

# Environmental

Science & Technology

SEPTEMBER 1972



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the  
BOD load**

**794**

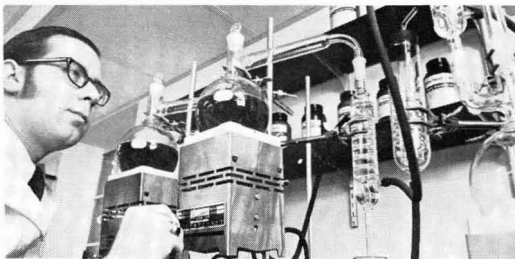
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*This year's edition of the annual Pollution Control Directory will be published in October as a separate issue of ES&T and not, as in previous years, as part of one of the regular fall issues*

## Current research

- Recent sedimentary history of Lake Mendota, Wis.** 799  
**G. C. Bortleson and G. F. Lee**

The extent to which man contributes to the accelerated enrichment of lake waters can now be revealed by analysis of core samples. The composition of the sediments with depth, and therefore with time, presents a pattern of change which documents the progressive increment of materials deposited to Lake Mendota.

- A pH-dependent succession of iron bacteria** 809  
**F. Walsh and R. Mitchell**

Degradation of iron pyrites found in coal leads to the formation of acidic waters, analogous to acid mine drainage. The rate of acid formation is described mathematically and is dependent on the ferrous ion concentration. The organism, *Thiobacillus ferrooxidans*, significantly catalyzed the oxidation in the pH range of 3.5-4.5.

- Effect of inhomogeneous mixing on atmospheric photochemical reactions** 812  
**C. duP. Donaldson and G. R. Hilst**

Turbulent fluctuation of photochemical concentrations plays a significant role in the production of photochemical materials in the atmosphere. Mathematical models have been developed which clearly show that atmospheric photochemical chain reactions can be suppressed by the inability to mix the reacting materials rapidly enough to prevent serious depletion of one of the reacting materials.

- Hydrogen peroxide formation from formaldehyde photooxidation and its presence in urban atmospheres** 816  
**J. J. Bufalini, B. W. Gay, Jr., and K. L. Brubaker**

Hydrogen peroxide has been found in the polluted atmosphere of urban areas. Under moderate smog condition, the urban atmosphere (Hoboken, N.J.) contained 4 ppm of hydrogen peroxide. Under severe smog conditions (Riverside, Calif.), the level of 18 ppm was recorded. The material is formed by a precursor formaldehyde; the reactions are described.

- Aerosol filtration by fibrous filter mats** 821  
**L. A. Jonas, C. M. Lochboehler, and W. S. Magee, Jr.**

One way to remove aerosol particles from the atmosphere is by filtration through fibrous filter mats. Mathematical relationships have been developed which correlate the theoretical data on penetration characteristics of a dioctylphthalate aerosol through mask filter mats with actual experimental data.

- Decontamination of noncombustible agricultural pesticide containers by removal of emulsifiable parathion** 826  
**D. P. H. Hsieh, T. E. Archer, D. M. Munnecke, and F. E. McGowan**

Used pesticide containers of parathion can be readily cleaned by washing with an alcoholic alkaline solution. These containers are noncombustible and represent a solid waste disposal problems since a large number of these containers have accumulated owing to the widespread agricultural use of this pesticide. The parathion residue in completely drained containers ranges from 150-45,000 mg. LD<sub>50</sub> for a rat is 3 mg/kg body weight.

- Distribution of cadmium and nickel of tobacco during cigarette smoking** 830

**E. E. Menden, V. J. Elia, L. W. Michael, and H. G. Petering**

Cigarette smoke may be a health hazard not only to smokers but to nonsmokers as well. These two toxic metals, cadmium and nickel, are not only in tobacco residues but are in smoke streams as well. For example, data show that 38-50% of the cadmium and 11-33% of the nickel are present in cigarette smoke sidestreams.

## Notes

- Infrared estimation of oil content in sediments in presence of biological matter** 833

**H. B. Mark, T.-C. Yu, J. S. Mattson, and R. L. Kolpack**

The estimation of the oil concentration in the presence of biological material in the water can be distinguished on the basis of infrared spectrophotometry. Basically, the estimation provides a method for correcting an absorbance band (2925 cm<sup>-1</sup>) to enable the estimation of the oil concentration alone.

- Brucine analysis for high nitrate concentrations** 835

**J. G. Holty and H. S. Potworowski**

If gross errors are to be avoided in the analysis of nitrate ion concentration in groundwater samples it is important to have an approximate knowledge of the nitrate ion concentration in the sample prior to the analysis. Otherwise, some samples yield higher concentrations of nitrate on dilution.

## Correspondence

- Singlet O<sub>2</sub> production from photoexcited NO<sub>2</sub>** 837

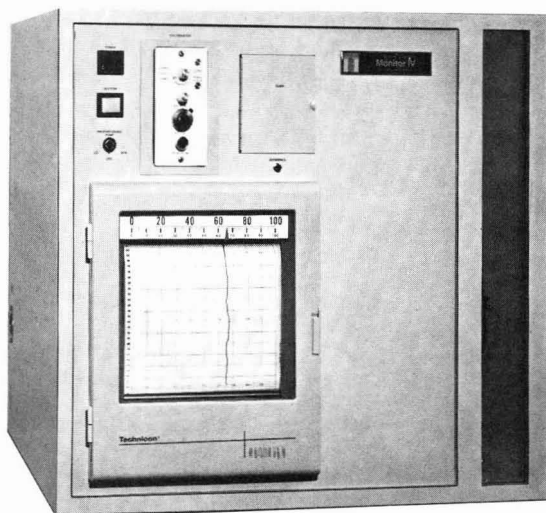
**J. J. Bufalini  
T. C. Frankiewicz and R. S. Berry**

Despite the large number of papers published on the role of singlet oxygen in smog formation, there is still no experimental proof either in the laboratory or in situ to suggest that this species in the photooxidation of hydrocarbons at realistic atmospheric concentrations.

**Credits:** 774, UPI; 776, Bell Laboratories; 779, ES&T's Stan Miller; 782, 783, Enviro-Engineers, Inc.; 788, ES&T's Carol Lewicke; 793, Koehne Studio; 798, William C. Rolfs

**Cover:** Joe Phillips

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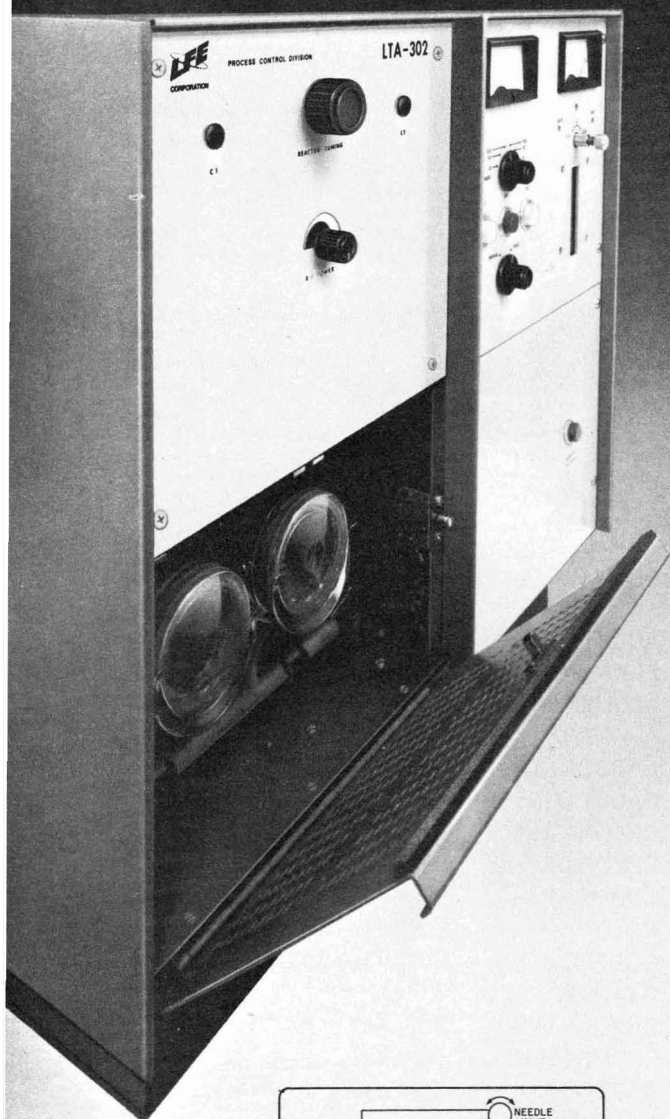
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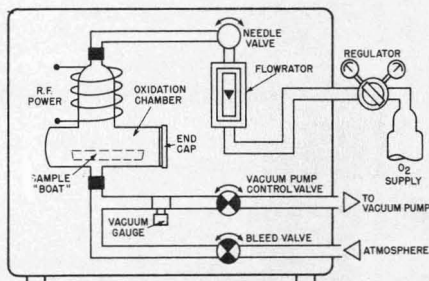
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# letters

## Transportation in "mock cities"

DEAR SIR:

Some omissions require comment in your otherwise excellent Special Report (June 1972) on auto engines and their emissions.

Cars are simply not acceptable means of mass transportation in genuine cities such as New York, Boston, and San Francisco. Mock cities such as Los Angeles and Houston, which are really clusters of suburbs with baseball stadiums, could not exist without cars. In fact, there is a synergistic relationship between cars and suburbs: Each vice feeds on the other.

In Manhattan, the most reasonable place for an environmentalist to live, our 1.5 million residents own only 200,000 cars. By way of contrast, the 7 million people in Los Angeles own and use 4 million cars, which amounts to some 5 times as many vehicles per person.

I and most Gothamites view the automobile as a generator of over 70% (by weight) of our air pollution, a creator of unwanted noise, a device which smells up our streets, clogs our traffic, and kills our pedestrians—in short, an unnecessary pestilential nuisance. When I tell younger people from the suburbs that I do not own a car, they usually assume that I am either too poor or that I have had my license lifted for reckless driving. But I and most of my relatively prosperous Manhattan friends use public transportation

by choice. If we must go to the hinterlands we can always rent cars.

Tinkering with auto engines does not appear to be a solution to the overall environmental problems created by unrestricted auto travel. If the future of the U.S.—where over 80% of the population will live in metropolitan areas—is to contain less noise, air pollution, dirt, death, and other environmental hassles, then mock cities must organize themselves along the lines suggested by Manhattan.

Cyrus Adler  
*The Electric Whale Co.*  
99 Nassau St.  
New York, N.Y. 10038

## Reverse osmosis plants

DEAR SIR:

Your May 1972 issue of *ES&T* mentions on page 459 that Permutit will be supplying the largest reverse osmosis water treatment plant ever ordered, and that this has a capacity of some 500,000 gpd.

I bring to your attention that as of December 20, 1971, an Ajax International reverse osmosis plant manufactured in Santa Barbara, Calif., was operating at its full capacity of 800,000 gpd at Kashima near Tokyo in Japan.

Peter K. Worsley  
*Ajax International Corp.*  
P.O. Box 4007  
Santa Barbara, Calif. 93103

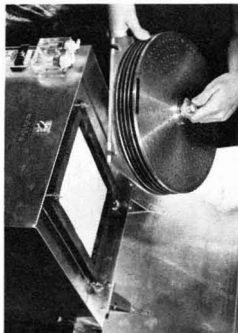
## Pollution-free power for the automobile

Reader Kendall Crawford, of Dearborn, Mich., has brought to our attention several points in *ES&T's* Special Report on auto pollution (June, p 512) that should be clarified:

- The Federal Clean Car Incentive Program is not restricted to gas turbines, steam engines, and stratified charge engines, as the *ES&T* report implied. These power sources are, however, the ones covered by EPA's Advanced Automotive Power Systems Program. The confusion appears to stem from the fact that both programs are administered by the same EPA division in Ann Arbor, Mich.

- The "new ignition systems that do away with spark plugs" (p 515 of the report) do not, in fact, do away with spark plugs! Electronic ignition systems require plugs, but allow them to be set with a wider gap and for a longer spark duration, which in turn permit leaner mixtures to be used (thus reducing hydrocarbon and carbon monoxide emissions).

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## Runoff poses next big control challenge

Whether or not pollution from outfalls is ever curbed, nonpoint sources will have to be tackled in earnest

**T**he major thrust of federal, state, and local water pollution control programs always has been, and continues to be, directed against the point source polluter. Of course, it must immediately be acknowledged that even where authorities have known where the discharge pipes were, and what was coming out of them, it has generally not been easy to curb pollution. Perhaps the main reason for this is that water quality standards, rather than effluent standards, have been the regulatory criteria with which water pollution control officials have had to work. Relating the character of one waste stream to the quality of a body of water that is simultaneously receiving many other streams from other sources has proved so difficult, indeed, that it is hardly surprising the federal EPA is pushing hard for specific effluent restrictions (story, this issue, p 778). If EPA has its way, and a new water pollution control law based on two bills being compromised in a House-Senate conference committee is passed, the government may at last have an enforceable weapon against point-source pollution.

With at least the prospect of point sources coming under better control, water pollution from nonpoint sources naturally assumes greater visibility. Indeed, a study performed for the Council on Environmental Quality and described in the just-released CEQ annual report suggests that nonpoint sources are often the dominant sources of water pollution, even in river basins with relatively uncontrolled point sources. Enviro Control, Inc., a Washington, D.C., consulting firm, was retained by CEQ to examine the mounds of water quality data collected over the years by federal and other agencies and to come up with an analysis of trends. There is certainly no shortage of data (see "Water quality surveillance: the federal-state network," *ES&T*, February 1971, p 114), but their accuracy and comparability leave a great deal to be desired. Nevertheless, Enviro Control was able to arrive at some conclusions based on the most reliable data

and some analysis tools specially developed for the study.

The "most startling" conclusion (to use CEQ's reaction) concerns the effect of increased stream flow on pollution. Whereas the popular notion is that heavy rain and the consequent increased flow in streams somehow "dilute" pollution, the figures for both rural and industrialized areas seem to indicate that pollution is no less, and often even worse, during high flow periods, suggesting a large contribution due to runoff from land. In fact, these runoff effects were so widespread that only 20% of the basins reviewed were seen to be dominated by point sources.

CEQ, in its report, is quick to try to allay any possible misconceptions that industrial and municipal pollution are not significant contributors to the overall problem. These sources, says the Council, dump "a large share" of pollutants into the country's waterways, and account for "most of" the toxic discharges. Nevertheless, "...if the Enviro analysis is confirmed by further work, it points up the need to place much greater emphasis on nonpoint sources of pollution." Behind CEQ's soothing generalities lies the stark fact that practical measures available to control feedlots, fertilizer and pesticide applications, unsewered urban runoff, building and ground clearing practices, and the like, have barely begun to be applied, let alone become effective. And most regulations promulgated so far have been entirely in the province of the states, which lack the manpower (and sometimes the enthusiasm) to enforce them.

