to sharply separate pyrites from coal down to a finer size than ash, because of its higher specific gravity.



Adjusting. *Wet concentrating table is most effective with finely pulverized coal*

Other methods

Other separation methods based on specific gravity that, though not yet in use, are being investigated, include the hydrocyclone, similar in concept to the units used to scrub particles from gas streams. For coal cleaning, water is the separation medium, and as the coal slurry is fed to the cyclone, centrifugal force generated effects the desired separation between high- and low-specific gravity material. An adaptation of this basic principle is the dense medium cyclone, which uses an aqueous suspension of finely ground magnetite to increase the specific gravity of the liquid phase and to allow sharper separation.

One particularly promising method for coal cleaning is froth flotation, which has already reached a considerable degree of sophistication in noncoal mineral industries. Raw, pulverized ore is fed to a water bath into which air is introduced under extreme agitation. The water phase contains a selective wetting agent which preferentially wets the surface of the mineral particles to be separated. The activated surface then adheres to the bubbles, which float to the surface as a froth, and are collected. The method can be highly efficient; in refining of sulfide ores, for example, near-quantitative separation of sulfides of various metals can be obtained by sequential treatment of the slurry with suitable wetting agents. This approach has not yet been very successful for pyrite removal from coal, as it will require an intensive screening program to identify suitable reagents that will effectively discriminate between coal and pyrite surfaces.

Several other methods for pyrite removal have been suggested—*e.g.,* the use of dielectric heating to convert the nonmagnetic pyrite into the ferromagnetic pyrrhotite, Fe_7S_8, which then could be removed magnetically. The method would seem to offer relatively low-cost removal, but its feasibility has yet to be explored, as is the case with electrostatic separation of pyrite particles from an air stream of pulverized coal.

A final possibility is chemical removal of pyrite, and Jolevil Association, Inc. has recently applied for a patent on selective oxidation of pyritic sulfur under controlled conditions with suitable oxidants such as air, oxygen, or carbon dioxide. The company has stated that its tests on the process have demonstrated sulfur reductions of 25 to 50% when suitable supplemental oxidants were added.

Programs

Much of the federal effort for bringing pyrite removal technology into fuller utilization throughout the coal industry is being funded by the National Air Pollution Control Administration (NAPCA), mainly through studies at the U.S. Bureau of Mines Energy Research Center at Bruceton, Pa., and Bituminous Coal Research (BCR) in Monroeville, Pa., an affiliate of the National Coal Association. Furthest along of the NAPCA programs, perhaps, is the nationwide assessment by the Bureau of Mines of the nation's coal reserves. The Bureau is sampling representative coal seams from producing beds throughout the U.S. to determine how much and which of the present day reserves might be susceptible to economical coal cleaning processes. NAPCA is also funding research at the Bureau on several of the coal cleaning processes, and will soon announce a major pilot plant at an as yet undisclosed location to further evaluate the efficiency and economics of such methods.

BCR, which has supported considerable research on coal preparation for some years, is also conducting some pyrite removal studies for NAPCA. Other BCR work is in line with NAPCA's total-utilization concept. Since the cost of any coal cleaning program would probably be prohibitive if the Btu content of the refuse was rejected, the NAPCA program envisages preparation of a low-sulfur coal for combustion in a conventional boiler, and the pyrite-rich refuse burned in a smaller, high sulfur combustion equipped with stack gas SO_2 recovery units.

Costs

Any discussion of the economics of coal desulfurization must still of necessity be speculative. Present coal preparation steps usually add something less than $1.00 per ton; extension of the present techniques to optimize pyrite removal would probably increase coal preparation costs considerably, largely because of the greater amount of material rejected. Most observers agree that the present premium prices paid for low sulfur coals do not yet make most pyrite removal practices economic. PJP

Blending technology and environment

New aluminum plant goes beyond installing pollution controls, seeks to harmonize industry and its rural setting

At a time when industry is under continuous pressure to abate pollution, it is interesting to see how the builders of new industrial plants are going about the business of constructing facilities which are both profitable and environmentally acceptable.

One such plant is the new aluminum reduction facility of Eastalco Aluminum Co. in Frederick, Md. Not only does this plant incorporate air and water pollution controls, but considerable effort was exerted to ensure harmony between the plant and its surrounding rural landscape.

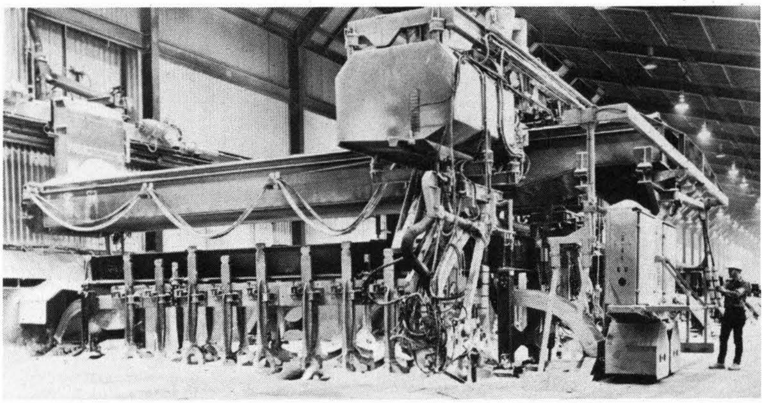
Aluminum production

Eastalco is a wholly owned affiliate of Howmet Corp. (Greenwich, Conn.) which, in turn, is largely owned by the French Pechiney group. At the new Frederick plant, located on a 1700-acre site that was formerly farmland, Eastalco is producing aluminum from alumina imported at Baltimore and transported from that port by railroad. Present capacity is 85,000 tons per year from a single potline. (A potline consists of 240 electrolytic cells, or pots, each of which produces 2000 lb of aluminum daily.) A second potline will be built when the demand for aluminum, now considerably oversupplied, picks up again.

The main potential source of air pollution from an aluminum reduction plant is the reduction cell. In each cell, alumina—Al_2O_3—is electrolytically reduced to aluminum. Molten cryolite—sodium aluminum fluoride, Na_3AlF_6—serves as the electrolyte, and the cell is supplied with 130,000 amps dc at 4 volts. Because of the high temperature in the cell, the cryolite is partly decomposed to hydrofluoric acid and other fluorine compounds, and the gases are emitted directly into the potline building. Contaminated air is drawn through 64 independent scrubbers housed in the building's roof, where high-pressure water sprays scrub out the contaminants before the air is discharged to the atmosphere. The scrubbers are of Pechiney design and treat about 7 million ft^3 of air per minute. (For a discussion of the adverse environmental effects of fluorides, see ES&T, August 1969, page 720.)

The contaminated scrubbing water is treated in a separate unit and the cleaned water is recycled to the scrubbers. The Potomac River, 8 miles away, supplies the plant with water, which is treated for silt and hardness before use.

Another water scrubbing unit cleans the air within the building where carbon anodes are produced from pitch and petroleum coke (the anodes are used in the reduction cells). Veteran aluminum industry observers have commented that the use of scrubbers in the anode fabrication and baking area is almost unheard of, so Eastalco's installation must be noted as an innovation.



Potline. *Each electrolytic cell in the line produces 2000 lb of aluminum every day. Fluorides emitted into the building are removed by 64 overhead water scrubbers*

Power demands

Any plant based on electrolytic technology is bound to have an indirect impact on the environment because, of course, it uses so much electricity. In the case of the Frederick plant, its peak demand will be 130,000 kW. Fortunately for residents of the Washington, D.C. area, only a short distance to the south, this power will be supplied by Potomac Edison Co., a utility that does not supply their region—which was occasionally subjected to blackouts and brownouts this summer.

Landscaping

The plant is positioned so that it is not visible more than a quarter-mile away. Trees have been planted on the property, and that part of the site that has not yet been developed (1400 of the total 1700 acres) has been seeded with grass. A specially commissioned piece of modern sculpture, made of carbon steel and aluminum and intended as "an interface between the serene Maryland countryside and the extremely sophisticated technology," is the dominant visual structure on a slight rise to the north.

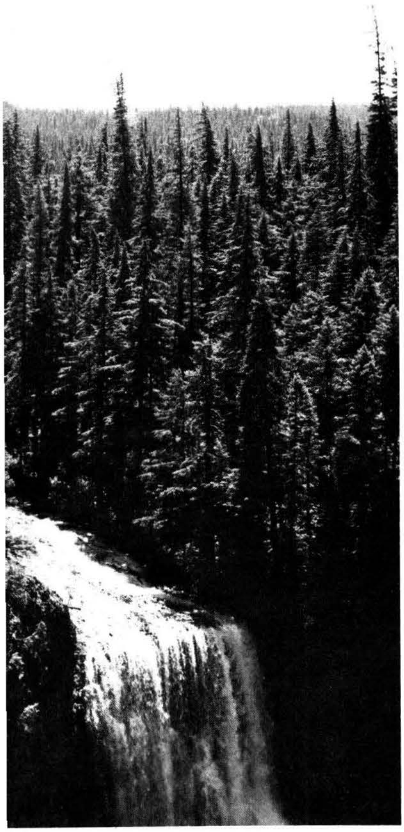
The pumphouse on the Potomac is built with native stone facing, and is an attempted reproduction of early 19th century architecture.

In a way, these esthetic considerations demonstrate how modern industrial companies are trying to solve a dilemma as old as the industrial revolution—to close the gap between technology and nature. To achieve complete harmony is, of course, an impossible task. But the Eastalco people have tried. DHMB

Optimum recovery and reuse ratios in a free market do not always maximize social benefits

Walter O. Spofford, Jr.
Resources for the Future, Inc.
Washington, D.C.

Closing the gap in waste management



"Recovered materials almost invariably must compete with the virgin output of other basic materials"

At a recent meeting of the American Chemical Society, a well-known ecologist described the potential agricultural value of composted municipal refuse as a soil conditioner (not as a fertilizer). He explained that soil conditioning was extremely important for maintaining long-term agricultural productivity, and we ought to do more about returning "waste" organic material to the land. He did not, however, discuss the costs and the associated generation of residuals of returning municipal refuse to the soil.

At the same meeting, a government official said composting municipal refuse was fine in principle, but was not "economic," that composting was the most expensive way of treating and disposing solid wastes. He further explained that most compost plants built in this country have run into financial trouble and have either discontinued operations or are presently running a deficit.

Obviously, the two gentlemen had differences of opinion, but oddly enough, they were both discussing economic issues—the allocation of scarce resources. Both were discussing the value (or lack of value) of the same material, municipal compost, but were they discussing the same resource allocation problem under the same ground rules? I think there is an explanation for their disagreement and that it lies partially in their concepts of economics. Hence, my motivation here is to attempt an economic explanation for the difference in opinion, and to point out that, although both were discussing the fate of municipal composting, they were discussing the problem from very different economic points of view.

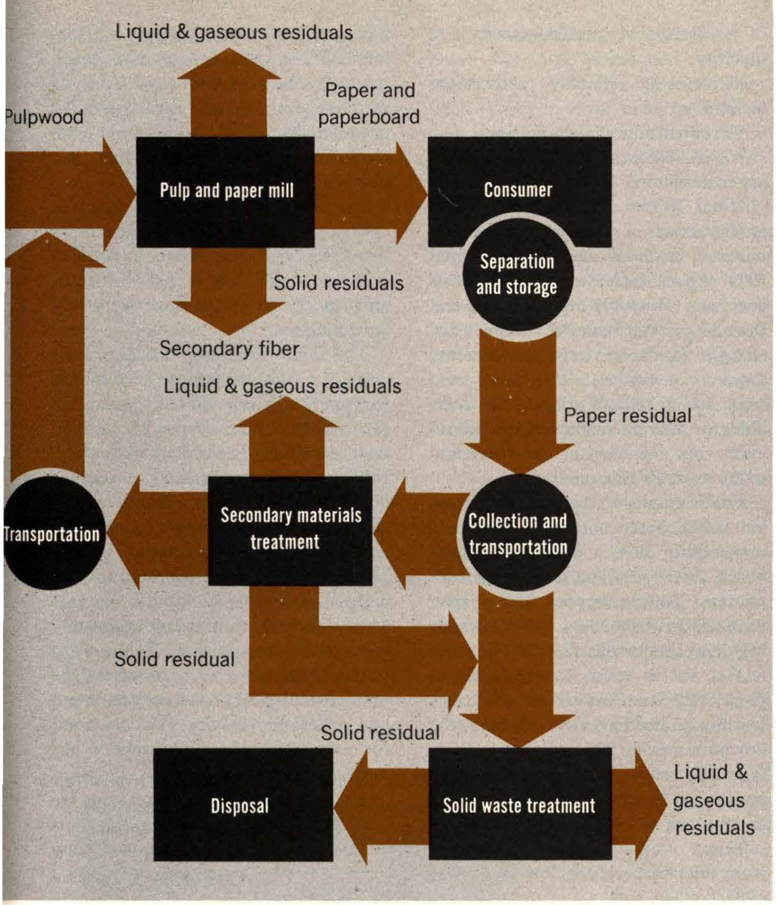
The ecologist was looking at the problem from society's point of view—the essence of welfare economics—although it is not at all clear just what value system he used to compare alternatives. The latter was looking at the problem from a more narrow, but nevertheless very real, "private" market point of view that is the essence of economics. The value system he used in comparing residuals management alternatives was market prices.

To provide a basis for examining the issue raised above, I would like to first discuss residuals management, in general, and the environment problems we face because of the failure of the private market system to allocate certain common property resources—air, water, and some aspects of the land—efficiently among all users. Then we can discuss a specific example—paper and paperboard production, consumption, recovery and reuse, and disposal—that conveniently points out the difference between the private market optimum and the optimum from the standpoint of society as a whole. In this regard, we should point out that although all rational decisions are based on costs and benefits, different activities or economic units face very different cost and benefit functions on matters of residuals disposal. For example, the private entrepreneur is rarely forced to take into consideration all the damages associated with his activities on the quality of the environment, whereas society as a whole (by definition) certainly would.

Finally, I will discuss what might be done to encourage the private market to conform more closely with society's optimal goals; after all, determination of society's goals and the means for closing the gap between the private and social positions is really the essence of politics.

I would hope that the discussion provides the ecologist, engineer, and economist with a better understanding of the problems we, as a society, face in common and, in addition, a basis

Production, recovery, and disposal of paper



for continued discussions of the problems of residuals management.

Residuals management—an overview

Residuals are generated at virtually every stage in the production and consumption of goods and services. These residuals can be either material or energy, and although we will discuss only material residuals, the management approach is equally relevant and essential for energy residuals. In an economy which is closed (no imports, exports) and no net accumulation of stocks, the amount of residuals discharged into the natural environment is approximately equal to the weight of basic fuels, food, and raw materials entering the processing and production system, plus material taken from the atmosphere. This result, while obvious upon reflection, leads to the rather surprising corollary that residuals disposal, in terms of sheer tonnage, is an even larger operation than basic materials production.

Most material residuals are readily transformed from one state to another in production, consumption, and residuals treatment activities. Changes in state, however, frequently involve energy inputs and energy residuals, and in the context of residuals management, it is helpful to remember that residuals can be changed in form, but they do not disappear. The total weight of the material is still with us in one form or another. Hence, solids may be considered the irreducible limiting form of residuals.

By the application of appropriate equipment and energy, all undesirable substances can be removed from water and air streams. As the restrictions on the discharge of material residuals to our air and water resources become more stringent, we can expect to be faced with the problem of handling greater and greater quantities of solid wastes. Both air and water pollution may be reduced, or even eliminated, with the application of the requisite resources, but we cannot eliminate the solid waste problem without essentially total material recovery and reuse. We include this discussion to emphasize the importance of considering all forms of energy and material residuals within a single analytical framework.

The discharges of sufficient quantities of residuals—*i.e.,* large amounts relative to the assimilative capacity of the environment—can, and generally do, impose external damages on other users of the environment. Normally, these damages are external to the operations of the discharger because there is no mechanism by which he is charged for the damages imposed on others, damages associated with his use of common property resources—specifically, the assimilative capacity of the environment. The extent of these externalities represent the failure of the private market system to allocate air, water, and land resources efficiently among all users. Stated differently, in terms of the many uses of the environment, the private market optimum does not correspond to the social optimum.

The ability of the natural environment to assimilate residuals is an extremely valuable resource. To eliminate completely all residuals, as in a spacecraft, would be an extremely costly procedure. Indeed, as we have already pointed out, it would require complete recycling of all residual materials. On the other hand, if no restriction were put upon the use of the assimilative capacity of the environment, it will be used too much (as we have already experienced in a number of cases). This, in fact, is what the pollution problem is all about.

Incentives

If we wish to realize the advantages of decentralized decision-making mechanisms—that is, the private market—we must find appropriate ways to mitigate these external environmental effects. The external costs of discharge of residuals must be compared with the costs of controlling the amounts of residuals discharged. A perfectly reasonable objective for a particular region might be the minimization of the costs of treatment plus all external damages associated with the remaining residuals in the environment.

Because the private market system fails to include all the relevant costs, governmental action is required. Incentives that have been used or proposed in an attempt to compensate for the failure of individual units to consider externalities can be classified as:

- Legislative, including direct regulation, quality standards, and license requirements.
- Litigation, including compensation for damages as well as restrictions on operations and (or) location.
- Economic, including effluent charges or taxes, subsidies, and tax incentives, including accelerated depreciation allowances.

Whatever the policy instrument, the intent is to achieve a more efficient allocation of resources from the standpoint of society as a whole.

Forms of external damages

Damages may be referred to broadly as the direct and indirect deterioration in the quality of the environments, and may assume many forms. Although in an economic sense, all damages are conceptually direct, it is useful to consider several categories of damages. Increased private market costs include increased costs of water and medical treatments and the cleaning of clothes, automobiles, and buildings. Increased nonmarket costs include decreased esthetic character of water, air, and land, and certain costs stemming from the impact of residuals such as persistent pesticides and heavy metals on flora and fauna, particularly in food chains.

Reducing residuals

The quantities of material residuals which are ultimately discharged in, or returned to, the environment may be reduced by decreasing the quantities of residuals generated in production and consumption activities, and also by increasing levels of material recovery and reuse, such as materials recycling, by-product production, and product reutilization.

The generation of residuals may be diminished in several ways, among them changes in product specifications, regulative price changes or taxes, use of substitute energy or raw material sources, more efficient processes, or increasing the useful lifetime of "durable" goods.

It is the second alternative—materials recovery and reuse—that I will emphasize here.

The extent of material recovery and reuse is a function of the combination of private market prices and public and private constraints and incentives. The economic feasibility of materials recovery and reuse depends on:

- Availability of a consistent supply of residuals of a specified quality and quantity.
- Processing and (or) reprocessing technology.
- Product output specification.
- Availability of markets for secondary materials.

Other factors remaining the same, as the extent of recovery and reuse of material residuals increases, raw material inputs decrease, treatment costs decrease (although not always), and the quantities of material residuals discharged to the environment decrease (again, not always). With few incentives, and at today's prices, it is profitable for private entrepreneurs to recycle only a portion of the many material residuals generated.

For example, let us look at the extent of recovery and reuse for some materials in 1966: paper and paperboard, 21%; iron and steel, 45%; aluminum, 20%; copper, 42%; zinc, 25%; and rubber, only 12%. For ferrous and nonferrous metals, the problem is not so much the costs of reprocessing itself as it is the costs (mostly collection) of inducing the flow of a specific residual (scrap autos, tin-plated steel cans, or aluminum products). In other situations, materials recovery is impeded because of insufficient output markets (compost from municipal refuse, low-grade secondary paper stocks), or excessive reprocessing costs (manual separation of paper from municipal refuse, or copper and other contaminants from automobile hulks).

Secondary materials

Given a market capacity to utilize secondary materials, relative pricing is probably the most effective means of influencing the flow of materials to and from production and consumption activities. There is probably no recovery operation or industry that could not be expanded if the market price of the output were higher. It is quite common for material recovery to expand during periods of shortage of (and higher prices for) the competitive virgin raw material. The most notable example was during World War II.

Recovered materials almost inevitably must compete with the virgin output of other basic industries. Furthermore, whenever a recorded material is qualitatively inferior in some respect to a virgin material, it must be deliverable at a lower price to compete with its higher-quality substitute.

In the past, prices have changed significantly with current supply and demand. What is not economically feasible today may be tomorrow. And, as we have seen, today's prices generally do not reflect all the social costs associated with residual generation and disposal.

If a fee were imposed on residuals discharged to the environment, relative prices of factor inputs to production would shift and increased materials recovery and reuse might very well be stimulated.

The same result would occur if the costs of reprocessing material residuals for inputs to production and consumption activities were decreased, through final product specifications which would reduce reprocessing costs, the development of more efficient reprocessing technology, new product uses for residuals, or new production processes which could process secondary materials along with other raw material inputs. Technological innovation then, probably represents the most important alternative for reducing the unit cost of both residuals treatment and materials recovery and reuse, and for expanding the opportunities for utilizing secondary materials.

A case for materials recovery and reuse, then, can be made on the basis of the market value of secondary material and the reduction in residual handling and disposal costs, and associated external damages. But, given levels of economic activities and consumption, what of the socially desirable extent of materials recovery and terial inputs. Technological innovation, reuse? To determine this, we must first specify a criterion for maximum social welfare. Minimization of the total cost of producing a product, the cost of handling and disposing of residuals, plus all external damages associated with remaining residuals in the environment, is only one possible criterion of maximizing social welfare. For example, this particular criterion is one of pure efficiency, and questions regarding the distribution of costs and benefits among both geographical areas and different income groups would certainly arise. Thus, in any real situation, the criteria used would probably be based on efficiency concepts with some adjustments related to the distributional problems.

Paper—a case study

To be more specific about the economics of solid waste management (including the possibilities of materials recovery and reuse), let's look at the production, consumption, and final disposal of paper products, and the role the secondary materials market can play in reducing the direct and indirect costs, as well as the associated externalities, or social costs, of disposing paper products in the form of solid waste.

Gross output of the paper and paperboard industry in the U.S. represented about $9.3 billion in 1969. In that year, approximately 53.5 million tons of paper and paperboard were produced, and 58 million tons used. The difference was made up by the excess of imports over export and changes in stocks. Of the total production, paperboard (including wet machine board) accounted for 25.7 million tons; paper products accounted for 23.5 million tons; and paper and paperboard for construction purposes, 4.3 million tons.

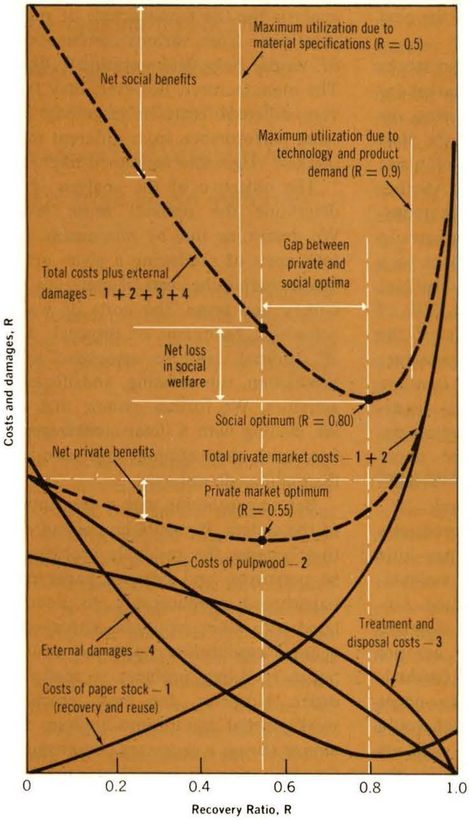
During the year, approximately 10.5 million tons of reclaimed paper stock was used in the production of paper and board. The percentage of paper stock (secondary paper fiber) in total fibrous materials consumed in board and paper production for 1969 was 19.0%. Although the total quantities of paper stock used by mills is increasing, 9.4 million tons in 1959 *vs.* 10.5 million tons in 1969, the percentage of reclaimed fiber is decreasing, 26.4% in 1959 *vs.* 19.0% in 1969.

Waste paper used in papermaking has been declining since the peak in World War II, when secondary fiber accounted for 35% of the raw material input for paper and paperboard production. Some reasons for this decline include "contamination" of waste paper by plastics, metals (paper clips, staples), clay coatings, and organic material (inks, laminants, and adhesives); increased costs of waste paper collection; technological advances in wood pulping, which result in higher fiber yields from virgin materials and more efficient, less costly production; and integration and expansion within the industry which have resulted in additions of virgin pulping capacity.

Paper represents between 40 to 55% (dry weight basis) of the municipal refuse collected from commercial and residential establishments. Of the paper stock consumed, 77.3% is used in the manufacture of paperboard (including wet machine), 13.8% is used in the production of paper (including newsprint), 8.6% is used in the manufacture of construction paper and paperboard, and 0.3% is returned to pulp mills. In 1969, approximately 87% of the total secondary fiber recovered was in the low-grade "bulkies"—mixed, news boxboard cuttings, and old corrugated containers. (In 1966, old corrugated boxes represented about 25% of the total reclaimed paper stock.) Of the remainder, 13% was made up of highly uniform wastes from commercial operations such as converters, printers, and paper mills.

Old corrugated boxes can sometimes be profitably collected from retail stores and supermarkets because the volume is substantial and the containers are usually clean and previously separated. In some areas of the country, old newspapers are collected by nonprofit organizations, including Boy Scouts, churches, and

Optimal recovery ratio for paper stock



The cost and damage functions shown are depicted as a function of the recovery ratio for paper stock.
For clarity, only functions which affect positions of the various optima are shown. Hence, production costs other than raw fiber inputs, as well as the associated external damages, both of which are assumed invariant with recovery ratio, are not included.
The external damage function shown includes externalities associated with both disposal activities and materials recovery and reuse. For each recovery ratio, the various costs and damage represent the minimum cost combination of the various alternatives.
This diagram is, of course, a gross oversimplification of all the costs and damages actually involved, and the functions shown represent an aggregate of a variety of cost functions only for purposes of exposition. In any real situation, this analysis would be made with use of linear or nonlinear programming techniques or simulation; the number of variables and complicating interrelationships would be too great in any to be presented in the form shown here

private collectors; in New York City, when sufficient demand was present, a surprising proportion of used newspapers collected in that area was supplied by apartment house janitors. The demand for old newspapers is especially high in areas served by newsprint or newspaper recycling plants such as Neenah, Wis., the home of Bergstrom Papers; and Garfield, N.J., Alsip, Ill., and Pomona, Calif., where the Garden State Paper Co. has plants. Garden State Paper Co. claims they will build a paper recycling plant anywhere that will guarantee an input of 300 tons of old newspapers per day.

Despite the absence of new incentives and regulations, three papermaking plants in 1969 converted 365,000 tons of old newspapers into 320,000 tons of fresh newsprint worth $45 million. Garden State Paper Co.'s plant in Alsip, Ill., sold their recycled newsprint for $146 a ton, which, at the time, was $7 less than the price of newsprint made from virgin pulp. As compensation for collecting these old newspapers, some $9 million went to such groups as the Salvation Army, Boy Scouts, churches, and so on.

These examples are encouraging, and indicate that present market forces are working in some areas. But before going any further in this discussion of secondary fiber reclamation, we should really examine more closely how one might determine an optimal reuse level for paper and board that would be desirable from the point of view of society as a whole.

Optimal recycling

Under present marketing conditions, paper stock comprises about 20% of the raw material input to paper and paperboard production. Although the relative prices of paper stock and virgin pulp play a major role in the extent of recovery and reuse, other factors are at work as well. For one thing, consumers of paper and board products may employ material specifications rather than performance specs. That is, they require that their products be made from 100% virgin fibers rather than specifying that it should have a given strength, softness, or color. Another problem is that secondary paper stock supply, as well as quality, is apt to vary significantly. To even out the quantity fluctuations, among other things, would require covered storage facilities.

Market prices for the various grades of paper stock fluctuate widely, and private investors are reluctant to make long-term investments in capital intensive equipment—the very equipment they need to minimize the unit costs of collection, storage, and reprocessing of these materials.

Recently, prices for the low-grade stock has been depressed because of slackening production of building paper and insulating board. It is a matter of record that the U.S. paper stock industry responds sensitively to activity at the building paper and board mills, which consume some 9% of total U.S. tonnage. Thus, when a dip in the housing industry afflicts the building paper and board mills, it develops a soft market for the low grades, thus weakening the entire pricing structure. For example, when the tight mortgage money created a sharp decline in housing starts in mid-1967, this was a disastrous period for dealers whose warehouses were stacked with inventories. With the return of housing starts, paper stock prices index rebounded from 78.1 (1957–59 = 100) in 1967 to 108.3 in 1969. For No. 1 mixed, the dip and surge were even more pronounced: from 103.2 in 1966 to 65.4 in 1967, 99.8 the next year, 110.0 in 1969.

However, prospects for paper stocks are improving. The current market for paper stock is influenced by rising virgin pulp prices and indicates the start of a trend to increased use of waste paper as a pulp substitute. Another bright spot in the paper stock industry has been the 1969 increase in export demand—up 36,000 tons to a total of 289,000 tons. It should be kept in mind, however, that almost 87% of the reclaimed paper stock is of the lower grades. These lower grades are used primarily for products that are subject to substantial variations in demand; most notably, construction paper and board. Hence, the paper stock industry is affected by variability in both supply and demand.

As I stated at the outset, producers and consumers have had to pay little or nothing for the use of the assimilative capacity of the environment. Unused paper residuals must be disposed of in some manner, if they are not recycled. In analyzing solid residuals management with respect to paper residuals, the question is: What would the degree of recycling be if such extended costs were included in the private market system?

In an attempt to determine an optimal recovery rate from society's point of view, we will use, as an example, a single paper stock category (such as No. 1 news or old corrugated) and assume it to be used for a single product.

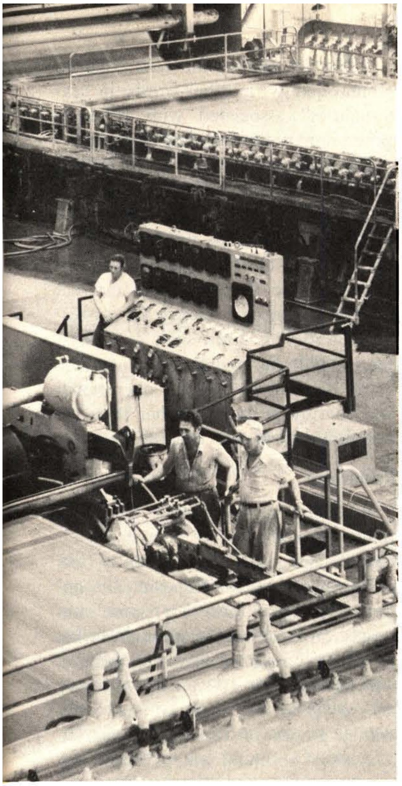
Optimal recovery ratio

For specifying an optimal recovery ratio, we will use the criterion of economic efficiency, free from institutional constraints. It should be kept in mind, however, that this is only one of the possible criteria that might be considered. From a methodological standpoint, the criterion chosen to represent society's welfare function is immaterial. In an operational situation, however, it would be most important.

For our analysis, we will assume that the consumption level of paper —but not, of course, paper stock— is fixed; that is, it is determined exogeneously. We will, however, use performance specifications rather than material specifications in our analysis, and will assume that the products are identical if the consumer of the product cannot distinguish between them in terms of his use of the product. Consequently, this allows in our analysis for the manufacture of products made from various combinations of virgin pulp and reclaimed fiber. The manufacturer, however, may face very different costs in providing the same performance from different mixtures of virgin and reclaimed fiber.

The objective of the analysis is to determine the optimal reuse level. We determine this by minimizing the total costs of producing a given product, including the costs of materials recovery and reuse, the costs of waste collection, treatment of disposal, and all external damages associated with production, reprocessing, and disposal activities. We further assume that we are dealing with a deterministic problem and that supply and demand fluctuations do not exist.

Before continuing with a description of the system, it should be pointed out that because the residuals problem is so pervasive, and because paper and paperboard products are so interrelated with other economic activities, a general equilibrium approach to the paper recycling problem is really in order. However, for most practical work, partial equilibrium analyses are almost always a necessary compromise. Concentration on a particular product chain which, except for specific situa-



"Waste paper used in papermaking has been declining since World War II because of technological advances that result in higher yields from virgin materials"

tions, neglects both location problems and interconnections with other economic activities (except through fixed market prices) is purely an heuristic device.

The system

To discuss the public and private benefits associated with recycling, we must be a little more specific about the system involved. Internal flows of materials, raw material inputs, and disposal of residuals to the environment must be depicted. The production, consumption, materials recovery and reuse, and disposal system that we will be using for this discussion is shown schematically (see box). Because we are only interested in the flows of materials, and pulp, paper and board in particular, the only input to the system that we consider explicitly is virgin pulpwood; we do not go back to the operations in the forest, or consider the transportation of pulpwood to the mill.

Even with such an apparently simple system, there are countless trade-offs that can be made. At the source of paper residuals generation, for example, we could separate the used paper from other solid residuals or refuse for special pickup. We might incinerate the paper at the user's location and dispose of the residue by way of the municipal collection system; we can store the material in various forms for periodic pickups of differing frequencies; we could compact and bail the material on site (to save storage space and reduce collection costs); or we could shred, grind, and pulp it and discharge it to the municipal sewerage system.

There are also a variety of alternative collection possibilities; frequencies, sizes and types of collection vehicles, sizes of collection crews, curb *vs.* backyard pickups—all are alternatives that might be considered in a complete analysis.

Locations of materials processing facilities and (or) disposal facilities play an important role in the transport of solid residuals. For example, are transfer stations feasible and, if so, where should they be located? Is separation at the source or at a transfer station, or other central processing activity, the more desirable alternative?

There are also many alternatives for treating and disposing of solid residuals. If ultimate disposal is in a sanitary landfill, volume-reduction operations—incineration, compaction, composting—should be considered. As the land available for landfill operations becomes more scarce, especially near urban areas, and the solids have to be transported further and further away, volume-reduction alternatives become more and more attractive.

Costs and external damages

To specify an optimal reuse rate, certain costs and damages must be delineated. We assume for this analysis that the market price of pulpwood encompasses all the social costs of employing this resource in paper- and board-making.

The costs of collection, recovery and reuse, treatment, disposal, and transportation are all determined by the market, and thus readily available, at least in principle. But nonmarket externalities are another matter. For our purpose, we assume the external damages associated with pulping and the manufacture of paper and board are the same for virgin pulp and reclaimed fibers and any combination thereof, although this is not likely. However, associated with collection, treatment, and disposal activities are certain "externalities" that must be included in the analysis. The kinds we are most familiar with are those associated with air and water pollution. And the actual external damages suffered by others will depend upon the assimilative capacity of the environment, all other dischargers in the area, the relative locations of emitters and receptors, and so on. Other forms of externalities associated with collection, recovery and reuse, and disposal that must be considered are: noise of collection and processing and (or) treatment activities, as well as those of an esthetic nature.

Before we leave this discussion, it is only fair to point out that although externalities are very real and more than one politician has either been put in office or deposed from office because of them, they are often difficult to quantify in meaningful dollar-terms. That is, explicit damage functions are generally lacking. This is especially true for those externalities associated with either the imputed or indirect costs.

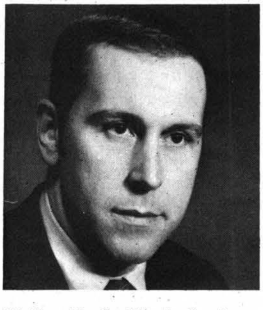
Optimal reuse rate

Given the cost and damage functions discussed above, the objective is to choose a level of recovery and reuse that minimizes the costs and damages of wood pulp, paper and board manufacturing costs; secondary materials recovery (including private costs for separation and preparation); processing and transportation; solid waste collection; treatment and disposal; and external damages. These cost and damage functions are depicted (see box) as a function of the recovery ratio. For this example, we show the position of the socially optimal recovery ratio at 0.80 and the location of the optimal recovery ratio for the private market at 0.55. From the municipality's standpoint, of course, the optimal recovery ratio is 1.0, and the cost of disposal is zero. These optimal recovery ratios are at the point where the respective costs are minimized.

From the point of view of society, the optimal recovery ratio is where all social costs, including damages, are minimized. This is the point where the marginal cost of using paper stock in the production of paper is equal to the sum of the marginal benefits (reduction in costs) of wood pulp, paper, and board manufacturing costs; solid waste collection; treatment and disposal; and all external damages.

But what about the point of view of the private entrepreneur? If he does not have to pay for disposal either directly or indirectly, his optimal position with respect to paper stock recovery will be the point where the marginal costs of employing paper stock in the production of paper are just equal to the marginal reduction in costs of pulpwood and paper and board manufacturing costs.

A numerical example of waste management costs, together with the remaining residuals discharged to the environment, might be helpful at this point. B. T. Bower and his coworkers, in their report on the Second Regional Plan for metropolitan New York ("Waste Management: Generation and Disposal of Solid, Liquid, and Gaseous Wastes in the New York Region," March 1968), have provided such an example. They have estimated for the year 2000, the waste management costs—incinerator, wet scrubber, settling basin, plus landfill of the incinerator residue—for two paper stock recovery ratios—20% and 80%. It is interesting to note that the annual cost of solid waste disposal, with only 20% of the paper recycled, is about 1.5 times the annual cost if 80% of the paper were recycled, a difference of almost $100 million for the New York region (31-county area in New York, New Jersey, and Connecticut). Their estimated costs are $300 million per year for 20% paper recycled and $120 million for 80% recycled.



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Almost as impressive are the quantities of residual particulates discharged to both the atmosphere and water course. Assuming good incineration (10 lb of particulates discharged per ton of waste incinerated), the particulates discharged to the atmosphere amount to 1020 tons per day for 20% recycling and 680 tons per day for 80% of the paper recycled. For the particulates discharged in the waste water, and also assuming good incineration (50 lb of particulates per ton of waste incinerated, 80% removal in the wet scrubber, and 90% removal in the settling basin), 20% recycled paper stock results in 408 tons of particulates per day, whereas 80% recovery and reuse results in 288 tons per day.

To relate physical quantities of residuals discharged in the environment to the externalities referred to above, damage functions would be required. We include this example here, however, to point out that even though solid residuals are treated and modified prior to disposal in the environment, externalities, generally, are not completely eliminated. The other reason for presenting this example is to indicate that substantial savings in waste management costs could be achieved by increasing the recovery rate of paper stock.

Public incentives

Given a "socially desirable" reuse level which has been evaluated by internalizing all the costs to society, and under conditions relatively free of constraints, how do we design new institutions that will attempt to compensate for our failure to reach the reuse ratio that maximizes social welfare?

Without drastic price alterations, and a reasonable expectation of prices remaining steady and favorable to the secondary materials market, there is probably no direct way to increase private sector recovery significantly in the short run other than through some form of public subsidy. Up to some point, such subsidy could be justified solely on the bases of:

- The savings in direct costs of residuals handling and disposal for a municipality, or other agency.
- Plus an improvement in environmental quality; in other words, in "externalities" associated with residuals generation, collection, and disposal.

For such a scheme, the cost of the subsidy might be internalized by including a disposal fee or tax in the price of the original product itself—the charge to be proportional or even equal to the direct and indirect costs it imposes on society for its disposal. Proceeds from such a disposal fee would be redistributed to the waste disposal agency for operational and subsidy purposes, rather than using funds from the general treasury.

Summary

Reducing residuals through either reduction at the source or material recovery and reuse is frequently less costly than residuals disposal. The optimal recovery ratio for most materials, from either the private market or social points of view, in general, will be less than 100% and will vary according to the material and even within grades of the same material. The social optimum will, except in unusual and extreme cases, represent a combination of virgin material inputs, material recovery and reuse, residuals handling and disposal, and even some external damages. Furthermore, because of residuals handling and disposal costs, and the associated external damages, the private market optimum will always be less than the social optimum, unless, of course, all costs are internalized, in which case they will be the same. And public incentives, in the form of subsidies, charges, taxes, or regulation, will be required to encourage the private market optimum to conform more closely with the socially optimal level of recovery and reuse.

Finally, whether a given alternative is considered "economic" depends on both the criterion used for ranking alternatives and the point of view of the unit making the decision—for example, the private entrepreneur or society as a whole. Decisions will be based on costs and benefits, but different activities will face different cost and benefit functions. Hence, for some locations, composting municipal refuse may not be economic for either a private entrepreneur or a municipality, but might very well be from the standpoint of society as a whole, assuming, of course that compost as a soil conditioner has the social value ascribed to it by some ecologist.

Fate of Phosphorus in Waste Treatment Processes: Enhanced Removal of Phosphate by Activated Sludge

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■ The activated sludge process achieves about 20% phosphorus removal from sewage containing 10 mg. P per liter to produce an activated sludge containing 2–3% P. Greater P removals and higher sludge P contents are caused by chemical precipitation, specifically, in hard water sewages by the precipitation of calcium phosphates which become entrapped in the activated sludge floc matrix. Precipitation depends on sewage pH, which depends on activated sludge CO_2 production. High mixed liquor CO_2 production causes low mixed liquor pH. As the mixed liquor proceeds down the aeration basin, the amount of degradable organics decrease and, in turn, both DO consumption and CO_2 production rates decrease. At a constant air supply rate, mixed liquor DO concentration increases and CO_2 content decreases, thus the pH of the mixed liquor increases. It is only fortuitous that at some point along the length of the aeration basin a rise in both DO and pH occurs. Operational parameters such as organic loading, mixed liquor suspended solids, and DO have no effect on the enhanced removal of phosphate by activated sludge.

In the considerable body of literature concerning the fate of phosphate in the activated sludge process, there appear to be two distinct schools of thought. The first viewpoint, represented in papers by Sawyer (1944), Sekikawa, Nichikawa, *et al.* (1966), Hall and Engelbrecht (1967), and Jenkins and Menar (1967) can be summarized as follows: The volatile mass (VSS) of activated sludge contains between 2 and 3% by weight of biologically incorporated phosphorus; the amount of phosphate incorporated biologically into activated sludge is not affected by the growth rate of the sludge or by process operating parameters such as organic loading, mixed liquor volatile suspended solids concentration (MLVSS), aeration rate, or mixed liquor dissolved oxygen (DO) concentrations; and phosphate removal is proportional to the net sludge growth.

With activated sludge P contents of 2 to 3%, domestic sewage P contents of 10 mg. P per liter and substrate removal rates in the standard rate range (0.4 to 1.0 lb. COD removed per lb. MLVSS-day), biological removal of phosphate can only account for a maximum of 20 to 30% of the influent phosphate or about 2 to 3 mg. of P per liter of an influent 10 mg. of P per liter.

The second point of view, expounded in papers by Levin and Shapiro (1965), Borchardt and Azad (1967), and Connell and Vacker, (1967), embodies the idea that under certain conditions, activated sludge is capable of removing more than the 2 to 3% phosphate-P that it requires for growth. The biological uptake of excess phosphate has been termed "luxury uptake." According to these authors, phosphate removal by this mechanism is enhanced by high-DO concentrations and, conversely, phosphate incorporated into sludges by the luxury uptake mechanism can be released easily under anoxic conditions and conditions of low pH, such as those that might be encountered in the sludge blanket at the bottom of a secondary clarifier or in an anaerobic digestor. Further, luxury uptake of phosphate leads to sludges with phosphate contents two to three times greater than normal sludges, and consequently, treatment of domestic sewage at standard organic loading rates can lead to phosphate removals of 60 to 90% of an influent 10 mg. P per liter.

A mechanism for the enhanced removal of phosphate must be consistent with these observations and, in addition, must provide satisfactory interpretation of the following observations made at the Rilling Road Plant, San Antonio, Tex.—a plant that has experienced phosphate removals as high as 90%.

At a point about $^3/_4$ of the way along the 300-ft. aeration basin where the DO concentration increases from about 1.2 to 5 mg./liter, there is a sharp drop in soluble orthophosphate concentration.

"Reversed tapered aeration," in which higher aeration rates are used at the tail end of the aeration basin than the head end of the basin, enhanced the removal of phosphate. During aeration at the Rilling Road Plant, the pH of the sewage increased from 7.3 to 7.9. Activated sludge with a high phosphate content had a very low (approximately 70%) volatile matter fraction.

Postulated Mechanism of Enhanced Phosphate Removal

Phosphate removal in excess of that predicted by biological growth requirements is caused by chemical precipitation. The phosphate precipitate is physically entrapped in the matrix of the activated sludge floc and is removed with the waste-activated sludge.

In hard water sewages, such as that at San Antonio, Tex., a significant phosphate removal is by calcium phosphate precipitation—the solubility of the calcium phosphate being a function of the pH of the sewage.

In the metabolism of organic matter activated sludge con-

Table I. Comparison of Mineral Characteristics of Water from San Antonio, Tex., and Sewage from San Ramon, Calif.

Constituent	San Antonio mg./liter	San Ramon mg./liter
PO_4 as P	9[b]	16
Ca	64[a]	66
Mg	17[a]	44
Total hardness as $CaCO_3$	230[a]	346
Alkalinity as $CaCO_3$	225[b]	405
pH	7.3[b]	7.7

[a] Durfor and Becker, 1964.
[b] Vacker, 1967.

sumes oxygen and produces CO_2, which controls the mixed liquor pH. CO_2 concentrations of 0.5% by volume (compared to typical atmospheric CO_2 contents of 0.03% by volume) have been determined by Weddle (1968) in the diffused air issuing from an activated sludge aeration basin.

In an activated sludge aeration basin the DO concentration is controlled by the rate of aeration and the rate at which the activated sludge consumes oxygen (for a constant rate of oxygen transfer). Since O_2 is consumed and CO_2 is produced by activated sludge in the metabolism of its substrate, the rates of O_2 uptake and CO_2 production should parallel each other.

In a conventionally operated activated sludge basin, return activated sludge and settled sewage enter at the head end of the basin. Here, the rates of CO_2 production and DO consumption are high and, consequently, the mixed liquor DO concentration is low. A high CO_2 production rate leads to high mixed liquor CO_2 concentrations and a low mixed liquor pH. As the mixed liquor proceeds down the aeration basin, the amount of degradable organic matter decreases; the DO consumption and CO_2 production rates decrease, the mixed liquor DO concentration increases; and the dissolved CO_2 content decreases and the mixed liquor pH rises. Thus, an increase in DO concentration should be accompanied by an increase in mixed liquor pH to a value that, at some point along the length of the basin, calcium phosphate precipitation will occur.

This point will coincide fortuitously with the point at which the mixed liquor DO concentration increases, and significantly with the point at which a decreased mixed liquor CO_2 content has allowed the pH to rise to a point where calcium phosphate precipitation occurs.

Several other changes that take place during aeration may influence the precipitation of calcium phosphate.

In settled sewage, the total phosphate consists of dissolved orthophosphate, some organic phosphate, both in solution and suspension, and condensed phosphates. Calcium may be present as Ca^{2+} and also as particulate salts with fatty acid anions and particulate or dissolved complexes with orthophosphate condensed phosphate anions.

Activated sludge treatment rapidly hydrolyzes condensed phosphates to orthophosphate, possibly releasing calcium from condensed phosphate complexes. Microbial degradation of fatty acid salts of calcium would release Ca^{2+} ions and degradation of organic compounds might release small amounts of phosphate. The net result of these processes is that both the postulated precipitating species—orthophosphate and calcium—would increase during activated sludge treatment.

Anoxic conditions develop in activated sludge when the DO consumption rate exceeds the oxygen supply rate. Since DO consumption is accompanied by CO_2 production, anoxic conditions should be accompanied by a pH decrease. The pH decrease should be more severe in the activated sludge floc matrix than in the liquid surrounding the floc, especially in a quiescent sludge blanket.

Because of the intimate association of the colloidal calcium phosphate particles with the activated sludge matrix, pH decreases associated with anoxic conditions will be especially felt by the particles and it is possible that in an anoxic floc interior locally acid conditions would cause calcium phosphate dissolution and release of orthophosphate into solution.

It has been observed that phosphate is released from activated sludge when the DO concentration is below 0.3 mg./liter (Levin and Shapiro, 1965) and that the released phosphate is from the acid-soluble fraction (Shapiro, 1967).

An enhanced phosphate removal mechanism involving calcium phosphate precipitation is therefore plausible in light of reported observations. This paper will provide experimental evidence that confirms the precipitation hypothesis.

Experimental

Effect of Aerating Gas on Calcium Phosphate Precipitation. Batches of activated sludge effluent from the Valley Community Services District (VCSD) Water Reclamation Plant, San Ramon, Calif., which has mineral characteristics similar but not identical to those of San Antonio sewage (Table I), were aerated with air, pure nitrogen, pure oxygen, and air + 5% CO_2. The results of this experiment (Figure 1) show that the important function of the aerating gas is CO_2-stripping, which subsequently causes an increase in the pH of the liquid.

DO concentration per se is unimportant in the removal of dissolved orthophosphate, since O_2 and N_2 were equally effective in causing calcium phosphate precipitation. These two gases raised the pH of the activated sludge effluent to an identical value and at an identical rate, while the DO in the effluent aerated with O_2 reached 34.4 mg./liter, the DO in the sample bubbled with N_2 fell from 7.2 to 1.7 mg./liter.

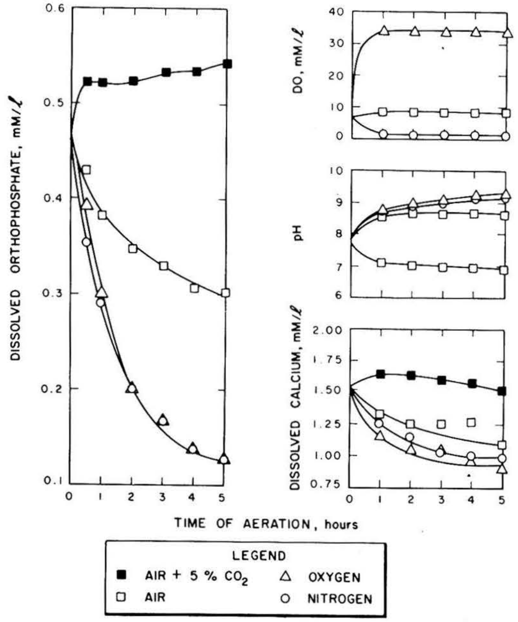

Figure 1. Batch aeration of activated sludge effluent with air, air + 5% CO_2, O_2, and N_2

Table II. Release of Orthophosphate from Activated Sludge

Analysis	Initial concentration	After 3-hr. aeration with		
		Air	Air + 0.5% CO_2	Air + 5% CO_2
DO, mg./liter	5.8	8.4	8.4	8.4
pH	8.17	8.43	7.60	6.85
Dissolved orthophosphate, m*M*/liter	0.33	0.25	0.51	1.04
Dissolved calcium m*M*/liter	1.49	1.36	1.72	2.45
Mole ratio of released calcium and orthophosphate: Ca:P	...	...	1.28	1.35

Air was not as effective as either N_2 or O_2 in causing the precipitation of orthophosphate because air, containing approximately 0.03% CO_2, is not as efficient a CO_2-stripper as pure N_2 or O_2. This is reflected by the pH changes caused by bubbling air, in comparison to those caused by N_2 and O_2. The final pH in the N_2- and O_2-bubbled activated sludge effluents was 9.20, whereas the final pH of the effluent bubbled with air was 8.65. Similarly, dissolved orthophosphate and calcium levels fell more rapidly and to lower values in the N_2- and O_2-aerated samples than in the effluent bubbled with air.

Aeration with air+5% CO_2 caused a pH decrease from 7.75 to 6.95, since the aerating gas mixture contained a higher CO_2 content than that to which the activated sludge effluent had been equilibrated. A small increase in dissolved orthophosphate and calcium took place, indicating that the sludge contained some calcium and orthophosphate that could be solubilized at a pH below 7.75.

Comparison of the results of aeration with air and with air +5% CO_2 provides further indication of the unimportance of DO concentration in orthophosphate precipitation. While the DO concentration in both samples was identical at all times during the experiment, the dissolved orthophosphate concentration fell from 14.6 to 9.4 mg. P per liter in the air-bubbled sample and rose from 14.6 to 16.9 mg. P per liter in the sample aerated with air+5% CO_2.

Release of Calcium Phosphate from Activated Sludge. Aliquots of activated sludge mixed liquor from a pilot plant that was being operated to produce a high phosphate sludge (5.2% P on a VSS basis) were bubbled with air, air+0.5% CO_2, and air+5% CO_2. After 3 hr., the DO concentration in all three aliquots increased from 5.8 to 8.4 mg./liter (Table II). In the sample aerated with air the pH increased from 8.17 to 8.43, and the dissolved calcium and orthophosphate decreased by 0.13 and 0.08 m*M*/liter, respectively. In the activated sludges aerated with air+0.5% CO_2 and with air +5% CO_2, the pH fell from 8.17 to 7.60 and 6.85, respectively. In both of these samples, dissolved calcium and orthophosphate were released (Table II), the releases being greater for the sample aerated with air +5% CO_2 (and having the lower pH).

Pilot Plant Experiments. A four-compartment, 300-liter aeration-capacity activated sludge pilot plant was located at the VCSD Water Reclamation Plant, San Ramon, Calif. The pilot plant was fed with primary effluent from the VCSD primary sedimentation basins. Samples of the influent and effluent flows were taken automatically every 15 min. and composited by pumping into refrigerated containers.

During each experiment, the pilot-plant performance (and where applicable, the performance of the VCSD plant) was characterized by organic loading, hydraulic residence time, mean cell residence time, and substrate removal efficiency.

For each experimental period the daily measurements of process performance were graphically summarized, and periods of steady operation were determined by inspection. The criterion for steady-state operation of the pilot activated sludge plant was ±30% deviation of daily values of MLVSS and substrate removal rate from the mean value and a ±15% deviation of daily sludge Ca and P values from the mean value. The data during periods of steady-state operation were then screened for conformance to a phosphate materials balance. The criterion for conformance to the phosphate materials balance was ±10% from completion. Only data that conformed to steady-state and phosphate materials balance criteria were used.

San Antonio Conditions. The pilot plant was operated to conform to the parameters reported to be important for enhanced phosphate removal by Connell and Vacker (1967) in their studies at the San Antonio Rilling Road Plant. The pilot plant aeration basin configuration with four 75-liter continuously stirred tank reactors (CSTR) in series and with settled sewage and return activated sludge entering at the first reactor, closely resembled the two-pass aeration basin of the Rilling Road Treatment Plant. The results of the six-week experiment (Table III) show that enhanced phosphate removal was not obtained in the pilot plant when the San Antonio conditions were matched almost identically. Thus, under conditions of identical MLVSS, BOD loading, effluent NO_3–N, and at mixed liquor DO concentrations that consistently exceeded the specified minimum of 1.5 mg./liter, the pilot plant reduced the phosphate concentration from 15.2 to 12.2 mg. P per liter—a removal of phosphate that could be accounted for entirely by incorporation into activated sludge cell material—*i.e.*, biological removal for growth. Indeed, during the entire period of operation under San Antonio conditions, the activated sludge P content in the pilot plant never exceeded 2.9% on a volatile matter basis and averaged 2.3% P—a figure which is in excellent agreement with the 2.6% P obtained in previous work (Jenkins and Menar, 1967).

It was concluded that the conditions of MLSS, BOD loading, effluent NO_3–N, and mixed liquor DO reported by Connell and Vacker (1967) were of no direct significance in the enhanced phosphate removal by activated sludge in this study.

Table III. Comparison of Average Operating Conditions and Phosphate Removal at San Antonio Rilling Road Plant and at Pilot Plant Operated under San Antonio Conditions

Parameter	Rilling Road[a] Plant	Pilot plant
MLSS, mg./liter	1130	1130
BOD loading, lb. BOD/lb. MLSS-day	0.5	0.5
Mean cell residence time, days (sludge age)	3.2	2.2
Mixed liquor DO, mg./liter	3.0	2.8
Effluent NO_3–N, mg. N/liter	1.0	1.5
Influent pH	7.3	7.7
Effluent pH	7.9	7.8
Influent total phosphate, mg. P/liter	10.5	15.2
Effluent dissolved phosphate, mg. P/liter	0.9	12.2
Phosphate removed, mg. P/liter	9.6	3.0

[a] Connell and Vacker (1967).

Table IV. Operating Conditions and Results of Pilot-Plant Preaeration Experiment

	Influent	Preaeration	Overall (preaeration + activated sludge)
Operating conditions			
Substrate removal rate, lb. COD removed/lb. MLVSS-day	...	2.4	0.8
Mean cell residence time, days	...	0.18	2.3
Hydraulic residence time, hr.	...	4.3	8.7
Air supply rate, cu. ft./gal. waste treated	...	14.0	28.0
MLSS, mg./liter	...	443	770
MLSS, volatile fraction, %	...	81.1	76.5
Results of operation			
Influent total COD, mg./liter	217		
Effluent dissolved COD, mg./liter	...	78	41
COD removal efficiency, %	...	64	81
Influent total P, mg./liter	15.3	...	...
Effluent dissolved P, mg./liter	...	11.0	10.1
MLVSS, P content, %	...	3.2	4.5
Influent total Ca, mg./liter	64.4	...	...
Effluent dissolved Ca, mg./liter	...	62.0	58.8
Influent pH	7.7	...	...
Effluent pH	...	8.3	8.3
Effluent DO, mg./liter	1.5	5.4	6.2

Preaeration Experiment. The purpose of this experiment was to determine whether the pH of the incoming sewage could be raised by preaeration to such a degree that phosphate precipitation would take place in the activated sludge aeration basins.

The pilot plant was divided into two sections of approximately equal volume, the first two reactors serving as preaeration basins and the latter two as the activated sludge aeration basins. Both the preaeration and aeration sections were further baffled to prevent short-circuiting by dividing each reactor into four compartments.

Table V. Operating Conditions and Results for Comparative Study

	Pilot plant	VCSD plant
Operating conditions		
Substrate removal rate, lb. COD removed/lb. MLVSS-day	0.25	0.29
Mean cell residence time, days	12.6	12.9
Hydraulic residence time, hr.	7.8	9.1
Air supply rate, cu. ft./gal. waste treated	97	3.0
MLSS, mg./liter	2780	2935
MLSS, volatile fraction, %	79.1	85.2
Mixed liquor temperature, °F.	68.4	67.5
Results of operation		
Influent total COD, mg./liter	267	264
Effluent dissolved COD, mg./liter	30	23
COD removal efficiency, %	88.8	91.3
Influent total P, mg./liter.	16.6	16.8
Effluent dissolved P, mg./liter	11.8	14.1
MLVSS, P content, %	4.0	2.1
Influent total Ca, mg. Ca/liter	69.6	68.0
Effluent dissolved Ca, mg. Ca/liter	56.0	58.0
MLVSS, Ca content, %	4.4	1.4
Influent pH	7.7	7.7
Effluent pH	8.3	7.2
Effluent DO, mg./liter	8.4	4.2

The operating conditions and the results of the three-week preaeration experiment are summarized in Table IV.

With average preaeration and aeration times of 4.3 and 4.4 hr., respectively, the pH of the influent settled sewage was raised from 7.7 to 8.3 during preaeration, a pH that was maintained in the mixed liquor aeration basins.

The phosphate concentration was reduced by 4.3 mg. P per liter (total influent P–dissolved effluent P) during preaeration and further reduced by 0.9 mg. P per liter by the activated sludge section of the plant. The overall reduction of 5.2 mg. P per liter is far greater than the approximately 2–3 mg. P per liter reduction that would be predicted by biological removal alone at a substrate removal rate of 0.8 lb. COD/lb. VSS-day (Jenkins and Menar, 1967). The activated sludge in the aeration basin contained 4.5% P on a VSS basis, a figure significantly greater than the average 2.6% found by Jenkins and Menar (1967) for activated sludge. Calcium concentrations were reduced by 2.4 mg. Ca per liter (total influent–dissolved effluent) by preaeration and by 5.6 mg. Ca per liter after aeration.

From these data, it could be reasoned that, as the pH rises and as calcium and orthophosphate are released during preaeration, precipitation of a colloidal calcium phosphate takes place. On contact with the mixed liquor in the aeration basin, the colloidal calcium phosphate particles agglomerate with activated sludge and are removed.

Comparative Study with VCSD Plant. The objective of the comparative study was to show that the phosphate removal of two activated sludge plants operated with identical flow patterns and organic loadings, and treating the same sewage could be regulated by the pH of the mixed liquor. The pilot plant was operated identically to the VCSD treatment facility—*i.e.*, as a sludge reaeration plant with 25% of the aeration basin used for sludge reaeration. The only operating variable that differed between the two plants was the air-to-liquid ratio, which was 3 cu. ft./gal. in the VCSD plant and approximately 97 cu. ft./gal. in the pilot plant.

Mean operating conditions and results of the 11-week comparative study (Table V) show that the pilot plant and VCSD plant operating parameters were identical, with the minor exception that the hydraulic residence time in the pilot plant was 7.8 hr. compared with 9.1 hr. in the VCSD plant.

In the VCSD plant the pH of the sewage fell from 7.7 to 7.2 during activated sludge treatment, while the increased rates of aeration in the pilot plant caused a pH increase of from 7.7 to 8.3 during treatment. The VCSD activated sludge plant removed 2.7 mg. P per liter to produce an activated sludge with 2.1% P (VSS basis)—figures entirely predictable on the basis of phosphorus requirements for biological growth (Jenkins and Menar, 1967). The pilot plant, however, effected a removal of 4.8 mg. P per liter and produced an activated sludge containing 4.0% P (VSS basis)—values far in excess of those predictable from sludge growth requirements.

The pilot plant activated sludge was significantly lower in volatile matter content than the VCSD sludge (79% compared with 85%), indicating that it contained a higher content of inorganic material. The calcium content of the pilot plant activated sludge was 4.4% Ca (VSS basis) compared with 1.4% Ca (VSS basis) in the VCSD activated sludge. The calcium removal effected by the VCSD plant was 10 mg. Ca per liter, whereas in the pilot plant 13.6 mg. Ca per liter was removed.