It is clear that all those concerned with the control of water pollution must think seriously about abandoning their traditional emphasis on point sources. What is needed instead is a much broader view, one that encompasses watershed management as well as waste treatment technology.

*D. H. Michael Bowen*

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# environmental currents

## WASHINGTON CEQ's third report adds up clean up costs

### Where the \$287 billion will be spent

|             |     |
|-------------|-----|
| Air         | 37% |
| Water       | 30% |
| Solid waste | 30% |
| Other       | 3%  |

During the 10-year period, 1971-80, the Council on Environmental Quality estimates that this nation's pollution control cleanup cost will be \$287 billion, notes that this cost does not pose any threat to the economic health of this country and represents 2.2% of the estimated Gross National Product (GNP) for the 10-year period. (The earlier estimate for cleanup in last year's annual report was \$105 billion for the six-year time span, 1970-75.) The report points out that the costs and risks of not cleaning up are infinitely greater than the price of cleanup although CEQ was unable to put a dollar value on the penalty. The annual cost for pollution control will increase from \$10.4 billion in 1970 to \$33.3 billion in 1980. On a per capita basis, the increase ranges from \$51 per person in 1970 to about \$145 per person in 1980.

## EPA completes its action on state implementation plans

By July 25, nearly all federal actions mandated by the Clean Air Amendments of 1970 on state implementation plans for clean air by mid decade were finalized. At a third press conference on the subject of implementation plans, the Environmental Protection Agency approved plans for a dozen states for one or more portions of each of their plans that had been disapproved earlier, in the May 31 decision (ES&T, July 1972, p 599). In another action on the same date, EPA approved proposed regulations for a dozen states (not necessarily the same as the above 12) to correct previously identified deficiencies in plans. So that only three plans—those for New York, California, and Washington, D.C.—were yet to be acted on before the July 31 deadline.

## Weather modification: some good and bad news

Weather modification is one of the most important scientific developments now visible on the horizon, says CEQ's Gordon MacDonald, but weather modification activity must be properly encouraged and managed, otherwise poor management could lead to calamitous environmental consequences. Much of the present effort in this area is devoted to the objective of clean water augmentation. In the Colorado River Basin, for example, snow augmentation is estimated to produce an annual increase of 2 million acre feet of clean water. The comments came to light in recent testimony on Senate Resolution 281 which proposes a treaty that would seek a complete cessation of research, experimentation, and use of environmental and geophysical modification activities as weapons of war.

## Commerce affirms need for deep port facilities

The Maritime Administration of the Department of Commerce reports that an offshore crude oil facility can be constructed off the Delaware Coast to help this nation meet its need for imported crude oil off the Atlantic Coast. It is expected that the U.S. consumption of energy will double in the remainder of this century, and since domestic energy sources are expected to remain essentially constant through this period, the U.S. will depend increasingly on foreign sources of oil for its energy demand. But Atlantic and Gulf Coast port facilities are limited to tankers of the 80,000-ton size, says Robert Blackwell, Assistant Secretary of Commerce for Maritime Affairs. The offshore facility off the Atlantic Coast would cost more than \$1.3 billion with 10% of the cost going for pollution control systems. The facility could be located about 8.5 miles east of Cape Henlopen, Del., according to the report prepared by the N.Y. engineering firm of Soros Associates. Deep ports are also needed in the Gulf (this issue, p 778).



Commerce's Asst. Sec. Blackwell



## **STATES Water quality under scrutiny across the states**

- In July, the federal EPA issued a 180-day notice to New York City and the Passaic Valley Sewerage Commission to submit updated abatement plans to stop degradation of New York Harbor and adjacent waters. The Justice Department also filed six civil suits charging New York City, the state of New Jersey, and a number of New Jersey communities with dumping raw or inadequately treated sewage into New York Harbor and its tributaries.
- The Oregon Department of Environmental Quality and the federal EPA have agreed upon a cooperative program based on a one-step waste discharge permit procedure which could save Oregon industries and municipalities \$40 million annually. Water pollution activities will be under a combined federal-state review; the state will issue permits consistent with federal and state water quality standards; and the state will enforce the terms of the permits.
- Livestock feedlot waste-disposal facilities must have operating permits, according to Montana State Board of Health regulations. Existing feedlots have a two-year grace period, but the health department will require new facilities to provide for both water pollution and odor controls.
- An amendment to New York's Environmental Conservation Law requires septic tank cleaners and collectors of commercial and industrial wastes to register with the Department of Environmental Conservation. Each registrant must also report annually to the department indicating the number and type of installations emptied or cleaned, the volume and nature of the products, and the disposal methods used.

## **Railroad cited for excessive noise in Chicago**

The Grand Trunk Western Railroad was fined \$5950, the largest fine ever imposed for noise violations, for 40 nonobservances of Chicago's (Ill.) Noise Pollution Control Ordinance. Department of Environmental Control inspectors issued the citations for excessively noisy operations from the railroad's piggyback crane operations.

## **Michigan, California enforce air quality regulations**

- The Wayne County (Mich.) Department of Health filed suit in July against the Ford Motor Co. operations at Rouge, Mich., for 143 violations of the county's air quality regulations between January 1970 and June 1972. The county charges that the plant emits smoke, sulfur dioxide, hydrocarbons, iron oxide, lime dust, slag dust, zinc oxide, fly ash, coke particulate matter, sand, and hydrogen sulfide.
- By January 30, 1973, the state of California will require emission control tests for 75% of automobiles produced in 1973 and subsequent years without obtaining a waiver under certain sections of the Clean Air Act. Tests will be conducted at delivery preparation sites, test centers, port of entry, distribution points, and by the Air Resources Board mobile laboratory. Any manufacturer who fails to meet assembly line tests will be subject to a \$5000 penalty for each violation.



Assembly line testing

## **50th state cracks down on solid waste dumping**

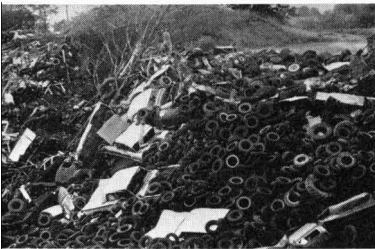
The state of Alaska is suing Alaska Packers Association, Inc., for \$120,000; the company allegedly dumped three million tin cans into Alaska's Larsen Bay and Uyak Bay. The state is also asking the court to require the firm to clean up the bays and remove the cans. This action is the first time Alaska has asked for punitive damages and is also the first solid waste case to be filed under Alaska's year-old environmental protection law.

## **TECHNOLOGY** New roles for methanol could increase market

Methanol is being touted in two separate environmentally related applications. • Methanol could conceivably replace natural gas as a clean-burning fuel. Although no confirmations have been received, Vulcan-Cincinnati is reportedly studying the feasibility of substituting methanol for liquefied natural gas. Although its heating value is roughly half that of natural gas, methanol could be made and shipped without the elaborate pressurized equipment necessary for importing LNG from North Africa and Venezuela. • Methanol also shows considerable promise in sewage treatment applications. EPA studies show that methanol can be injected into an anaerobic sludge system where bacteria use it as a carbon source to aid in conversion of nitrates to nitrogen gas and carbon dioxide gas.

## **Furnace burns whole tires cleanly**

One way to get rid of the millions of scrap tires generated by the motoring public each year is to burn them, according to Lucas American Recyclers, Inc. (San Francisco, Calif.), in a specially designed incinerator manufactured by the company. The furnace is of the rotary hearth type with tires automatically deposited on the periphery of the combustion chamber. Putting another tire in the furnace displaces the carcass of the previous tire and initiates its trek along the spiral path leading to a central ash discharge aperture. Along the way, the heat generated is so intense it oxidizes the bead wire and converts it to sterile ash. Gases pass through a high-temperature combustion zone, a cyclone, and desulfurizer before being emitted to the atmosphere. Cooling water can be recirculated.



Mounds of scrap tires

## **RESEARCH** Quick lead test perfected for blood samples

Martin Marcus, chief chemist at Fordham Hospital (New York City) has perfected a procedure based on atomic absorption spectrophotometry for the analysis of lead levels in blood. The method has been accepted by the city's municipal hospital system and is a modification of the combustion boat method pioneered by London chemist H. T. Delves. The new method detects lead accurately in microgram quantities using a 10- $\mu$ l blood sample; older methods required 3–5-ml samples which were difficult to obtain from small children, the chief sufferers from urban lead poisoning. Marcus' method eliminates the need for dithizine extraction and complex sample handling which plagued earlier methods.

## **ERTS-1 is up and working well**

Earth Resources Technology Satellite-(ERTS) 1, a 1965-lb remote-sensing satellite launched from NASA's Western Test Range (Lompac, Calif.), is circling the globe in a 560-mile circular polar orbit and transmitting its first data to NASA receiving stations on earth. NASA bills the ERTS program as a major step in establishing a comprehensive information base dealing with the earth's resources and surface environment. "Glitches" marred the satellite's early transmissions—a power surge forced NASA to shut off a wide-band tape recorder and a return beam Vidicon imaging system to prevent failure—but backup systems are functioning well and multispectral scanners continue to send good pictures back to earth, NASA officials say. ERTS-1 has a life expectancy of about one year. ERTS-2 will be launched late in 1973, pending approval of the rest of the ERTS program by the Office of Management and Budget.

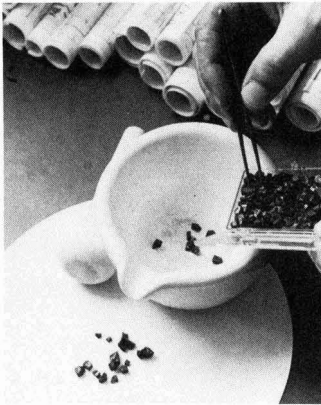
# environmental currents

## **INDUSTRY** Paper industry wins praise from CEP

The Council on Economic Priorities (CEP), a nonprofit, New York City-based business watchdog corporation, says that the pulp and paper industry will have adequate pollution control at most of its mills by 1975 and is "years ahead" of such industries as steel and utilities, in coping with major environmental problems. An earlier 1970 CEP study was highly critical of the industry's efforts. The Council credits the industry's rapid improvement to the fact that well-developed technology has enabled the industry to clean up with equipment now commercially available. In addition, CEP says, government regulatory efforts have been persistent and effective. Data on 24 major pulp and paper corporations—representing about three quarters of the industry's pulping capacity—indicate that the cleanup price tag for the 1971-75 period will be about \$840 million.

## **Bell's catalyst doesn't shake Engelhard**

Bell Labs may have a base metal catalyst to clean up auto emissions, but Engelhard Industries isn't impressed. Bell announced that a proprietary lanthanum lead manganite compound might "rival platinum" as a catalyst for removing carbon monoxide from auto exhausts because of its inherent cheapness. Engelhard, which makes platinum catalytic converters and will supply at least 60% of Ford's needs for the 1975 model year, cried foul. Engelhard charged, and Bell confirmed, that Bell's testing had been carried out with synthetic gas mixtures containing only CO and O<sub>2</sub>, and that no test using auto exhaust had been run. Engelhard also complained that its platinum converters were crushed to make comparison tests, and that crushed catalysts weren't as effective as the whole converters.



**Bell's inexpensive catalyst**

## **Water expert says Canadian water is coming**

The transmission of Canadian water to the United States to meet this country's need for supplementary capacity during peak demands and periodic dry periods is "inevitable" and awaits "only political considerations," according to Abel Wolman, professor emeritus of sanitary engineering at the Johns Hopkins University. In an interview appearing in the *Journal of the American Water Works Association*, Wolman says that importation of water would allow the U.S. to build only the facilities it would normally need and the U.S. wouldn't have to provide surplus water for its relatively rare dry periods. "The quantities of water in Canada are so prodigious they couldn't possibly be used locally, even with the maximum estimates the Canadians have made," Wolman said.

## **Key to energy crunch is better utilization**

Increased efficiency of energy use would help to slow energy consumption growth rates, thereby relieving pressure on scarce energy resources and reducing environmental problems associated with energy production, conversion, and use, according to scientists at Oak Ridge National Laboratory. About one fourth of total U.S. energy consumption is attributable to transportation, but some modes of transportation—trucks, airplanes, and automobiles—are relatively inefficient. More efficient are trains, pipelines, waterways, and buses so that changes in the national transportation mix could effect considerable energy savings. Residential space heating and cooling are also major energy consumers. Increasing insulation, adding storm windows, and installing more efficient air conditioners and electric heat pumps could also cut energy needs.



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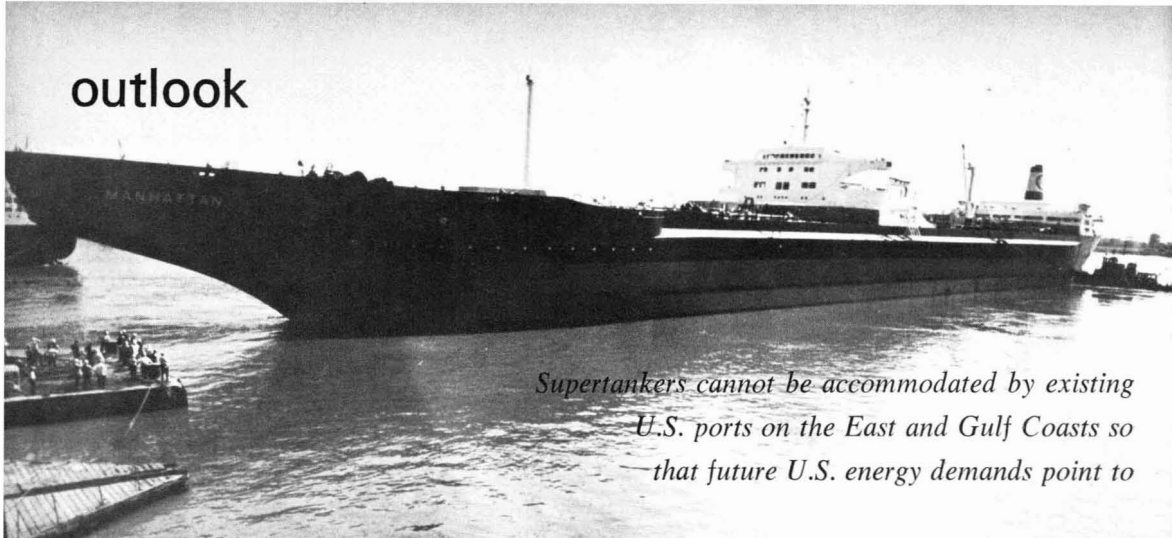
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*Supertankers cannot be accommodated by existing U.S. ports on the East and Gulf Coasts so that future U.S. energy demands point to*

## The case for deep port construction

Superport development plays an important part in the overall energy issue now attracting so much attention. The benefits and risks of such development are being specifically considered as part of the National Fuels and Energy Policy Study. The public's awareness of and attention to the subject are arriving on the scene none too soon, because several factors sharply point up the need for large new ports:

- world trade of the future will be dependent on both supertanker and supercargo carriers
- 60% of the total world oil production is now transported by sea, and the percentage will increase in the future
- foreign countries already have 50 deep ports (either natural or under construction), including 5 in Canada, 10 in Japan, and 15 in Europe
- by 1985, more than half of the oil needed by the U.S. may have to be imported, since domestic production, including the anticipated Alaskan oil, will meet only half the expected demand.