Two additional pilot plant experiments, the first conducted at an average substrate removal rate of 0.2 lb. COD/lb. VSS/day and MLSS of 4950 mg./liter and the second at an average substrate removal rate of 0.59 lb. COD/lb. VSS/day and MLSS of 1850 mg./liter demonstrated that all the conditions associated with enhanced phosphate removal in the previous pilot-scale experiments were effective in low-rate, high-solids units and in standard rate activated sludge units (Table VI).

Parallel between Ca and P Removal. During the comparative study a cold spell caused the performance of the relatively exposed pilot plant to deteriorate, especially with regard to phosphate removal. Figure 2 shows that the phosphate and calcium contents fell simultaneously at the onset of the cold weather and recovered in perfect step following the return of normal temperatures. The parallel behavior of calcium and phosphate removals and sludge calcium and phosphate contents is consistent with the precipitation mechanism postulated for enhanced phosphate removal by the pilot plant.

Discussion

Laboratory and pilot plant experiments have shown that enhanced phosphate removal by activated sludge in hard water sewages can be rationally explained by calcium phosphate precipitation followed by trapping of the precipitate by the activated sludge floc. Biological uptake of phosphate by activated sludge treating domestic sewage produced an activated sludge with 2 to 3% P on a VSS basis and results in a phosphate removal of 20 to 30% of an influent 10 mg. P per liter. Laboratory experiments demonstrated the insignificance of DO as a parameter in calcium phosphate precipitation and showed that pH, which in an activated sludge aeration basin is largely controlled by the CO_2 content of the mixed liquor, was of decisive significance. The pilot plant experiments show the aeration basin DO fortuitously reflects the pH value of the mixed liquor (Figure 3) with high DO concentrations being associated with high pH values for a given set of operating conditions.

Pilot plant activated sludge experiments have shown that decreases of dissolved phosphate were accompanied by decreases of dissolved calcium and that the activated sludge phosphate and calcium contents paralleled each other (Figure 4). Further evidence that increased activated sludge phosphate

Table VI. Operating Conditions and Results for Low Loading–High Solids, and Standard Rate Activated Sludge Studies

	Low loading–high solids system	Standard rate system
Operating conditions		
Substrate removal rate, lb. COD removed/lb. MLVSS-day	0.2	0.59
Mean cell residence time, days	14.5	4.0
Hydraulic residence time, hr.	6.7	6.0
Air supply rate, cu. ft./gal. waste treated	83	75
MLSS, mg./liter	4950	1850
MLSS, volatile fraction, %	66.1	72.6
Mixed liquor temperature, ° F.	77.6	75.9
Results of operation		
Influent total COD, mg./liter	273	232
Effluent dissolved COD, mg./liter	33	36
COD removal efficiency, %	87.7	84.3
Influent total P, mg./liter	17.7	15.8
Effluent dissolved P, mg./liter	11.1	10.4
MLVSS, P content, %	6.8	6.0
Influent total Ca, mg./liter	64.3	62.8
Effluent dissolved Ca, mg./liter	55.5	56.0
MLVSS, Ca content, %	10.0	8.3
Influent pH	7.5	7.7
Effluent pH	8.1	8.1
Effluent DO, mg./liter	6.0	6.2

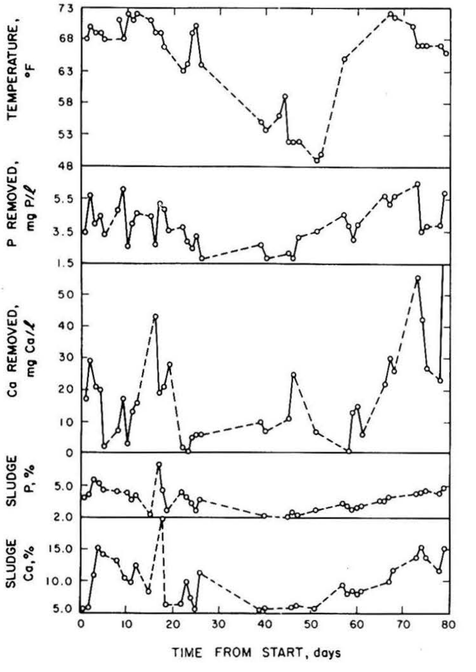

Figure 2. Parallel between Ca and P removal and Ca and P in sludge for pilot plant

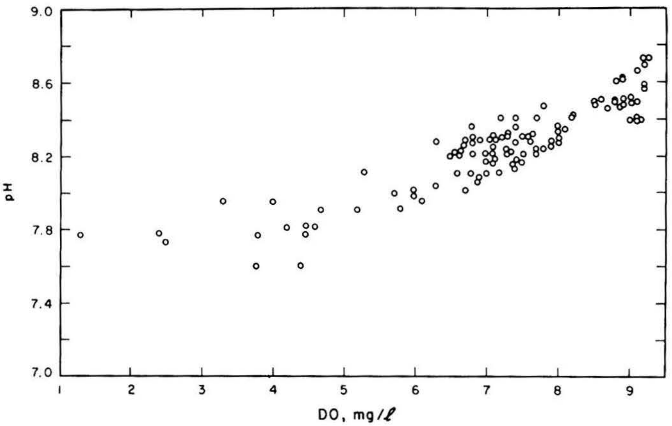

Figure 3. Illustration that mixed liquor DO reflects mixed liquor pH in pilot plant experiments

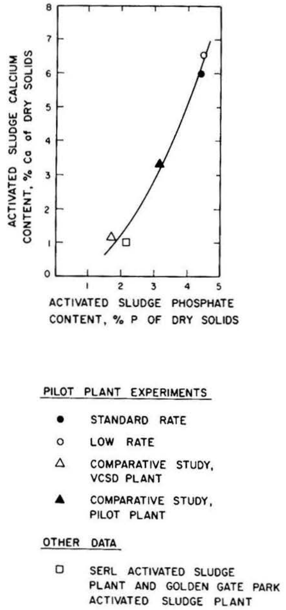

Figure 4. Correlation of activated sludge phosphate and calcium contents

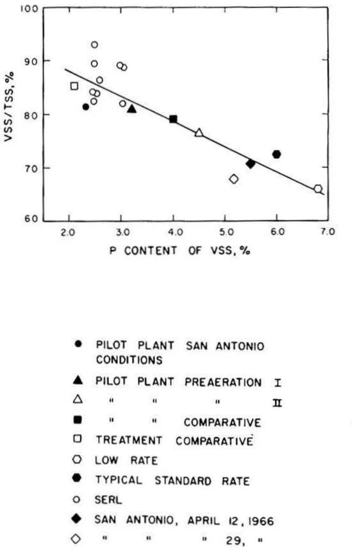

Figure 5. Correlation of activated sludge phosphate content and volatile fraction

content was associated with an inorganic compound and not caused by a biological uptake was obtained from the relationship of activated sludge phosphate content to the volatile fraction of activated sludge (Figure 5). As the phosphate content of the activated sludge increases, its volatile fraction decreases. Data included in Figure 5 from the current pilot plant studies, from the San Antonio Rilling Road Plant and from prior studies by Jenkins and Menar (1967), show that as phosphate incorporation into activated sludge increases, a progressively more nonvolatile sludge is produced.

An examination of all laboratory and pilot plant data shows that there is an empirical correlation between the concentration product (Ca^{2+}) (orthophosphate) and pH (Figure 6). While this correlation at the present time is empirical it does provide a consistent representation of the data and confirms the hypothesis that the solubility of calcium phosphate in sewage systems is a function of pH.

Several activated sludge treatment operating parameters claimed to be necessary for enhanced phosphate removal (Connell and Vacker, 1967; Levin and Shapiro, 1965) do not appear to be significant. High DO concentrations per se did not cause enhanced phosphate removal in these experiments. Connell and Vacker (1967) report that the particular organic loading of 0.5 lb. BOD/lb. MLSS-day and the particular MLSS concentration of 1000 mg./liter were most favorable for enhanced phosphate removal. Pilot plant activated sludge experiments showed that enhanced phosphate removals could occur at a wide range of organic loadings and MLSS concentrations. Other correlations of Vacker, Connell, *et al.* (1967) relating enhanced removal of phosphate to sludge volume index, effluent nitrate content, effluent SS concentration, and the effluent ammonia concentration were not substantiated.

The involvement of a precipitation mechanism in the enhanced removal of phosphate by activated sludge has been demonstrated by this research. In hard water sewages such as those of San Antonio and VCSD, the precipitation appears to

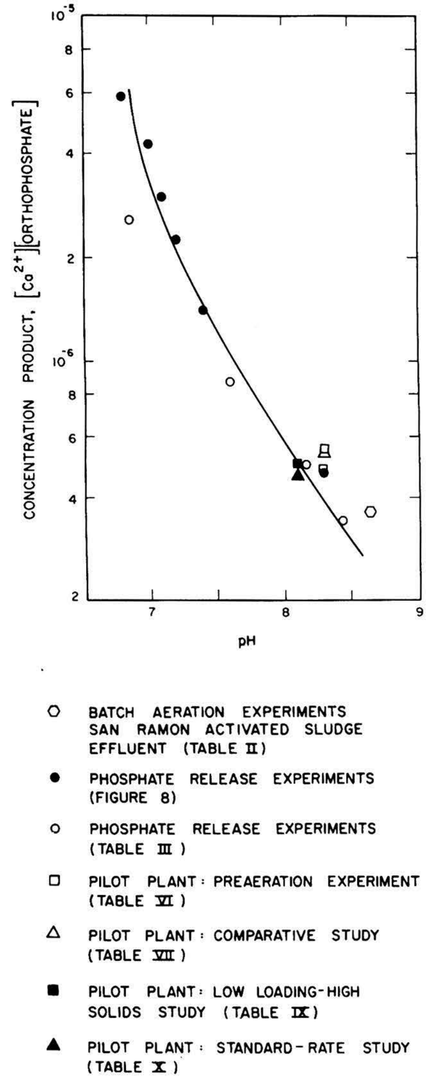

Figure 6. Correlation of the concentration product (Ca^{2+})(orthophosphate) with pH

be calcium phosphate. However, it should be noted that the residual dissolved orthophosphate concentrations obtained at San Antonio at the pH values reported by Connell and Vacker (1967) for this plant are much lower than would be predicted by the correlation curve in Figure 6. Moreover, the dissolved orthophosphate residuals obtained in the pilot plant experiments at no time approached those low values of <1 mg. P per liter reported for the Rilling Road Plant at San Antonio (Connell and Vacker, 1967). The reasons for this disparity are not evident at this time and data on the nature of the calcium phosphate precipitate are inconclusive. It is indeed possible that the divergence of the results reported at San Antonio and those found for San Ramon is caused by differences in the ionic and organic nature of the system in which precipitation takes place. No evidence was found that would support the postulate that biological luxury uptake accounted for the enhanced removal of phosphate by activated sludge in hard water sewages.

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Nitrogen Fixation by Nonsymbiotic Microorganisms in Some California Soils

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■ The rate of nitrogen fixation by soil samples from various California environments was determined at monthly intervals for a period of one year by comparing direct isotopic observations of fixation rates with rates determined by the acetylene–ethylene method. Annual fixation rates of approximately 5 kg. nitrogen per hectare per year were observed in the most favorable environment examined, and rates as low as 2 kg. per year were observed on a more arid site with native vegetation. Observations made by direct isotopic methods compared reasonably well with those obtained with use of the acetylene–ethylene method, but some variability between the two occurred. Limiting factors in the fixation reaction are reported and the significance of observed rates is discussed.

Contributions from free-living microorganisms to the nitrogen balance of the biosphere have not been fully assessed. A carefully drawn balance sheet of nitrogen transformations is needed, however, since nitrogen plays an important part in the nutrition of both animals and plants. As pressures for food production increase and agricultural methods place greater emphasis on maximizing production potential, the management of nitrogen assumes greater importance because of the degradation of environment quality which mismanagement can produce. This degradation of quality applies particularly to food and to water resources, both of which could attain excessive levels of nitrate ion.

Legumes are presently considered to be the prominent nitrogen fixers of the earth, but contributions may nevertheless be considerable from nonlegumes, blue-green algae, and bacteria. Organisms capable of fixing nitrogen nonsymbiotically were reviewed by Stewart (1966), who included at least 18 bacterial genera, several yeasts, and blue-green algae. The relatively little attention given to free-living nitrogen-fixing organisms during the past 50 years or more is ascribed by Stewart (1966) to the prevailing assumption that the only organisms involved were *Clostridium* and *Azotobacter*, both unlikely to be important in relation to soil fertility. As reviewed by Stewart (1966), however, certain "unexplained phenomena" suggest that free-living soil organisms fix considerable amounts of nitrogen. Efforts to estimate the rate of fixation have been limited because the rate of fixation is low and (or) methods are too insensitive to detect small changes in nitrogen content. The methods used include total nitrogen determinations (Kjeldahl nitrogen) (Jaiyebo and Moore, 1963; Moore, 1963; Moore and Abaelu, 1959; Olsen, 1932; Olson, 1958; Parker, 1957; Stevenson, 1958, 1959), lysimeter determinations (Chapman, Liebig, *et al.*, 1949; Gel'tser, 1961; Smith, 1944), N_2^{15} studies (Delwiche and Wijler, 1956; Stewart, 1965), and acetylene–ethylene studies (Hardy, Holsten, *et al.*, 1968; Stewart, Fitzgerald, *et al.*, 1967). Since the Kjeldahl determination is too imprecise to detect small changes, large numbers of samples must be assayed and given statistical analysis. Lysimeter studies do not permit evaluation of rates of nitrogen fixation, for they cannot determine losses through denitrification.

Nitrogen fixation rates can be determined with greater sensitivity by incorporating the stable isotope N_2^{15} and subsequently making a mass spectrometric analysis than by determining total nitrogen. This method theoretically allows determination of the net rate of fixation by free-living organisms in the complicated soils system. Results obtained with this method under conditions simulating those in nature (Delwiche and Wijler, 1956) indicated fixation rates that were low in unamended soils and about three times as high in soil amended with the equivalent of 4 tons of straw per acre. The study of Delwiche and Wijler (1956) provided a direct estimate of free-living nitrogen fixation, although the values obtained did not extend over a full year and only a limited set of conditions were included in their work.

A method, based on the reduction of acetylene to ethylene, that can be 10^3 times as sensitive as the N_2^{15} method and 10^6 times as sensitive as the Kjeldahl method (Hardy, Holsten, *et al.*, 1968) resulted from discoveries that acetylene can inhibit nitrogen fixation (Dilworth, 1966; Schollhorn and Burris, 1967), that the inhibition is competitive (Schollhorn and Burris, 1967), and that the ethylene formed is not further reduced and does not interfere with further acetylene reduction (Dilworth, 1966).

The reduction of acetylene to ethylene involves the transfer of two electrons, whereas the reduction of nitrogen to ammonia involves six electrons. No consistent ratios between moles of N_2 fixed to moles of acetylene reduced have yet been obtained for complex soil systems, although they have been reported for enzyme preparations from bacterial cells (Hardy, Holsten, *et al.*, 1968; Schollhorn and Burris, 1967; Stewart, Fitzgerald, *et al.*, 1967) and from cultures of bacteria (Hardy, Holsten, *et al.*, 1968). Even though the acetylene–ethylene method has several advantages over the N_2^{15} method, it remains an indirect method, so calibration by direct methods is necessary.

The work reported here is an effort to determine nitrogen fixation by free-living organisms in different soils under different management regimes over a period of one year. The N_2^{15} method is used under conditions simulating those prevailing in the field. The acetylene–ethylene method is also used to establish a calibration between the two methods and to determine any variability in the calibration.

Because of the large number of variables which can contribute to error in the estimation of fixation, the significance of any single observation is questionable. The precision of determination of the isotope ratio is about 0.002 atom $\%\ N^{15}$ at low levels of enrichment and relatively constant within the procedures used in this study. This makes possible the detection of a dilution of about 1 part in 5×10^4. For this reason, sensitivity was predominantly a function of total nitrogen, which varied considerably among samples and between sites.

There was, moreover, a significant variability in total nitrogen content of soil samples at any given site and a considerable variability in fixation. It was for this reason that a large number of samples was taken and, although the extent of fixation undoubtedly varies greatly in time and location, the figures obtained probably represent a reasonable mean for each site.

Materials and Methods

Four sites were sampled monthly for one year. Site 1 was on Yolo clay loam on which the dominant vegetation, the perennial morning glory (*Convolvulus arvensis* L.), was controlled by herbicides and hoeing. Site 2 was on Yolo clay loam under perennial lawn grass irrigated during the dry season. The turf consisted mainly of *Poa pratensis* L., *Festuca rubra* L., and *Cynodon dactylon* L., the last of which become dormant during winter. Site 3 was on unirrigated Pleasanton gravelly loam with native vegetation. The dominant vegetation, left undisturbed, was *Avena barbata* Brot., *Stipa pulchra* Hitchc., and *S. cernua* Stebbins and Love. Site 4 was on Yolo loam on which wheat had been grown. The residues were plowed under in July 1968, and the field was irrigated after the August sampling, left fallow until planted with safflower (in April 1969), and irrigated during the dry season. The soil types employed were described series with the following characteristics.

Yolo series consists of neutral to mildly alkaline soils formed from recently deposited alluvium from sedimentary rock sources. In profile, the soils have dark brown, medium to moderately fine-textured surface soils 30- to 50-cm. thick, overlying brown similarly textured materials more than 1.5-m. thick, which offers no significant impediment to root or water penetration.

Yolo clay loam has a clay loam surface soil overlying clay loam or silty clay loam subsurface material extending more than 1.5-m. deep.

Yolo loam has a loam surface soil overlying stratified layers of very fine sandy loam, fine sandy loam, and loam, extending more than 1.5-m. deep.

Pleasanton series consists of neutral to moderately acid gravelly soils formed on nearly level to gently sloping alluvial fans and terraces. The parent materials were derived from mixed rock sources. In profile, the soils have dark grayish-brown, gravelly, medium-textured surface layers, 27- to 60-cm. thick, overlying brown to dark brown, very gravelly, moderately fine-textured subsoils 30- to 75-cm. thick. These, in turn, rest on brown to yellowish-brown, gravelly, medium-textured materials extending more than 1.8-m. deep.

Pleasanton gravelly loam has a dark grayish-brown, gravelly, loam surface that is massive and hard when dry. At about 40 cm., it rests on a subsoil of very gravelly, sandy clay loam that has a weak, blocky structure and offers a slight to moderate impediment to root and water penetration.

Two locations about 15 cm. apart were selected at each of the different sampling sites, and soil cores 22 mm. in diameter were sampled at each location for depths of 0 to 5, 10 to 15, and 30 to 35 cm. and placed in plastic bags. In the laboratory, each core was cut into disks, the disks were quartered, and quantities of 4 to 10 g. each were placed in each of four modified Thunberg tubes. Since the enriched nitrogen sometimes contained contaminant oxides of nitrogen, giving rise to highly inaccurate fixation figures, two of the four tubes were used as controls and sterilized in an autoclave for 1 hr. Later, as methods for elimination of contaminant oxides of nitrogen proved effective, the number of control samples was reduced.

Tests for sterility were made by including in the sterilization process four cotton-stoppered test tubes, each containing 4 g. of soil. These were incubated for 24 hr. at 26°C., and 10 ml. of sterile nutrient broth was then added to each tube. The tubes were incubated for seven days and observed for microbial growth. The sterilization process proved adequate. The two remaining tubes were paired with the sterilized samples and evacuated in batches of 16. Nitrogen gas of at least 95% enrichment with respect to N_2^{15} (BioRad Laboratories, Richmond, Calif.) was admitted into the tubes through an ascarite filter to a pressure of 5-cm. Hg, and a gas mixture (Matheson Co.) consisting of O_2 (22%), CO_2 (0.04%), and Ar (the balance) was used to attain a pressure of 3 cm. below ambient. The stopcocks were closed, and the tubes were incubated for 72 hr. at 26°C. Two tubes were selected randomly from each batch of 16, and the initial composition of the gases was analyzed mass spectrometrically for mass/charge (*m./e.*) 44 (CO_2), 32 (O_2) 30 (N_2^{15}), 29 ($N^{14}N^{15}$), and 29 (N_2^{14}). At the end of the incubation period the gas composition of all the tubes was analyzed similarly, and the contents of the tubes were transferred to 50-ml. beakers, dried overnight at 105°C., and ground with a porcelain mortar and pestle. One-gram quantities were digested and steam-distilled according to the microKjeldahl procedure (Bremner, 1965). The titration end point was determined potentiometrically with a pH meter to avoid the use of an indicator. The samples were further acidified with $0.1N$ HCl and evaported to near dryness.

The ammonia was converted to N_2 with alkaline sodium hypobromite and passed through two consecutive liquid nitrogen traps to remove contaminating gases which could have interfered with the mass spectrometric analysis. Mass spectrometric analyses were carried out with a Consolidated-Nier isotope-ratio mass spectrometer (Model 21-201). A standard $0.01M$ NH_4Cl solution (Baker Analyzed Reagent, lot no. 30369) was run between every five samples after the liquid nitrogen traps were cleaned. The N^{15} content of the samples was calculated by the method of Wijler (1954), and the results obtained were adjusted by a correction factor which was the product of two independent factors: The first of these was calculated from the ratio between *m./e.* 30 and *m./e.* 28 of the initial gases, assuming the ion voltage to be directly proportional to the partial pressure of the ion species. The second correction factor was calculated with the Michaelis-Menten equation (Briggs and Haldane, 1925), correcting for the partial pressure of N_2 in the initial incubation gas, and

Table I. Nitrogen Fixation Rates Obtained by Direct Isotopic Method in Profile of Four Sites

	Fallow soil		Irrigated lawn		Native vegetation		Wheat field	
Month	g. N per g. soil per day × 10^9	kg. N per hectare per month	g. N per g. soil per day × 10^9	kg. N per hectare per month	g. N per g. soil per day × 10^9	kg. N per hectare per month	g. N per g. soil per day × 10^9	kg. N per hectare per month
Aug. '68	1.5	0.15	4.9	0.60	2.5	0.13	2.8	0.39
Sept.	2.8	0.41	5.7	0.51	2.7	0.13	3.6	0.49
Oct.	1.0	0.12	2.5	0.21	4.1	0.18	0.2	0.02
Nov.	1.6	0.15	1.7	0.16	3.0	0.14	0.7	0.07
Dec.	1.4	0.15	0.0	0.00	7.6	0.37	5.6	0.73
Jan. '69	4.8	0.59	9.6	1.08	6.8	0.33	5.4	0.74
Feb.	4.1	0.43	5.1	0.56	8.0	0.35	5.3	0.71
Mar.	6.5	0.85	5.1	0.45	...	0.26	...	0.38
Apr.	1.0	0.14	2.1	0.23	1.3	0.06	1.3	0.1
May	0.9	0.11	2.5	0.25	2.1	0.09	1.6	0.22
June	1.8	0.24	3.0	0.33	1.1	0.05	0.5	0.05
July	0.8	0.11	2.2	0.26	0.5	0.02	0.9	0.10
Total	**28.2**	**3.46 ± 0.20**	**44.4**	**4.76 ± 0.25**	**39.7**	**2.11 ± 0.10**	**27.9**	**4.07 ± 0.16**

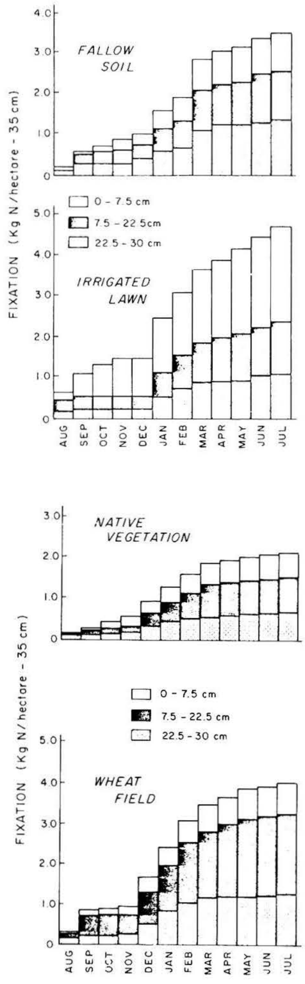

Figure 1. Cumulative nitrogen fixation on four sites

taking km. = 0.02 atm. (Wilson, Burris, *et al.*, 1942) for N_2 during nitrogen fixation. Although this value for km. appears to be low compared with experience with cell-free preparations, test samples, supplied partial pressures of nitrogen three times that normally employed confirmed the validity of the assumption.

Some lots of N_2^{15} contained significant contamination of fixed nitrogen, probably as oxides of nitrogen. To eliminate these contaminates, acidified 0.3*M* $FeSO_4$ (pH 2) was admitted into the gas container prior to use, and a liquid nitrogen trap and ascarite filter were used in series, in that order, between the gas container and the manifold, when introducing gas into test chambers.

The acetylene-reduction capacity of soil was determined by methods similar to those used by Hardy, Holsten, *et al.* (1968). Soil cores of 1-cm. diameter were obtained with a no. 9 cork bore and placed in a test tube of 1.2-cm. i.d. and 10-cm. long to approximately 2 cm. from the top. A paper disk, 1 cm. in diameter, was placed on top of the soil core to prevent direct contact between the soil and the serum stopper (Scientific Glass Apparatus Co., R7950). The volume of the tube, with the stopper inserted, was 13 ml. The tubes, with soil cores, were attached to a manifold previously described by means of modified plastic syringe cylinders and hypodermic needles, and evacuated. The control samples were filled with the $Ar–O_2–CO_2$ gas mixture previously described. Treated samples received 0.1 atm. of high-purity acetylene (Matheson Co.) passed through a concentrated H_2SO_4–acetone scrubber and adjusted to atmospheric pressure with the $Ar–O_2–CO_2$ gas mixture. Since the acetylene always contained some ethylene, each group of 16 vials included four empty vials as internal controls. The tubes were shaken to move the soil core up against the stopper, inverted, incubated for 1 hr. at 26° C., and then transferred to an ice bath to stop the reaction. After 15 min., the tubes were withdrawn one at a time and shaken to move the soil core to the bottom of the test tube; 1.5-ml. of distilled water, previously boiled to remove gases, was injected into the containers; and 0.5-ml. gas was withdrawn for analysis with a Varian Aerograph 600 C gas chromatograph. The carrier gas was high-purity nitrogen (Matheson Co.) at a flow rate of 20 ml. per minute, and H_2 was supplied by a hydrogen generator at a flow rate of 20 ml. per minute (Varian Aerograph, Model 650). The oxidant in the hydrogen flame was high-purity dry O_2

(Matheson Co.) at a flow rate of 60 ml. per minute. Separation was achieved on a 6-ft. $^1/_8$-in. Porapak R 50–80 mesh column (Varian Aerograph) at an oven temperature of 72.5° C., and ethylene was detected by hydrogen flame ionization. The standard was a mixture of air and 10 p.p.m. high-purity ethylene (Matheson Co.). The volume of gas was calculated from the total volume of 13 ml., with the assumption that soil particle density was 2.65 g. per cc., and soil–water density was 1 g. per cc. Acetylene reduction was calculated according to the perfect gas law and corrected with the Michaelis-Menten equation (Briggs and Haldane, 1925) assuming $km_{(acetylene)} =$ 0.005 atm. (Hardy, Holsten, *et al.*, 1968).

The soil samples were further analyzed for ammonia, nitrite, and nitrate nitrogen, as well as moisture content. Determinations were carried out as described by Jackson (1958) but scaled down to accommodate 2.5-g. samples. Further modifications included the determination of ammonia nitrogen by means of Nesslerization and photometry after steam distillation of the soil extracts. For nitrate determinations, the phenoldisulfonic method was used (Jackson, 1958), and nitrite was determined by the Shinn (1941) method.

The water retentiveness of soil was determined by the ceramic plate method (Richards, 1965). Moisture equivalent (m.e.) was determined at $^1/_3$ bar, and "permanent wilting point" (p.w.p.) at 15 bar.

Soil temperature data were obtained from the Department of Agricultural Engineering, University of California, Davis. Mean monthly temperatures were calculated from daily maximum and minimum soil temperatures recorded at 10 cm.

Results

Nitrogen Fixation Rates. Fixation rates are reported in Table I, and cumulative nitrogen fixation is shown in Figure 1. The gravelly loam of the native foothill site contained 50% gravel in the 0–7.5-cm. layer, 66% in the 7.5–22.5-cm. layer, and 68% in the 22.5–35-cm. layer. Fixation rates were corrected accordingly. The fixation rates for Sites 3 and 4 during March having been lost, were estimated by interpolation. Annual fixation rates never exceeded 4.8 ± 1.9 kg. N per hectare 35-cm. deep, which was recorded for the irrigated turf of Site 2. The annual fixation rate of the "fallow" soil of Site 1 was 3.5 ± 1.7 kg. N per hectare 35-cm. deep. The lowest fixation rate was in the gravelly soil with native vegetation in Site 3, namely, 2.1 ± 0.8 kg. N per hectare 35-cm. deep per year, in contrast to 4.0 ± 1.3 kg. N in the wheat field soil of Site 4. Figure 1 shows that fixation rates at all sites were highest in winter. In the "fallow" soil of Site 1, fixation rate increased significantly in January, remained relatively high through March, and decreased thereafter. The trend was the same in the irrigated turf of Site 2, but in the gravelly soil of Site 3 and the wheat field soil of Site 4, significant increases occurred in December, lasted through February, and became relatively low April through July. From August through March, Sites 1 and 2 were sampled in the first week of the month, and Sites 3 and 4 in the second week.

Effect of Temperature. Mean monthly temperatures were compiled from soil temperatures recorded at a depth of 10 cm. on the Davis campus over a period of one year (Table II). Mean soil temperatures in August through September fell within the range optimal for nitrogen fixation (Jensen, 1965). A decrease was observed in October, and a low mean temperature of 6.5°C. was recorded during December through January. This was still within the limits that allow fixation to occur, according to Jensen (1965), and an increase was observed from February through July but it never exceeded the optimal range for fixation.

Table II. Mean Monthly Soil Temperatures Recorded at 10 cm.

Month	Maximum	Minimum	Average
Aug. '68	31.4	22.1	26.7
Sept.	33.1	23.6	28.4
Oct.	22.4	15.2	18.8
Nov.	14.0	9.9	12.0
Dec.	8.1	4.9	6.5
Jan. '69	7.8	5.2	6.5
Feb.	10.2	6.3	8.2
Mar.	16.3	8.9	12.6
Apr.	21.1	13.3	17.2
May	29.5	20.3	24.9
June	31.9	22.9	27.4
July	34.4	25.6	30.0

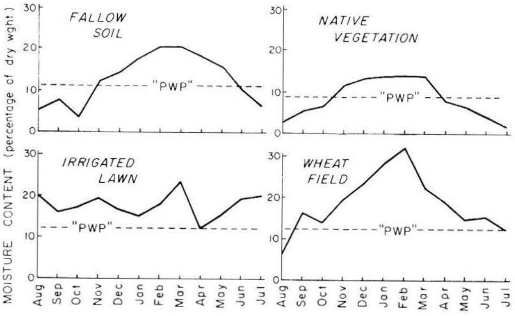

Figure 2. Moisture status of test sites

Effect of Soil Moisture. Table III gives soil moisture contents of the different soil samples, and Figure 2 presents values for samples from the 10 to 15-cm layers. Table IV shows the soil moisture relationships of the different sites and depths. The unirrigated fallow soil was completely dependent upon rainfall, whereas the lawn turf was irrigated regularly during the dry season. The gravelly soil with native vegetation was likewise dependent upon rainfall, and the wheat field was irrigated after the August sampling, before which the residue of the preceding wheat crop was plowed under, and also during the dry season after having been planted with safflower in the spring of 1969.

On the unirrigated sites, moisture content of the soil fell below the p.w.p., particularly in the upper 10 cm., during the dry season, and at these times little or no fixation was observed. Figure 2 shows that the moisture content of samples taken from the unirrigated soil of Site 1 fell below the p.w.p. at 10 cm. in August through October, and again in June through July.

Energy Source. Various figures have been reported for the ratio of nitrogen fixed to carbohydrate utilized by nitrogen-fixing organisms. These values range from 1 to 27-mg. N fixed per gram of carbohydrate consumed, depending upon conditions (Stewart, 1966). If it is assumed that 5-mg. N were fixed for each gram carbohydrate utilized, a carbohydrate input of 70 g. per square meter would have been needed on the fallow site. Although the dominant vegetation (morning glory) was largely controlled by herbicides, the input of plant material from this source was estimated to be more than

Table III. Total Nitrogen and Soil Moisture Content of Soils Investigated

	Fallow soil		Irrigated lawn		Native vegetation		Wheat field	
Month	mg. N per g. soil	Percent moisture	mg. N per g. soil	Percent moisture	mg. N per g. soil	Percent moisture	mg. N per g. soil	Percent moisture
Aug. '68	3.7	5.9	3.6	17.7	4.7	2.4	2.6	7.0
Sept.	3.7	7.0	4.8	20.7	4.5	5.5	2.7	14.6
Oct.	3.9	4.9	4.1	18.7	5.5	9.3	3.0	16.4
Nov.	3.4	14.1	4.3	20.5	5.3	13.7	2.8	19.6
Dec.	3.5	12.2	4.1	19.6	4.4	14.7	2.7	22.9
Jan. '69	3.6	16.5	5.5	19.3	4.3	17.8	2.5	29.1
Feb.	3.5	19.5	4.5	22.4	3.8	18.1	2.8	3.02
Mar.	3.4	19.5	4.7	24.9	4.5	17.6	2.8	21.4
Apr.	3.3	17.6	4.3	16.3	4.4	13.4	2.7	19.8
May	3.5	15.8	4.2	21.1	3.9	5.3	2.6	14.0
June	3.3	8.4	4.4	27.0	3.6	4.3	2.7	13.4
July	3.1	6.3	4.8	23.6	3.6	2.4	2.7	10.0

Table IV. Acidity and Moisture Relationships of Soils Investigated

		Moisture retention at	
Site and depth, cm.	pH	$^1/_3$ bar	15 bar
Fallow soil			
0 to 7.5	6.3	25.7	12.1
7.5 to 22.5	6.3	25.2	11.1
22.5 to 35	6.3	29.2	11.2
Irrigated lawn			
0 to 7.5	7.0	32.8	16.6
7.5 to 22.5	7.3	24.6	11.9
22.5 to 35	7.2	26.7	13.0
Native vegetation			
0 to 7.5	5.7	24.2	12.7
7.5 to 22.5	5.8	18.2	8.6
22.5 to 35	6.1	18.8	10.1
Wheat field			
0 to 7.5	6.3	24.5	18.0
7.5 to 22.5	6.6	27.0	12.4
22.5 to 35	6.8	27.2	13.0

Table V. Correlation between the Acetylene–Ethylene and Direct Methods of Assaying for Nitrogen Fixation

Site and depth, cm.	Acetylene reduction moles/g. soil/day $\times 10^{12}$	Nitrogen fixation moles/g. soil/day $\times 10^{12}$	$\frac{\text{Acetylene reduced}}{\text{nitrogen fixed}}$
Fallow soil			
0 to 7.5	109	13.0	8.4
7.5 to 22.5	278	32.5	8.6
22.5 to 35	152	39.9	3.8
Irrigated lawn			
0 to 7.5	719	114	6.3
7.5 to 22.5	203	66.5	3.1
22.5 to 35	211	56.4	3.8
Native vegetation			
0 to 7.5	9	0.0	...
7.5 to 22.5	102	0.0	...
22.5 to 35	219	54.0	4.1
Wheat field			...
0 to 7.5	256	46.4	5.5
7.5 to 22.5	200	0.0	...
22.5 to 35	145	46.6	3.1

adequate for the fixation observed. On all other sites, energy input was estimated to meet or exceed these requirements.

Nitrogen Status of the Soils. Table III gives the total nitrogen contents of the soils as determined by the Kjeldahl method. Nitrite was never observed, and nitrate and exchangeable ammonia did not represent a significant fraction of the total nitrogen.

Effect of Acidity. The acidity of the soils from various sites and depths (Table IV) fell within the limits and ranged around the optimum (near neutrality) for fixation (Jensen, 1965). Values ranged from pH 5.7 to 6.1 (in the gravelly soil with native vegetation of Site 3) to pH 7.0 to 7.3 (in the irrigated turf of Site 2).

Acetylene Reduction as a Measure of Nitrogen Fixation. Table V gives comparative values between acetylene reduction and direct determination of nitrogen fixation during July. No ethylene was detected in any of the control samples. In five of the nine instances in which comparisons were possible, the molar ratio of acetylene reduced to nitrogen fixed fell between 3.0 and 4.5, which approaches the theoretical value of three, and is in close agreement with values obtained with *Azotobacter vinelandii* (Hardy, Holsten, *et al.*, 1968). In the "fallow" soil of Site 1 the ratios obtained for the 10 to 15- and 30 to 35-cm. layers both exceeded 8.0, whereas the ratio in the top layer of the irrigated turf of Site 2 was greater than 6.0. Acetylene reduction occurred in three instances where no fixation was detected by isotopic methods, and a ratio of 5:5 was observed in the 0 to 5-cm. layer of Site 4. Acetylene reduction is more sensitive than direct observation of nitrogen fixation. However, there are a number of possibilities for interference. Production of ethylene by soil organisms (Freebairn and Buddenhagen, 1964; Ilag and Curtis, 1968; Young, Pratt, *et al.*, 1951) or by plants cannot be excluded, nor can the possibility that ethylene may be metabolized. Adsorption of ethylene to soil surfaces, resulting in lower reduction rates is possible, and acetylene reduction may not be linear with time. We obtained good linearity for periods up to 5 hr., but 24-hr. incubation periods sometimes gave anomalous results. Hardy, Holsten, *et al.* (1968) reported a linear rate of acetylene reduction up to 18 to 20 hr. for *A. vinelandii*, and 6 hr. for *Clostridium pasteurianum* in pure cultures. An initial lag often observed with *A. vinelandii* was presumably the effect of transfer and dilution. Inoculum from a culture in the late log phase of growth had a longer lag than that from the early log phase.

Discussion

No effort was made to carry out investigations *in situ*, primarily because of the cost of isotopic nitrogen. Such procedures would be possible with the acetylene–ethylene assay, and for this reason, comparisons were made in the laboratory between the acetylene–ethylene and direct isotopic methods. Contributions from free-living photosynthetic nitrogen-fixing microorganisms would not have been detected, although there are indications that they may be important in soil under certain conditions (Jaiyebo and Moore, 1963; Stewart, 1965; Tchan and Beadle, 1955). Photochemical reduction of nitrogen and accretions through rainfall were likewise not included in this study.

Fixation rates were significant in all sites, but the annual rate of fixation never exceeded 4.8 kg. N per hectare 35-cm. deep per year (in the irrigated turf of Site 2). Under favorable conditions, however, this rate was exceeded for shorter periods. The lowest rate, 2.0 kg. N per hectare 35-cm. deep per year, was observed in the gravelly soil of Site 3, which was under undisturbed native vegetation. Figures obtained are in reasonable agreement with estimates of Lipman and Conybeare (1936) of 6.7 kg. N per hectare per year, and findings of Delwiche and Wijler (1956) of 6.2 kg. N per hectare 15-cm. deep per year. These rates also fell within the same region as findings by Hardy, Holsten, *et al.* (1968) of 0.42 kg. N per hectare 23-cm. deep per month under anaerobic conditions in soil in Chester County, Penna. The fixation rates observed were significantly lower than gains of 44.9 kg. N per hectare per year obtained by Chapman, Liebig, *et al.* (1949), 50.5 to 74 kg. N obtained by Gel'tser (1961), and 274 kg. N found by Smith (1944) in lysimeter studies under nonlegumes. Fixation rates observed in these experiments were also significantly lower than some values obtained with Kjeldahl determinations. Jaiyebo and Moore (1963) found gains of 56 kg. N per hectare per year under a mulch, and 89.8 kg. N under star grass in Nigeria. In this latter work, contributions by green algae cannot be excluded. In greenhouse studies, Moore (1963) found gains of 112 to 145.8 kg. N per hectare per four months in soil under grass. Moore and Abaelu (1959) reported an increase equivalent to 157 kg. N per hectare per year in bare soil kept moist in pots in a greenhouse. On observing succession rates on Southern Lake Michigan sand dunes, Olson (1958) estimated annual nitrogen accretions to be 4.03 kg. N per hectare 1-dm. deep. Stevenson (1959), studying the increase in nitrogen content of the ecosystem of *Pinus radiata* forest developed over a period of 25 years on depleted hill country in New Zealand, found an average annual increment of 35.9 kg. N per hectare per year. From data obtained in our study, it seems unlikely that free-living nonphotosynthetic microorganisms alone could have been responsible for the relatively high rates of nitrogen fixation mentioned above. From an agronomic point of view, nitrogen fixation by free-living organisms may not be economically important, since nitrogen additions in the same site run to about 120 kg. N per hectare, compared with 4.0 kg. fixed. Under range conditions nitrogen fertilizer is usually not added, and the soils are usually nitrogen deficient. Therefore, any addition is significant. From data given by Chapman, Liebig, *et al.* (1949) for Riverside, Calif., and a seasonal total precipitation of 61.7 cm. for the Davis area from July 1968 to June 1969, the amount of nitrogen contained in rainwater was estimated to be 0.97 kg. N per hectare per year. Free-living bacteria, therefore, contribute a significant fraction of the total nitrogen input in unfertilized range soils under the conditions studied.

Since the acidity and nitrogen status of all soil samples were not limiting to nitrogen fixation, the limiting factors might have been soil moisture, temperature, and available energy sources, and fluctuations in nitrogen fixation rates during winter in all sites was clearly a response to rainfall, although temperatures were close to the lower limits for fixation (Jensen 1965). Rainfall may be responsible for a downwash of soluble organic substrate into the soil, making it available to nitrogen-fixing organisms. The fixation rates for the "fallow" soil of Site 1 and the gravelly soil of Site 3 showed significant increases during the month following increase in soil moisture content. In the "fallow" soil of Site 1, a sixfold decrease in nitrogen fixation rate occurred during April, although soil moisture content remained favorable into May. This may reflect the depletion of available soluble organic matter as soil temperature became more favorable. In the gravelly soil of Site 3, a similar decrease took place. In the irrigated turf of Site 2, soil moisture was never limiting. The dominant vegetation consisted of three grass species, of which Bermuda grass became dormant during winter. The foliage was killed by frost, and it may be that available soluble organic substrate serving as energy source for nitrogen fixation was washed into the soil. The 2.5-fold decrease in fixation rate in April from that in March may again signify a depletion of such energy sources.

The wheat field soil of Site 4 had an even more complex situation. The fixation rate for August was relatively high although soil moisture was below the p.w.p. throughout the profile examined. The residue of the preceding wheat crop was plowed under prior to the August sampling, making available a substantial amount of organic matter low in nitrogen. During September the soil moisture content was more favorable and an increase in nitrogen fixation was observed.

The effect of available energy sources was demonstrated by relative fixation rates observed in the different sites, and the consistently higher rates in the upper layer than in deeper layers of the irrigated turf of Site 2.

At the 10-cm. level, soil temperatures remained within the limits for nitrogen fixation even in winter. The samples could not be incubated at ambient temperatures, for reasons already stated. Comparisons were made between direct observation of nitrogen fixation and the acetylene–ethylene method, and since the latter method lends itself excellently to *in situ* assays, more precise measurements may be possible if certain precautions are taken, as will be discussed later.

In comparisons between the acetylene–ethylene method and direct observation of nitrogen fixation, several ratios were obtained that corresponded with those found by Hardy, Holsten, *et al.* (1968), and Klucas (1967), between 3.0 and 4.5. Variations were observed, however, with ratios larger than 8.0 in some cases and in others acetylene reduction occurred where no nitrogen fixation was observed. No ethylene was ever detected in the control samples in the absence of added acetylene.

These variations cannot be ascribed to lack of sensitivity on the part of the direct isotopic method, since the relatively high ratios were obtained where nitrogen fixation should have been easily detectable with the isotopic method.

The usefulness of the acetylene–ethylene method lies in its flexibility and simplicity. It is inexpensive, and its sensitivity is not affected by the total nitrogen content of the system, whereas the sensitivity of the direct method is inversely proportional to the total nitrogen content of the system. The more extensive time of incubation required to get sensitivity from the direct method and the cost and complexity of the procedure limit its application. However, since correlation between the two methods is not rigid, the direct method is still necessary as a reference.

Summary and Conclusions

The contribution of free-living nitrogen-fixing microorganisms to the nitrogen balance in soil was studied. Assays were carried out in the laboratory, simulating field conditions, by both the direct isotopic and acetylene–ethylene methods. Four different sites were investigated. Site 1 was Yolo clay loam on which the vegetation was controlled with herbicide and by hoeing. Site 2 was irrigated turf on Yolo clay loam. Site 3 was a gravelly loam in the Pleasanton series with undisturbed native vegetation. Site 4 was wheat field in Yolo loam. The residues of the preceding wheat crop on this site were plowed under, sampled in August, irrigated, and left fallow until planted with safflower the next spring, and irrigated during the dry season.

Fixation never exceeded 4.8 ± 1.9 kg. N per hectare per year (in the irrigated turf of Site 2). The lowest fixation rate, 2.1 ± 0.8 kg. N per hectare per year, was observed in the gravelly loam of Site 3. Fixation was 3.5 ± 1.7 kg. N per hectare per year in the unirrigated Yolo loam of Site 1, and 4.0 ± 1.3 kg. N in the wheat field of Site 4.

Fixation rates in all sites were highest in winter.

Depth had no consistent effect on fixation rates except in the upper layer of the irrigated turf of Site 2, where fixation, whenever measurable, was consistently higher in the upper than in the deeper layers.

No nitrite was detected, and ammonia and nitrate nitrogen never constituted a significant fraction of the total nitrogen content of the soil.

The acidity of all soils fell within the limits for fixation, ranging around the optimum pH value (near neutrality).

Soil temperatures at 10 cm. never exceeded the limits for nitrogen fixation. The effect of temperature, especially during winter, was somewhat obscured by incubation at 26° C.

Limiting factors seemed to have been soil moisture and soluble available energy sources.

Free-living microorganisms do not seem likely to be the sole contributors to the relatively high fixation rates observed by some other workers.

Free-living nitrogen fixation does not seem to be economically important in intensive agronomic agriculture but, augmented by nitrogenous compounds in rainfall, may contribute significantly to the nitrogen balance in unfertilized range soils.

Reasonable correlation was obtained between the acetylene–ethylene and direct methods of assaying for nitrogen fixation. In the majority of cases, ratios ranged between 3.0 and 4.5. Variations were observed, and in all such instances the values were larger than 4.5. In only one of these instances could the apparent discrepancy be ascribed to insensitivity of the direct method.

The acetylene–ethylene method has much to recommend it, but the direct method must still be used as reference since correlation between the two methods is not rigid.

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Turbulence Promoters for Hyperfiltration with Dynamic Membranes

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■ Experimental studies of turbulence promoters for hyperfiltration show that detached promoters can be fabricated which possess characteristics of "ideal" promoters—*i.e.*, they do not block the membrane surface nor provide stagnant regions where solids can accumulate or where the concentration of rejected salts can build up. Also, with dynamically formed membranes, turbulence promoters cause marked increases in transmission rate and reduce transmission rate losses with time. Economic evaluation of conditions for which application of turbulence promoters to the hyperfiltration process might be attractive was carried out by using an optimization computer code. Results show that use of turbulence promoters markedly affects optimum plant geometry; by virtue of higher fluxes when using turbulence promoters (known to be experimentally possible with dynamic membranes), appreciable reduction in water cost may be possible when the dynamic membrane is not strained to meet product water quality requirements.

One of the most promising applications of hyperfiltration with dynamic membranes is pollution control where removal of organic contaminants and reduction of inorganic salt concentration are the principal objectives (Kraus, Shor, *et al.*, 1967; Perona, Butt, *et al.*, 1967; Savage, Bolton, *et al.*, 1969). Economic optimization studies (Griffith, Keller, *et al.*, 1968) show that low water costs may be possible with ion exchange-type dynamic membranes provided the intrinsic rejection of the membrane is well above the minimum theoretically required and provided sufficiently large membrane permeabilities are available.

Significant increases in dynamic membrane permeability have been observed in exploratory studies (Thomas and Watson, 1968) of the effect of detached spiral turbulence promoters on membrane performance. In these studies, the turbulence promoters were located in the downstream half of a porous tube, otherwise the operating conditions were the same. In one test at 400 p.s.i. pressure, the flux in the turbulence promoted half of the tube was 190 g.p.d./ft.^{2} compared with 150 g.p.d./ft.^{2} in the unpromoted half of the tube.

The object of the present study was to determine the effect of various turbulence promoter designs on permeability and rejection of dynamic membranes and to assess the effect of turbulence promoters on desalinated water costs. To minimize effects of membrane chemistry (Kraus, Shor, *et al.*, 1967; Shor, Kraus, *et al.*, 1968b), hydrous zirconium oxide was used to form the membrane and $MgCl_2$ solutions were used as feed.

Turbulence Promoters. The performance of a wide variety of turbulence promoter configurations has been evaluated experimentally (Bergles and Morton, 1965) largely with the goal of enhancing the rate of heat transfer. As yet, there is neither a preferred configuration nor a general theory which predicts the amount of enhancement (Bergles and Morton, 1965; Nunner, 1956; Koch, 1958; Dipprey and Sabersky, 1963; Owen and Thomson, 1963). Consequently, it is common practice to develop specific configurations tailored for the particular requirements of a given process. For heat transfer, the promoters are usually made as an integral part of the surface (Kays and London, 1964; Sheriff and Gumley, 1966). This gives, in addition to the turbulence generated by the promoter, a fin effect due to the increase in surface area for heat transfer. In membrane processes, spacers between the membrane surfaces often act as turbulence promoters. However, in some cases the spacers may block from 20 to 40% of the membrane surface (Katz, 1960). Other spacer designs which block a smaller fraction of the surface and may also act as turbulence promoters are plastic screens and ridged perforated plastic sheets (Saline Water Conversion Report, 1966).

An ideal requirement for turbulence promoters for hyperfiltration is that the turbulence promoter neither blocks the membrane surface nor provides stagnant regions where solids can accumulate or where the concentration of rejected salts can build up. Prevention of stagnant regions is essential in the hyperfiltration process because the salt concentration may build up in these regions, resulting in "breakthrough" and marked deterioration of membrane separation performance (Johnson, Dresner, *et al.*, 1966).

A potentially attractive turbulence promoter design which meets many of the "ideal" requirements outlined above is the "detached" promoter in which the promoter is supported away from the surface. Fundamental studies of such promoters have been reported previously (Thomas and Kraus, 1964; Thomas, 1965; Watson and Thomas, 1967) as have exploratory studies aimed at reduction of concentration polarization at dynamically formed hyperfiltration membranes (Thomas and Watson, 1968).

Optimization studies (Mixon, 1968) of detached promoters for hyperfiltration with hydrous zirconium oxide dynamic membranes using $MgCl_2$ solution feeds have been completed with use of promoters fabricated from a wire in the form of a spiral, supported away from the surface by a continuous wire runner 0.5 to 1.5 the diameter of the wire spiral.

These studies showed that, with $^1/_4$-in. i.d. tubes, optimum performance occurred when the spiral and runner wires both had a diameter 0.1 the tube diameter. With these promoters the maximum increase in mass-transfer coefficient was 400% and the flux was doubled (based on smooth tube values measured under the same conditions). The maximum effectiveness of these turbulence promoters occurred for Reynolds numbers from 2×10^3 to 4×10^3.

Empty Channel Hydrodynamics. The effect of turbulent flow on concentration polarization in hyperfiltration systems is given by

$$\ln \frac{1 - R_{obs}}{R_{obs}} = K \frac{v}{u} N_{Re}{}^{1/4} N_{Sc}{}^{2/3} + \ln \frac{1 - \mathbf{R}}{\mathbf{R}} \qquad (1)$$

provided the intrinsic rejection, **R**, is a constant. Although real hyperfiltration membranes frequently do not possess constant intrinsic rejection [*e.g.*, with neutral membranes, such as cellulose acetate the intrinsic rejection may be a function of flux (Sheppard and Thomas, 1970) and with ion-exclusion membranes the intrinsic rejection may be a function of both flux and the concentration at the membrane solution interface (Shor, Kraus, *et al.*, 1968a,b)], for a test with constant feed composition Equation 1 may be used to represent the variation of observed rejection with velocity on a plot of ln $[(1 - R_{obs})/R_{obs}]$ *vs.* $v/u^{3/4}$ (Shor, Kraus, *et al.*, 1968a; Cooney and Rabe, 1968). From the experimental results of several studies with ion-exclusion type membranes (Shor, Kraus, *et al.*, 1968a; Mixon, 1968), it is apparent that the affect of nonconstancy of R is reflected primarily in the value of K in Equation 1 and not in the value of the exponent on u. Equation 1 may also be used to obtain the intrinsic rejection at infinite circulation velocity (Shor, Kraus, *et al.*, 1968b). However, accurate calculation of the concentration at the membrane solution interface at finite axial velocities requires correction for the nonconstancy of the intrinsic rejection. Equation 1 may be rearranged to a form similar to that used in correlating heat-transfer data

$$j = \frac{v N_{Sc}{}^{2/3}}{u \ln \left[\dfrac{1 - R_{obs}}{R_{obs}} \Big/ \dfrac{1 - \mathbf{R}}{\mathbf{R}} \right]} = \frac{1}{K N_{Re}{}^{1/4}} \qquad (2)$$

Equation 2 has the advantage that when results are plotted as log j *vs.* log N_{Re}, the value of the exponent on the Reynolds number can be readily determined as can the value of the coefficient K. When plotting heat-transfer data as j *vs.* N_{Re}, the laminar, transition, and turbulent flow data have a slope of $-^1/_4$, and a smooth curve connecting the laminar and turbulent curves may be drawn through the transition regime data. Usually the Reynolds number for the beginning of fully developed turbulent flow heat transfer is a factor of 4 or 5 greater than the Reynolds number for the end of the laminar flow regime.

Turbulence Promoter Performance. In turbulent flow, the principal effect of turbulence promoters on dynamic membrane performance is reflected in the transmission velocity, v, and the coefficient K of Equations 1 and 2. A secondary effect which may occur is a different value of the exponent of the Reynolds number. Determination of the value of K and of the exponent on the Reynolds number is readily accomplished by plotting results for turbulence promoters as j factor *vs.* Reynolds number, with use of Equation 2.

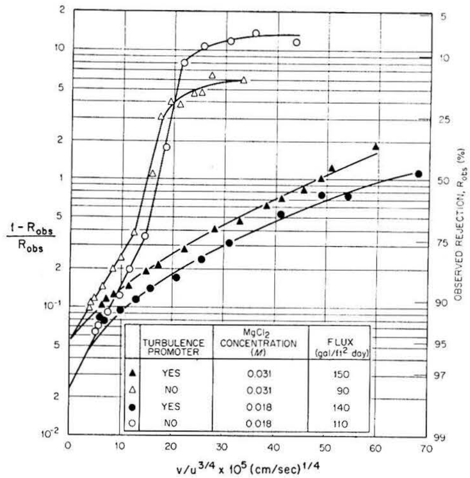

Figure 1. Effect of turbulence promoter with partial runner on observed rejection in hyperfiltration studies with dynamically formed membrane of hydrous Zr^{IV} oxide (600 p.s.i.g.)

Equipment and Procedure

Turbulence promoter tests were carried out in a stainless steel recirculation loop. The loop consisted of a 50-g.p.m. canned rotor pump, a heat exchanger to maintain the circulating stream at a steady temperature, air-operated control valves, and a line bypassing the test section. High flow rates were measured with a calibrated venturi and low flow rates were measured with a high-pressure rotometer. Feed was introduced with a Hydropulse pump rated at $3^1/_2$ g.p.m. This capacity was sufficient to permit a large portion of the circulating steam to be let down to atmospheric pressure, mixed with product water and returned to the loop, thus minimizing concentration changes during a run.

Porous carbon tubes were used as support for the dynamic membranes; they were 20-in. long, 0.39-in. o.d., 0.23-in. i.d., and were capable of withstanding a pressure of 1000 lb. per square inch when pressurized internally.

For most of the tests, the membrane was formed by circulating a solution of $0.0001M$ hydrous zirconium oxide, 0.015 to $0.04M$ $MgCl_2$, and sufficient HCl to give a pH of 3, through the carbon tube at a linear velocity of 5.8 ft. per second (a Reynolds number of about 13,000) under a pressure of 600 p.s.i.g. After a membrane formation period of 16 to 18 hr., the membrane was sufficiently stable to give reproducible results for circulation velocities from 0.5 to 18 ft. per second using the same feed composition as during the membrane forming portion of the run.

Turbulence Promoters. To determine the effect of runners on detached turbulence promoter performance, spiral promoters were fabricated from wires with diameters of 0.025 in., a diameter previously (Mixon, 1968) found to be near optimum for the tube diameter used in this study. The pitch of the spiral was 0.25 in. Three different designs were tested.

CONTINUOUS RUNNERS. Four continuous wire runners with diameters of 0.010 in. were spot welded to the outside of the wire spiral. The runners thus served to hold the spiral away from the membrane surface, to maintain the pitch of the spiral, and to stiffen it.

PARTIAL RUNNERS. Short pieces of runner with diameters of 0.010 in. and length of 0.7 in. were spot welded to each end and to the middle section of the spiral. To provide rigidity and to maintain spiral pitch, two wires with a diameter of 0.025 in. were spot welded to the inside of the spiral.

NO RUNNERS. This spiral had no runner on the outside and two runners spot welded to the inside for rigidity. The nominal outside diameter of the spiral was 0.001 in. less than the inside diameter of the carbon tube; some turns of the spiral were as much as 0.008 in. smaller in diameter than the inside diameter of the tube. Considering the slight eccentricity of the hand-bored carbon tube, it is probable that on the average the spiral was separated from the surface by 0.002 to 0.004 in. with occasional point contact.

Since dynamic membranes presumably can be formed on irregular surfaces, an attempt was made to remove material from the inside of a carbon tube, leaving a ridge with a pitch of 0.25 in. This was not accomplished but it was possible to use a screw-thread die to produce a turbulence promoter with 20 turns per inch of tube length with a thread height of 0.032 in. This tube had a surface area 65% greater than a smooth tube with the same diameter.

In all cases, the turbulence promoter was positioned in the downstream half of the tube. Such an arrangement permitted the efflux to be divided into two streams, so that the promoted and unpromoted performance of the membrane could be evaluated under as nearly identical experimental conditions as possible.

Experimental Results

Figure 1 shows results of two tests with the same design "partial runner" turbulence promoter but different feed concentrations plotted as ln $[(1 - R_{obs})/R_{obs}]$ *vs.* $v/u^{3/4}$, a form which permits determination of the intrinsic rejection, R, by extrapolation to infinite circulation velocity, u. The validity of this procedure has been demonstrated (Shor, Kraus, *et al.*, 1968b). Values of the intrinsic rejection at the two different concentrations are in excellent agreement with those of previous studies (Shor, Kraus, *et al.*, 1968b), and are characteristic of results with ion exchange-type membranes. The results for the portion of the tube containing no turbulence promoters have the initial straight line form predicted by Equation 1 for the turbulent flow regime. As the linear velocity is decreased, there is a sharp reduction of rejection in the transition flow regime and finally very low rejection in the laminar flow regime. The results for the portion of the tube containing a turbulence promoter fall along a curve with almost constant slope and do not have the sharp break characteristic of the transition from turbulent to laminar flow. It is notable that for $v/u^{3/4} \sim 20 \times 10^{-5}$ (cm./sec.)$^{1/4}$, the observed rejection of the portion of the tube containing no turbulence promoters was less than 20%, whereas the observed rejection of the portion of the tube containing turbulence promoters was greater than 80%—*i.e.*, the presence of turbulence promoters caused a marked improvement in membrane rejection. The shape of the curves shown in Figure 1 is characteristic of the bulk of the results we have obtained with and without turbulence promoters.

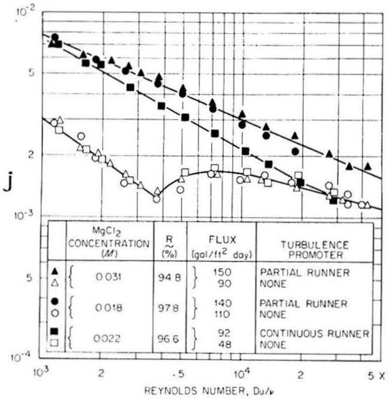

Figure 2. Comparison of effect of partial and continuous runners on hyperfiltration *j* factor

Dynamically formed hydrous Zr^{IV} oxide membrane, 600 p.s.i.g.

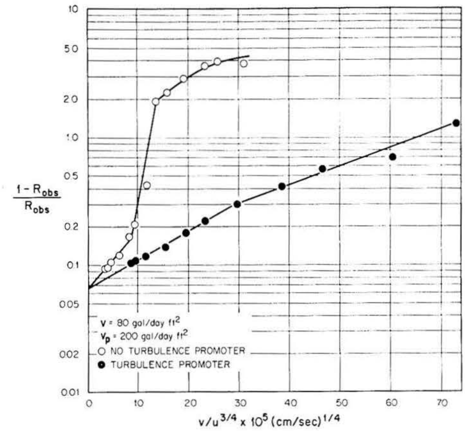

Figure 3. Effect of spiral turbulence promoter with no runners on observed rejection and product water flux

0.023*M* MgCl$_2$, 600 p.s.i.g., hydrous Zr^{IV} oxide membrane

The results shown in Figure 1 are replotted in Figure 2 as *j* for hyperfiltration *vs.* N_{Re} (see Equation 2) using the same symbols as in Figure 1 for the different conditions. In addition, there is a new set of results for turbulence promoter with a "continuous runner." There is good agreement among all three no-turbulence promoter tests which had transmission rates from 48 to 110 g.p.d./ft.² and feed concentrations from 0.018 to 0.031*M*. The line through the laminar flow data has a slope of $-^2/_3$, as expected from heat-transfer results, and the line through the smooth tube turbulent flow data has a slope of $-^1/_4$, as indicated by Equation 2 and also as expected from the heat-transfer results. The slope of $-^1/_4$ also supports the validity of the linear, slope intercept model in which ln $\{[(1 - R_{obs})/R_{obs}]/[(1 - R)/R]\}$ is plotted *vs.* $v/u^{3/4}$ and the results extrapolated to obtain the intrinsic rejection at infinite circulation velocity—*i.e.*, the nonconstancy of R primarily affects the value of K in Equations 1 and 2, not the value of the exponent of u.