Basically, two types of terminals are being considered—crude oil terminals and dry bulk cargo terminals. If benefits of any superport project can be shown to outweigh any risks, the U.S. Congress would probably have to appropriate the actual money for construction.

Supercarriers handle oil or dry bulk goods. For example, a supertanker is a vessel of more than 100,000 deadweight tons (dwt) which carries in excess of 2 million barrels of oil. More than 300 supertankers are operating today and at least 200 such vessels are currently on

order in the world's shipyards. A few vessels of 1 million dwt are being designed or built.

The argument for superport development recognizes that fully laden supercarriers require channel depths which U.S. ports simply cannot accommodate at present. For example, a fully laden 150,000-dwt tanker requires a channel depth of 60 ft, a 200,000-dwt tanker requires 64 ft, a 250,000-dwt tanker requires 75 ft, and so on.

At present, the U.S. has only three ports which would accommodate some of these supercarriers. All three are on the West Coast—Puget Sound, with a natural depth of 100 ft; Los Angeles/Long Beach, whose channel has been developed to a 60-ft depth; and the Gulf of Alaska. Major ports along the Atlantic and Gulf coasts have channel depths of only about 40–45 ft.

### Why Alabama?

To say that every state has the potential for a deep port, truly wants a deep port, needs a deep port, and would help alleviate the oncoming energy crisis if it had one, is certainly not true. But it is undoubtedly true that Alabama wants a superport.

Alabama Governor George Wallace personally asked State Sen. L. W. "Red" Noonan to spearhead the Alabama effort on superport development. Noonan is chairman of the Alabama Senate Seaports Committee. Dubbed Ameraport, the proposed Alabama superport envisions the location of a deep-port facility in the Gulf of Mexico within an approximate 30–40-mile

radius of the Alabama coastline. Ameraport is the name coined to convey the idea that a port off the Alabama Coast would serve most of America better than most other locations. The current thinking favors an offshore facility—the natural depth at Port Morgan in Mobile Bay is already 50–54 ft.

One of the noteworthy features of Alabama's case for Ameraport is that it has marshaled a statewide effort and has enlisted the support of many environmentalists, developers, and legislators.

Ameraport has an operating environmental office in the form of a new state agency—the Marine Environmental Sciences Consortium (MESC). MESC represents all 17 universities and colleges in the state; the consortium will be used in conducting research on the ecology of the Gulf of Mexico and estuarine areas. It will provide the best environmental answers on development affecting Alabama's coastline.

The initial legislative proposal for the creation of MESC was, in fact, introduced by Sen. Noonan in the 1971 regular session of the Alabama legislature (which meets every other year). The legislature met during all of 1971 and in January and February of 1972, and although its next regular session will begin on May 3, 1973, pressing matters such as superport development may lead to one or more earlier sessions.

MESC is a public, nonprofit corporation dedicated to providing marine education, research, and service to the state of Alabama. It now has a facility of its own to help it play its environmental education role.

On July 6 of this year, more than 30 acres of land on Dauphin Island, off the Alabama coast in the Gulf of Mexico, were transferred to the consortium. Formerly, the land was part of a U.S. Air Force station; it was declared excess federal land and is part of President Nixon's program of returning underutilized federal land to the people for their use and enjoyment.

According to the 1970 census, the population of the 48 contiguous states was close to 207 million. Population of the 23 states and the District of Columbia served directly by waterways and railroads starting at Mobile is almost 104 million people, about one half the total population. Mobile may in some ways be the hub of Southern rebirth. Governor Wallace commented at a Mobile hearing, "There can be no doubt that more people and more communities will be served more expeditiously and economically and receive more direct and indirect benefits as a result of a deep-water port off the Alabama coast than from any other location on the entire Gulf."

**Other developments**

In May 1971, the U.S. Congress authorized a regional study for the Gulf of Mexico, a main consideration being superport development. Then, in October 1971, Congress authorized a regional study for the North Atlantic region. Both studies were initiated with fiscal-year-1972 funds, but now are budgeted for continuation into fiscal year 1973.

In April and May of this year, the U.S. Army Corps of Engineers held public hearings on superport development at the headquarters locations for each of its four district offices on the Gulf Coast. Thus, public hearings were held in Mobile, Tampa, New Orleans, and Galveston. These hearings provided strong statements by high-level officials in favor of supercarrier facilities.

Headquartered in Vicksburg, Miss., the Corps' Lower Mississippi Valley district office ultimately will make the site selection on the Gulf superport, but its final decision on site selection is far off. Meanwhile, additional information and facts must be developed before a final choice can be made.

Last month, the Corps' Vicksburg office announced a contract with the R&D firm of A. D. Little, Inc. (Boston, Mass.) to perform an assessment of the environmental impact of superport, bulk ore facilities, and both pe-

**Distances between foreign and Gulf ports (nautical miles)**

|                            | Mobile, Ala. | New Orleans, La. | Galveston, Tex. |
|----------------------------|--------------|------------------|-----------------|
| <b>Persian Gulf</b>        | 12,448       | 12,501           | 12,683          |
| <b>Yokohama, Japan</b>     | 17,553       | 17,606           | 17,790          |
| <b>Sydney, Australia</b>   | 13,511       | 13,564           | 13,748          |
| <b>Dakar (West Africa)</b> | 4,215        | 4,268            | 4,452           |

roleum and nonpetroleum facilities for the entire Gulf Coast—from Brownsville, Tex., to Tampa, Fla. The A. D. Little study will divide this Gulf area into a number (possibly as many as 10) dissimilar ecological regions, and assess the effect of a superport on each. The report is due to the Corps on April 1, 1973. Then, by June 30, 1973, the Corps will report to Congress on the feasibility of constructing a superport in the Gulf based on the three E's—engineering, economics, and environmental considerations. But a specific site or sites will not be announced until some time after June 30, 1974. Later, the Corps will be making specific recommendations on superport construction which will then find their way into the appropriations machinery of Congress.

Further arguments in favor of Mobile include the belief that Mobile is the natural point of entry of the Gulf for bulk cargoes that would be moved to the greater steel-producing centers of Birmingham, Pittsburgh, Youngstown, Chicago, and St. Louis. In addition to

the inland waterway system, railroad service is available from Mobile to 23 states and the District of Columbia.

At the same time, a number of other studies are under way; these findings will shed more light on the final choice of superport sites in the U.S. These studies are being conducted by the Council on Environmental Quality, A. D. Little, Inc., Soros Associates (New York, N.Y.), and Robert Nathan Associates (Washington, D.C.).

Each of the southern Gulf states probably would like a superport off its coastline. While it is true that Alabama, with more miles of inland waterways than any other state, may be the choice for an offshore bulk commodity facility, it is also argued at the same time that the deep-port oil facility might more logically be built off the Texas or Louisiana coast, since oil and gas interests are firmly established there. But it is important to remember that the Texas and Louisiana facilities are operating to capacity today, and known oil reserves and seismographic data indicate under-surface oil domes in the mid- and east Gulf—suggesting an eastward movement of oil and gas interests. Meanwhile, the reports to Congress should provide stimulating reading as the nation moves into its energy crunch time and as superport development surfaces as one solution to the energy issue.

Whether the benefits outweigh the risks or whether ports will be onshore or offshore, no one can say with any assurance today. If the U.S. started superport construction tomorrow, it still would not likely become a reality until 1977; further, the total cost for each superport might be between \$0.5-1.2 billion. Auxiliary crude oil buoy installations of the bell or doughnut type cost between \$2-5 million. How many superports are necessary and where these developments should be located to help satisfy the nations' overall energy needs are questions which cannot as yet be answered. ssm



State Senator L. W. "Red" Noonan  
*Spearheading Alabama's superport*

*Nashville plans a system that not only will incinerate its solid wastes, but also will produce the energy to air-condition city buildings*

## Local trash cuts downtown fuel bills

In an aggressive bid to solve two problems at once, the city of Nashville, Tenn., is planning to use its solid waste as a basic source of energy to heat and cool downtown buildings.

Nashville's approach is based on the well-known advantages of "district" cooling and heating, in which steam or chilled water from a central facility is piped for use in many buildings in the same general area. Such a system has many advantages for Nashville, as it is both the center of metropolitan government (Nashville and surrounding Davidson County have had metro government since 1963) and the Tennessee state capital. Many downtown buildings are therefore government owned, resulting in few of the difficulties in getting multiple owners to agree to tap into a distribution system that might arise in a business district.

### NTTC is born

Nashville originally had in mind a conventionally fired district heating and cooling plant to serve metro government buildings only, and in 1969 contracted with the local consulting firm of I. C. Thomasson and Associates to come

up with a design. But in 1970, before any designs were finalized, the state of Tennessee passed a law requiring that by 1972 all landfills must employ daily earth cover. When the city realized that, in addition to the extra cost imposed by this law on operations at its five landfills, the sites themselves would last only another 12 years, the idea of using the solid waste as a fuel first arose.

Because the local gas and electric utilities in Nashville did not have authority under the metropolitan charter to build or operate a central district heating and cooling plant (even a conventionally fueled one), an organization—the Nashville Thermal Transfer Corp.—was chartered under Tennessee law in May 1970, and empowered to issue revenue bonds for construction. The corporation has no assets, and when the bonds have been paid off, the plant will revert to the metro government.

Thomasson Associates, after extensive modification of original plans, concluded that a district system fueled by solid waste was indeed feasible. "Then," says Nashville Mayor Beverly Briley, "the NTTC found itself in the incineration business."

Initial plans for the plant call for it to be completed by 1974, and to burn about 720 tons/day of solid waste, most of it collected in the mid-city area and delivered to the central plant by compactor truck. The plant, to be built on a 3-acre site alongside the Cumberland River, will at first serve 27 downtown buildings, 12 of them state office buildings (one is the state capitol); the state has signed a 30-year contract with NTTC. The rates charged for steam and chilled water will save customers 25-30% on costs of running their own heating and cooling units, claims Mayor Briley.

### Clean burning

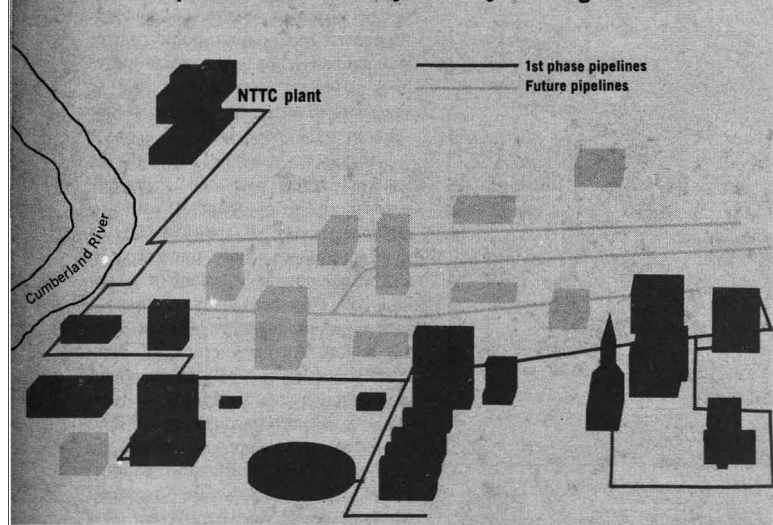
Key to the planned system is the specially designed incinerator, a multiple grate unit with a Babcock & Wilcox boiler, dry cyclone particulate matter collector, and wet scrubber. In Phase I of the project (slated for completion in 1974), the unit will generate 215,000 lb/hr of steam, which can be supplied to the distribution system at 125 psi or used to drive turbine chilling machines (manufactured by Carrier Corp., Syracuse, N.Y.) which produce water for distribution at 40°F.

The incinerator will reduce the solid waste to one tenth of its original weight, and the inert residue can be landfilled without earth cover, according to Thomasson's Maurice Wilson. NTTC is, however, exploring ways in which values can be reclaimed from the residue. Because the city retains title to the waste it supplies at no cost to NTTC, it stands to benefit if salable products can be produced from the residue.

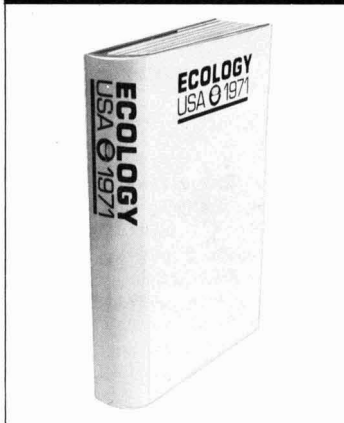
By 1978, city officials think, the plant could generate as much as 500,000 lb of steam an hour, and double the number of buildings served. They visualize all of the 1300 tons/day of solid waste currently generated by the 500,000 people in the metropolitan Nashville area eventually being burned in the NTTC plant, with three centrally located transfer stations being established to prevent traffic jams of garbage trucks at the plant.

DHMB

### Central plant will serve many mid-city buildings

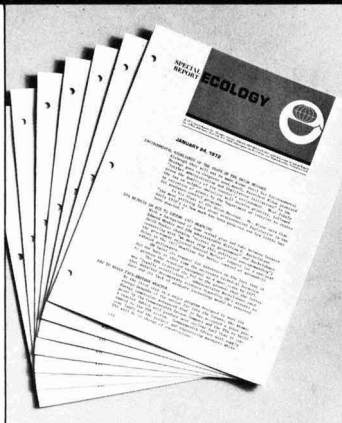


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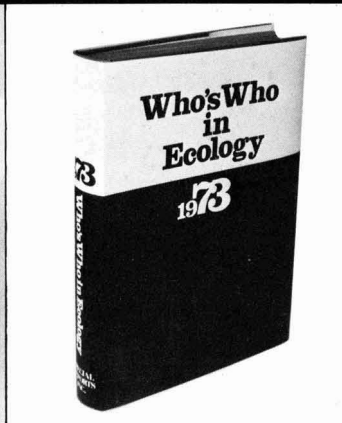
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# Cleveland opts for physical-chemical

Several years ago the Cuyahoga River near Cleveland, Ohio, literally caught fire as a result of semitreated and often untreated municipal and industrial wastes pouring into the river. Conditions have improved somewhat since, but Cleveland's existing Westerly Water Pollution Control Facility (one of three waste water treatment plants), located on Lake Erie near the mouth of the Cuyahoga, was built in 1922 and cannot adequately treat its share of the metropolitan area's waste water.

The plant provides primary treatment to approximately 40 million gallons per day (mgd) of municipal and industrial wastes in an Imhoff tank complex. (An Imhoff unit consists of two-story sedimentation tanks with sludge accumulation in the bottom.) At present, the average dry weather flow of waste water through the plant is 50 mgd, and the dry weather peak is 70 mgd, which the outdated plant cannot handle. Nor can the plant produce effluent meeting federal and state water quality standards.

## Criteria

Three years ago, the Cleveland Clean Water Task Force (created to look into water pollution problems and solutions) began looking at two alternatives to the old plant. One was

### U.S. physical-chemical treatment plants

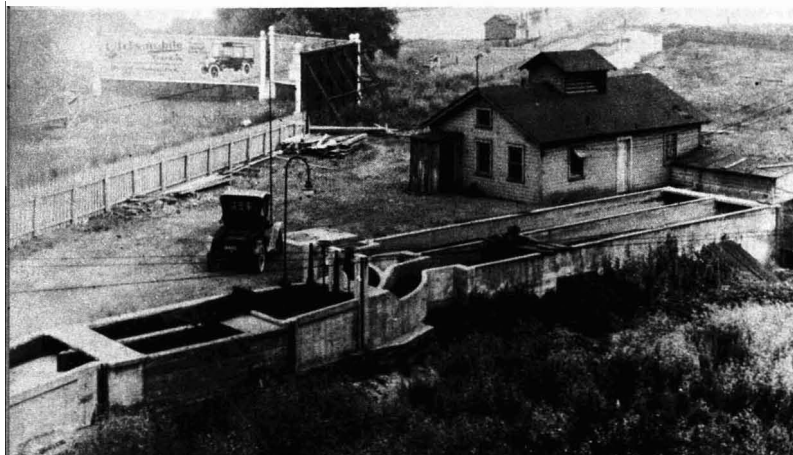
| Plant                                | Flow, mgd |
|--------------------------------------|-----------|
| Fitchburg, Mass.                     | 15        |
| Cortland, N.Y.                       | 10        |
| LeRoy, N.Y.                          | 2         |
| Niagara Falls, N.Y.                  | 60        |
| Alexandria, Va.                      | 25        |
| Arlington, Va.                       | 30        |
| Lower Potomac, Va.                   | 36        |
| Prince William County, Va.           | 15        |
| Cleveland (Westerly), Ohio           | 50        |
| Rocky River, Ohio                    | 10        |
| Owasso, Mich.                        | 6         |
| Rosemount, Minn.                     | 1         |
| St. Charles, Mo.                     | 8         |
| Garland, Tex.                        | 30        |
| Los Angeles, Calif. (Hyperion Plant) | 5         |
| Orange County, Calif.                | 17        |
| Selma-Kingsburg-Fowler, Calif.       | 10        |
| Total                                | 330       |

Under design or construction.

to construct an island in Lake Erie with waste activated sludge from the plant—this was deemed impractical, ineffective, and expensive. The other—later adopted—was to build a new waste water treatment plant while the old plant continued to operate.

A new plant must meet certain stringent criteria, the Task Force decided. Besides meeting effluent quality objectives, the plant must be capable of handling, without upset, widely varying flows from combined storm and waste water sewers. It must also handle assorted constituents from industrial discharges, which account for nearly 50% of the flow into the plant. The plant site, only eight acres in area, is almost completely built up, but waste water treatment must continue during demolition of the old plant and construction of the new facilities. The design must be flexible for future expansion and addition of new processes. Also, the facility must minimize the effects of toxic materials and provide a potential for removing heavy metals.

What type of plant could handle such a big order? The Task Force knew that biological treatment plants are sensitive to weather changes and that unusual or strong effluents could result in a completely disrupted treatment process. Furthermore, many Task Force mem-



**Transformation.** The original waste treatment plant for Cleveland, Ohio (left), was torn down in 1922. A 40-mgd Imhoff tank facility (right) was built but is now outdated and unable to handle the amount and variety of wastes passing through to meet water quality standards. It will soon be replaced by a \$41 million physical-chemical treatment plant (upper right) capable of handling up to 100 mgd. The new plant, to be completed by 1974, will be the world's largest physical-chemical treatment plant

*The big Ohio city is turning its back on biological treatment as it gears up to modernize its Westerly plant*

bers felt that biological treatment plants cannot provide the high degree of solids and BOD removal required to meet water quality standards.

Physical-chemical treatment is the answer the Task Force decided upon, and the city awarded the design contract to Zurn Environmental Engineers, an affiliate of Enviro-Engineers, Inc. (Washington, D.C.). Physical-chemical treatment is not in widespread use; in fact, only 17 such plants are under design or construction in the U.S. (see box). Nevertheless, it is receiving increasingly serious consideration as effluent restrictions tighten.

**Advantages**

The 50-mgd plant will be the largest physical-chemical treatment plant in the world, and will be capable of handling up to 100 mgd hydraulically (see

below). Effluent quality will represent 90% BOD removal, 93% suspended solids removal, and 90% phosphorus removal.

One advantage of a physical-chemical treatment plant is that unit processes are based upon hydraulic (rather than biological) requirements. This means that waste water flows above and beyond the design flow capacity do not necessarily mean deterioration in effluent quality. For example, filters can catch solids carried over from the clarifiers. Another benefit is high internal recycle of process waste water. The Cleveland plant will be capable of an instantaneous recycle flow of approximately 30 mgd for backwashing the filters and adsorption columns. The plant is designed to handle recycle flows superimposed upon the peak dry weather flows (70 mgd)—thus total

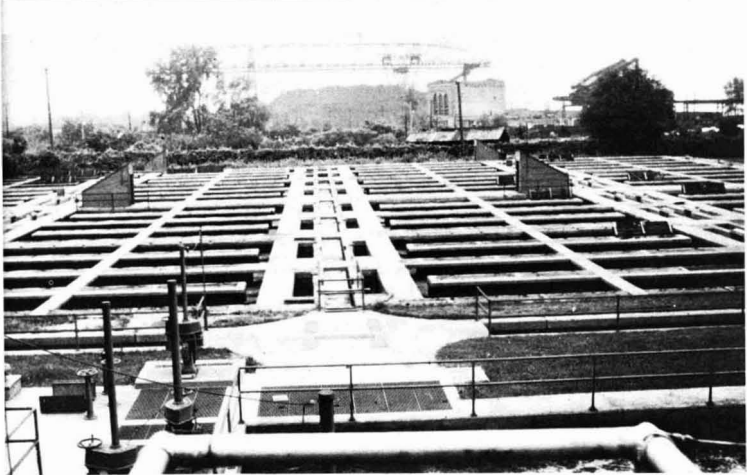
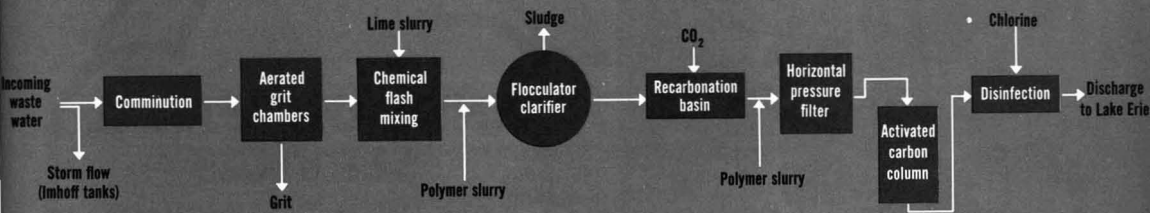
capacity can be 100 mgd for sustained periods.

Not all of the old plant will be demolished. The Imhoff tanks will remain and be modified (for screening and disinfection) to provide storm flows a minimum of treatment. Combined storm and sewer flows up to 100 mgd will be taken into the main treatment plant, and the remainder will be diverted to the storm-water holding Imhoff tanks for later treatment.

**Plant processes**

Here's how the new plant will work: Incoming waste water will undergo preliminary screening and settling to remove debris, sand, grit, and other large particles, and to provide some protection for the comminators which will finely grind the influent. After passing through aerated grit-removal

**Flow through Cleveland's physical chemical treatment plant**



chambers (flow diagram), the waste water will flow into two flash mixing tanks where propeller mixers will stir in a 10% lime slurry. The lime will convert influent phosphorus into insoluble calcium phosphate.

Water from the flash mix tanks will go into two channels, each serving two flocculator-clarifiers. The flow will again be divided and fed to the center flocculating well in each clarifier. Polyelectrolytes can be added at this point as a coagulant aid. Virtually all settleable solids will be removed here as waste particles coagulate and rapidly settle to the bottom of the basins.

The waste water, with a pH of 10.5-11.5 from the lime clarification step, then will pass into the recarbonation

basin. There, carbon dioxide will be bubbled through the water to lower the pH.

The dephosphated effluent next will go through a series of pressure filters operating at 10 psi. These 14 horizontal filters will be stacked in two levels of seven each to minimize space. The filter medium has not yet been chosen, but could well be beds of sand or crushed anthracite coal, or a combination of the two. This filtration step will virtually complete removal of the remaining suspended solids in the waste water.

After the filtration step, the semi-treated water will flow into activated carbon sorption columns (30 columns, each 20 ft in diameter, 28 ft high, and having a carbon bed depth of 17 ft) to remove any remaining dissolved organic material. The columns will be stacked in two levels of 15 columns each. Approximately 2000 tons of carbon will be used, and each column will be in service for 43 days between regeneration cycles.

Spent carbon will be regenerated in two multiple-hearth furnaces to burn off the collected organic material. The plant will be able to reuse regenerated carbon again and again. The filtration

and sorption units will be housed in a building equivalent in height to 13 stories.

The treated effluent will finally be disinfected by liquid chlorine. Studies are under way, however, to determine the feasibility of using ozone both for disinfection and as a method to achieve higher BOD removal if it should be required.

#### Sludge handling

Sludge will be pumped from the flocculator-clarifiers to two sludge-holding tanks equipped with sludge-thickener mechanisms. Although sludge concentrations of 10-14% could be achieved in the flocculator-clarifiers, the solids-handling system is conservatively being designed for 5% solids. Centrifuges will further dewater the sludge. Each centrifuge will have a capacity of 15,000 gph, although the design loading is 9850 gph, thus providing capacity for sustained plant operation at 100 mgd. Additional sludge can then be handled easily when waste water flow rate is as high as 100 mgd. Solids capture is expected to be above 90% and sludge cake solids above 30%.

Sludge cake will be fed to the re-

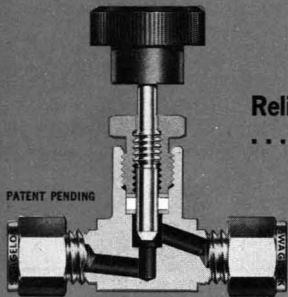
calcining furnaces at approximately 12,500 lb/hr. Zurn Environmental Engineers hopes for a recyclable lime product of 80% purity which can be reused at the flash mixing stage.

Instrumentation, control, and monitoring for the Westerly plant will be automated with economical use of manpower. A programmable computer will monitor all measurements, control positions, and alarms and provide feedback control.

About 60% of the plant design is complete, and bids on major equipment packages will be received this fall. Construction will begin before the year ends, and all phases of the physical-chemical treatment plant are expected to be operating by late 1974. The cost of the entire plant is estimated to be \$41 million, and the designers expect to achieve a waste water treatment cost of approximately 26-28¢ per 1000 gal.

This plant represents a significant breakthrough in a waste water treatment alternative not previously explored on a large scale. C. J. Touhill, vice president, Enviro-Engineers, Inc., believes, and will do much for the general acceptance of physical-chemical treatment.

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Circle No. 21 on Readers' Service Card

# New Jersey checks auto exhaust

*Annual safety inspection now includes emission testing for carbon monoxide and unburned hydrocarbons as part of the state's fight for cleaner air*

Don't be surprised when your late model car—which you think is in perfect condition—fails to pass the New Jersey state inspection this year. It flunked because the exhaust was too dirty.

That's not likely to cause you any great inconvenience—this year. The inspector will just give you a leaflet entitled "Your car and its pollution test" and tell you what to do to correct the problem. But after July 1, 1973, the state will be playing for keeps. If your car fails then, you will have two weeks to correct the problem and present it for reinspection—just as you would, for say, worn tires.

New Jersey is the first state to require emissions testing as part of the annual state inspection. Under Chapter 15 of the New Jersey Air Pollution Code, passed last June, the state will attempt to put a significant dent in pollution coming from light duty, gasoline-fueled motor vehicles.

Three sections of the code are of major importance. The first enacts a "public highway standard" which makes visible emissions from the engine or crankcase illegal after July 1, 1973 and provides fines ranging from \$25 to \$100.

The second section describes new motor vehicle dealer inspection standards. Under New Jersey law, the dealer must inspect new cars and certify that they meet state inspection standards. After July 1, 1973, the dealer will also have to certify that new cars meet emission standards for smoke, carbon monoxide (CO), and unburned hydrocarbons (HC).

The third section of the act provides for emission testing of all cars as part of



**Sniffer.** Technician measures tailpipe emissions at N.J. inspection station

the annual state inspection. The two-part emission test is an idle mode test which is not strictly comparable to the multicycle test prescribed by the federal government for new cars, according to John Elston, principal environmental engineer with the New Jersey Department of Environmental Protection. The inspector first checks for visible emissions from the engine or crankcase as the engine is raced. Then, with the engine idling, the inspector inserts a sampling probe in the tailpipe and checks to see if CO or HC levels exceed the standard. The test does not include measurement of nitrogen oxides (NO<sub>2</sub>).

The test equipment, manufactured by Sun Electric Co., uses nondispersive infrared monitors to measure pollutant levels. Most of the test equipment has been installed, according to Elston, and the remainder will be in place by the end of this month.

The timetable looks something like

this. Beginning July 1, 1973, motorists must meet the emissions requirements or fail the inspection. With the initial pollution standards, Elston says, about 12-15% of the state's estimated 3.5 million cars will fail the test. There are different standards for different model years (see table) and Elston says that approximately equal numbers of cars will fail the test in each of the standard categories.

As of July 1, 1974, the standards will get tighter. Based on the model year distribution of cars now on the road, Elston expects that about 20% of all vehicles inspected would not pass. Standards will get even tighter after July 1, 1975, and Elston says that about one third of all cars now on the road would fail the test under those standards.