In Figure 2, the solid circles and triangles are results obtained by using the same "partial runner" turbulence promoter; as with the unpromoted data the agreement of the two tests is quite good. The solid squares in Figure 3 are results obtained with a spiral turbulence promoter identical with the turbulence promoter used in the other tests shown in Figure 2, except that it had "continuous" runners instead of "partial" runners. At a Reynolds number of 10^3, both turbulence promoter designs increased the *j* factor by an equal amount (a factor of 2.6). At larger Reynolds numbers the effectiveness of the promoter with continuous runners decreased continuously until, at a Reynolds number of 3×10^4, it had no effect on the *j* factor when compared with smooth tube results. In contrast, the results for the promoters with the partial

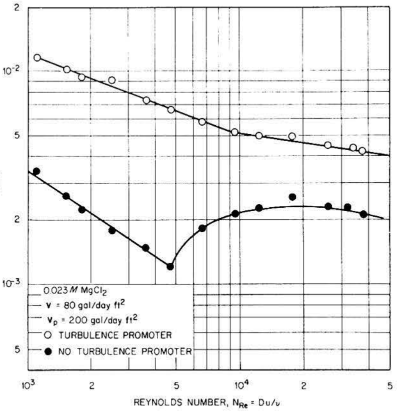

Figure 4. Effect of spiral turbulence promoter with no runners on hyperfiltration *j* factor

600 p.s.i.g., hydrous Zr^{IV} oxide membrane

runners were considerably above the smooth tube results even at a Reynolds number of 5×10^4 (a factor of 1.48). Note that the transmission rate in the half of the tube containing the turbulence promoter was always greater than the value for the corresponding test in the unpromoted half of the tube.

Results of a test with the spiral with no runners are shown in Figures 3 and 4. As pointed out above, despite the absence of runners, it is believed that this 0.025-in. diameter wire spiral was 0.002 to 0.004 in. away from the surface over most of its length because of irregularities in spiral manufacture and in the diameter of the hand-bored carbon tube. Notable features of these results are: the same intrinsic rejection (93.7%) for both promoted and unpromoted half of the tube; pronounced enhancement well into the normal laminar flow regime; maximum mass-transfer enhancement in the transition Reynolds number regime (a factor of 5.7 in this instance); marked increase in transmission rate in that portion of the tube containing the turbulence promoter (from 80 to 200 g.p.d./ft.^{2} in this instance); and significant increase in *j* factor well into the turbulent flow regime (a factor of 2 at a Reynolds number of 4×10^4).

The behavior of an attached "screw-thread" promoter is illustrated in Figures 5 and 6. With this promoter a choice must be made of which surface area to use in calculating the transmission velocity from the measured volumetric production rate—*i.e.*, the area corresponding to the nominal tube diameter or the true surface area of the screw thread. If the nominal diameter is used to calculate the surface area, the transmission rates for the unpromoted and promoted surfaces are 110 and 260 g.p.d./ft.^{2}, respectively. If the true surface areas are used the transmission rates of the unpromoted and promoted surfaces are 110 and 160 g.p.d./ft.^{2}, respectively. The true surface area was used in the calculation of the *j* factors shown in Figure 6, and the nominal surface area was used for Figure 5.

Comparison of Figures 3 and 5 shows a major difference in the performance of detached and attached promoters in hyperfiltration—*i.e.*, with detached promoters, both the promoted and unpromoted halves of the tube gave the same intrinsic rejection (Figure 3) whereas with the attached (screw-thread) promoter, the intrinsic rejection of the promoted half of the tube was 95% compared with 99% for the unpromoted half of the tube. [Note that in terms of product quality, the proper comparison is of the value of $(1 - R)$—*i.e.*, 0.04 and 0.01, a factor of four difference largely attributable to stagnant regions at the root of the screw thread.] These values of the intrinsic rejection were used in the calculation of the *j* factors shown in Figure 6. In the laminar, transition, and turbulent flow regimes, the screw-thread turbulence promoter gave *j* factors twice the value for the smooth tube when the true surface area was used to calculate the transmission velocities. When the transmission velocity was based on nominal tube diameter, the screw-thread turbulence promoter *j* factor was 3.3 times the value for the smooth tubes. In heat transfer studies with air as the fluid (Draycott and Lawther, 1961; Furber and Cox, 1967), a screw-thread turbulence promoter with 24 threads per inch gave *j* factors twice the value for the smooth tube when the nominal tube diameter was used in the calculation of heat flux. The apparent greater effectiveness of the screw-thread promoter at the high Schmidt numbers of the present study is consistent with similar observations with both attached (Smith and Gowen, 1965) and detached (Watson and Thomas, 1967) turbulence promoters.

Time Dependence. The effect of turbulence promoters on the transmission rate of dynamic membranes occurs in two different ways, as illustrated in Figures 7 and 8. These results were obtained by using a carbon tube which was brushed and acid washed between each test to remove the membrane. A new membrane was formed at three different velocities: 47, 160, and 540 cm./sec., with a spiral detached turbulence promoter

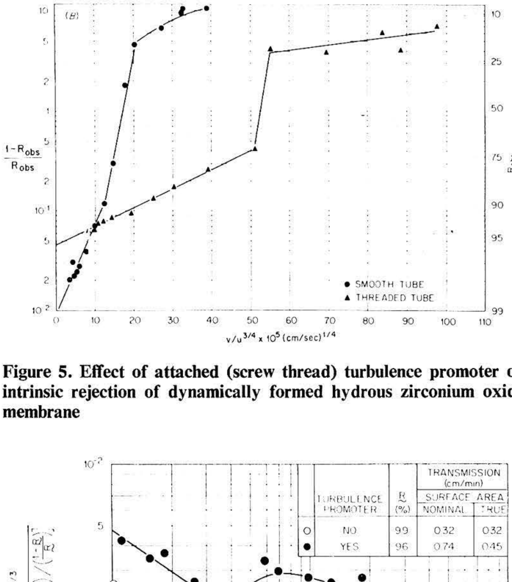

Figure 5. Effect of attached (screw thread) turbulence promoter on intrinsic rejection of dynamically formed hydrous zirconium oxide membrane

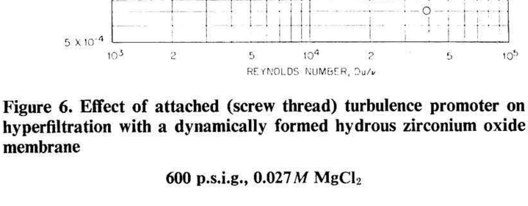

Figure 6. Effect of attached (screw thread) turbulence promoter on hyperfiltration with a dynamically formed hydrous zirconium oxide membrane

600 p.s.i.g., 0.027M $MgCl_2$

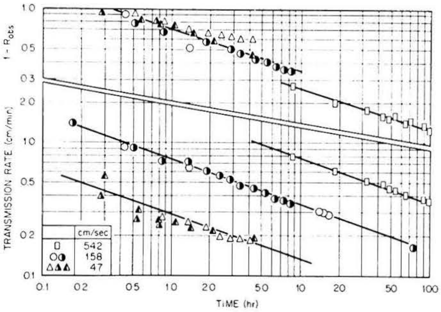

Figure 7. Effect of circulation velocity and time on formation of dynamic membrane

No turbulence promoter, feed: 0.032M $MgCl_2$, membrane: 0.0001M Zr^{IV} oxide

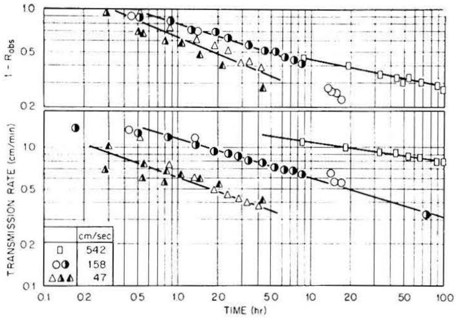

Figure 8. Effect of detached turbulence promoter, circulation velocity, and time on formation of dynamic membrane

Feed: 0.032M $MgCl_2$, membrane: 0.0001M Zr^{IV} oxide

with longitudinal runners located in the downstream half of the tube. Duplicate tests, indicated by differently shaded points, showed good agreement. At the lowest linear velocity (47 cm./sec., or $N_{Re} = 3100$, corresponding to a low transition region Reynolds number), both promoted and unpromoted transmission rates decreased as the -0.3 power of time. However, the transmission rate of the promoted half of the tube was 2.3 times greater than the unpromoted half of the tube. At the intermediate velocity (160 cm./sec., $N_{Re} = 10{,}500$), the transmission rate of the promoted half of the tube was again greater than that of the unpromoted half. However, at this velocity the transmission rate of the promoted half of the tube decreased at a slower rate than the unpromoted half—*i.e.*, with the -0.25 power of time compared with the -0.33 power of time for the unpromoted half of the tube. At the highest velocity (542 cm./sec., $N_{Re} = 35{,}000$), the transmission rate of the promoted half of the tube was again greater than the unpromoted half and the rate of decrease with time was much smaller—*i.e.*, the -0.12 power of time for the unpromoted tube. Thus, a detached turbulence promoter with spiral runner apparently caused both a higher transmission rate and a slower decrease of transmission rate with time than was observed in the absence of turbulence promoters.

Friction Factors. Friction factors for carbon tubes containing wire spiral with no runners, with a partial runner, and with a continuous runner were within ±10% of each other and were almost a factor of 10 greater than the friction factors for a carbon tube with no turbulence promoter in the Reynolds number range 2×10^3 to 4×10^4. The results for the three spiral promoters in carbon tubes were fitted by

$$f = 0.77/N_{Re}^{0.23} \tag{3}$$

and the results for the carbon tube with no promoters were fitted by

$$f = 0.12/N_{Re}^{0.28} \tag{4}$$

The results for carbon tube with no promoters were somewhat above the conventional smooth tube line; the results fitted curves (Schlichting, 1968) for an equivalent sand grain roughness of $k_d/D = 5 \times 10^{-3}$.

Economic Calculations

Computer Code. The effect of turbulence promoters on the economics of hyperfiltration with dynamic ion exchange-type membranes was briefly explored using computer code developed by Griffith, Keller, *et al.* (1970). A general description of the code and results of a parametric study of tubular systems have been published elsewhere (Griffith, Keller, *et al.*, 1968b).

The computer code determines optimum flow conditions to give minimum water costs by using a general nonlinear optimization procedure based on gradient search (Zellnik, Sondak, *et al.*, 1962; Cooper and Kephart, 1965; Cross, 1968). The numerical procedure developed to approximate the differential process is based on subdividing the tube into a number of subsections, such that the concentration change in each section is equal and arbitrarily small. For given feed concentration, concentration ratio, tube diameter, inlet flow conditions, and membrane properties, the concentration polarization, effective pressure, and salt concentration in the product are calculated at the inlet to the first subsection. An iterative procedure is used to calculate concentration polarization, effective pressure, and salt concentration in the product at the end of the first subsection, as well as the length of the subsection, the incremental water recovery, and the associated pressure and velocity drop over the subsection. This procedure is continued recursively down the tube and the pertinent variables are summed to obtain the overall water recovery, tube length, and pressure drop. From these results, the area and pumping requirements are calculated. Then a cost can be calculated for given economic parameters.

Although the hydrodynamics was treated in a sophisticated manner, a simplified cost equation was used. This equation contains two parameters: (1) a daily capital and maintenance charge per square foot of membrane area, C_A, and (2) a unit cost for pumping power, C_E. If the ratio of area to energy costs is defined as

$$R_{AE} = C_A/C_E \tag{5}$$

then the unit cost of product water, C_p, may be expressed as

$$C_p = C_E \frac{R_{AE}A + P_E}{W_p} \tag{6}$$

A simplified equation of the Equation 6 type is most meaningful if the cost parameters are interpreted as incremental costs. The area cost, C_A, would then be the additional capital charge and operating expense (expressed as cent/ft.^{2} day) associated with increasing the size of the plant; this includes, for example, capital charges arising from additional membranes, backing materials, collection systems, space requirements, as well as additional operating expense to maintain the increased area. The capital charges arising from the cost of pumps might be included in C_A, though it seems more appropriate to include pump costs in C_E, the cost of energy (per k.w.h.), since additional pump costs are, as a first approximation, proportional to the energy consumption.

The costs developed by using this computer program are thus relative and incremental; to obtain total water costs, terms not proportional to area or energy consumption would have to be included. For rough estimates of total water costs for a given set of conditions (or designs), however, it is probably sufficient to evaluate C_A from the total daily plant cost and the area; C_E may then be the unit energy cost (with or without pumps).

In the present calculations, the ion exchange-type membrane characteristics were the same as those used in previous calculations (Griffith, Keller, *et al.*, 1968). The effect of turbulence promoters on hyperfiltration was based on the experimental results shown in Figures 3 and 4, and their effect on friction factor was estimated from Equations 3 and 4. In particular, membrane permeabilities were 2 and 5 g.p.d./ft.^{2} atm. for the smooth tube and turbulence promoter cases, respectively. Friction factors for the turbulence promoter cases were assumed to be 10 times those for a smooth tube; the effect of turbulence promoters on concentration polarization was accounted for by using $K = 12$ in Equation 1 rather than the smooth tube value (Shor, Kraus, *et al.*, 1968b) of 25.

Results of Optimization Calculations. Figure 9 illustrates the difference between optimum conditions for turbulence promoters and no turbulence promoters as well as the detailed nature of the computer output. Most notable is the marked decrease in plant length (from 245.7 to 75.2 ft.) associated with turbulence promoters. The decrease in plant length is caused by both decreased velocity and increased permeability in the turbulence promoter case.

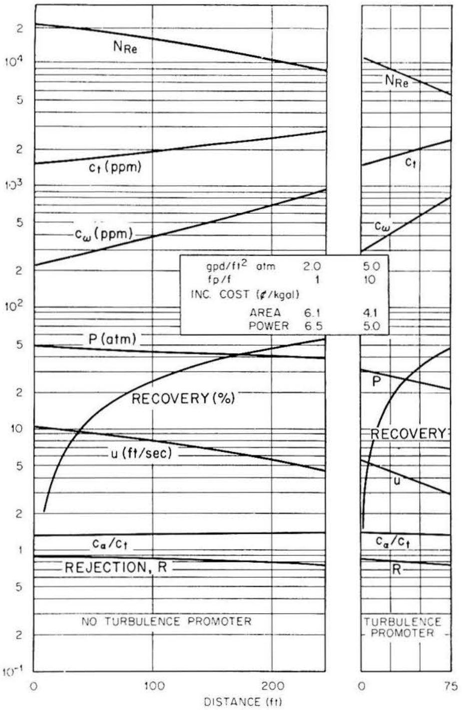

Figure 9. Profile of optimum operating conditions for dynamic hyperfiltration membrane formed in the presence and absence of turbulence promoters

The results of a series of calculations are summarized in Table I. These results are for minimum incremental water costs for a plant with C_A = 0.5 and 1¢ per day ft.^{2}, and C_E = 0.5¢ per k.w.h. C_A and C_E costs are not inconsistent with those used in previous economic studies (Keilin and DeHaven, 1965; Menzel, 1967). At a feed concentration of 2000 p.p.m., the ion-exchange membrane characteristics assumed for the calculation are strained to produce product water of 500 p.p.m. quality. Consequently, there was little or no economic advantage for use of turbulence promoters with their attendant higher permeability membrane.

When the inlet feed concentration is reduced to 1500 p.p.m. the membrane capabilities are no longer strained to produce 500 p.p.m. product water with appreciable water recovery and the increased flux possible with turbulence promoters resulted in a significant economic advantage.

With a feed concentration of 1500 p.p.m. and an area cost of 0.5¢ per ft.^{2} day, the difference in optimum water cost without and with turbulence promoters was 2.9¢ per kgal., (total cost of 12.1 and 9.2¢ per kgal., respectively). Increasing the area cost to 1¢ per ft.^{2} day increased the difference in optimum water cost without and with turbulence promoters to 5.4¢ per kgal. (total cost of 18.0 and 12.6¢ per kgal., respectively). Since the same area cost was used in the no-turbulence promoter and turbulence promoter calculations, the difference in cost represents the maximum that can be paid for turbulence promoter manufacture.

The results given in Table I provide considerable insight into the details of how operating conditions were changed to achieve the optimum costs. The principal input changes due to turbulence promoters were an increase in permeability from 2 to 5 gal. per day ft.^{2} atm., a decrease in K (Equation 1) from 25 to 12, and an increase in the friction factor by a factor of 10. The first two items lead to decreased costs, the last to increased cost. In arriving at a new optimum for a system with turbulence promoters, the optimization procedure determined optimum operating conditions with nearly equal plant and pumping costs as was the case in previous optimization calculations for smooth tubes (Griffith, Keller, *et al.*, 1968). To maintain the approximate balance between plant and pumping costs, the optimization procedure in the computer program reduced the entrance pressure to 65% of the smooth tube value and it reduced the entrance velocity to 50% of the smooth tube value. Despite the reduction in inlet pressure, these conditions gave a 48% increase in flux because of the increased permeability of the membrane in the presence of turbulence promoters.

Discussion

The experimental results of the present study support the definition of an ideal turbulence promoter for hyperfiltration as being one which neither blocks the membrane surface nor provides stagnant regions where solids can accumulate or where the concentration of rejected salts can build up.

The screw-thread promoter design apparently permitted stagnant regions to form at the root of the thread, resulting in a significant decrease in intrinsic rejection compared with that observed on the smooth upstream half of the tube (Figure 5). In contrast, the spiral turbulence promoter with no runners (separated from the surface by an estimated 0.002 to 0.004 in.) gave the same intrinsic rejection as observed with the smooth upstream half of the tube (Figure 3).

Comparison of the results obtained with turbulence promoters with continuous runners, partial runners, and no run-

Table I. Results of Economic Optimization Calculations for Tubes with and without Turbulence Promoters and Ion Exchange-Type Membrane

Tube diameter = 1/4 in., C_E = 0.5 cent/k.w.h.

Feed concn (p.p.m.)	Inlet pressure (atm.)	Inlet velocity (ft./sec.)	Inlet Reynolds number	No. of tubes	Tube length (ft.)	Av. flux (g.p.d./ft.^{2})	Water recovery (%)	Plant cost, cent/ kgal.	Pumping cost, cent/ kgal.	Total cost, cent/ kgal.	Blended water cost,[a] cent/ kgal.
No-turbulence promoter, f_p/f = 1.0 permeability = 2 gal./ft.$^2\cdot$day$\cdot$atm.											
1500[b]	40	8.6	16,800	996	222	69	53	7.2	5.7	12.9	12.3
	60	13.1	25,600	555	279	98	63	5.1	7.3	12.4	
	48.3[c]	10.5	20,600	761	246	82	57	6.1	6.5	12.6	12.1
2000[d]	40	11.4	22,300	1230	193	65	32	7.8	9.4	17.2	
	60	17.0	33,400	681	261	86	39	5.8	11.7	17.5	
	46.6[c]	13.2	25,800	983	213	73	35	6.9	10.1	17.0	
1500[b]	40	8.1	15,900	1210	179	71	46	14.1	6.6	18.9	
	60	12.2	23,800	616	243	102	61	9.8	7.5	17.3	
	65.1[c]	13.7	26,800	595	235	110	56	9.1	8.9	18.0	17.1
2000[d]	40	11.0	21,600	1300	178	66	32	15.2	9.6	24.8	
	60	15.8	31,000	774	210	94	37	10.6	12.3	22.9	
	59.8[c]	15.8	31,000	773	211	94	37	10.7	12.3	22.9	
Turbulence promoter, f_p/f = 10 permeability = 5 gal./ft.$^2\cdot$day$\cdot$atm.											
1500[b]	40	7.0	13,600	1270	83	145	52	3.4	5.9	9.4	
	60	10.2	19,900	793	102	189	56	2.6	8.1	10.8	
	31.9[c]	5.6	11,000	1670	75	121	48	4.1	5.0	9.2	
2000[b]	40	9.5	18,500	2390	47	136	20	3.7	15.2	18.8	
	60	12.6	24,800	1430	59	182	25	2.7	18.2	20.9	
	39.9[c]	9.4	18,500	2390	47	136	20	3.7	15.1	18.8	
1500[d]	40	6.5	12,700	1480	67	157	49	6.4	6.3	12.6	
	60	9.8	19,100	860	86	208	54	4.8	8.5	13.3	
	42.2[c]	6.9	13,500	1320	71	162	50	6.2	6.5	12.6	
2000[d]	40	9.3	18,200	2450	45	140	20	7.1	15.3	22.4	
	60	12.5	24,600	1450	56	188	25	5.3	18.3	23.6	
	43.8[c]	9.9	19,400	2150	48	150	21	6.7	15.7	22.3	

[a] Economically advantageous to blend product with feed to produce desired end-product.
[b] R_{AE} = 1.
[c] Indicates optimized value. Inlet velocity and water recovery optimized in all cases.
[d] R_{AE} = 2.

ners clearly indicated the necessity of minimizing contact with the dynamic membrane surface, particularly for Reynolds numbers in excess of 10^4.

A novel feature of the detached turbulence promoter is that it maintains its effectiveness well into the normal laminar flow regime. Generally, this type of behavior is not observed with attached promoters (Bergles and Morton, 1965; Dipprey and Sabersky, 1963; Kays and London, 1964).

A feature of all the turbulence promoters we have studied is that they increase the flux over that observed from the unpromoted portion of the tube in the same experiment. The greatest increase in flux (from 80 to 200 g.p.d./ft.^{2}) was observed with the spiral promoter with no runners. In addition to larger values of flux observed with turbulence promoters over the whole laminar to turbulent velocity range at any given time, flux decline with time was much slower for the turbulence promoter half of the tube than for the unpromoted half of the tube operating at the same velocity when the velocity was above 160 cm./sec.

Based on economic optimization calculations, use of a turbulence promoter with dynamic membranes can result in a significant economic advantage, largely because of the increased permeability. Use of turbulence promoters also results in markedly different operating conditions and plant geometry compared with no-turbulence promoter plant—*i.e.*, a 50% reduction in inlet velocity, a 35% reduction in inlet pressure, and a 65% reduction in tube length.

Acknowledgment

The authors wish to acknowledge the support and suggestions of Kurt A. Kraus and the assistance of W. A. Wilburn in fabrication of the turbulence promoters.

Nomenclature

A = area, ft.^{2}
C_A = unit cost of area, cents/ft.^{2} day
C_E = unit cost of energy, cents/k.w.h.
C_p = product water cost, cents/kgal.
D = tube diameter, ft.
f = smooth tube friction factor, $(D\Delta P/4L)(\rho u^2/2g_c)$ dimensionless
f_p = turbulence promoter + smooth tube friction factor, dimensionless
g_c = conversion factor, (lb.$_m$/lb.$_f$)(ft./sec.^{2})
j = j factor (see Equation 2) dimensionless
K = coefficient in Equation 1, dimensionless
L = tube length, ft.
N_{Re} = Reynolds number, dimensionless
N_{Sc} = Schmidt number, dimensionless
P = pressure, atm.
ΔP = pressure drop, lb. force/ft.^{2}

P_E = energy consumed per day, k.w.h./day
ρ = fluid density, lb. mass/ft.^{3}
R_{AE} = cost ratio, C_A/C_E
$\mathbf{R}$ = intrinsic salt rejection
R_{obs} = observed salt rejection
v = production rate, ft./sec.
u = axial velocity, ft./sec.
W_p = daily production, kgal./day

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The Monitoring of Hydrogen, Methane, and Hydrocarbons in the Atmosphere

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■ A simple, automatic system of recording only methane and (or) methane plus all other hydrocarbons using a selective combustor and a flame ionization detector is reported. In addition, another system is presented using the selective combustion technique and a water sorption detector where hydrogen, methane, reactive hydrocarbons, and nonreactive hydrocarbons are separately recorded. In the latter instrument, the air is first dried and led through a combustion tube and then to a water detector. Reactive and nonreactive hydrocarbons are distinguished by ease of combustion.

In monitoring the atmosphere for hydrocarbons, the flame ionization detector (FID) is most often used. This sensitive instrument responds to hydrocarbon and partly oxidized hydrocarbon. Methane accounts for 60 to 90% of the atmospheric hydrocarbons, but it is photochemically inert. The large methane signal obscures the active smog-producing hydrocarbons. Thus, a method for simple registration of all nonmethane hydrocarbons has been sought. Gas chromatography is used, but it is expensive and normally reports only the light hydrocarbons. Ortman (1966) described a method presently used in some monitoring stations where all hydrocarbons except methane are removed from the air with use of an activated carbon filter with the resulting air analyzed for methane via the FID. This is a simple technique; however, filters require careful preparation and replacement. In addition, there is a 5-min. delay between methane concentration changes and the observed result.

The decomposition energy required for methane is significantly higher than other hydrocarbons; it is also photochemically inactive, and by the same token, advantage can be taken of methane's inertness to analyze for it in the presence of other hydrocarbons by using a selective catalytic combustor. Methane analysis is almost instantaneous using the combustor, and life is in excess of six months. Another class distinction can be made between the remaining hydrocarbons by altering combustor temperature.

Three basic methods of monitoring hydrocarbons will be considered in the following discussion. These are diagrammed in Figure 1. The advantage of these three techniques over the other methods lies not only in the selectivity of the combustor to H_2, CH_4, and other hydrocarbons, but in sensitivity. Also, it does not depend as much on compound type as do such techniques as nondispersive infrared.

Method 1 depends on the flame response being proportional to the number of carbons burned per second. Dietz (1967) summarizes the FID weight basis response factors for many hydrocarbons. For 83 paraffins, 20 aromatics, and 5 olefins, the response factors are within 5% of each other (1 ± 0.05), while oxygenated compounds run 40 to 85% lower than paraffins.

Method 2 produces signals proportional to the hydrogen content of the hydrocarbon, while Method 3 yields a carbon content signal. The carbon signal is the most faithful for reporting the weight fraction of hydrocarbon in the air. Unfortunately, CO_2 analyzers are not yet available with adequate sensitivity to use on ambient air hydrocarbon monitoring. Rosenbaum (1959) has applied the technique to gas chromatography effluents where concentrations far exceed 1 p.p.m.

Method 2 should be preferred since a coated crystal sorption detector for water is sensitive enough, simple, rugged, and long-lived. The equipment requires only the air sample and electricity. The response time is a few minutes, far slower than the FID; however, it is adequate for air monitoring.

Method 1 is a modification of the usual method of monitoring the atmosphere with the FID. The FID is rapid, sensitive enough, already in use, and popular. With this method, the methane plus hydrocarbons are determined by operating the combustor cold; next, the combustor heat is increased to the point where all hydrocarbons except methane are consumed. Thus, the FID signal is for methane alone, and subtraction yields the nonmethane hydrocarbon signal. The disadvantages of the FID are that hydrogen and combustion air cylinders are required, and it is a subtractive and not a direct technique for reactive hydrocarbons. However, this is an accepted approach and will be widely used, especially since most air monitoring stations already have FID's, and all they need to add is the programmed selective combustor to measure methane. The combustor also permits the flame background to be measured.

Experimental

The character of Methods 1 and 2 were determined and evaluated for several months in conjunction with automatic programmed selective combustor units. The selective combustor consisted of a $^1/_4$-in. o.d. quartz tube containing a 2-in.-long coil of 16 mil platinum wire 24-in. long. This coil was connected to a transformer which could vary the power input from 0 to 64 W manually or by an automatic timer. At 64 W all hydrocarbons, including methane, were burnt. Thus, a zero level for the FID was determined. This procedure, then, eliminates the bother and expensive "zero gas" to determine background levels. Wire temperatures were estimated from the resistance of the coil and known coefficients.

Analysis of the selective combustor products was accomplished with a Perkin-Elmer F-11 chromatograph equipped with a flame ionization detector. One-cc. samples were used, and the column was $^1/_8$ in. × 5 ft. Porapak Q operated at 100° C.

The output of the selective combustor was fed to either the F-11 FID or to a water-sensing sorption detector. The selective sorption detector for water consisted of two piezoelectric quartz crystal resonators coated with a hygroscopic polymer. The uncombusted dried air flowed over one crystal through the combustor to the second detector crystal. Thus, when hydrocarbons were present the frequency of the second crystal would decrease because it received the water of combustion. The net frequency difference was recorded *vs.* time. Calibration was affected by passing precombusted air through a small KOH electrolysis cell at the inlet. Thus, known amounts of hydrogen were generated, creating known water concentrations.

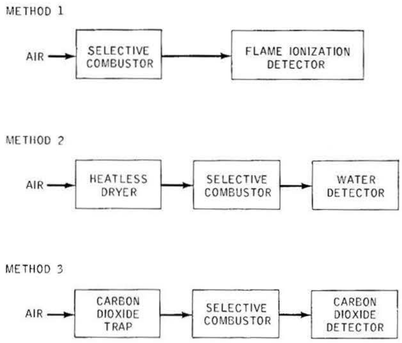


Figure 1. Three basic methods for hydrocarbon monitoring

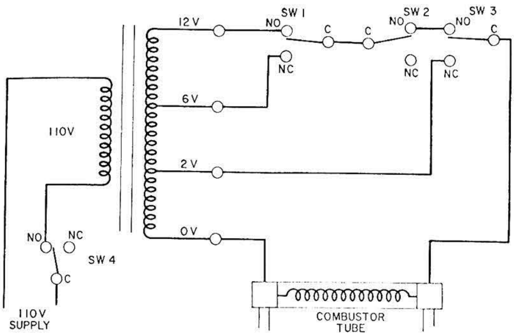
Under Method 2, a dryer must be used in front of the combustor to keep the large amount of atmospheric water from swamping the water analyzer. Cartridges packed with Dowex 50 W × 8 (Na^+) form ion-exchange resin dried at 300°F. in dry nitrogen were most effective in passing hydrocarbons, alcohols, olefins, and the like, and yet highly effective in trapping the water. Samples of C_1 to C_{11} paraffins were injected at the pump inlet to test the overall system for hangup, and the expected yields of water were found. C_{10} to C_{11} gave long tails lasting 5 to 10 min., but lighter materials were much faster. Polar materials such as alcohol, acetone, and toluene had negligible tailing as long as the cartridge was reasonably dry. The water picked up by the dryer tended to hold polar materials. This problem and cartridge replacement were eliminated by the use of a heatless dryer developed by Skarstrom (1960). The heatless dryer was also packed with Dowex 50 W × 8 (Na^+). This type of dryer regenerates itself every 30 sec. at the expense of purging some dry air. It is simple and long-lived, and each drying cycle produces product air a little dryer than the previous cycle until the dew point is not observed, even at liquid nitrogen temperatures (78°K.). Rejection of water to this extreme is not a requirement. In addition, the dryer is maintained in a constant condition of dryness which greatly reduces polar compound hangup.