Much of the success of the program will depend on the private garage owner's ability to service autos that don't come up to snuff. That's a major reason for the gradually tightening standard schedule. New Jersey hopes to convince mechanics that the equipment is valuable as a diagnostic aid. High HC usually means ignition malfunction, for example, Elston says, and excess CO tends to indicate carburetion problems. "We look on high emissions as pollution," he says, "garage mechanics should look on them as diagnostic signs." HMM

## Upper limits of CO and HC in auto exhaust

| MODEL YEAR | JULY 5, 1972                     |         | JULY 1, 1974 |         | JULY 1, 1975 |         |
|------------|----------------------------------|---------|--------------|---------|--------------|---------|
|            | CO, %                            | HC, ppm | CO, %        | HC, ppm | CO, %        | HC, ppm |
| pre-1968   | 10.0                             | 1600    | 8.5          | 1400    | 7.5          | 1200    |
| 1968-1969  | 8.0                              | 800     | 7.0          | 700     | 5.0          | 600     |
| 1970-1974  | 6.0                              | 600     | 5.0          | 500     | 4.0          | 400     |
| 1975       | (to be promulgated by amendment) |         |              |         |              |         |

# Effluent guidelines are on the way

*With most of its statutory enforcement authority jeopardized by recent court decisions, EPA is looking to a better method for controlling industrial water pollution*

Although it's not too well known yet, there's been a definite shift in EPA's strategy in the war against industrial water pollution. The agency's Office of Water Programs is readying its guns to fight water pollution at the industrial outfall, using a tactic adopted by the Office of Air Programs to halt air pollution from stationary sources, by promulgating effluent guidelines and performance standards.

The shift in position is tantamount to an admission that the agency's previous control strategy—based on water quality standards—simply has not worked. Enforcement conferences and 180-day notices—the major enforcement tools provided by the Federal Water Pollution Control Act, have proved to be costly and cumbersome remedies, virtually devoid of clout. One agency official, who declines to be quoted, labels them "ludicrous."

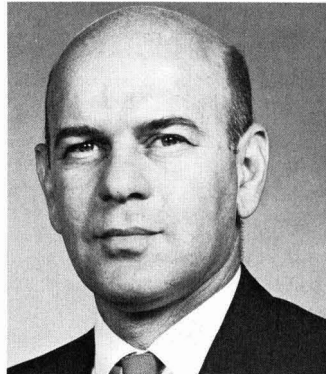
Similarly, the utility of the discharge permit provisions of the Rivers and Harbors Act of 1899—the so-called Refuse Act, pressed into service by the Nixon Administration in December 1970 to patch up the holes in EPA's armamentarium—is in serious trouble because of a pair of court decisions. In December 1971, Federal Judge Aubrey E. Robinson of the District Court for the District of Columbia, issued an injunction forbidding the issuance of any discharge permits until environmental impact statements for each major permit could be prepared. Some 20,000 applications for the permits are on file, according to EPA assistant administrator for enforcement and general counsel John R. Quarles, Jr., and preparation of environmental impact statements for each major one would be a "bureaucratic nightmare." EPA has appealed the decision, but until the appeal can be heard and decided, the ban on permits stands.

To make matters worse, in May of this year, the U.S. Court of Appeals in Philadelphia, Pa., ruled in a case involving the Pennsylvania Industrial Chemical Corp., that industrial polluters may not be prosecuted under the Refuse Act unless permits are available. "That

case," Quarles complains, "could stop us dead in our tracks. Something must be done or the Refuse Act—our principal legal weapon against industrial water polluters—may become a dead letter." Quarles has asked the Justice Department to intervene and speed up the appeals in the District of Columbia case.

## Full speed ahead

EPA isn't waiting for a congressional mandate to set effluent guidelines before gearing up to do battle with the industrial polluters, although such a



**Guideline chief Cywin**  
*Not waiting for Congress*

mandate is expected as a result of new legislation (see below). For example, there has been a quiet restructuring of the Office of Water Programs—specifically, it appears, to provide a framework for developing effluent guidelines. (See chart, page 779.) The office of Deputy Assistant Administrator for Water Programs, formerly headed by Eugene Jensen, has been split, creating two new positions—deputy assistant administrator for water programs operations and deputy assistant administrator for water programs planning and standards. Jensen has been named to the operations post; the planning and standards position is still vacant. The new effluent guidelines program is headed by division director Allen Cywin, former acting chief of Water Quality Research

for EPA, and is administered out of the planning and standards branch.

There is little doubt that legal authority to operate the effluent guidelines program will soon be forthcoming. Both H.R. 11896 and S. 2770—the House and Senate versions of the omnibus water pollution control amendments being thrashed over in joint committee—have virtually identical language requiring that the EPA administrator adopt and enforce effluent guidelines and standards for industrial point sources. "The Environmental Protection Agency is not waiting for this legislation to be passed before beginning to carry out and develop the necessary guidelines and standards that are required," says Michael B. La Graff, Cywin's second in command. "The time schedules of the legislation are very stringent and we need every minute of time in order to satisfy completely the requirements of the legislation," he adds.

The proposed water legislation (section numbers refer to H.R. 11896) has four separate sections dealing with effluent guidelines and standards:

- Sec. 304 (b): Effluent Limitation Guidelines
- Sec. 306: Standards of Performance for New Sources
- Sec. 307(a): Toxic Pollutant Standards and
- Sec. 307(b): Pretreatment Standards.

## Technology key

Under the effluent limitation guidelines called for in Sec. 304(b), EPA would identify both the "best practicable technology" currently available and the "best available demonstrated technology." Guidelines would be published within one year of the adoption of the new water amendments. By 1976 all industrial waste sources—no matter how old—would be required to adopt, as minimum acceptable treatment, the best practicable technology currently available.

The proposed legislation specifies several parameters to be considered in the development and application of the regulations, including the age of equip-



ment and facilities involved, the processes employed, process changes, engineering aspects of the application of various types of control technology, and the cost of achieving effluent reductions.

Regulations promulgated under Sec. 304(b) would establish the minimum requirements each industrial source would have to meet by 1976 and maximum effluent requirements that could be achieved, where necessary, within the allotted time. Such "practicable" control technology would be based on end-of-the-line treatment techniques rather than on cleaning up the process itself. The technology to be used would be determined purely on technical considerations and not on the quality of the receiving waters. It would be uniform regardless of the local pollution situation.

EPA interprets "currently available," to mean a control technology which in "demonstration projects, pilot plants, and general use has demonstrated a 'reasonable' level of engineering and economic confidence and viability in the process at the time of commencement of actual construction of the control facilities," La Graff says.

On the other hand, "best available demonstrated technology" embraces in-process control technology as well as outfall cleanup. Such levels will be set by technology that "through pilot plant operation or full-scale use has demonstrated both technological performance and economic viability at a level sufficient to reasonably justify the making of investments in such processes," according to La Graff. An important aspect of the legislation provided in Sec. 304(b) is that it would apply to all plants, and not just newer ones.

### Performance standards

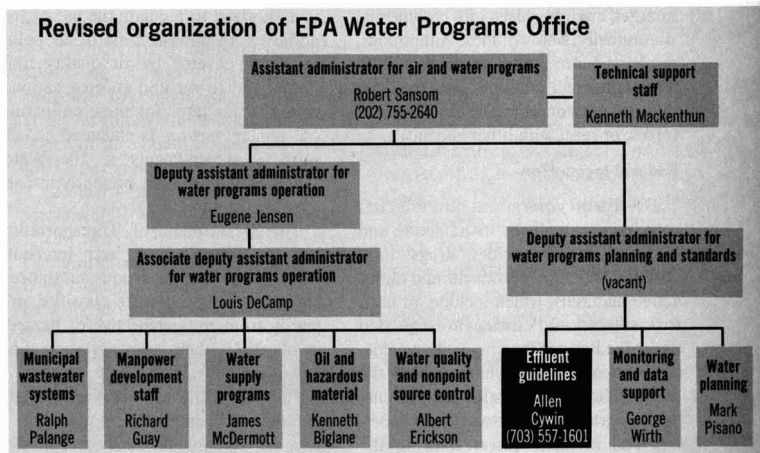
Sec. 306 of the proposed water law would require the administrator to promulgate performance standards within 15 months after passage of the law for new sources or all old sources which undergo "major modification." Such sources would have to incorporate the "best available demonstrated technology" at the time of construction or modification. While "best available" legally means the same for both new and old sources, EPA will probably require lower discharge levels from new plants because of greater opportunity to incorporate in-plant controls. This section of the bill specifically delineates about 30 industrial categories for which standards will be prescribed. EPA will probably end up with more categories than that.

Section 307(a) would require that within 90 days of enactment of the legislation, the administrator must publish a list of pollutants or combination of pollutants that are determined to be toxic. Toxic is distinguished from hazardous, La Graff says, in that a hazardous substance presents an "imminent or substantial danger," while for a substance to be declared toxic "requires evidence that it will cause death, disease, behavioral abnormalities, cancer, . . . or physical deformations in affected organisms or their offspring." Molasses is being considered as a hazardous substance "because when discharged into a body of water it has caused a fish kill," he says. "However, in a normal toxicity study it would require enormous amounts of molasses in order to be toxic, and therefore it would not normally be considered a toxic pollutant per se."

Within six months after publishing the toxic substances list, EPA would publish proposed effluent standards for

standards which will limit discharge of specific pollutants to municipal systems.

Just how EPA will implement the provisions of the water legislation remains open at this time. Clearly the time constraints are formidable, even considering that the bills have not yet become law. The first step for the agency is to develop categories and subcategories which take into account the parameters specified in the bills. A start, at least, has been made in a pilot study with the American Petroleum Institute. Following the sub-categorization of refineries by class—A, B, C, D, and E class refineries as defined by the industry—EPA has begun studies aimed at characterizing the effluents—no mean task in itself. The next step will be to assess the treatment technology available for application by each of the various classes. EPA must repeat the process for all industrial sources. The end result will be a set of output standards, in terms of hard numbers such as pounds of BOD/unit of raw material in-



each toxic pollutant. Such a standard could require a total ban, but standards could also be varied from industry to industry depending upon the degree of treatment technology available. Such variances among industries would not be granted simply because it is more expensive for one industry to treat a toxic substance than it is for a different industry to treat the same pollutant.

Section 207(b) would establish two provisions for the publication of effluent pretreatment guidelines. The first is for publication within six months of pretreatment guidelines aimed at aiding municipal systems, with some specific considerations that should be taken into account when accepting industrial wastes for treatment. The second is for publication within six months of pretreatment

put or production.

The job is complicated by the fact that, depending upon the amount of horse trading that goes on in the conference committee, the law may provide for a program to begin issuing discharge permits upon passage of the statute. "We must be prepared to support this effort immediately upon enactment of the legislation," La Graff says, "and not a year or 15 months following the enactment."

Amid all the uncertainty about specifics, one thing remains clear: With its current legal authority to check industrial water pollution seriously eroded, EPA is pinning its hopes on the effluent guidelines. Enforcement chief Quarles has called on Congress for speedy action. HMM

*Manufacturers of all types of chemicals and subsequent products wait for legislative proposals to gel as . . .*

## **Congress considers strict control of toxic substances**

**Chemicals.** *All new products may have to be tested before they can be marketed*



About two million chemical compounds are known, several thousand new chemicals are discovered each year, and several hundred are introduced into commercial use annually. Many of these compounds, discharged into the environment in both large and small amounts, can be either diluted or concentrated by physical forces, or react with other chemicals.

### **Federal legislation**

The federal government now exercises some control over the manufacture and distribution of pesticides, drugs, food additives, consumer products, and radioactive materials, which include, in part, toxic substances. Pesticides are regulated under the Federal Insecticide, Fungicide, and Rodenticide Act which protects the user and handler of pesticides by requiring registration with EPA, proper labeling, and in some cases, coloring the pesticide product. The Food and Drug Administration (FDA) also regulates pesticides by examining food to see that pesticide residues do not exceed allowable limits.

FDA, under authority of the Food, Drug, and Cosmetic Act, regulates food labeling, food additives, food containers, drugs, and cosmetics. The Atomic Energy Commission, under the Atomic Energy Act, controls almost the entire spectrum of activity associated with handling, transportation, and disposal of radioactive materials.

The Federal Water Pollution Control Act and the Clean Air act empower EPA to control direct release of pollutants into the environment. However, the Federal Water Pollution Control Act is generally aimed at accidental discharges of such substances into water.

The Clean Air Amendments of 1970 contain a section specifically aimed at toxic substances. The EPA administrator is authorized to regulate the use of fuel additives, to publish a list of air pollutants not covered by air quality standards, and to set and enforce national emission standards for these pollutants. (A similar section is included in the proposed amendments to the Water Pollution Control Act presently in congressional conference.)

The Department of Transportation has regulatory power over interstate transportation of hazardous substances. However, substances are classified primarily from the perspective of hazards involved in their transportation and possible spills from accidents.

The Resource Recovery Act calls only for the formulation of a plan for a system of national disposal sites for storing and disposing of hazardous wastes. In most instances, the other acts do not take into account disposal of wastes.

The Hazardous Substances Act of 1970 covers toxic materials in household products and toys, but not the raw materials from which they are manufactured. The Act does call for banning hazardous substances from interstate commerce, but the definition of hazardous substances is quite restrictive—a substance may be banned only if special labeling or packaging is found to be ineffective in preventing a hazard. (Only three household products have so far been banned.)

### **Senate bill**

In 1971, both houses of Congress introduced toxic substances control legislation. In May of this year, the Senate passed the Toxic Substances Control Act

(S. 1478) by a 77-0 vote. Under terms of this bill, within one year of enactment, EPA would specify test protocols (standardized methods of performing tests) for various classes and uses of chemical substances and set results that must be achieved "to protect human health and environment."

EPA would also determine standards of use for a product. For example, a regulation might say that a certain detergent could be used only if the phosphate content were very low. If it were higher, it could be used everywhere except the Great Lakes Basin, where overfertilization is a problem.

One controversial section (the Spong Amendment) would require premarket screening of new chemical substances. Any manufacturer of a new chemical would have to submit test results of intended uses of the substance to EPA at least 90 days prior to its commercial production. During this 90-day period, the EPA administrator would propose any rules or regulations governing the use or distribution of the substance.

For existing chemical substances (those on the market prior to enactment of the law), the EPA administrator would require testing if he had reason to believe that manufacturing, processing, distribution, use, or disposal of that substance posed an "unreasonable" threat to human health or the environment. Furthermore, any new use for an existing chemical would require new testing and authorization, according to S. 1478.

If an "imminent hazard" existed, U.S. district courts, upon petition by the EPA administrator or the Attorney General, could restrain the uses or distribution of the substance responsible for the immi-

ment hazard. Chemical substances which the administrator found manufactured, processed, distributed, used, or disposed of in violation of regulations and which of themselves constituted an imminent hazard could be seized. Under the law, the administrator would require reports from manufacturers indicating the names and identities of the chemical substances produced, the categories of use, the amounts of each substance produced, and a description of the by-products. "Trade secrets" would not be made public.

The Spong Amendment to the Senate bill also contains a citizen suit section. Citizens would be allowed to bring suits to enjoin violations of the act and to require the performance by the EPA administrator of his mandatory duties.