For automatic operation of the selective combustor in Method 2, four voltages were selected by a four-switch timer. The circuit and program of Figure 2 produce the following combustion conditions shown in Table I.

For automatic operation of Method 1, where H_2 and reactive hydrocarbons cannot be determined, the last two program steps are omitted. The first step is 7 min. of high heat to combust all hydrocarbons and establish the FID, zero. The next 7 min. of the medium heat establish the methane level, and then the power is turned off for 40 min. to record total hydrocarbons.

Results and Discussion

The performance of the selective combustor was determined by feeding p.p.m.-level hydrocarbons in air at various flow rates to the combustor and analyzing the product by gas chromatography. Methane is the most difficult to burn; however,



TIME	COMBUSTOR VOLTS	SW 1	SW 2	SW 3	SW 4
		SWITCH POSITION			
0 TO 45 MINUTES	12	NO	NO	NO	NO
45 TO 50 MINUTES	6	NC	NO	NO	NO
50 TO 55 MINUTES	2	NC	NC	NC	NO
55 TO 60 MINUTES	0	NC	NC	NC	NC

Figure 2. Electrical circuit for the selective combustion tube

Switch positions are shown for the Industrial Timer Corp. MC8/4SW/A12 unit

Table I. Temperature Program of the Selective Combustor

Part of the hour[a] (min.)	Temperature level	Remarks
0 to 39	High	H_2, C_1, plus hydrocarbons burnt
39 to 46	Medium	H_2 plus all hydrocarbons except C_1 burnt
46 to 53	Low	H_2, olefinic, and reactive hydrocarbons burnt
53 to 60	Very low	Only hydrogen burnt

[a] A cycle time of 1 hr. was selected because this is the frequency of data logging at our air monitoring station. This particular program records total hydrocarbons most of the time. The other species show up as steps down from the total once per hour.

at an estimated wire temperature of 1200° to 1300°C., combustion is complete provided the residence time exceeds 0.4 sec. Efficiency data obtained at several flows for 1.6 p.p.m. methane feed are shown in Table II. For air flow rates below 60 cc./min., at least 97% of the methane reacted as indicated by the residual of 0.05 p.p.m. This low value is an analytical error produced by the syringe injection method since introducing only the syringe needle indicated 0.05 p.p.m.

The results of gas chromatographic analysis of combustor products *vs.* combustor temperature are shown in Figure 3, p.p.m.-level hydrocarbons were used. At 400°C., the two olefins were combusted to extinction; however, at this point, methane is generated by thermal cracking, etc. At about 1000° C., most of the ethane and olefins were burnt and some methane is lost, while at 1300°C., all hydrocarbons, including methane, are consumed. While not shown, a sharper distinction is obtained between methane and propane. For methane/ethane the selection is about 87% effective, while for methane/propane it is 95%.

Hydrogen is very easily consumed on platinum in air because H_2 absorbs in the platinum as atomic hydrogen, and reaction with oxygen is complete at 150°C. as evidenced in Table III. It has thus been shown that several compound types are selectively burnt by the platinum combustor.

Table II. The Combustion Efficiency of Methane *vs.* Flow Rate[a]

Flow rate (cc./min.)	Residence time (sec.)	Product p.p.m. CH_4
10	2	0.05
20	1	0.05
40	0.5	0.05
60	0.4	0.05
130	0.2	0.2
290	0.1	0.7

[a] Ambient air containing 1.6 p.p.m. methane passed through a combustor at various flow rates. The exhaust was analyzed by gas chromatography.

Optimum temperatures can be obtained on synthetic mixtures containing typical hydrocarbons. Tests on ambient air during high pollution were conducted to check the selected temperatures. A temperature scan on polluted air from complete combustion to zero showed two breaks: one at high temperature, indicating the methane/paraffin separation; and one in the 250 to 500° C. range, indicating the nonreactive/reactive split. These separations are by no means precise or as well defined as obtained with the synthetic blends because of the large smear of materials in polluted air. The important point is that the separation is directionally the same as one could expect the reactivity to be in the atmosphere. A better definition of the separation must await detailed studies on the catalytic combustion of trace materials to water. This is now possible with the sensitive water sorption detector.

Innes and Andreatch (1970) reported on a selective combustor using vanadia catalyst in a heat of combustion detector operating at high concentrations. They showed a reasonable correlation of low severity combustion with smog effects.

By employing a flame ionization detector as Method 1 was diagrammed in the introduction, new and useful atmospheric hydrocarbon analyses result. A simple timer programs the combustor through two temperatures. Full on for 5 min. removes all hydrocarbons, thus establishng a zero level. This

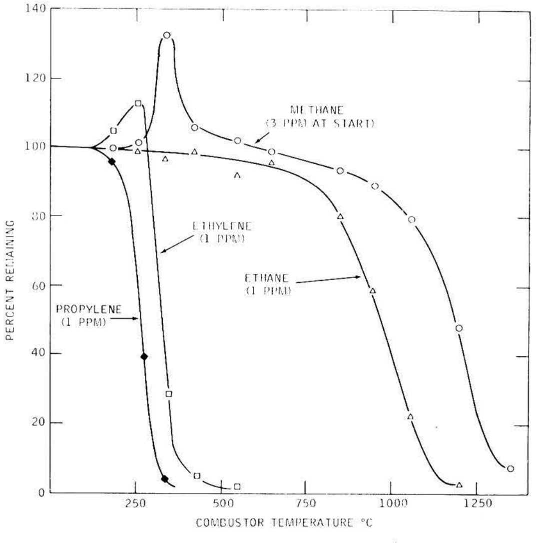


Figure 3. Analysis of combustor products at various temperatures demonstrating degree of selectivity

is advantageous for checking drift automatically without using expensive "zero gas", which is never really zero. After full on has established zero, the timer switches to a new heat for 5 min. where methane is not combusted, but all other hydrocarbons are, and the FID now registers the value for methane. Next, the combustor switches off and total hydrocarbons are sensed. But what about the olefins that were so beautifully separated by the combustor? Why not add a third heat to indicate olefins? Alas, Mother Nature has been unkind because near the olefin temperature, methane and other hydrocarbons are produced by cracking and recombination reactions, and the flame response increases with increasing temperature. This is shown by Figure 4.

An automatic zero, methane, and total hydrocarbon analyzer using the combustor and a Beckman FID was operated on laboratory air before being installed in an air monitoring station for long-term evaluation. Typical results are shown by a reproduction of a recording in Figure 5. The recording shows several hours of monitoring. At the points marked 1, the combustor was turned full on, establishing the zero level at 2. At Point 2 the combustor was turned down to pass methane only, thus establishing the methane level at 3, where the power was removed to permit recording total hydrocarbons for the remainder of the hour when the whole cycle repeats. The curious spike at 1 was determined to be due to oil vapor in the air, which condensed on the combustor during the off period. This was confirmed further by other analyses. When the cycle was repeated after short "off" intervals, no spike resulted. When the combustor was off for several hours, a giant spike occurred. By integrating the spike area, the oil concentration was estimated to be 0.1 p.p.m. No systematic workup or check on this conclusion was made.

Methods 2 and 3 are capable of all three selectivities because only products of the combustion are sensed. In Method 2 the air sample is first dried and then combusted. The resulting water is selectively detected by a sorption detector, which responds to water, but not hydrocarbons. Several models of the Method 2 analyzer were built. One, using a Du Pont 510 moisture analyzer and a Gow-Mac combustor (13-750), is still undergoing a side-by-side comparison test with a Method 1 analyzer at the Esso Research Air Monitoring Station (ERAMS). At this point in time, one year has been logged with no maintenance on Method 2, and two failures by Method 1. Both analyzers track each other well, as shown by Table IV. Method 1 is by flame ionization and Method 2 is called the King Method.

A second, and less expensive, analyzer using Method 2 is installed at the author's home in Florham Park, N.J. This is practical since the method is simple, requiring only a small pump, a dryer, a combustion tube, a timer, a sorption detector, and an inexpensive Heath Kit recorder. An "at home" recording of methane, paraffins, and reactive hydrocarbons is shown in Figure 6. In this recording, the combustor program was set for 42 min. to combust all, then from Points 1 to 2 for 6 min. to combust all except methane, from Points 2

Table III. Selective Catalytic Combustion at 150 °C.

Vapor	Percent converted Platinum	 Palladium
Hydrogen	100	100
Methanol	2	0.012
Ethanol	2	0.05
Acetone	0.05	0.04
Pentane	0.001	0.0002
Benzene	0.001	0.0002
Methane	0.0003	0.0006

Table IV. Percent of Time Concentration Is Exceeded[a]

Total hydrocarbons	0.1	1	10	50
By flame	5.0	4.1	3.2	2.3
By King	5.6	4.4	3.6	2.2

[a] These are hourly p.p.m. data for August 1969. Average for the month was 2.4 p.p.m. Beckman FID and 2.4 p.p.m. King.

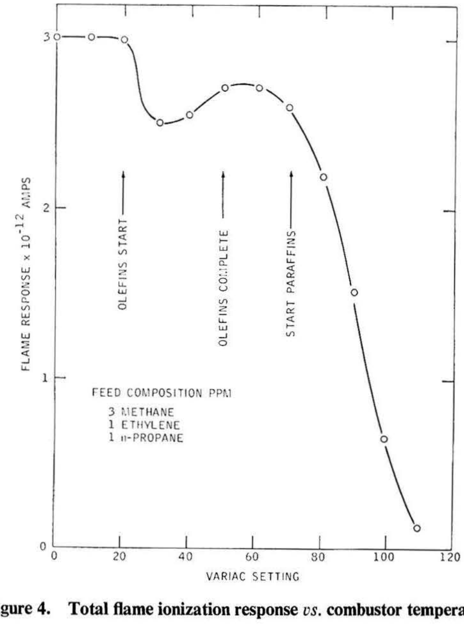


Figure 4. Total flame ionization response *vs.* combustor temperature

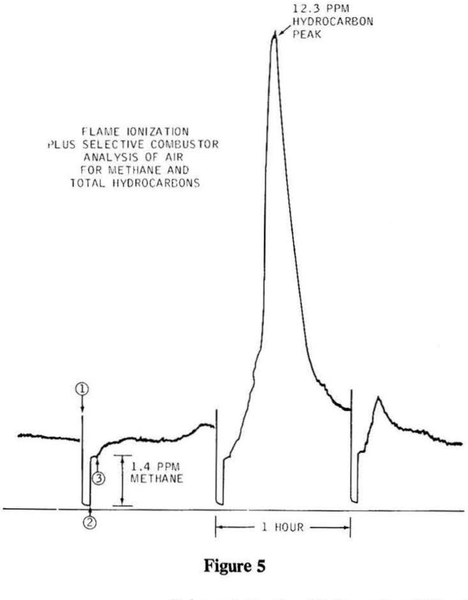


Figure 5

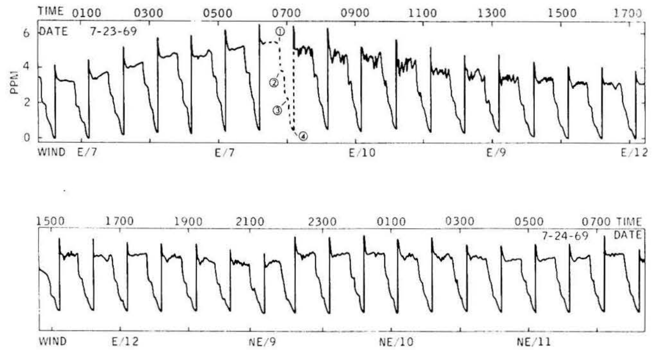


Figure 6. Reactive hydrocarbons and methane recorded at authors home, Florham Park, N.J., 30-ft. elevation

to 3 for 6 min. to combust olefins plus hydrogen, and from Points 3 to 4, 6 min. to combust only hydrogen.

At 07:00 hr. on July 23, 1969, where these points are depicted in Figure 6, the hydrocarbon concentrations are 1.6 p.p.m methane (Points 1 to 2), 1.15 p.p.m paraffin type hydrocarbons (Points 2 to 3) and 1.9 p.p.m. olefin and other reactive hydrocarbon types (Points 3 to 4). Methane values were fairly constant, rarely reading 2 p.p.m., while the other hydrocarbons varied widely in October 1969, 1.4 p.p.m. methane was observed for long periods. Other hydrocarbons were less than 0.2 p.p.m. before the traffic started on S. Orange Ave., which is 700 ft. away from the sampling point. The effect of traffic is readily discernible from the general background. Compare hours 06:00 to 07:00 and 07:00 to 08:00. The rapid fluctuations correlate with traffic density. The use of low power (150° C.) between Points 3 and 4 establishes a zero level where hydrogen only is burnt. Thus, if hydrogen should change, the zero level will change. Other measurements have convinced me that this rarely happens. If the hydrogen level is desired, the combustor can be programmed for an "off" period.

Hydrogen was monitored for long periods of time at Bayway, N.J., with use of a slight modification of the above system. The heatless dryer was packed with activated charcoal, using a purge to feed ratio of 7:1, water and all hydrocarbons including methane were rejected. The hydrocarbon rejection efficiency was 100% and methane was 97%. This product was then led through a combustor and thence a water analyzer. The reason for the initial separation is because the combustor makes a 100% selection between methane and hydrogen. The selection between hydrogen and anything else in the atmosphere must be open to some question simply because it is difficult to test everything else. After several months of monitoring, the 1-p.p.m. level was found to be very steady. Only once did the level reach 10 p.p.m. for a few minutes. The data suggest a slight diurnal effect with a maximum at 2:00 p.m. The deviation from average was only 0.1 p.p.m., and further investigation away from the heavy industrial area is needed to confirm or deny the diurnal effects. The ultraviolet conversion of formaldehyde to H_2 and CO is known. McQuigg and Calvert (1959) suggested the high altitude conversion of formaldehyde as a possible source of diurnal H_2.

Summary and Conclusions

Three new ways to monitor hydrocarbons in the atmosphere were discussed. Method 1 involves a selective combustor and a flame ionization detector. With this method, an automatic zero level, methane, and total hydrocarbons are recorded. Method 2 involves converting the hydrocarbons to water with a selective combustor. Here, hydrogen, olefins, paraffins, and methane are recorded. The third method is

Table V. Comparison of Flame and King Detector Methods of Continuous Atmospheric Hydrocarbon Analysis

	FID and combustor[a]	XTAL and combustor
Response	Fast (0.1 sec.)	Adequate (5 min.)
Sensitivity	Good (4 p.p.b.)	Good (10 p.p.b.)
Sample	Total carbon	Total hydrogen
	Methane by difference; not capable of reactive HC	Reactive HC direct; other HC and methane by differences
Complexity	Requires H_2 and air cylinders	No extra gases
	Sensitive, expensive electrometer	Simple electronics (4 transistors)
	Entire unit thermostated (100 liters)	One small cell thermostated (2.5 cc.)
	Flow of air and H_2 controlled	Not flow sensitive
Life	Jets foul and require maintenance	No critical orifices
Calibration	Requires known blend	Simple. H_2 by electrolysis—a first principle method
Portability	Not portable	Easily made portable and battery operated

[a] The combustor has another important use in FID work. By placing one in the flame support air line all hydrocarbons are removed and noise reduced such that 1-p.p.b. hydrocarbons are resolved by a gas chromatograph using 5-cc. samples.

analogous to Method 2, except the carbon dioxide of combustion is sensed.

The preferred technique is Method 2 for the reasons summarized in Table V. Since most air monitoring stations now have flame units, Method 1 will probably prevail after combustors are commercially available. It is expected that Method 2 or 3 will be popular when and if reactive hydrocarbon monitoring becomes important.

Acknowledgment

I thank R. S. Brief of our Medical Research Division for conducting the long-term evaluation of both Methods 1 and 2.

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Singlet Oxygen in the Environmental Sciences. Possible Production of $^1O_2$ by Energy Transfer following Oxygen-Enhanced Absorptions

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■ A reversible absorption of actinic light ($\lambda > 300$ nm.) by collision complexes of tetramethylethylene (TME) and trimethylethylene (TrME) with ground-state molecular oxygen $O_2(^3\Sigma_g^-)$ has been examined. The Benesi-Hildebrand treatment of the reversible enhanced absorption gives the extinction coefficients of the collision complex. Using Mulliken's concept of charge transfer between olefin as donor and oxygen as acceptor, a mechanism for the production of singlet molecular oxygen [$O_2(^1\Delta_g)$ and (or) $O_2(^1\Sigma_g^+)$] is suggested. The applicability of these processes to photochemical air pollution, to the photodegradation of polymers, and to biological systems is discussed.

Four routes have been proposed to account for the formation of singlet molecular oxygen, $O_2(^1\Sigma_g^+$ or $^1\Delta_g)$, in polluted urban atmospheres of the Los Angeles type (Pitts, 1969; Pitts, Khan, *et al.*, 1969). They are (*a*) direct absorption of solar radiation by ground-state molecular oxygen, $O_2(^3\Sigma_g^-)$ (Leighton, 1961), (*b*) absorption of solar radiation by organic pollutant molecules, such as aldehydes, ketones, and polynuclear aromatic hydrocarbons, followed by transfer of energy to ground-state molecular oxygen, the Kautsky (1939) mechanism (Khan, Pitts, *et al.* 1967), (*c*) photodecomposition of ozone (Kummler, Bortner, *et al.*, 1969), and (*d*) as a product of certain exothermic chemical reactions (Murray and Kaplan, 1968).

Coomber and Pitts (1970) have observed the first two processes under simulated atmospheric conditions using an infrared spectrophotometer fitted with 40-m. pathlength cells. These authors suggested a fifth route for formation of singlet molecular oxygen which involves absorption of uv light by an oxygen–olefin collision complex. The $^1O_2$ production is due to the perturbation and enhancement of the "forbidden" singlet-triplet absorption of the olefin by ground-state molecular oxygen followed by transfer of energy from triplet olefin to $O_2(^3\Sigma_g^-)$ to give $^1O_2(^1\Sigma_g^+$ or $^1\Delta_g)$.

In the present research, we hoped that by determining the uv absorption spectra of TME, TME + O_2, TME + C_2H_5Br mixtures, and the difference spectra of TrME–O_2–TrME, we would be able to detect this O_2-enhanced transition and could then investigate the importance of this mechanism to photochemical air pollution.

Experimental

UV absorption spectra were measured by use of a Cary 15 spectrophotometer. Two quartz sample cells, having 5- and 7-mm. pathlengths, were used for liquid samples. They were fitted with two side arms for degassing, bulb-to-bulb distillations, and sample transfer under vacuum, and could be evacuated via a Teflon greaseless stopcock to 10^{-6} torr.

Materials

Tetramethylethylene (TME) (Chemical Samples Co.) was treated with $LiAlH_4$ overnight, filtered, and the filtrate run three times through a 4-cm. column of fresh alumina. The sample was stored *in vacuo* and was better than 99.9% pure by g.l.p.c. Trimethylethylene (TrME) (Chemical Samples Co., 99.9%) was purified by passage through an alumina column until a minor, second peak completely disappeared. Ethyl bromide (Matheson, Coleman, and Bell) was purified by g.l.p.c. with use of a 15-ft. by 0.25-in. column of 20% Carbowax 20M/HMDS Chromosorb W (60/80 mesh) at 75° C. with He as the carrier gas. No impurity was detected in the final sample. Cyclohexane (Matheson, Coleman, and Bell, spectroquality reagent), oxygen (Matheson, ultrahigh purity grade), and air zero gas (Matheson) were used without further purification.

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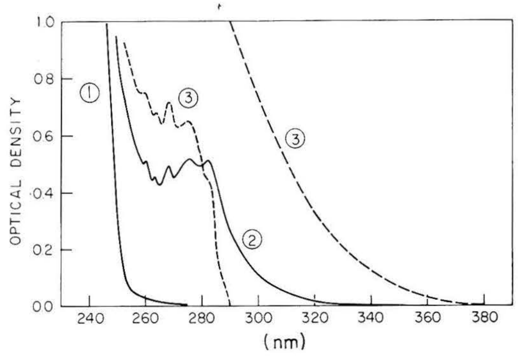

Figure 1. Effect of dissolved oxygen on absorption spectrum of TME at 25°C., pathlength 5 mm.

Curve 1. Neat TME degassed at 10^{-6} torr
Curve 2. Partially oxygenated TME
Curve 3. Oxygen saturated TME

Procedure

TME was thoroughly degassed by freezing, pumping, warming, and agitating until three consecutive pumpings gave "sticking vacuum." For the solution spectra, TME was transferred to the 5-mm. cell and a spectrum obtained in the 230–400 nm. region. The sample was saturated with oxygen and its spectrum taken. This TME–O_2 mixture was frozen, pumped, and warmed and its spectrum retaken. This procedure was repeated until all the oxygen had been removed. In experiments with TME–C_2H_5Br mixtures, the spectrum of degassed TME was run and then ~2μl C_2H_5Br was distilled into 15-ml. TME and another spectrum were taken. The TrME–cyclohexane solution was saturated with oxygen and its spectrum taken in the 230–400 nm. region. Immediately afterwards the mixture was thoroughly degassed by freezing, pumping, warming, and bulb-to-bulb distillation to establish rapid equilibrium of olefin and residual oxygen between the gas and liquid phase. This procedure was repeated until no further change in the uv spectrum occurred, usually after six to seven cycles.

Results and Discussion

The spectrum of degassed liquid TME shown in Figure 1 agrees well with the literature spectrum, (API, 1959). There is no absorption at wavelengths longer than 275 nm. When the sample was saturated with oxygen the long wavelength limit of absorption was shifted to 380 nm. (Figure 1, Curve 3). Reducing the amount of dissolved oxygen by freeze–pump cycles reduced the intensity of the absorption (Figure 1, Curve 2).

When the same procedure was followed with a thoroughly degassed sample of 2-ml. TME in 10-ml. cyclohexane, the following results were obtained (Figure 2). With no oxygen, the long wavelength cutoff remained constant at 250 nm. (Figure 2, Curve 1). This was shifted to 350 nm. on saturation with oxygen (Figure 2, Curve 2). The effect of flushing the oxygenated solution with nitrogen is also shown in Figure 2, Curve 3. The absorption still persists between 250 and 310 nm., showing that some oxygen remains. Obviously, degassing is to be preferred for removing dissolved oxygen. Curve 4 in Figure 2 shows that even careful degassing does not completely remove the increased absorbance. G.l.p.c. analysis of the TME–O_2 mixture showed that several products (~1% of the starting material) had been formed, of which only the hydroperoxide of TME (2,3-dimethyl, 3-hydroperoxy, 1-butene) could be identified. These products may be responsible for the remaining irreversible enhancement of the absorption.

The absorption spectrum of 2μl C_2H_5Br/15 ml. TME is shown in Figure 3. Compared to the spectrum of neat TME the long wavelength cutoff has again been shifted toward the red and no structure is visible in contrast to the TME–O_2 mixture.

As TME is very reactive toward O_2, a less reactive compound, trimethylethylene, was chosen for study. Again, an O_2-enhanced reversible absorption was found. G.l.p.c. analysis of the TrME/O_2 mixture showed that less than 0.01% products had been formed. Figure 4 shows the difference spectrum of (TrME/O_2/cyclohexane-TrME/cyclohexane)—*i.e.*, the enhanced reversible absorption due to oxygen.

For these mixtures the modified Benesi-Hildebrand equation has been used (Scott, 1956; Trotter and Hanna, 1966). If a donor D and an acceptor O_2 form a complex C with an additional absorbance $A = (C)(\epsilon_c)1$, assuming that $(D) = (D^\circ) - (C) \cong (D^\circ)$, one gets on rearrangement the following equation:

$$y = \frac{(O_2{}^\circ)(D^\circ)1}{A} = \frac{1}{\epsilon_c Q_c} + \frac{(D^\circ)}{\epsilon_c}$$

The value of y plotted against different donor concentrations on the molar, molal, and mole fraction scale (subscripts c, m, and x) yields ϵ_c, ϵ_m, and ϵ_x, respectively, as the inverse of the slope and $\epsilon_c Q_c$, $\epsilon_m Q_m$, and $\epsilon_x Q_x$, respectively, as the inverse of the intercept. The equilibrium quotients Q's (rather than equilibrium constants, because no activity coefficients are included) and extinction coefficients for TrME–O_2 complex are shown in Table I.

The values of ϵ_c and ϵ_m or ϵ_x, respectively, often represent upper and lower bounds for the "true" extinction coefficient (Trotter and Hanna, 1966). The 95% confidence limits for the different Q's vary between ±5 and ±11%, but systematic errors are likely to be higher than that.

Although the equilibrium constant cannot be evaluated accurately because no activity coefficients are included, the equilibrium quotient may be used for the following order of magnitude calculation. Using a diffusion constant $k_q \cong 10^{10} M^{-1} s^{-1}$, a donor concentration $(D) \cong 10M$, and an oxygen concentration $(O_2) \cong 10^{-3}\ M$, the change in complex concentration in unit time is $d(C)/dt = k_q(D)(O_2) \cong 10^8$ mole s^{-1}.

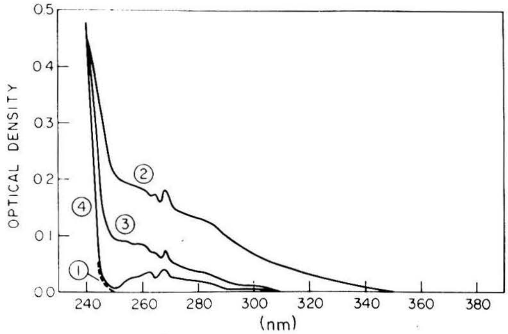

Figure 2. Effect of oxygen on absorption spectrum of 2-ml. TME in 10-ml. cyclohexane at 25°C., pathlength 5 mm.

Curve 1. Degassed initial solution (~10^{-6} torr)
Curve 2. Oxygen saturated solution
Curve 3. Nitrogen flushed solution
Curve 4. Final solution, degassed to ~10^{-6} torr

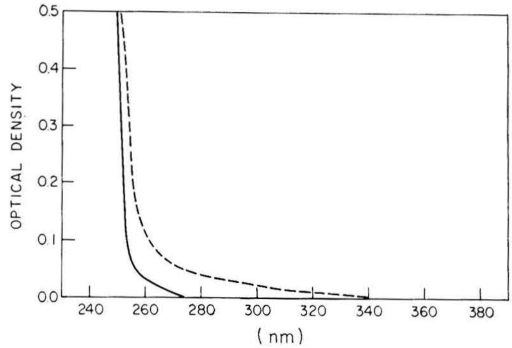

Figure 3. Effect of ethylbromide (2 μl. in 15 ml. TME) on absorption spectrum of degassed TME at 25 °C.

—— neat TME; - - - TME + C_2H_5Br; optical pathlength 5 mm.

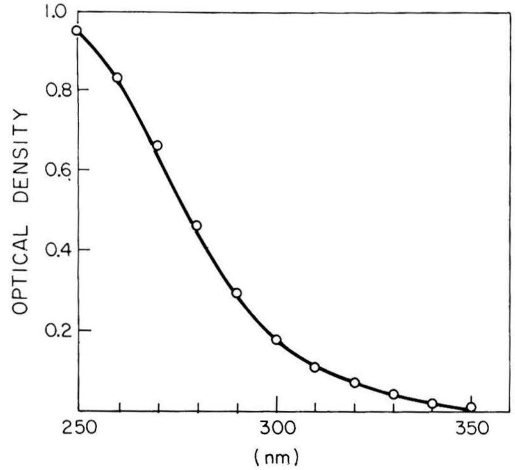

Figure 4. Difference spectrum of TrME/O_2/cyclohexane—TrME/-cyclohexane, [TrME] = 4.5M, pathlength 7 mm.

As the stationary complex concentration is $(C) = A/\epsilon_1 \cong 10^{-2}\ M$ (A = absorbance), one gets a contact time of the collision complex on the order of $10^{-10}\ s$ in good agreement with other estimates (Kearns and Khan, 1968).

Unfortunately, the results obtained in solution cannot be transferred easily and reliably to the gas phase (Mulliken and Person, 1969). Nevertheless, an order of magnitude calculation may be carried out by keeping in mind that the figures may well be off by a factor of 10. Using a gas diffusion constant $k_q \cong 10^{11} M^{-1} s^{-1}$, an equilibrium quotient $Q_c \cong 1$, and a contact time of 10^{-10} sec., a 500-m. layer of 1 p.p.m. polluted atmosphere would absorb 1% of the light at a wavelength where the complex extinction coefficients are $\Sigma_{\epsilon_1} = 20\ M^{-1}$ cm.$^{-1}$ Although these results may quantitatively be subject to a large error, qualitatively they may prove to be very important. Previously, classes of compounds such as olefins and aromatics have been dismissed as being unimportant in environmental systems because they do not absorb in the solar region. Many of these compounds now have to be reconsidered because of the "red" shift in the presence of oxygen.

Table I. Equilibrium Quotient and Extinction Coefficient for the TrME/O_2 complex on the Molal, Mole Fraction, and Molarity Scale (m, x, c)

λ nm.	ϵ_m	ϵ_x	ϵ_c
250	68	74	73
260	59	64	66
270	48	53	55
280	33	38	37
290	21	24	24
300	13	14	14
310	8	9	8
	$Q_m = 0.7$	$Q_x = 8$	$Q_c = 0.85$

Oxygen-enhanced effects on the gas- and liquid-phase uv absorption spectra of olefins and aromatic hydrocarbons of which many have been identified as atmospheric pollutants have been observed by Evans (1953, 1957a,b, 1959), Mulliken and Tsubomura (1960), and others (for references, see Hoijtink, 1969). Examining mixtures of ethylene, benzene, toluene, styrene, m-cresol, naphthalene, phenanthrene, pyrene, benzopyrenes, and anthracene, as well as many other compounds with oxygen at high pressures, Evans assigned this shift to enhancement of the forbidden singlet-triplet transition of the compounds by formation of a collision complex with oxygen (a paramagnetic perturber) and subsequent light absorption. Mulliken and Tsubomura found an increased absorption by simply bubbling oxygen into ethanol, dioxane, n-butylamine, benzene, mesitylene, pyrrole, triethylamine, aniline, N,N-diethylaniline, etc. As their extinction coefficient is about a hundred times stronger than the ϵ of known $T \leftarrow S$ absorptions, they advocate the formation of a contact charge transfer complex between oxygen and the different donors. The enhanced absorption observed in this work is comparable to the one found by Mulliken and Tsubomura, and therefore it is believed that the reversible absorption is due to a charge transfer complex. Furthermore, the unstructured absorption is in favor of such an explanation. The structure which appears near 270 nm. (= 37,000 cm.$^{-1}$) in Figures 1 and 2 must be due to product formation and not to $T \leftarrow S$ absorption because the triplet energy of TME was proposed to lie at 416 nm. (= 24,000 cm.$^{-1}$) by Cundall and Griffiths (1965) and at 340 nm. (= 29,400 cm.$^{-1}$) by Itoh and Mulliken (1969).