A major section of the bill deals with transporting chemical substances on navigable waters. The Coast Guard, after notification from EPA of potential harm from the transport of hazardous chemical substances, would establish a system for ports, harbors, and other waters to prevent environmental harm. The Coast Guard would be the enforcing arm of such a system of regulations.

#### House bill

The wording of the House bill is generally similar to that of the Senate bill. Overall, however, the House version (backed by the administration) is less harsh than the Senate version.

In the House bill, new chemicals would not have to be screened before

marketing. The manufacturers would send reports to the EPA administrator describing the characteristics of the chemical, and action could be taken at that time if the substance were considered hazardous. Also the House bill has no provision for citizen suits.

The Council on Environmental Quality (CEQ), under the House bill, would develop a standard classification system for toxic chemicals. On the basis of this system, reports submitted by industry and inspections of facilities, EPA would be able to make initial judgments as to which substances posed problems; not all new chemicals would be tested. Protocols would be required only for new chemicals (the Senate bill covers both new and existing chemicals).

An area of controversy in both bills is the absence of regulations covering intermediate chemicals—those chemical substances that are converted chemically in the course of manufacture of products and subsequently sold publicly. Intermediates are not covered in either bill and are exempt from regulation. However, a potentially dangerous chemical could be shipped intrastate to a processor who might convert it into an environmentally innocuous substance which in turn could be introduced into interstate commerce.

Another area of dispute is that of environmental impact statements. Should EPA write a statement for each and every chemical? And could the agency be sued if an EPA-approved substance turns out to be harmful to the environment?

The House is presently looking at its bill in respect to the one the Senate has passed. At press time, sources on Capitol Hill expected the bill to be voted on before the end of the summer session of Congress. However, it is probable that joint meetings between the House and Senate would be necessary to iron out the differences in the bills.

#### Office of Toxic Substances

Perhaps in anticipation of forthcoming legislation, EPA recently created the Office of Toxic Substances within the Office of Categorical Programs. Although, at press time, the EPA administrator was not required by legal mandate to establish it, the Office is staffing up and has begun a number of activities of its own. Under existing legislation, the Office does not have any specific regulatory or statutory authority. "We have a coordinating role," says Charles Gregg, Jr., temporary acting head of the Office, "and we're interested in seeing that the agency looks at the problems associated with a substance, for instance, mercury, as a single problem, rather than a number of problems that everyone handles his own way."

Gregg and the other staff members feel that many toxic substances problems can be solved even if no act emerges from Congress. They hope that their persuasive powers and what little authority other environmental acts impart will enable government and industry to sit down and rationally solve problems concerning toxic substances.

#### Industrial reaction

Industry sources feel that in view of the regulatory statutes already in force, that there is no need for "sweeping" new legislation. For example, C. Boyd Shaffer, Manufacturing Chemists Association, believes that not all new chemicals need be tested. Of those tested, not all need be tested to the same degree, he says.

Shaffer also objects to the possible time lag pending approval of new chemical substances. Smaller firms have indicated that they will be hesitant about introducing new chemicals if they face expensive delays, recalls, or bans of new or existing chemicals.

EPA Deputy Administrator Robert Fri and CEQ Chairman Russell Train both agree that the Spong amendment requirement for premarket screening should be revised. EPA does not want to be inundated with thousands of premarket tests on which to make a decision "within 90 days." CKL

**Proposed bills contain several basic differences**

**H. R. 5276**  
92<sup>ND</sup> CONGRESS  
1<sup>ST</sup> Session

IN THE HOUSE OF REPRESENTATIVES  
MARCH 1, 1971  
Mr. SPOONER (for himself and Mr. SPENCER) introduced the following bill; which was referred to the Committee on Interstate and Foreign Commerce

**A BILL**  
to amend the Federal Hazardous Substances Act, as amended, and for other purposes.  
Be it enacted by the Senate and House of Representatives of the United States of America in Congress assembled, that this Act may be cited as the Toxic Substances Control Act of 1971.

SEC. 2. The Federal Hazardous Substances Act is amended by inserting before section 1 of such Act the following:

SECTION 1—HAZARDOUS CONSUMER PRODUCTS.  
Sec. 3. Such Act is further amended by adding...

SENATE  
92<sup>ND</sup> CONGRESS  
2<sup>ND</sup> Session

REPORT  
No. 92-789

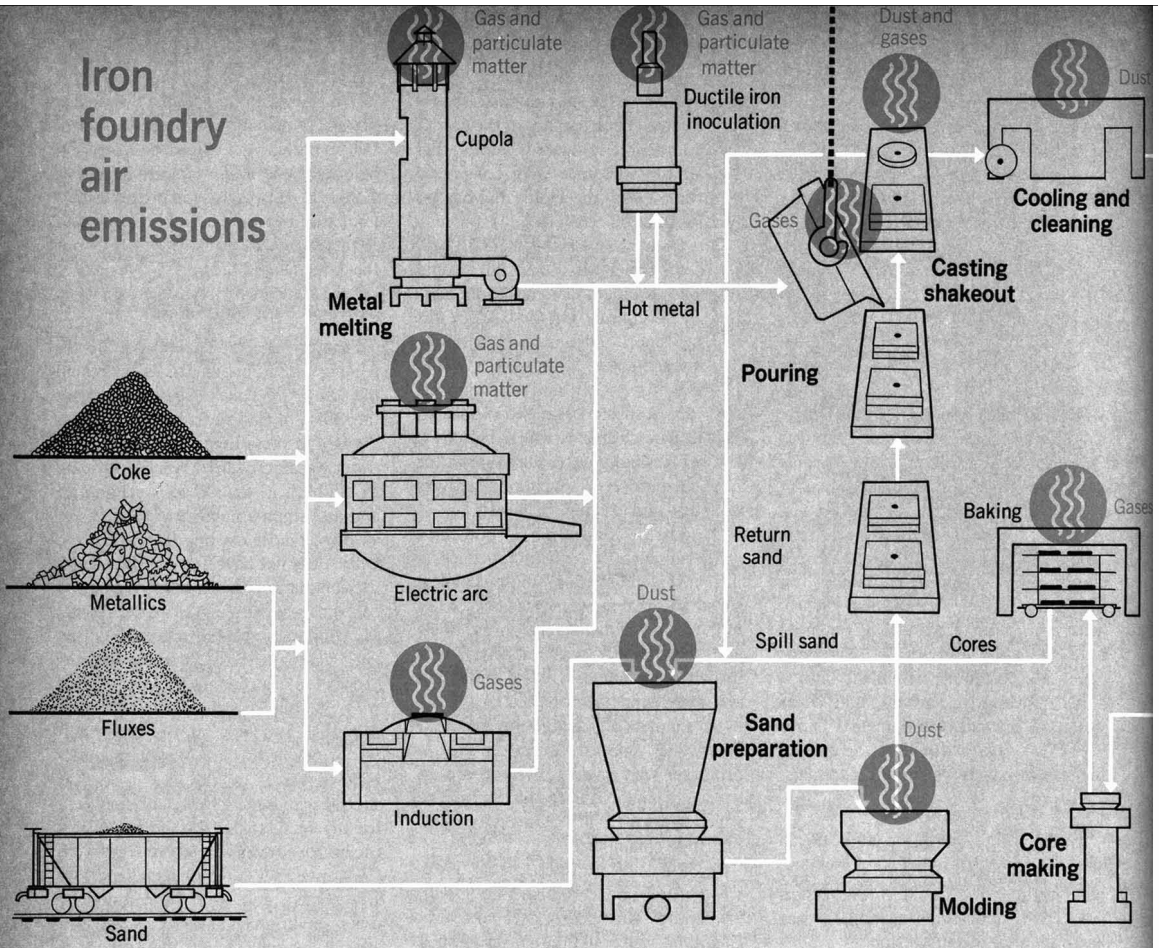
TOXIC SUBSTANCES CONTROL  
ACT OF 1972

REPORT  
OF THE  
SENATE COMMITTEE ON COMMERCE  
ON  
S. 1478  
(TOGETHER WITH SUPPLEMENTAL VIEWS)  
TO AMEND THE FEDERAL HAZARDOUS SUBSTANCES ACT,  
AS AMENDED, AND FOR OTHER PURPOSES

MAY 5, 1972

U.S. GOVERNMENT PRINTING OFFICE  
WASHINGTON : 1972

## Iron foundry air emissions



# Impact of foundry pollution

**Bernard S. Gutow**

*A. T. Kearney, Inc.  
Chicago, Ill. 60606*

Within the next 10 years, control expenditures could result in one third of U.S. iron foundries closing their doors and the eventual layoff of 26,000 employees

The iron foundry industry is defined as those shops that melt iron in furnaces, pour it into molds, and alloy and/or treat the iron in either the molten or cast state. Foundry processes are limited to making gray, malleable, and ductile iron castings. The industry is composed of some 1635 foundries (in 1971) of which 71% were small, less than 100 employees; 25% medium, between 100 and 500 employees; and only 4% large, over 500 employees.

Foundries are widely distributed and are located in almost every state with half of them in the Great Lakes states. Approximately 25% of all iron foundries are captive (the remainder being independent), largely producing jobbing type castings.

Most foundries are relatively old, although many have been modernized by installing new equipment. Many of the small foundries are marginal oper-

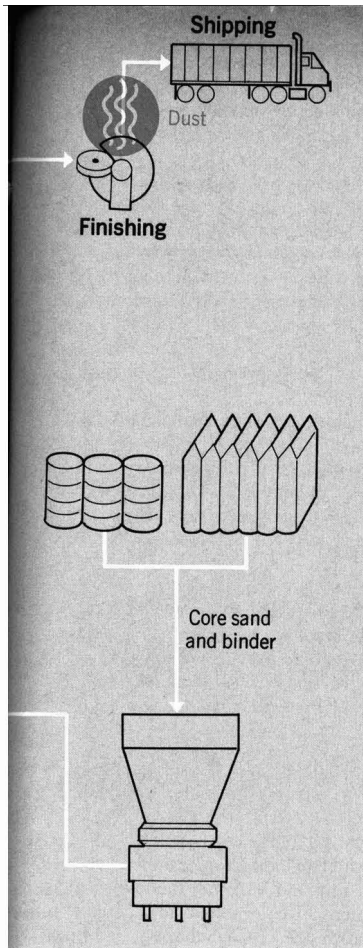
ations with old or obsolete equipment and facilities. Melting is still principally accomplished by cupolas (vertical cylindrical furnaces), but output from electric arc and induction furnaces is increasing in importance and tonnage.

The principal environmental problem of the iron foundry industry is air pollution caused largely by melting operations. Air pollution from non-melting operations is more easily controlled, and emissions are considered to be more of an in-plant environmental problem than an air pollution problem. Water pollution results principally from wet scrubbers installed on cupolas for air pollution control and from slag quenching on cupolas.

### Production

Iron castings production has varied widely during the past 10 years, from 10 million to 15 million tons per year.





## control

Although yearly figures have fluctuated, the general trend has been moderately upward, with a continuing growth projected at 2 wt %/year. Malleable iron output has remained at about one million tons per year, while ductile iron production has shown steady growth and now exceeds malleable production.

Principal production categories include cast iron pipe and fittings—representing 23% of product cast; ingot molds, 11%; and miscellaneous castings, 66%. However, only 65 foundries produce pipe and molds, resulting in 4% of the foundries producing 34% of the tonnage.

The miscellaneous iron castings category includes all malleable and most of the ductile iron output as well as gray iron castings. Principal users are automotive and agricultural equipment industries, which when combined, account for over 33% of all castings produced

(Table 1). Only 66% of the iron casting production is accounted for by 30 major industries, with over 2.5 million tons per year distributed among all other industries.

Markets for iron castings have been projected to increase to approximately 17 million tons per year by 1980. The only area in which competition from other products is expected to be a major consideration is in cast iron pressure and soil pipe. Export markets for iron castings are expected to diminish, and imports are expected to increase. However, these represent only a minor factor in the total market.

Iron foundry production processes can be divided into two broad categories: melting and nonmelting. Melting operations involve cupolas, electric arc, induction, and reverberatory furnaces. These account for the more important pollution control problems in the iron foundry (see flow diagram). Nonmelting operations include molding, pouring, shakeout, sand preparation, cleaning, finishing, and coremaking. Emissions from these operations are more easily controlled with lower cost, readily available equipment.

Iron foundry population has declined steadily from 3200 in 1947, to 1635 in 1971, and is projected to continue declining to about 1000 by 1980. The foundries that have closed, or are expected to close in the next decade, are primarily the small ones without the capital to modernize and mechanize.

The necessity for large capital expenditures for pollution control has been a contributing factor, but has not been the principal reason for the closures. Despite the reduction in the number of operating foundries over the past years and the projected continuance of that trend through 1980, the industry will continue to meet the demand for iron castings. Since the average iron castings production per foundry has increased offsetting the loss in foundry population, about 16,500 tons per year will be produced by 1980. With the exception of pipe and ingot mold foundries, the vast majority of iron foundries produce

a variety of iron castings, mostly on a jobbing basis.

Total employment was about 230,000 in 1968, with average labor input being 23 man-hr per ton of castings. Although almost all levels of skills are utilized in iron foundries, most of the production labor can be classified as unskilled or semiskilled.

### Emission control

Emission control costs, measured against such factors as sales, total assets, and cost per ton of castings, generally show a declining percentage as foundry size increases. Therefore, a greater emission control burden is placed on the smaller foundries, which also accounts for their inability to cope with this cost.

The effect of environmental control on cost of castings varies widely from more than \$14 per ton for the smallest foundries to under \$2 per ton for the largest foundries. Except for the smallest foundries, these cost increases are not a significantly high percentage of the casting cost. However, the profit structure of the industry is not sufficiently strong enough to absorb this added cost. As a result, the cost will have to be passed on to the castings customers as a price increase. Since the entire industry is faced with the same problem, price movements may have a negligible effect in shifting demand between foundries. However, it will probably result in some losses to competitive materials in pipe products and to imported castings.

Technological changes taking place in the iron foundry industry involve almost every area of activity, but are concentrated primarily in three general directions: melting, mechanization and automation, and pollution and environmental control. Although the first two result in lower labor costs and higher productivity, the high capital costs involved in all areas have accelerated the rate of closing of small foundries.

The effect of government influence, both federal and local, on iron castings purchase is minimal, since very few iron castings are bought directly by governments. The one exception is cast



TABLE 1

*Distribution of miscellaneous iron castings*

| Industry user                             | 1967 Distribution |      | Industry user                           | 1967 Distribution |       |
|---|-------------------|------|---|-------------------|-------|
|   | Tons<br>× 1000    | %    |   | Tons<br>× 1000    | %     |
| Motor vehicle parts and accessories       | 2593              | 27.4 | Printing trades machinery               | 67                | 0.7   |
| Farm machinery                            | 558               | 5.9  | Hardware                                | 55                | 0.6   |
| Motor vehicles                            | 505               | 5.3  | Textile machinery                       | 55                | 0.6   |
| Internal combustion engines               | 295               | 3.1  | Industrial trucks and tractors          | 51                | 0.5   |
| Construction machinery                    | 247               | 2.6  | Household laundry equipment             | 47                | 0.5   |
| Enameled sanitary ware (1965)             | 207               | 2.2  | Special industry machinery              | 44                | 0.5   |
| Heating equipment (1965)                  | 199               | 2.1  | Machine tools—metal forming             | 44                | 0.5   |
| Valves and pipe fittings                  | 165               | 1.7  | Special dies, tools, jigs, and fixtures | 40                | 0.4   |
| Metal cutting machine tools               | 160               | 1.7  | Paper industries machinery              | 29                | 0.3   |
| Pumps and compressors                     | 144               | 1.5  | Ball and roller bearings                | 24                | 0.3   |
| Cooking utensils (1965)                   | 140               | 1.5  | General industrial machinery            | 22                | 0.2   |
| Refrigeration machinery                   | 132               | 1.4  | Food products machinery                 | 20                | 0.2   |
| Power transmission equipment              | 106               | 1.1  | Woodworking machinery                   | 20                | 0.2   |
| Railroad and street cars                  | 104               | 1.1  | Metalworking machinery                  | 19                | 0.2   |
| Motors and generators                     | 91                | 1.0  | All other                               | 3212              | 33.9  |
| Miscellaneous machinery except electrical | 75                | 0.8  | Total                                   | 9470              | 100.0 |

Note: Does not include cast iron pipe or ingot molds.

Source: Department of Commerce, Bureau of the Census, 1967 Census of Manufactures.

iron pipe, where government specifications and cost control tend to promote lower cost, competitive products.

Price increases of \$2 to \$14 per ton, caused by the need to recover costs of installing and operating pollution controls in iron foundries, will have some effect in promoting the use of competitive products and materials over iron castings, particularly in pressure and soil pipe. It will also, at least temporarily, adversely affect the foreign balance of trade by reducing exports and increasing import of iron castings. Export markets, however, represent a minor factor in the total market.

Competition within the iron foundry industry will be affected to only a limited degree since all foundries are faced with the same need for installing pollution controls. However, the need for higher increases, \$14 per ton or more, among the very small foundries will undoubtedly adversely affect their competitive positions and will result in increased closings among small shops.

#### Foundry closings

The rate of closing of small foundries, undiminished for the past 25 years, is expected to continue at least for the next 10 years. The reasons have been economic—principally the need for

capital expenditures to replace equipment, reduce labor costs, and increase productivity. The added need for high-cost pollution controls, which yield no return on investment and, in fact, actually increase operating costs, has accelerated the rate of closing of smaller and marginal foundries. The number of foundries having fewer than 20 employees that manage to survive until 1980 will be very small, probably under 100, compared with over 700 only 10 years ago. Older foundries, and those still operated manually, will also experience a high percentage of closures.

Since foundries expected to close are primarily small ones with low capacity, the total displaced tonnage is not expected to be great in relation to total available capacity. Principal problems will be that as the very small jobbing foundries disappear, there will be few foundries left that will be willing to take small orders for one or two special castings.

Most foundries obtain their metallic and nonmetallic raw materials from suppliers and dealers located in their general areas. These in turn get their materials from steel plants, refractory firms, quarries, and similar companies. The principal exceptions are the scrap dealers located in every community

who buy local scrap, process it, and sell it to foundries. Since the total foundry tonnage is expected to continue to grow, the closing down of individual foundries is not expected to have any national effect on suppliers. Local dealers and supply firms may be affected if the only foundry in an area closes down, but most will continue to supply the same materials to other foundries in the area.

The net effect of the continuing decrease in the number of iron foundries, while the total casting tonnage has continued to grow, has been to increase the average output per foundry from 3800 tons per year in 1947 to 8700 tons in 1969. This is projected to be 16,500 tons in 1980, and further illustrates the rapid disappearance of the small foundries.

Since pollution control costs result in price increases, products such as pipe and molds, which are sold as finished products directly to consumers, will experience a direct increase in the cost of final products. However, for most jobbing castings, which constitute only a small percentage of the weight of the product in which they are used, the overall effect on the final product cost is relatively minor. For example, the cost of the average automobile has been

estimated to increase about 50 cents owing to the installation of pollution control equipment in iron foundries.

### Employment effects

The principal effect of the closing of foundries is expected to be on local employment and to a lesser degree on national employment. An estimated distribution of foundry closures has been made, resulting in a state-by-state analysis of the effect on employment (Table 2).

The total number of employees estimated to be dislocated by foundries projected to close in the next 10 years is 26,630, or about 11% of total foundry employment. Approximately half or their equivalent will be reemployed in other iron foundries, which will increase their business by picking up that given up by the closed foundries. Net unemployment is therefore estimated to be approximately 13,300. However, many of these foundries are expected to close for reasons other than the need

for installing pollution controls. Pollution control will only accelerate the rate of closings.

Approximately 2266 of the 13,300 foundry workers estimated to be unemployed as a result of foundry closings through 1980 will possess skills directly transferrable to other industries. If local demand for these skills exists at the time of a foundry closing, these workers will be absorbed into other industries. However, the majority of foundry workers are semiskilled or unskilled which creates a need for retraining and, in some cases, relocation to new areas.

Expenditures for air pollution control in iron foundries are estimated at \$24 million in 1972, increasing annually to \$131 million in 1975, after which controls are assumed to have been largely installed and annual expenditures will drop off. The major problem facing foundries has been identified as raising capital funds for installing controls. It represents a problem of financing non-productive expense in an industry with earnings always marginal.



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Special inducements may have to be provided by various levels of government to assist and encourage foundries to make the necessary expenditures rather than closing their doors. Of the many alternatives considered, those which are most likely to be successful have been identified as subsidies or grants covering large portions of the capital investment for pollution control, and/or large direct offset charges against income taxes.

Because iron castings output is expected to continue to grow, even though many iron foundries will close, the overall effect on the industry will not be as catastrophic as might otherwise be expected. Raw materials will continue to be required in undiminished quantities, and castings customers will continue to be supplied in spite of some local inconveniences. Even the unemployment, created by closing of many small foundries, will be compensated for partially by the need for many surviving foundries to expand to pick up the displaced castings tonnage.

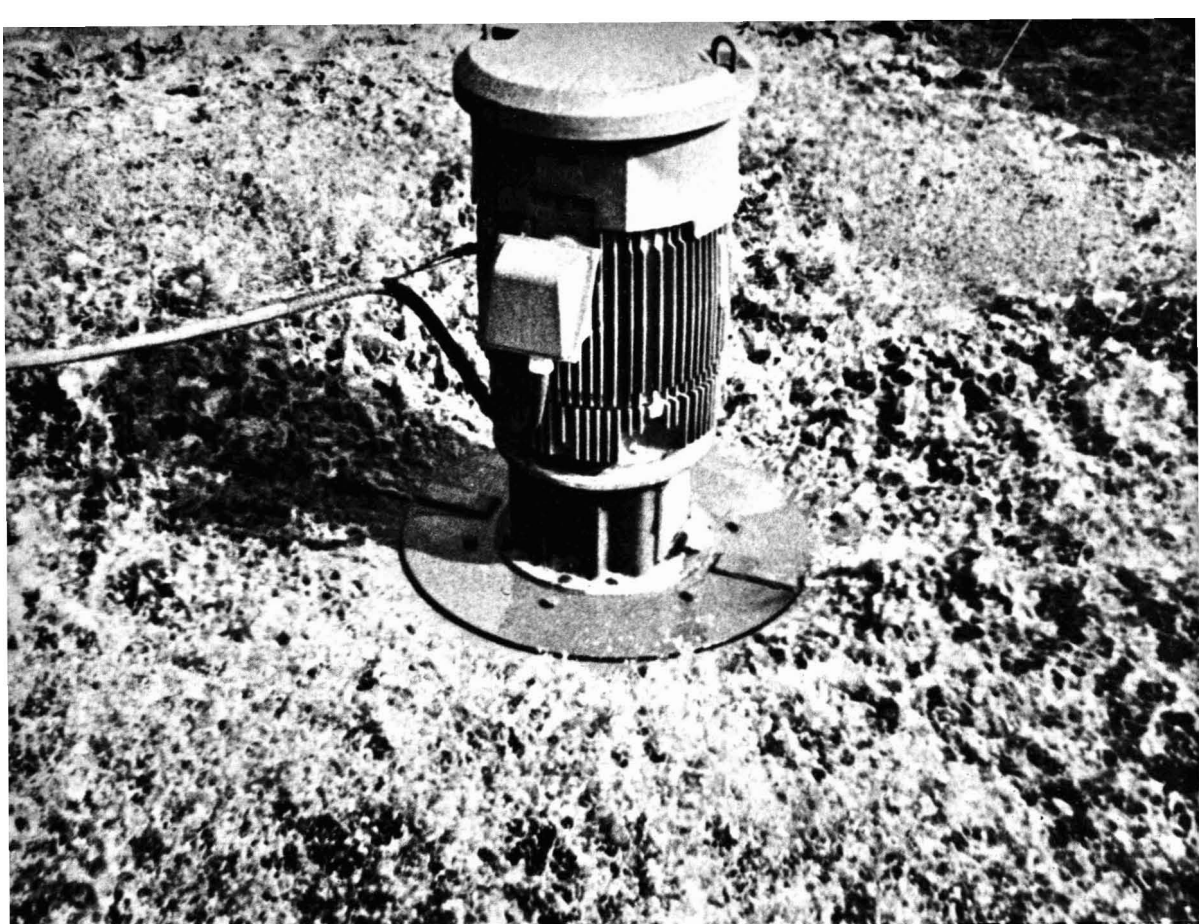
The widespread distribution of iron foundries, and the location of foundries in almost every community, are expected to create a local, rather than a national, problem. This will be true particularly where a small foundry is practically the only industry in a community. In these cases, attraction of new industry or relocation of some workers to other communities will be necessary. With the possible exception of some scrap yards serving isolated communities where a foundry closes, the effect of iron foundry closures on supplier industries in most areas is expected to be very minor.

TABLE 2

### Projected iron foundry employee dislocations (1971-1980)

| State       | Foundry distribution | Foundry closings | Employee dislocations | State        | Foundry distribution | Foundry closings | Employee dislocations |
|-------------|----------------------|------------------|-----------------------|--------------|----------------------|------------------|-----------------------|
| Alabama     | 65                   | 23               | 1,025                 | Montana      | 2                    | —                | —                     |
| Alaska      | —                    | —                | —                     | Nebraska     | 7                    | 2                | 85                    |
| Arizona     | 3                    | —                | —                     | Nevada       | 1                    | —                | —                     |
| Arkansas    | 9                    | 4                | 40                    | N.H.         | 9                    | 4                | 65                    |
| California  | 86                   | 41               | 1,585                 | New Jersey   | 44                   | 18               | 565                   |
| Colorado    | 15                   | 6                | 265                   | New Mexico   | —                    | —                | —                     |
| Connecticut | 28                   | 12               | 595                   | New York     | 85                   | 36               | 1,315                 |
| Delaware    | 1                    | —                | —                     | N. Carolina  | 29                   | 16               | 465                   |
| D.C.        | —                    | —                | —                     | N. Dakota    | 3                    | 1                | 10                    |
| Florida     | 16                   | 9                | 165                   | Ohio         | 164                  | 59               | 2,745                 |
| Georgia     | 31                   | 16               | 415                   | Oklahoma     | 18                   | 9                | 420                   |
| Hawaii      | 1                    | —                | —                     | Oregon       | 14                   | 8                | 170                   |
| Idaho       | 3                    | 2                | 20                    | Pa.          | 166                  | 63               | 2,865                 |
| Illinois    | 104                  | 35               | 1,820                 | Rhode Island | 10                   | 3                | 120                   |
| Indiana     | 79                   | 27               | 1,190                 | S. Carolina  | 15                   | 9                | 205                   |
| Iowa        | 38                   | 14               | 740                   | S. Dakota    | 1                    | —                | —                     |
| Kansas      | 24                   | 13               | 425                   | Tennessee    | 43                   | 17               | 745                   |
| Kentucky    | 11                   | 5                | 165                   | Texas        | 59                   | 31               | 920                   |
| Louisiana   | 11                   | 7                | 120                   | Utah         | 12                   | 5                | 190                   |
| Maine       | 8                    | 5                | 140                   | Vermont      | 8                    | 3                | 95                    |
| Maryland    | 11                   | 1                | 75                    | Virginia     | 33                   | 18               | 600                   |
| Mass.       | 51                   | 25               | 1,065                 | Washington   | 21                   | 12               | 195                   |
| Michigan    | 122                  | 48               | 1,950                 | W. Virginia  | 13                   | 6                | 150                   |
| Minnesota   | 35                   | 20               | 775                   | Wisconsin    | 93                   | 33               | 1,540                 |
| Mississippi | 7                    | 5                | 115                   | Wyoming      | —                    | —                | —                     |
| Missouri    | 26                   | 13               | 475                   | Total        | 1635                 | 685              | 26,630                |

Note: Of the 26,630 employee dislocations, approximately 13,000 employees are absorbed by remaining foundries and 2000 are absorbed by other industries, leaving a net dislocation of about 11,000 employees.



# The case for higher rate waste water treatment

No "universal" design standard for biological waste water treatment plants exists in the United States. Each state has its own body of regulations, design guidelines, or statutes which set forth in greater or lesser detail acceptable design criteria. Often, even where detailed design guides exist, these are subject to judgmental modification and interpretation by regulatory agency officials.

Perhaps the nearest approach to a universal design standard is the "Recommended Standards for Sewage

Even so-called "overloaded" plants may in fact be capable of treating larger flows; modified operation is the key to better utilization of design capacity

Works," published and revised periodically by the Great Lakes-Upper Mississippi River Board (GLUMRB) of State Sanitary Engineers. This document is frequently referred to as the "Ten States Standards" since the Board consists of Illinois, Indiana, Iowa, Michigan, Minnesota, Missouri, New York, Ohio, Pennsylvania, and Wisconsin. Other states follow these recommended standards at least to some extent and, in any event, these standards are fairly representative of regulatory agency thinking and practices generally.

With reference to the "permissible loadings" for several variants of the activated sludge process of waste water treatment, GLUMRB permits organic loadings to vary from a low of 12.5 lb BOD (signifies BOD<sub>5</sub>) per 1000 ft<sup>3</sup> of aeration tank capacity (extended aeration process) to a high of 50 lb BOD/1000 ft<sup>3</sup> (contact stabilization or step aeration processes). For plants designed to treat 500,000 gal./day of waste water or less (5000-person contributing population or less), the loading range is 12.5–30 lb BOD/1000 ft<sup>3</sup>, depending on the process variant selected.