Mulliken and Tsubomura (1960) have given a plausible explanation for the intensity of the charge transfer band. As the oxygen-donor pair is a very weak complex or contact pair, the overall state is a triplet state consisting of the singlet ground state of the donor ${}^1D_0$ (TME or TrME) and of the triplet ground state of the acceptor $O_2({}^3D\ldots O_2({}^3\Sigma_g^-)$:

$$ {}^1D_0 + O_2({}^3\Sigma_g^-) \leftrightarrows {}^3[D\ldots O_2({}^3\Sigma_g^-)] \qquad (1) $$

This collision complex may absorb light and transfer an electron to the acceptor, resulting in the formation of a charge transfer complex. This CT state must be either a triplet or singlet as O_2^- and D^+ are both in doublet states.

$$ {}^3[D\ldots O_2({}^3\Sigma_g^-)] \xrightarrow{h\upsilon} {}^3[D^+\text{–}O_2^-] \qquad (2a) $$

$$ {}^3[D\ldots O_2({}^3\Sigma_g^-)] \xrightarrow{h\upsilon} {}^1[D^+\text{–}O_2^-] \qquad (2b) $$

In Reaction 2a, both the ground state and the CT state are triplet spin states that make the transition allowed by spin-conservation laws.

The first excited singlet and triplet state of the donor and the corresponding 1:1 pairs with ground-state oxygen $O_2({}^3\Sigma_g^-)$ are ${}^1D_1$, ${}^3D_1$ and ${}^3G$, ${}^{1,3,5}F$, respectively (Figure 5). The

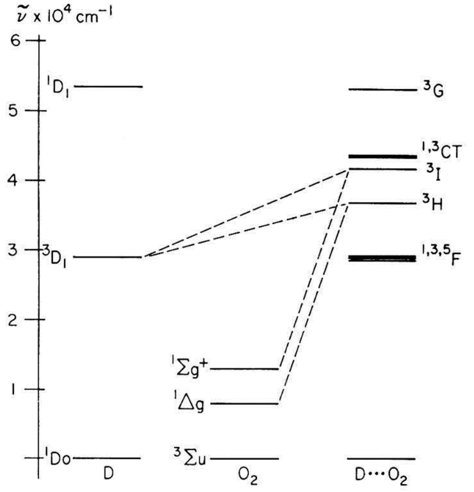

Figure 5. Energy level diagram for a donor, oxygen and their 1:1 contact pair

first excited singlet state $^1D_1$ forms with ground-state $O_2(^3\Sigma_g^-)$ a triplet ^3G, whereas the first excited triplet state $^3D_1$ with O_2 in the ground state can make quintet (^5F), triplet (^3F), and singlet (^1F) states. If 1:1 pairs of triplet donor $^3D_1$ with singlet oxygen in the $^1\Delta_g$ or $^1\Sigma_g$ state are included, two additional levels designated as ^3H and ^3I arise.

The *CT* state may interact with ^3G, borrowing its intensity from the strongly allowed transition between the donor ground state and the donor singlet excited state. In turn, ^3F may interact with ^3CT, therefore, borrowing intensity from the *CT* band and leading to an enhanced $T \leftarrow S$ absorption. Mulliken concluded that a direct interaction between ^3F and ^3G has a much smaller effect on the intensity of the $T \leftarrow S$ band than the interaction between these states through ^3CT. So the observed absorption may be due to an allowed *CT* band, which borrows its intensity mainly from the strongly allowed $^1D_1 \leftarrow {}^1D_0$ transition, and to a much smaller extent to a $T \rightarrow S$ band which is enhanced through this ^3CT state.

If this pathway of internal conversion from ^3G to ^3F via ^3CT is effective, ^3F may fall apart to produce triplet state donor and ground-state molecular oxygen

$$^3F = {}^3[^3D_1 + O_2(^3\Sigma_g^-)] \rightarrow {}^3D_1 + O_2(^3\Sigma_g^-) \qquad (3)$$

Another mechanism may involve the radiationless decay of ^3CT into ^3I and ^3H, respectively, which possibly dissociate to produce $^1O_2(^1\Delta_g/^1\Sigma_g^+)$ plus $^3D_1$

$$^3CT \rightarrow {}^3I \rightarrow {}^3D_1 + {}^1O_2(^1\Sigma_g^+) \qquad (4a)$$

$$^3CT \rightarrow {}^3H \rightarrow {}^3D_1 + O_2(^1\Delta_g) \qquad (4b)$$

Reaction 3 is known to produce singlet molecular oxygen by energy transfer from the triplet donor to ground-state oxygen $O_2(^3\Sigma_g^-)$ (Kautsky mechanism), whereas Reaction 4 produces $O_2(^1\Sigma_g^+, {}^1\Delta_g)$ directly. It has been shown that O_2 $(^1\Delta_g)$ reacts with olefins to produce hydroperoxides which could be identified in the case of TME, the most reactive of the examined olefins.

Thus, in the presence of oxygen, every organic pollutant molecule which has donor qualities is capable of both shifting into and enhancing the absorption within the solar region ($\lambda > 290$ nm.). Consequently, we propose that the oxygen-enhanced absorption of light by organic pollutant molecules is a possible significant source of $^1O_2$ in polluted urban atmospheres. The general mechanism, ignoring reactions that will not give $^1O_2$, is given by Reactions 1 to 4.

There are other observations in the literature which demonstrate the general applicability of this mechanism. Reinisch and Gloria (1968) noted that *in vacuo* the long wavelength limit for photodegradation of PVC was 332 nm., whereas in the presence of oxygen the limit was "red" shifted to 435 nm. Light of the latter wavelength has energy of 65.7 kcal. mole^{-1}, but ~73 kcal. mole^{-1} are required to break the weakest bond in PVC, the secondary C—Cl linkage. PVC is transparent at wavelengths longer than 200 nm., and Reinisch and Gloria established that photodegradation of the polymer between 200 and 332 nm., *in vacuo*, was due to energy transfer to PVC from polyenic impurities. They suspected that photooxidation caused the enhanced rate of degradation in oxygen although the polyenes were transparent above 332 nm. We feel that their surmise was correct and that singlet molecular oxygen had been formed by the oxygen enhanced absorption of the polyenes. Singlet molecular oxygen could then attack and degrade the PVC. Polyenic compounds also occur in biological systems. It is interesting to speculate whether oxygen enhanced absorptions have any bearing on their degradation.

It is possible that this oxygen-enhanced absorption mechanism plays a part in the photoconversion of provitamin D to vitamin D in animal skin (Fieser and Fieser, 1959). 7-Dehydrocholesterol (provitamin D_3) does not absorb radiation of wavelengths longer than 300 nm., while human (Caucasian) skin transmits only ~52% of the incident radiation between 290 and 340 nm. (Thomson, 1955). Leighton (1961) has shown that no solar radiation of wavelengths smaller than 290 nm. reaches the lower atmosphere and that the actinic irradiance below 310 nm. is also small. Thus, the photoconversion of provitamin D_3 to vitamin D_3 apparently occurs in a region where the small amount of solar irradiance is further decreased by the filter effect of human skin. We propose that the presence of oxygen could enhance the charge transfer absorption of 7-dehydrocholesterol with molecular ground-state oxygen. This absorption will be at longer wavelengths where the actinic irradiance of the lower atmosphere is some 20 times greater than at 300 nm. and the conditions for conversion are more favorable.

The "red" shift in the absorption spectra of such differing compounds as ethylene (Evans, 1960a) and mesitylene when oxygen is present has one other very important implication. Previously, many compounds have been dismissed as being unimportant in environmental systems because they do not absorb in the solar region. However, the "red" shift caused by the oxygen enhanced absorption means that many of these compounds do absorb in that region. TME and TrME are examples. Thus, many compounds which were dismissed as unimportant will have to be reconsidered.

Acknowledgment

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COMMUNICATION

Sludge Dewatering by High-Rate Freezing at Small Temperature Differences

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■ When sludge is frozen via the film-freezing principle, the dewatering characteristics are comparable to those obtained with extended freezing, but freezing time and ΔT are greatly reduced. Freezing is complete within 5 min. at $\Delta T = -5\,°\mathrm{C}$. in $^1/_8$-in. sludge canisters with an overall heat transfer coefficient of $U = 29$ Btu/ft.^{2}-hr.-°F. The addition of at least 20 p.p.m. Al [as $Al_2(SO_4)_3$] is necessary for efficient dewatering. The film-freezing principle takes advantage of the high thermal admittance of thin-ice films, so that the controlling heat removal mechanism is the cooling bath stirring rate.

Earlier workers have shown that sewage sludge can be dewatered by freezing, thawing, and filtering with addition of certain chemicals (Bruce, Clements, *et al.*, 1953; Clements, Stephenson, *et al.*, 1950; Katz and Mason, 1970). However, freezing as a means of dewatering does not appear economical, because the long times and high ΔT required would lead to high equipment and operating costs. The present treatment is intended to revive interest in a freeze-dewatering process because a set of operating conditions has been found which combines satisfactory dewatering with economical operation, and recently developed techniques of desalination, some still unpublicized, may permit sludge freeze-dewatering to be conducted at low cost.

A fundamental objection to freeze-dewatering is the apparent need for slow, complete freezing. Clements *et al.* arrived at this conclusion firmly; when sludge was flash frozen at dry-ice temperatures, there was no change in the dewatering properties upon thawing. Their hypothesis was that a network of fine ice crystals had formed and enveloped the colloidal solids, preventing them from coagulation. They also observed that addition of chemicals (especially trivalent ions) enhanced the dewatering effect of freezing very strongly.

In the present investigation, it is postulated that film freezing may permit adequate dewatering within sufficiently short times to make the process economically attractive. One of the present investigators (C.Y.C.) observed that an ice film of small thickness possesses a thermal admittance ($k/\Delta x$) of about 200 Btu/ft.^{2}-°F.-hr. is high enough to permit rapid removal of heat even at small temperature differences. Therefore, it should be possible to freeze sludge within a few minutes at low ΔT levels. The present investigation has been undertaken to study the dewatering characteristics of sludge frozen in this way.

Experimental

Samples of sludge were obtained from the Clear Creek Valley (Colo.) sewage treatment plant, with solids composition as follows:

	%
Primary sludge	2.2
Activated sludge	0.2
Return activated sludge	0.3
Digested sludge	1.6

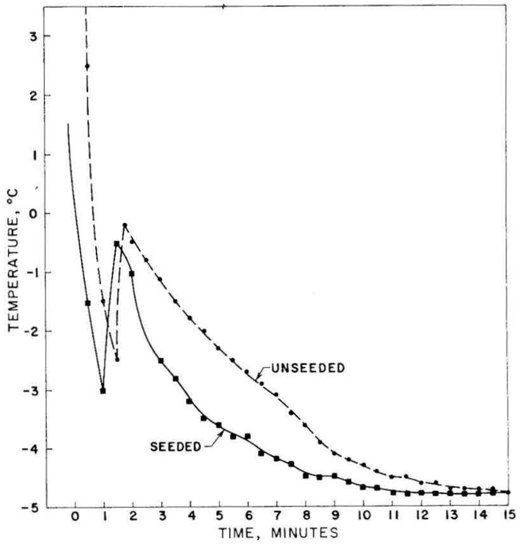

Figure 1. Typical freezing curves for digested sludge in $^1/_4$-in. canisters at the initial rate of cooling bath stirring

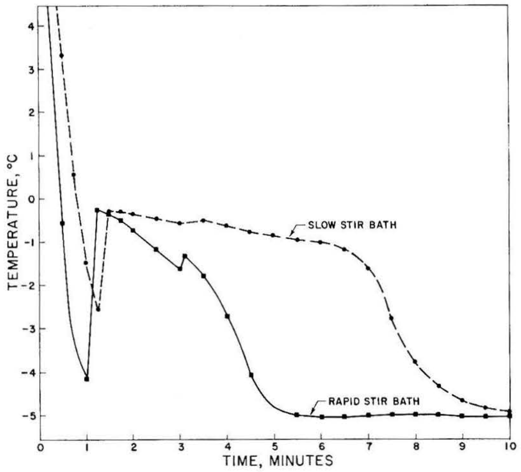

Figure 2. Effect of raising overall heat transfer coefficient from 12 Btu/ft.^{2}-°F.-hr. (upper curve) to 29 (lower curve) by increasing the cooling bath stirring rate

Digested sludge, $^1/_8$-inch canisters

Sludge was frozen in rectangular brass canisters with sides 5 × 6 in.^{2} and either $^1/_4$- or $^1/_8$-in. spacing, holding about 42 or 21 ml. of sludge, respectively. When loaded, the surface for heat transfer was about 290 cm.^{2} Wall thickness of the brass was 0.125 in. For freezing, the canisters were suspended in a stirred, controlled-temperature bath of ethylene glycol. Temperatures were measured by thermistor probes.

Alum was the only chemical added to the sludge. The alum concentrations were chosen the same as those used by previous investigators, so that results could be compared.

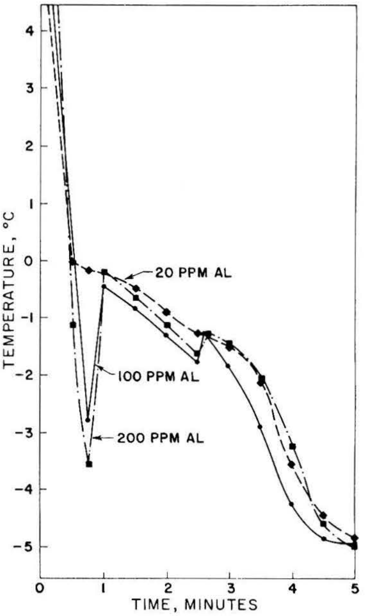

Figure 3. Effect of Al concentration on freezing of digested sludge in $^1/_8$-in. canisters, at the higher rate of cooling bath stirring

Filtration rate was not computed in the present study, since an arbitrary criterion of filtration completeness was employed.

Results and Discussion

Sludge was frozen as described above, employing two rates of stirring of the cooling bath. In the first case, the overall heat transfer coefficient was calculated as $U = 12$ Btu/ft.^{2}-°F.-hr., and the ΔT from bath to sludge was $-3°$ to $-5°$C. The percent content of dry solids after freezing [with addition of 100 p.p.m. Al, as $Al_2(SO_4)_3$], thawing, and filtration was as follows:

	Ambient	$\Delta T =$ $-3°$C.	$\Delta T =$ $-4°$C.	$\Delta T =$ $-5°$C.
Primary sludge	11.7	23.8	20.6	25.0
Activated sludge	23.3	30.1	30.4	27.6
Return activated sludge	14.9	27.9	...	...
Digested sludge	8.9	11.9	21.2	21.1

These results are comparable to those of Clements *et al.* for slow freezing. But typical profiles of temperature *vs.* time (Figure 1) reveal that freezing is complete within 10 min. in the present study.

Without Al addition, the percent dry solids is about half that obtained with Al addition. The ΔT was increased to $-29°$ C. in the case of digested sludge as a check; the percent dry solids then increased to 24.0.

The second set of experiments employed a higher rate of cooling bath stirring, and the heat transfer coefficient rose to 29 Btu/ft.^{2}-°F.-hr. The dry solids content of the filter cake was very similar to that obtained at the lower rate. However, the freezing time is much shorter, as shown in Figure 2. The effect of Al addition is shown in Figure 3. The distinct peak in three curves of these two figures at 2.5 to 3 min. apparently reveals the presence of bound water that is released after the free water has been frozen.

Conclusions

The principal conclusion from these results is that freezing by the film-freezing principle permits efficient dewatering of sludge in short times at low ΔT. The ice film conducts heat sufficiently rapidly that the external heat transfer mechanism controls the process.

Chemical addition is necessary to dewatering by freezing. The effectiveness of the alum addition points to a coagulation phenomenon. There is evidence that the coagulation (or whatever) process releases bound water irreversibly when a certain threshold condition, presumably Al concentration in the supernatant, is achieved.

Finally, it seems clear that sludge dewatering by freezing deserves renewed attention.

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CORRESPONDENCE

Hartley Photolysis of Ozone as a Source of Singlet Oxygen in Polluted Atmospheres

The article by R. H. Kummler, M. H. Bortner and Theodore Baurer on the "Hartley Photolysis of Ozone as a Source of Singlet Oxygen in Polluted Atmospheres" [ENVIRON. SCI. TECHNOL. **3,** 248–50 (1969)], states:

> On p. 249, that "the ozone density is much greater in polluted urban environments than in the upper atmosphere"; and
>
> On p. 250, that the photodissociation of ozone produces singlet oxygen, $O_2(^1\Delta_g)$, whose "reactivity approaches that of O-atoms."

In conjunction with certain other data, the authors seem to regard this as evidence that photolysis of ozone at ground level is sufficient to produce significant quantities of singlet oxygen and that this is a more important oxidizing agent in photochemical smog formation than atomic oxygen.

This appears to be unsupportable for two reasons:

> The fact that the ozone density in urban environments exceeds that in the upper atmosphere only on infrequent occasions and then in only one urban area—Southern California; and
>
> The fact that such concentrations occur in urban environments only in the afternoon *after* the principal photochemical reactions involving hydrocarbons and oxides of nitrogen have taken place. That is, the ozone occurs primarily as a product of these reactions, not an initiator, and so must the singlet oxygen.

For example, to enlarge on the first reason, the ozone concentration in the upper atmosphere exceeds 3 to 5 p.p.m. At the level of ozone maximum (approx. 25 km.), the barometric pressure is about 33 one-thousandths of the ground-level pressure, and the temperature is about minus 53°C. Under these conditions, one mole occupies about 550 liters. One liter at 3 p.p.m., therefore, contains 6×10^{23} molecules $\times\ 3 \times 10^{-6}/550 = 3.3 \times 10^{15}$ molecules of ozone. Similarly, at 5 p.p.m., the ozone density $= 5.5 \times 10^{15}$ molecules/liter. At ground level, if the ozone concentration is 0.1 p.p.m. (a high value for most cities), then the ozone density is 2.45×10^{15} molecules/liter. The conclusion should therefore be that the air aloft is more dense in the number of ozone molecules than at ground level.

The single exception to this conclusion occurs in Los Angeles, only after the photochemical smog-forming reactions have proceeded almost to completion and the NO_2 concentration begins to decline, and only on those days when the temperature inversion has remained low all day. This inversion allows the ozone to accumulate. When the ground-level concentration reaches 0.15 p.p.m. by volume, it is about the same as that of the upper air, and only when it reaches or exceeds 0.25 p.p.m. does the ozone density of the ground-level concentration exceed that of the upper atmosphere.

Further, in support of the second reason cited above, elevated concentrations of ozone occur only in the afternoon. If singlet oxygen—or any less usual form of oxygen molecule, such as atomic oxygen or ozone—is to be important in the photochemical reactions, it must be there in quantity in the early morning. This is the time of initiation of such reactions involving oxygen atoms from the dissociation of NO_2 and hydrocarbons, especially those termed "reactive" such as olefins and such substituted aromatic compounds as xylenes. At this time of day, the ozone concentration is so low it is not measurable. Since the significant production of $O_2(^1\Delta_g)$ is dependent upon the presence of relatively high concentrations of ozone, the concentration of $O_2(^1\Delta_g)$ at that time of day must be so vanishingly low as to be nonexistent.

The most commonly accepted interpretation of the sequence of photochemical smog-forming reactions involves, first, the conversion of NO to NO_2 followed by the photodissociation of NO_2 to produce atomic oxygen. In the competition for oxygen atoms then taking place among oxygen molecules, nitric oxide, and hydrocarbons, the last named appeared to be favored. This is illustrated by the fact that introduction of such compounds, especially the more reactive types, accelerates the conversion of NO to NO_2 to a rate which is fantastic compared with that of the usual three-body reaction of $2NO + O_2 \rightarrow 2NO_2$. How this occurs is not clearly understood, but it is known that:

> It occurs at very low ozone concentrations.
>
> It occurs, therefore, at very, very low $O_2(^1\Delta_g)$ concentrations.

The *rate* at which oxygen atoms are produced is maximized at maximum NO_2 concentration in sunlight. This occurs at or just prior to the complete disappearance of nitric oxide concentrations.

Ozone does not accumulate (increase in concentration) until after NO_2 reacts or decreases. It accumulates only when NO is not available to scavenge it.

Most of the more reactive hydrocarbons have disappeared in reactions prior to the time either O_3 maximizes or $O_2(^1\Delta_g)$ can be formed in quantity from O_3; only the slow or relatively slow reactors such as paraffins, and ethylene because of its relatively high concentration, remain.

Oxygen atom concentration should maximize after the time of maximum rate of production of oxygen atoms—*i.e.*, sometime after the NO_2 maximum concentration. This may be prior to the ozone maximum or at about the same time as the ozone maximum.

$O_2(^1\Delta_g)$ concentration should maximize after the O_3 maximum concentration and must be much less in concentration if it depends upon the photolysis of ozone. Kummler, Bortner, *et al.* (p. 249) indicate this to be true

$$\frac{O_2(^1\Delta_g)}{O_3} = (1\text{–}12) \times 10^{-6}$$

By the time O_3 maximizes, eye irritation has become strong, plant damaging agents are already forming, and visibility reduction has occurred.

The question then is: Where lies the importance of singlet oxygen from the dissociation of ozone in the smog or air pollution problem? Pitts' suggestion that a complex organic donor molecule in the triplet state is transformed and the energy is transferred to oxygen molecules, seems to be more reasonable and has greater possibility of being important than the photodissociation of ozone in the photochemical smog problem, but it is so far unsubstantiated by any evidence that this occurs in Los Angeles air.

The relative importance of oxygen atoms, ozone and singlet oxygen molecules from photodissociation of ozone is shown in the following schematic equations:

$$NO + O_2 + NO \rightarrow N_2O_4 \leftrightarrows 2NO_2 \qquad (1)$$

$$NO_2 + h\nu \rightarrow NO + O \qquad (2)$$

$$\left[\,O\,\right]\begin{array}{lll} + O_2 + M \rightarrow O_3 & & (3a) \\ + (HC)_R \rightarrow [HCO^{\cdot}] & \left\{\begin{array}{l}\text{Important and increases} \\ \text{fast in importance as} \\ \text{the reactivity of } HC \text{ is} \\ \text{increased.}\end{array}\right. & (3b) \end{array}$$

$$\left[\,O_3\,\right]\begin{array}{lll} + NO \rightarrow NO_2 + O_2 & \left\{\begin{array}{l}\text{NO keeps } O_3 \text{ from} \\ \text{accumulating.}\end{array}\right. & (4a) \\ + (HC)_R \rightarrow [HCO_3] & \left\{\begin{array}{l}\text{Important and in-} \\ \text{creases slowly in im-} \\ \text{portance as the ``reac-} \\ \text{tivity'' of } HC \text{ is in-} \\ \text{creased.}\end{array}\right. & (4b) \\ + h\nu \rightarrow O_2(^1\Delta_g) & \left\{\begin{array}{l}\text{Cannot become im-} \\ \text{portant until } O_3 \text{ in-} \\ \text{creases or maximizes} \\ \text{which must occur after} \\ \text{NO disappears.}\end{array}\right. & (4c) \end{array}$$

If any importance can be attached to singlet oxygen from the photodissociation of ozone, it might be in one or both of the following ways:

That it puts an upper limit on ozone concentration since the higher the concentration, the more light can be absorbed, which reduces the ozone concentration by forming singlet oxygen molecules.

That it changes slightly the number of oxygen atoms in the organic products of photochemical oxidation of hydrocarbons; say, from 3 to 2.

We must conclude, therefore, that the importance of singlet oxygen from O_3 photodissociation cannot compete with that of atomic oxygen in the photochemical smog process, especially during the morning hours when the photochemical reactions are really just getting started, and neither ozone nor singlet oxygen are present in measurable quantities.

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As in our previous article on this subject (Kummler, Bortner, *et al.*, 1969), we will confine our remarks to the Los Angeles area for which the availability of solar flux data (Nader, 1967) enables us to present our calculations on a quantitative basis. In an environment like the L.A. area, the ozone concentration at noon typically exceeds 20 p.p.hm. (*e.g.*, Stern, 1968; State of California, 1966) or a number density of over 4.9×10^{15}/liter. For comparison, Bortner and Kummler (1968) reviewed the composition of the minor constituents in the upper atmosphere. They concluded on the basis of experimental data (Johnson, Purcell, *et al.* 1952; Miller and Stewart, 1956; Horton and Burger, 1966) that a typical maximum ozone concentration at about 30 km. is 3×10^{15} molecules/liter. This unique situation applies only to Los Angeles, and only during late summer or early fall, the "smog season," which is the season of concern to us as the pertinent solar flux data were taken from Oct. 6–20, 1965. In other cities and in clean air, an ozone maximum in vertical profile does not occur near ground level. At no location, however, may conclusions regarding the importance of particular mechanisms be made on the basis of the absolute ozone concentration. Rather, the relative ozone content of the air is the important parameter. In this discussion, the ratio of ozone to atomic oxygen densities should be the focal point. The reactions for the definition of this ratio are

$$NO_2 + h\nu \rightarrow NO + O \qquad (1)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$

$$NO_2 + O_3 \rightarrow NO_2 + O_2 \qquad (3)$$

Reactions of O with hydrocarbons are several orders of magnitude slower than the ozone formation by Reaction 2 and play no significant role in determining the O-atom concentration (Leighton, 1961). Similarly, the steady-state ozone concentration is determined by Reactions 2 and 3. Reactions of the hydroxyl radical (Heicklen, 1969) cause slow changes in the cyclic relationship above, but at any given time the O and O_3 steady-state concentrations should be excellent approximations to the actual case

$$(O)_{ss} = \frac{k_1(NO_2)}{k_2(O_2)(M)} \tag{4}$$

$$(O_3)_{ss} = \frac{k_2(O)(O_2)(M)}{k_3(NO)} = \frac{k_1(NO_2)}{k_3(NO)} \tag{5}$$

Hence,

$$(O_3)_{ss}/(O)_{ss} = \frac{k_2(O_2)(M)}{k_3(NO)} \tag{6}$$

Thus, a mechanism dependent on ozone tends to be more important than an O-atom mechanism in regions of low NO concentration—*i.e.*, in "clean" air or in smaller and meteorologically favored cities, even though the absolute ozone concentration there is relatively lower than that in Los Angeles. Thus, the work of Kummler, Bortner, *et al.* (1969) applies more strongly out of Los Angeles than in all other parameters assumed constant. This was not previously noted.

Since the rate constants k_2 and k_3 are well established (DASA Reaction Rate Handbook, 1968), the time-dependent ratio of $(O_3)_{ss}/(O)_{ss}$ may be readily calculated from knowledge of the diurnal behavior of the NO concentration by substitution into Equation 6,

$$\frac{(O_3)_{ss}}{(O)_{ss}} = \frac{2.3 \times 10^6}{(NO)} \tag{7}$$

where the NO concentration is in p.p.hm. This relationship is especially useful near the NO peak concentrations, when the ozone concentration, even though undetectable by presently employed instruments, is by no means unimportant. The e-folding time constant for the achievement of a steady state in atomic oxygen is very nearly constant (14 μsec.). Thus, for all practical purposes, the O-atom peak coincides with the NO_2 peak. The ozone steady state is achieved more slowly, but even at an NO concentration of 1 p.p.hm., the steady-state assumption should be valid after 1 min, based on Reaction 3. At the NO_2 peak, the NO concentration (Stern, 1968; State of California, 1966) is typically 1 p.p.hm., and in Los Angeles this occurs at about 8 to 9 a.m. At this time, the solar flux in the wavelength region of interest is about one-third that at noon. Therefore, the rate constant for the production of $O_2(^1\Delta_g)$ by Hartley photolysis of ozone should be decreased by one-third (Kummler, Bortner, *et al.*, 1969).

The recent, more accurate $O_2(^1\Delta_g)$ quenching data of Clark and Wayne (1969), indicate a lower effective lifetime of $O_2(^1\Delta_g)$ (0.088 sec.) at ground level than that previously employed. Thus the ratio of $O_2(^1\Delta_g)$ to O_3, based on the conditions of Table I in Kummler, Bortner, *et al.* (1969) will range from 8×10^{-8} to 6×10^{-7} at the early morning NO_2 peak. This implies a $[O_2(^1\Delta_g)]_{ss}/[O]_{ss}$ ratio of from 0.2 to 1.4 at the peak O-atom concentration. At any later time, the $O_2(^1\Delta_g)$ produced by Hartley photolysis alone will exceed the O concentration. Then even at 8:30 a.m. PDST, the presence of $O_2(^1\Delta_g)$ is as real as that of O-atoms, although neither is present in measurable quantities. Hence, little insight into the importance of $O_2(^1\Delta_g)$ is to be gained from a study of the diurnal variations of smog formation alone.

Of greater significance is the recent work of Herron and Huie (1969), in which the rate of constants for $O_2(^1\Delta_g)$ reactions with several hydrocarbons relative to that with tetramethylethylene (TME) (1.0) were obtained as: 2,3 dimethyl-2-pentene, (0.7); 1-methylcyclopentene, (0.015); 1,2 dimethylcyclopentene, (0.4); 1,2 dimethylcyclohexene, (0.9). These rate constants were compared to the absolute TME value of $k_{TME} = (1.0 \pm 0.3) \times 10^9$ cm.^{3} mole^{-1} sec.$^{-1}$, which places the $O_2(^1\Delta_g)$ reactivity at less than 1/1000 of the O-atom reactivity. For this reason the Hartley photolysis will not generate enough singlet oxygen to make $O_2(^1\Delta_g)$ generally important in the photochemistry of air pollution.

However, the Hartley photolysis of ozone is not the only mechanism for $O_2(^1\Delta_g)$ production in urban atmospheres. Kummler and Bortner (1969) have verified the energy transfer mechanism originally suggested by Khan, Pitts, *et al.* (1967), as have Snelling (1968), Star, Sprung, *et al.* (1969), and others. This mechanism, if it proceeds with unit quantum yield, according to Pitts, Khan, *et al.* (1969), would produce nearly 1000 times as much $O_2(^1\Delta_g)$ as would the Hartley photolysis. Chemiexcitation, particularly via the O_3 reaction with organics noted by Murray (1970), might also produce 1000 times as much as ozone photolysis (Kummler and Bortner, 1970). Hence the criterion of Herron and Huie (1969), for $O_2(^1\Delta_g)$ importance may still be met.

Both O_2^* and O will produce the radicals—*e.g.*, *R*CO or OH—necessary to convert NO to NO_2 (Altshuller and Bufalini, 1965), perhaps via the mechanism suggested by Heicklen (1969)

$$OH + CO \rightarrow CO_2 + H \tag{8}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{9}$$

$$HO_2 + NO \rightarrow NO_2 + OH \tag{10}$$

Before making a final decision on the importance of $O_2(^1\Delta_g)$, its concentration in urban atmospheres must be measured to ascertain whether the ratio of $O_2(^1\Delta_g)$ to O will be greater than that required by the data of Herron and Huie (1969).

Quite recently, Herron and Huie (1970) have reiterated the contention that, based on the relative concentrations of O and $O_2(^1\Delta_g)$ listed by us (Kummler, Bortner, *et al.*, 1969), the reactions of $O_2(^1\Delta_g)$ with hydrocarbons of interest (Herron and Huie, 1969) are of relatively minor importance. However, we would again point out that the $O_2(^1\Delta_g)$ concentration cited by Kummler, Bortner, *et al.* (1969) was designated specifically as a minimum value, based only on the Hartley photolysis of ozone as a generating mechanism, and subject to significant enhancement by other mechanisms (Pitts, Khan, *et al.*,1969).

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CORRECTION

SPECTROPHOTOMETRIC DETERMINATION OF ATMOSPHERIC FLUORIDES

In this article by P. W. West, G. R. Lyles, and J. L. Miller [ENVIRON. SCI. TECHNOL. **4,** 487 (1970)], paragraph 4, page 489, should read as follows:

> Lanthanum nitrate buffer ($2 \times 10^{-3}M$). Dissolve 0.866 g. $La(NO_3)_3 \cdot 6H_2O$ and 102 g. NaOAc (anhy) in 250 ml. H_2O. The pH of this solution, when diluted 1:10, and containing acetone to the extent of 25% (v./v.) (see Sampling Technique), should be 4.1 to 4.2.

Coastal Services (Braintree, Mass.), a division of Ocean World Corp., has acquired the Chem-Kleen Co. (Rahway, N.J.), a company specializing in the maintenance of tanks used for petroleum and chemical product storage. Coastal Services is in the oil pollution control business and the acquisition will enable it to introduce services in the New York City area.

Chemical Separations Corp. (Oak Ridge, Tenn.) has been awarded a contract by the Office of Saline Water to construct a plant for removal of minerals from seawater prior to desalination. The company's technology is capable of removing 65 to 95% of the calcium and 30 to 45% of the magnesium, thus greatly reducing scale problems in desalination equipment. The plant will be built at Freeport, Tex., and is due on stream in late 1970.

Resource Management Corp. (Bethesda, Md.), under a contract with the federal Bureau of Solid Wastes Management, will study costs connected with littering and ways to combat it. The company will specifically look for areas of future research that promise the best chances for progress.

Pollution Control, Inc. (Birmingham, Ala.) has been established as an independent consulting and engineering service. The company will concentrate initially on the performance and analysis of field tests on gas and particle emission rates, and on providing complete gaseous emission studies. Currently, studies are under way in Tennessee.

Wellman-Lord, Inc. (Lakeland, Fla.) has announced successful operation of the SO_2 recovery unit installed at Olin Corp.'s sulfuric acid plant (Paulsboro, N.J.). W-L claims the unit has been in continuous operation since July 1970, and has recovered SO_2 in more than design amounts. The process involves absorption of SO_2, SO_3, and fly ash (if present) in a sodium sulfite solution. The company guarantees more than 90% removal.

Chemical Construction Co. has received a $4 million contract to design and install a pollution control system for a new steam-generating unit of Pacific Power and Light Co. at Glenrock, Wyo. Three venturi scrubbers on the unit will remove fly ash from stack gases at 99.8% efficiency. The system is said to have built-in capability for SO_2 removal, if later required.

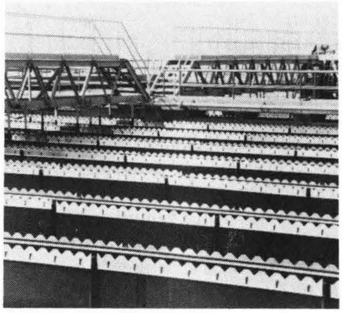
Aerojet-General Corp. has further expanded its activities in the water desalting field by forming a new company called Envirogenics Co. Envirogenics will market evaporation plants, reverse osmosis systems, and cryogenic storage facilities for natural gas. Aerojet says the new company already has a backlog of $45 million.

J. F. Pritchard & Co. (Kansas City, Mo.) is offering a recently developed process for removing SO_2 from the discharged gases of Claus-type sulfur plants. Pritchard says the process should result in 99%+ removal for most new or existing plants. The company developed the process jointly with Texas Gulf Sulphur Co., The British Gas Council, and The North Western Gas Board.

Enviro Control Inc., a partly owned subsidiary of Diversified Computer and Management Services, Inc., has been established in Washington, D.C. Enviro will market a line of water pollution control instruments, assist companies to identify and recover valuable by-products, and undertake planning and management studies for regulatory authorities. The company's first product, to be marketed within seven months, is a compact instrument package for use on industrial waste streams.

Research-Cottrell, Inc. (Bound Brook, N.J.) has been awarded a contract for two incinerator pollution control systems by Combustion Engineering, Inc. The systems, which consist of a cooling tower and electrostatic precipitator, will be installed on two 72-ton-per-day incinerators in Reading, Mass. R-C guarantees 96.5% collection efficiency for these units.

new products



Stainless weirs

Weirs, made of thin-gauge, Type 304 stainless steel, can be used for years in the water treatment plant with minimum care or cleaning. The weirs can be fabricated with a brake-formed edge that adds to the rigidity of the thin-gauge sections. Because thin gauges are used, stainless steel weirs are economically competitive with weirs made of other materials. Because stainless steel resists corrosion and the accumulation of water-borne deposits, weir maintenance is negligible. Basford Inc. **61**

Flammable gas detection

Model FFA is designed for the detection of flammable vapors that have characteristics which make conventional instrumentation unreliable or inoperative. This unit is recommended for the protection of solvent dryers when silicones are utilized in the product or in applications where long-term stability and reliability warrant the additional initial investment. Control Instruments Inc. **62**

Pesticide pollution reduction

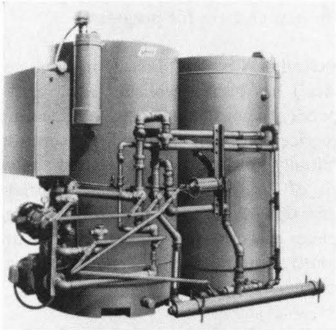
Nu-Film-17, containing Pinolene, a film-forming compound, can be sprayed in combination with various pesticides and markedly reduces pesticide pollution in the environment. The film incapsulates the pesticide and holds it tenaciously to the crop foliage or target area of the spray application. Because of the film's waterproof nature, it holds the pesticide deposit on this target area and keeps it from being washed off by rain. The pesticide is held in place on the plant foliage until it has been completely degraded, thus rendering it inactive and harmless. The Nu-Film-17 film is broken down by natural weathering and disappears after being completely degraded. Miller Chemical & Fertilizer Corp. **63**

Computation service

To assist designers of waste gas and liquid incinerators and other combustion equipment, a new computation service predicts the equilibrium and nonequilibrium products of combustion of completely arbitrary mixtures of waste gases, fuels, and oxidizers with use of a generalized thermochemistry computer program. Quantitative evaluations of nearly 100 species are obtained including such common pollutants as NO, NO_2, and SO_2. Aerotherm Corp. **64**

Sulfur gas chromatography

Model 1490-5, a sophisticated gas chromatograph for the most advanced air pollution studies, was developed specifically for determining sulfur gas in low ppb concentrations. The instrument can identify all sulfur gases, not merely SO_2. Varian Aerograph **65**



Pilot waste treatment

This scaled-down biological waste treatment plant consists of primary and secondary clarifiers, flow-through aeration tanks, and positive displacement pumps to handle waste water, sludge return, and wasting. The 240 gpd plant provides 6-hr aeration and 2-hr settling. Oxygen transfer efficiencies approach full-scale plant levels. Biospherics Inc. **66**

Evaporative coolers

A complete line of custom-designed evaporative coolers are used to reduce gas temperatures prior to an air pollution control device such as an electrostatic precipitator or a baghouse. Among the available options are sonic atomizers used to create the fine fog of water necessary for optimum operation of evaporative coolers. Standard Havens Systems **67**

Solid waste incinerator

The Mark VI Radicator is the first controlled air solid waste incinerator to meet Department of Health, Education, and Welfare (HEW) standards for emission of air pollutants at its rated capacity. Tests were conducted with the unit charged at rates above its normal capacity of 600 lb per hour, with results still lower than the HEW standards. Midland-Ross Corp. **68**

Effluent filter

Aero jet filter systems treat secondary sewage treatment plant effluent providing phosphate reduction, BOD reduction, and suspended solids reduction. This filter provides aeration, chemical mixing, precipitation, coagulation, flocculation, filtration, and upflow clarification. New plant installations have shown phosphate reduction of 97 to 98%. Jetflo Systems **69**

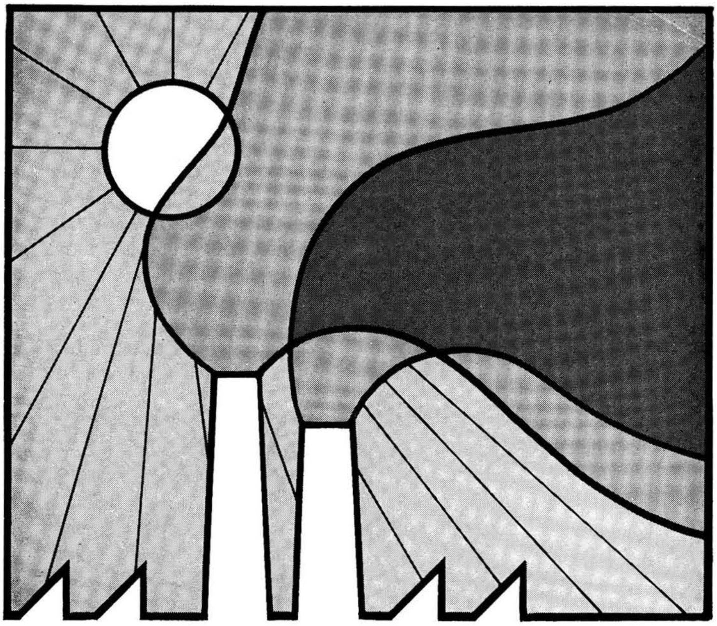
Smog collector

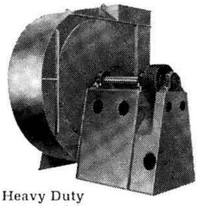
Polycomplex R, when sprayed into smog-laden air, rapidly absorbs the dirt particles, sulfur dioxide, and other acid gases, and then precipitates in the form of a fine rain, with the particles and gases securely blocked in the droplets. By absorbing water in the air, the droplets become larger until they settle as rain. A single treatment can reduce the particulate matter more than 60% and acid content of the air by more than 75%. Guardian Chemical Corp. **70**

Water pollution indicator

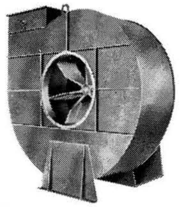
The Quick Microbial Indicator and Quantifier can quickly determine whether estuarine water is likely to be polluted from human sources. This O/SD biological water pollution indicator uses the fungus *Candida albicans* as the indicating organism. Offshore/Sea Development Corp. **71**

(*continued on page 1154*)

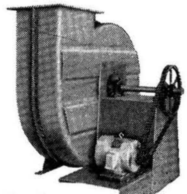




Heavy Duty Industrial Fans



Alloy Fans

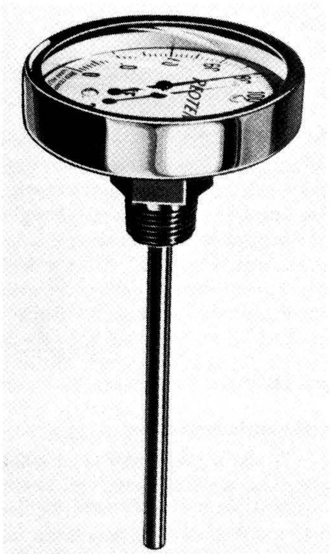


Fiberglass Fans

(*continued from page 1153*)

Pollution sterilization

A new system has been introduced for the sterilization of polluted liquids through the utilization of ultraviolet radiation and ozone. The equipment involved in the system is designed to generate an unsupported thin film of the liquid to be treated which cascades past a cluster of high-intensity lamps in the form of a corona. The liquid does not contact the lamps which would impair the process of irradiation. The thin film of liquid is precisely controlled by an annular nozzle diffuser which retains the shape of the corona in spite of pressure fluctuations. Performance tests indicate the capability of the system to devitalize pathogenic organisms besides reducing BOD, COD, and dissolved solids. Pure Water Systems, Inc. **72**



Thermometer

The Reotemp dial thermometer can be found in oil refineries, chemical plants, steam generators, pulp mills, and water and waste works. Used where heat measurement is a requirement, the Reotemp is available in a range of Fahrenheit or Centigrade scales. Reotemp Instrument Co. **73**

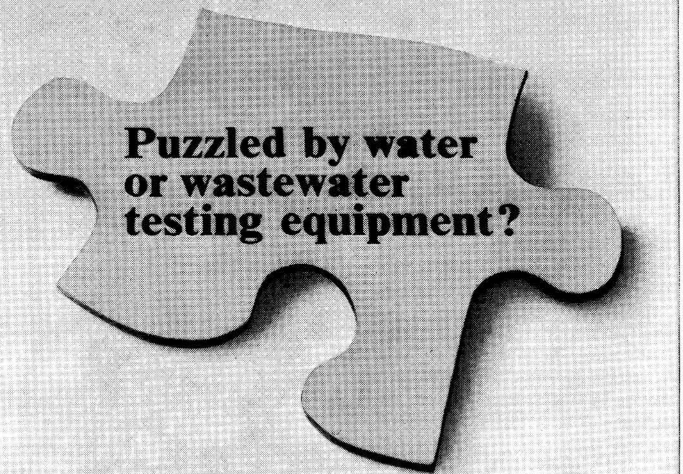
CO detector

Model 1004-AR has an instrument span of 100 ppm, which means measurement of carbon dioxide in the air of 10 ppm or less. Since the unit is strictly selective to CO, hydrocarbons, sulfur compounds, and other gases or vapors do not affect the reading. Ambient temperature operating range is −20° to +140°F. Devco Engineering, Inc. **74**

Noise abatement

Perma-HUSH is a muffler for reducing the noise of escaping compressed air from compressors, cylinders, air motors and tools, instrumentation and relief valves, etc. Constructed of aluminum pellets and glass beads under a sound-deadening process, Perma-HUSH features no cartridge replacement, its compact size, corrosion resistance, and high noise reduction. Permafilter **75**

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.



new literature

Mn indicator. The brochure "Mn Indicator and Test Papers" covers test papers for pH determination, cation and anion detection, and nondestructive determination of some alloy compositions, as well as a wide range of reagent test papers for the detection of numerous other substances. Gallard-Schlesinger Chemical Mfg. Corp. **91**

Fume washers. Bulletin describes a new series of Unitized Fume Washers for removal of entrained liquid particles from industrial exhaust air streams. Provides detailed data on units in 2000-, 4000-, and 8000-cfm sizes and their application in metal finishing and other industrial operations. Complete specifications, performance data, and dimensions are provided. The Ceilcote Co. **92**

Sludge treatment process. An eight-page brochure describes rapid chemical oxidation of sludge in municipal and industrial waste water treatment systems. The process stabilizes and coagulates sludge in a single cycle, requiring only a few minutes with no pretreatment beyond the usual removal of gross debris and the breaking up of larger solids. BIF Purifax, Inc. **93**

Tilted plate separators. Bulletin contains a detailed description of the Tilted Plate Separators (TPS), which eliminate pollutants from the waste water of such industrial plants as oil refineries, chemical processing plants, starch manufacturing plants, paper mills, sugar mills, etc. The TPS is inexpensive, requires no power for operation, has no maintenance because it has no moving parts, and requires very little space. The Pielkenroad Separator Co. **94**

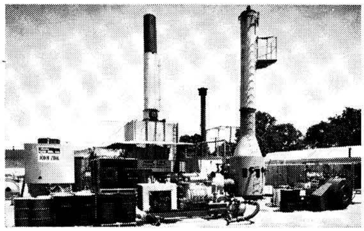
Noise suppression. Publication details how air-stream noise from a giant electric power plant was reduced from a roar to a whisper. Description covers the entire noise attenuating plan in a problem-solution-results format. The IAC Power-FLOW silencing system was designed to be compatible with the general plant architecture and to reduce noise with a minimum pressure drop in air flow to the forced-draft fans that furnish combustion air to two 450-mW units. Industrial Acoustics Co. **95**

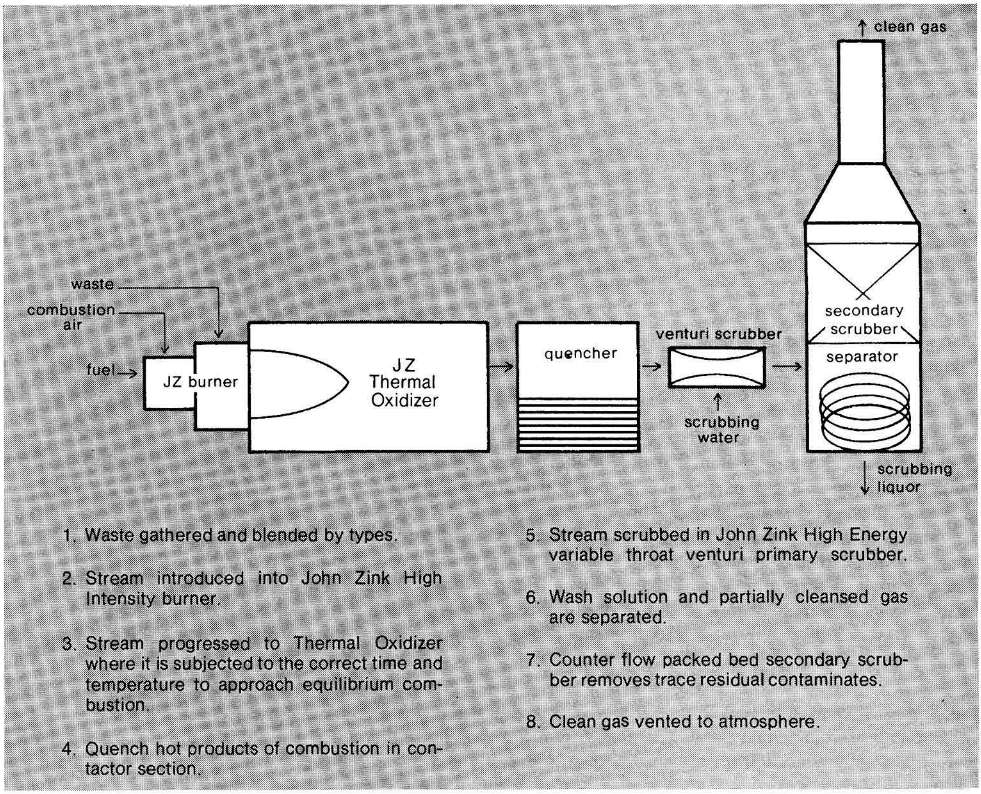
Clean water. Eight-page brochure details how the Pamispa Process, developed for the pulp and paper industries, can provide the most economical means for solving water pollution problems. The services include pilot studies, water profiles, water analysis, reports for regulatory agencies, process engineering, and start-up services required for the installation of the Pamispa Process. Clarcom, Inc. **96**

Flow meters. Brochure describes Model 61 Total Flow Meters housed in high-impact Cycolac plastic cases and neoprene-gasketed covers to provide protection against moisture and dust. These meters are used for measuring flow rates and totalizing volume in open channels as well as converting water-level measurements to flow data for continuous indication or graphic strip-chart record. The instruments will operate from flows as low as 14,000 gpd up to several hundred million gpd. Leupold & Stevens, Inc. **97**

Pollution control engineering. Brochure outlines AESCO's capabilities in a complete water and air pollution control consulting engineering service. All phases of consultation are available, from feasibility laboratory budget studies to detailed specification writing and start-up services. American Environmental Systems Co. **98**

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.





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Proceedings Workshop on Mosquito Control in North Carolina. viii + 144 pages. Water Resources Research Institute of the University of North Carolina, 124 Riddick Bldg., N.C. State University, Raleigh, N.C. 27607. 1970. Gratis, paper.

The proceedings of the workshop present an assessment of mosquito control technology and public and private control programs with a discussion of water resource management and ecological implications. Discussions dealt with the transition away from persistent pesticides and minimization of other forms of ecological impact. ■

No Deposit–No Return: Man and His Environment: A View toward Survival. Huey D. Johnson, Ed. xvi + 351 pages. Addison-Wesley Publishing Co., Inc., Reading, Mass. 01836. 1970. $2.95, paper.

This primer for environmental awareness is meant for all concerned citizens, not just students. It could be used as a text in interdisciplinary courses treating the wide spectrum of man and his environment, and for supplementary use in introductory nonmajor biology courses. ■

Preliminary Air Pollution Survey of Asbestos. xi + 94 pages. U.S. Department of Commerce, National Bureau of Standards, Clearinghouse for Federal Scientific and Technical Information, Springfield, Va. 22151. 1969. $3.00, paper.

This document, a preliminary review on asbestos, is being used as a basis for further evaluation both internally by the National Air Pollution Control Administration and externally by contractors. These reports can be significant to air pollution control officials, whether state or local, as a library of information on which to base informed decisions on the control of pollutants in their geographic regions. Also, these reports may stimulate scientific research and provide information for interested citizens. ■

Developments in Water Quality Research. Hillel I. Shuval, Ed. xiv + 312 pages. Ann Arbor-Humphrey Science Publishers, Inc., Drawer No. 1425, Ann Arbor, Mich. 48106. 1970. $17.50, hard cover.

This book contains the proceedings of the Jerusalem International Conference on Water Quality and Pollution research. This conference provided an international forum for reviewing some acute problems concerning water and its use. The papers published are grouped into three categories—water quality management, waste water treatment and utilization, and marine pollution. ■

Concepts of Pest Management. R. L. Rabb and F. E. Guthrie, Eds. xi + 242 pages. North Carolina State University at Raleigh, Department of Entomology, Box 5215, Raleigh, N.C. 27607. 1970. $4.00, paper.

"This book (proceedings of a conference held in March) is a major step in devising ecologically sound and environmentally compatible pest control programs," says editor Guthrie. Editor Rabb says, "Pest control is directly relevant to two of the world's most pressing problems: population expansion and pollution." ■

Surfactant Biodegradation. R. D. Swisher. xxiii + 496 pages. Marcel Dekker, Inc., 95 Madison Ave., New York, N.Y. 10016. 1970. $33.50, hard cover.

This book presents the theory and practice of biodegradation studies as they were applied to the waste surfactant problem. It details the state of knowledge, as of mid-1969, concerning biodegradable surfactants. Indicated by the increasing masses of foam wherever sewage entered the environment, the waste surfactant problem is one small part of the world's growing pollution problem. The book is useful to scientists and research workers in the fields of surfactants and detergents, as well as in many areas of pollution control. ■

Meteorological Aspects of Air Pollution. v + 69 pages. Unipub, Inc., P.O. Box 433, New York, N.Y. 10016. 1970. $4.50, paper.

This publication contains the full texts of three papers which were presented during the scientific discussions at the 1969 annual session of the World Meteorological Organization. Devoted to the meteorological aspects of atmospheric pollution, these papers represent the latest information on the meteorological aspects of both high- and low-concentration atmospheric pollution. ■

The Human Environment and Business. Henry Ford II. 63 pages. Weybright and Talley, Inc., 750 Third Ave., New York, N.Y. 10017. 1970. $3.50, hard cover.

Three essays written by Mr. Ford consist of "verbal bluntness and practical boldness," says Kingman Brewster, Jr., president of Yale University. The first talk is a "hard-headed analysis of the options which are open to the young." The second reaffirms the "value and essentiality of the profit motive if private business is to do its job in the public interest." The third presents the demands of society and the natural environment upon private enterprise while also accepting the inevitable role of government. ■

Man and His Environment. Sidney Dorros, Ed. 56 pages. Publications-Sales Section, National Education Association, 2101 Sixteenth St., N.W., Washington, D.C. 20036. 1970. $1.75, paper.

This booklet presents an interdisciplinary approach to environmental education. Intended to help teachers expand their classrooms to include all of man's environment, this booklet uses five concepts of the environment—variety and similarities, patterns, interaction and interdependence, continuity and change, and adaption and evolution. ■

Proceedings of the Symposium on Respirable Coal Mine Dust. 297 pages. Superintendent of Documents, Government Printing Office, Washington, D.C. 20402. 1970. $2.25, paper.

This symposium dealt with the various engineering methods of controlling dust in underground coal mines, including ventilation, water suppression, machine design, dust collection, and respirators and life-support systems. The merits of these procedures and their potential application to underground coal mining were examined. ■

meeting guide

December 28
American Association for the Advancement of Science

137th Annual Meeting and Symposium

Chicago, Ill.

The symposium "Industrial Approaches to Urban Problems" will explore the human and technical problems a city faces in the pursuit of improved urban housing, solid waste management, education, and transportation. Each subject will be examined by a panel of experts from government and industry. Write: American Association for the Advancement of Science, 1515 Massachusetts Ave., N.W., Washington, D.C. 20005

January 25-28
Louisiana State University

LSU Symposium on Air Pollution

Baton Rouge, La.

The theme "Air Pollution and Its Problems" is to be discussed by NAPCA and other government officials, as well as representatives from universities and research institutions. Fee: $15. Contact: Dr. J. W. Robinson, Department of Chemistry, Louisiana State University, Baton Rouge, La. 70803

January 28-30
The University of Wisconsin—Green Bay College of Community Sciences, and the Bureau of Community Environmental Management of USPHS

Conference on the Ecology of Human Living Environments

Green Bay, Wis.

Meeting deals with the assumption that the human habitat profoundly influences human behavior—that an individual's behavior often depends on the surroundings in which he lives, works, studies, and socializes. Contact: William M. Smith, College of Community Sciences, The University of Wisconsin—Green Bay, Green Bay, Wis. 54302

February 3-5
American Chemical Society

Sixth Middle Atlantic Regional Meeting

Baltimore, Md.

A Division of Environmental Chemistry will be included in the program. More than 18 symposia are scheduled, and there are over 51 exhibit booths planned. Contact: Donald E. Jones, General Chairman, Western Maryland College, Westminster, Md. 21157

February 15 and 16
Illinois Environmental Protection Agency, and the Department of Civil Engineering, U. of Ill.

13th Water Quality Conference

Urbana, Ill.

This conference is planned for engineers and scientists in education, government, industry, and private practice, and for water and waste water works managers and operators. For more information, contact: V. L. Snoeyink, Assistant Professor of Sanitary Engineering, 3230 Civil Engineering Bldg., University of Illinois, Urbana, Ill. 61801

February 21-26
Engineering Foundation of the United Engineering Trustees, Inc.

1971 Engineering Foundation Conferences

Pacific Grove, Calif.

"Environmental Engineering in the Food Industry" and "Stack Gas Emissions and Measurements" are the two conference themes. Attendance, limited to about 100 persons, is by invitation or application. Fee: $160. Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

February 22-24
Technical Association of the Pulp & Paper Industry (TAPPI)

1971 Pulp and Paper Exhibit, and 56th Annual Meeting of TAPPI

New York, N.Y.

Over 250 exhibit booths are planned with such features as equipment for air and water treatment. Over 19 technical sessions are scheduled. Contact: Technical Association of the Pulp & Paper Industry, 360 Lexington Ave., New York, N.Y. 10017

Courses

Present, through June 1971
National Air Pollution Control Administration—Office of Manpower Development

Institute for Air Pollution Training

Research Triangle Park, N.C.

Studies are conducted relating to the manpower required to control the quality of our air. Short courses are run at various intervals throughout the coming months. For details, write: Office of Manpower Development, P.O. Box 12055, Research Triangle Park, N.C. 27705

December 8-11
Virginia Polytechnic Institute and State University

Short Course on Gas Chromatographic Analysis of Air Pollutants

Blacksburg, Va.

This course is designed for industrial, academic, and institutional people, primarily chemists, who are concerned with analysis of air pollutants. No previous experience is required. The course presents background information, proper means of sampling and determining air pollutants, and discussion of the latest instrumental techniques. Registration limited to 30 persons. Fee: $120. Write: Continuing Education Center, Virginia Polytechnic Institute and State University, Blacksburg, Va. 24061

December 9-11
Iowa State University

Short Course on Pesticide Analysis

Ames, Iowa

The course is directed toward the needs of health and related occupations to allow them to concentrate on pesticide analysis in the environment. Fee: $30. Write: Extension Courses and Conferences, 111 Curtiss Hall, Iowa State University, Ames, Iowa 50010

December 14 and 15
Practising Law Institute

Short Course in Legal Control of the Environment

New York, N.Y.

Course is designed to prepare the attorney for the environmental law explosion. Litigation techniques from the viewpoints of both plaintiff and defendant will be discussed in depth, as will the role of federal, state, and local administrative agencies. Detailed attention will be given to remedies for damages and injunctive relief, actions in nuisance and trespass, class actions, and interviewers' actions as they relate to air, water, and land pollution. Contact: Practising Law Institute, 1133 Ave. of Americas, New York, N.Y. 10036

February 15-19
Sadtler Research Laboratories, Inc.

Short Course on Air Pollution Instrumentation

Philadelphia, Pa.

The course includes lecture and laboratory sessions. Tuition: $325. Contact: Sadtler Research Laboratories, Inc., Subsidiary of Block Engineering, Inc., 3316 Spring Garden St., Philadelphia, Pa. 19104

Call for papers

December 15 deadline
Air Pollution Control Association

64th Annual Meeting

Atlantic City, N.J.

An invitation for submission of papers is now open to everyone. Any interested author should submit three copies of the title and summary of his paper to Franklin B. Flower, Department of Environmental Sciences, CAES, Rutgers University, New Brunswick, N.J. 08903

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VOLUME 4—1970

January	1–82	July	533–614
February	83–172	August	615–704
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Indexed below are the names of all authors of Current Research papers, together with the full title of the paper(s), and the names of Feature article authors. Also indexed are names appearing in the Editorial, Viewpoint, Environmental Currents, Outlook and Letters sections. Refer to the listing above to determine the issue in which a given name appears.

SUBJECT INDEX VOLUME 4—1970

January	1–82	July	533–614
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Information is indexed under specific terms where possible, but the nature of the environmental field is such that index users will need to look for synonymous or related entries.

Please note that this year's subject index is both less deep and narrower in scope than those of previous years. Information indexed appears in the Editorial, Viewpoint, Letters, Environmental Currents, Outlook, Feature, and Current Research Sections. Sections that have not been indexed are Industry Trends, New Products, New Literature, Bookshelf, and Meeting Guide. A full list of books and of meetings can be found in one of the Pollution Control Directory Issues (October 1968, October 1969 or November 1970).

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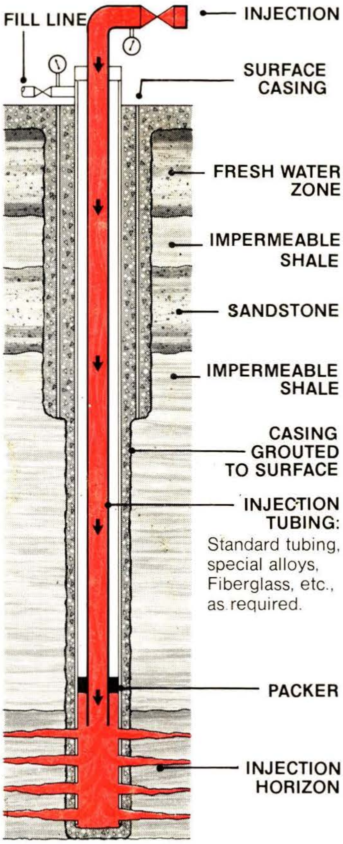

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