The contention exists (with supporting data) that substantially higher loadings should be permitted. It has also been contended (and demonstrated) that utilizing higher design loadings in properly designed waste water treatment plants would not result in deterioration of plant performance or effluent quality. Furthermore, "volumetric loading" criteria such as "lb BOD/1000 ft<sup>3</sup> of aeration tank volume/day" are meaningless both from a practical and a fundamental standpoint. Such criteria ignore completely the fact that the food-to-microorganisms ratio governs characteristics and performance of biological waste water treatment systems. In short, volumetric criteria leave unanswered the question, "How many, if any, microorganisms are in the aeration tank with the BOD?"

#### Case for higher loadings

Data supporting the soundness of higher loading levels abound in the published literature and have been freely available to regulatory agencies and consulting engineers alike for many years. In the early 1950's for example, the University of Florida studied a waste water treatment system designed on a 3.8-hr aeration period. A "typical activated sludge" was produced when the unit was operated as a combined chemical-biological treatment system, the Florida researchers reported in *Sewage Ind. Wastes* (February 1952). During this phase of the study, water-softening sludge (principally calcium carbonate) was added at various dose rates ranging from 25–200 mg/l. (as

CaCO<sub>3</sub>). At air inputs of 0.28–0.30 ft<sup>3</sup>/day (waste-treated basis) BOD removals averaged 91%, and suspended solids removals averaged 94%.

Experiments (begun in 1937) conducted by the Federal Institute of Water Supply, Sewage Purification and Water Pollution Control, Swiss Federal Institute of Technology, Zurich, Switzerland, covered a range of aeration periods of from 1.07–9 hr and a range of aeration tank loadings of from 23.1–202 lb BOD/1000 ft<sup>3</sup> (*Sewage Ind. Wastes*, January 1954). Mixed liquor suspended solids ranged between 2830 and 3930 mg/l. Treatment system effluent BOD values ranged from 8–32 mg/l. while effluent suspended solids values ranged from 8–47 mg/l. Effluent suspended solids and BOD concentrations of 20 mg/l. or less were achieved at aeration tank loadings of 160 lb/1000 ft<sup>3</sup> or less.

Experiments from 1948–1951 by the Research Institute for Public Health Engineering, National Health Research Council, The Hague, Netherlands, and the Institute for Sewage Purification indicated that if sufficient aeration capacity was available, the aeration period could be greatly reduced (*Sewage Ind. Wastes*, February 1954). Loadings of 6–8 times "normal" (normal being 20–60 lb BOD/1000 ft<sup>3</sup>) could be treated by activated sludge. At a loading of 300 lb BOD/1000 ft<sup>3</sup> of aeration tank capacity, an average effluent BOD level of 39 mg/l. was achieved with individual values as low as 16 mg/l. At a loading of 150 lb BOD/1000 ft<sup>3</sup>, an average effluent BOD of 15 mg/l. was obtained in one run and 11 mg/l. during another. Effluent BOD averaged 23 mg/l. at a loading of 197 lb BOD/1000 ft<sup>3</sup>. At 275 lb. BOD/1000 ft<sup>3</sup>, effluent BOD concentration averaged 15 mg/l. As explained in "Biological Treatment of Sewage and Industrial Waste" (Reinhold, 1956), treatment of a beet sugar process waste at an aeration tank loading of 625 lb/1000 ft<sup>3</sup> produced 90% BOD removal.

In the same publication, operating data from 65 waste water treatment plants in the U.S. support the contention, that, as long as a minimum aeration period of 1.0–1.5 hr is provided, activated sludge plant performance is in-

dependent of aeration time and is, beyond that point, dependent on loading in terms of lb BOD/lb MLSS (mixed liquor suspended solids). Data indicate about 93% removal of applied BOD up to at least a loading of 0.5 lb BOD/lb MLSS/day. Activated sludge plants with loadings ranging from 150–600 lb BOD/1000 ft<sup>3</sup>/day removed 89–92% of the applied BOD at plant loadings from 150–400 lb BOD/1000 ft<sup>3</sup>.

In 1959, an activated sludge waste water treatment plant utilized series aeration and clarification, described in *Water Sewage Works* (February 1959). A total aeration period of 1.6 hr at design flow was provided. The BOD loading averaged 124 lb/1000 ft<sup>3</sup>/day. The observed average effluent BOD concentration was 13 mg/l. or a removal efficiency of 92.9%. Experiments in the Netherlands showing that an activated sludge system loaded at 3746 lb BOD/1000 ft<sup>3</sup>/day produced an effluent with a 28 mg/l. BOD level are discussed in "Advances in Biological Waste Treatment" (Macmillan Co., 1963).

Experiments conducted by the Department of Sanitary Engineering, College of Technology, Hanover, Germany, described in *J. Water Pollut. Contr. Fed.* (October 1960), revealed that BOD removals averaging 87% were achieved at a loading of 200 lb BOD/1000 ft<sup>3</sup>/day. At another location, aeration tank loadings of 225–644 lb BOD/1000 ft<sup>3</sup> resulted in effluent BOD values averaging 27 mg/l. (an average removal of 87%).

From observations and experiments conducted in Hungary, BOD removals of 90% or greater are reported in "Advances in Water Pollution Control" (Pergamon Press, 1965) at loadings ranging from 199–268 lb BOD/1000 ft<sup>3</sup>/day for 1.0–1.5-hr aeration periods. In 1965, high-rate activated sludge was recognized as a valid process variant. The successful development of this process variant depended on first developing high-intensity aeration devices (*J. Water Pollut. Contr. Fed.*, February 1965). High mixed liquor solids and short aeration periods were process characteristics. In studies by the Hydraulic Research Institute, Prague, Czechoslovakia, BOD removals of 90%



or greater were reported at the Third International Conference on Water Pollution Research (1966) for volumetric loadings of 96–324 lb BOD/1000 ft<sup>3</sup>/day.

In 10 high-rate plants in Canada, 200 samples were collected and subjected to analysis. Design volumetric loading was 125 lb BOD/1000 ft<sup>3</sup>/day with a minimum aeration tank detention time of 1.75 hr. High-rate data were compared to data from 57 conventional activated sludge plants (1200 samples) and 28 extended aeration plants (240 samples) (Ontario Water Resources Commission). The mean effluent BOD concentration for the high-rate systems was 14.4 mg/l. and the suspended solids concentration was 13.5. Effluent mean BOD levels for conventional and extended aeration plants were 17.2 and 14.8 mg/l., respectively. Both capital and operating costs for high-rate plants were less than for conventional plants.

The University of Iowa studied volumetric loadings up to 200 lb BOD/1000 ft<sup>3</sup>/day (*Water Wastes Eng.*, July, August, and October 1967). At a loading of 151 lb BOD/1000 ft<sup>3</sup>, an effluent BOD of 13 mg/l. was reported.

BOD removal of 90% or greater was reported in "Advances in Water Quality Improvement" (Univ. of Texas Press, 1968) for loadings of 53–358 lb BOD/1000 ft<sup>3</sup>/day at 13°C and 52–247 BOD/1000 ft<sup>3</sup>/day at 11°C. Data presented indicate that 90% BOD removal was associated with mixed liquor suspended solids loadings of 0.6 lb BOD/lb MLSS/day or less within the range of temperatures studied.

During 2½ years of operations at the Grand Island, Neb., waste water treatment plant, volumetric BOD loadings increased over the period from 66 lb BOD/1000 ft<sup>3</sup>/day to a high of 136. BOD removal efficiencies increased from 94% in 1967 to 98% in 1969 with a 99% removal achieved for 2½ months of 1969 (effluent BOD = 5 mg/l.) (*J. Water Pollut. Contr. Fed.*, May 1970).

An operating plant at Pentrych, Wales, had an average volumetric loading for a six-month period of 203 lb BOD/1000 ft<sup>3</sup>/day. According to *Water Waste Treat.* (January-February 1969), aeration detention time varied between 1.17 and 2.32 hr. Effluent BOD concentration averaged 23.7 mg/l. including one high-value sample. Excluding this one sample, the average effluent BOD level was 15.7 mg/l.



**Aeration.** The Grand Island, Nebraska complete mixing activated sludge plant above, like the two 0.5-mgd contact stabilization tanks at the right, can achieve about 98% BOD removal

A study carried out at Rutgers, the State University (New Jersey), and reported in *J. Water Pollut. Contr. Fed.* (January 1971), determined the removal rate of soluble organics:

- Soluble TOC (total organic carbon) is reduced to a relatively stable level after 30 min of aeration. Initial concentration reduction averaged 70%.

- Soluble COD is reduced to a relatively stable level after 1 hr of aeration. Initial concentration reduction averaged 77%.

- COD:TOC ratios decrease steadily over the first hour of aeration and fluctuate irregularly thereafter.

- Over a 30-min to 1-hr aeration interval, the COD:TOC ratio decreased while the TOC concentration remained constant. This combination of events suggested the transfer of soluble organics between the aqueous phase and bacteria.

- Estimated net increase in the mean oxidation state of soluble carbon averaged 1.61 units after 1 hr and 1.67 units after 6 hr of aeration. Thus, over 96% of the apparent oxidation occurred within the first hour of treatment.

In a field study, an activated sludge plant operated at volumetric loadings ranging from 75.2–145 lb BOD/1000 ft<sup>3</sup>/day. Removal of BOD from primary clarified effluent, explained in *J. Water Pollut. Contr. Fed.* (March 1971), averaged 83%; thus, overall plant removals are presumed to have averaged over 90% (unfortunately plant influent BOD data was not collected).

#### Design and loading criteria

The preceding literature review sets forth ample justification for an upward revision of the permissible design loading presently extant generally in the U.S. However, a simple increase alone will not take maximum advantage of the activated sludge process. The mixing mode must also be considered. Many

U.S. activated sludge plants have been designed in the past as plug flow or semiplug flow aeration systems. (Wastes added to the aeration tank at any given time move through the tank to the effluent end without substantial mixing with the remainder of the tank contents.) Such systems are subject to upset resulting from relatively large organic loading surges. They are even at some considerable disadvantage owing to "normal" daily peak loadings since the effect of peak or surge loads is concentrated on those microbes at and near the influent end of a plug flow tank at the time of such peak or surge. Perhaps one fourth or less of the total microbial population of the system must, under these circumstances, attempt to cope with loadings ranging from two to three times design to many times that level. The microorganisms involved suffer metabolic upset as well as inability to produce the desired removal of applied organics. Frequently, hydraulic overloading occurs during surge organic loading, thus reducing the time available to the microbes to react.

Contrasted with the "concentration of effect" inherent in plug flow systems is the "dilution of effect" inherent in completely mixed systems. In completely mixed aeration systems, organic load increases are essentially immediately dispersed throughout the aeration tank contents—the effect on any single microbe is one fourth or less that in a plug flow system. Any increase in aeration tank effluent-soluble BOD will be minimized owing both to dilution and to the fact that a far greater number of microbes are involved in the process of adsorbing, absorbing, and metabolizing

the applied BOD even though the time to do so is reduced by an accompanying hydraulic surge.

The importance of complete mixing, to more fully utilize the inherent treatment capacity of the activated sludge process, is nowhere better illustrated than at Grand Island, Neb. This complete mixing activated sludge plant was

plants (100,000 gal./day or 1000 population equivalent and greater) at least 125 lb BOD/1000 ft<sup>3</sup>/day (contrasted with 30-50 presently) loadings could be employed.

#### Beyond activated sludge

If treatment levels are desired beyond those possible with activated sludge

to design properly the final clarification portion of the system. System effluent suspended solids concentrations of 10-15 mg/l. can result in effluent BOD concentrations 6-9 mg/l. higher than those indicated by the foregoing calculations. Observed BOD removals could then be reduced to 92% or less, depending on the actual losses of solids in the system effluent.

To ensure low effluent suspended solids levels and, consequently, low effluent BOD values, tertiary filters are more frequently employed today. By using dual media (crushed anthracite and sand) effluent filters operating at filtration rates of 3-5 gal./min/ft<sup>2</sup>, filtered effluent BOD and suspended solids concentrations of 2-4 mg/l. are achieved. It is, therefore, possible to achieve 99% BOD removal through combined biological and physical treatment units.

For higher removals of applied organics, carbon adsorption columns can be added to the system following filtration. My associates and I also included phosphorus removal. Adding phosphorus-precipitating chemicals directly to the aeration tank, prior to aeration, or following the aeration step, can remove 90% or more of the applied phosphorus.

Recently, chemical-physical treatment processes have been advocated as alternatives to biological, biological-chemical, and biological-chemical-physical treatment systems. A number of laboratory and pilot plant chemical-physical treatment systems have been studied. However, to date, no full-scale chemical-physical treatment plants are in operation in the U.S. The first such plant will be operated by the City of Rosemount, Minn., when it is completed. Valid comparisons between biological and chemical-physical waste water treatment systems must await collection and analysis of routine operational data from Rosemount and other full-scale chemical-physical plants.

#### Outlook

Generally accepted U.S. design loading criteria for activated sludge waste water treatment plants are shown to be "over-cautious" as indicated by the demonstrated efficiencies of higher rate treatment systems in many parts of the world. Increases in permissible design loading rates, which are modest by comparison with established practice

designed to treat the waste waters from a 130,000-head-of-cattle/day slaughterhouse and the City of Grand Island. The flow sheet consists of, in order, grit removal, primary sedimentation, completely mixed aeration, and final sedimentation. Over the course of the day, the BOD loading to the aeration portion of the treatment system varied from a 800-lb/hr high level during midafternoon to a 100-lb/hr low during the early morning hours. Despite this wide range of process loading levels, BOD removal efficiencies were 94% in 1967, 95% in 1968, and 98% in 1969. During the first 2½ months of 1970, 99% removal was achieved. In addition, observed plant performance followed very closely that predicted by fundamental complete mixing activated sludge relationships.

With these considerations in mind, completely mixed aeration tanks could be employed (with or without preceding primary clarification) and permissible BOD volumetric loadings could be increased to at least 60 lb BOD/1000 ft<sup>3</sup>/day (contrasted with 12.5-30.0 presently) for small plants (less than 100,000 gal./day or 1000 population equivalent daily treatment capacity). For large

treatment alone, chemical and/or physical treatment units can be added to the basic biological treatment system. This, of course, raises the question of the degree of treatment possible with biological treatment systems alone. I have observed (as have American Society of Civil Engineers members and University of Kansas researchers) BOD removal rates of 173-360/day at 20°C with completely mixed activated sludge systems. Utilizing, for example, a value of 203/day, the unmetabolized BOD remaining (*F*) after 3 hr of aeration in a completely mixed system (assuming an influent BOD of 240 mg/l.) would be:

$$F = \frac{240}{203(0.125) + 1} = 9 \text{ mg/l.}$$

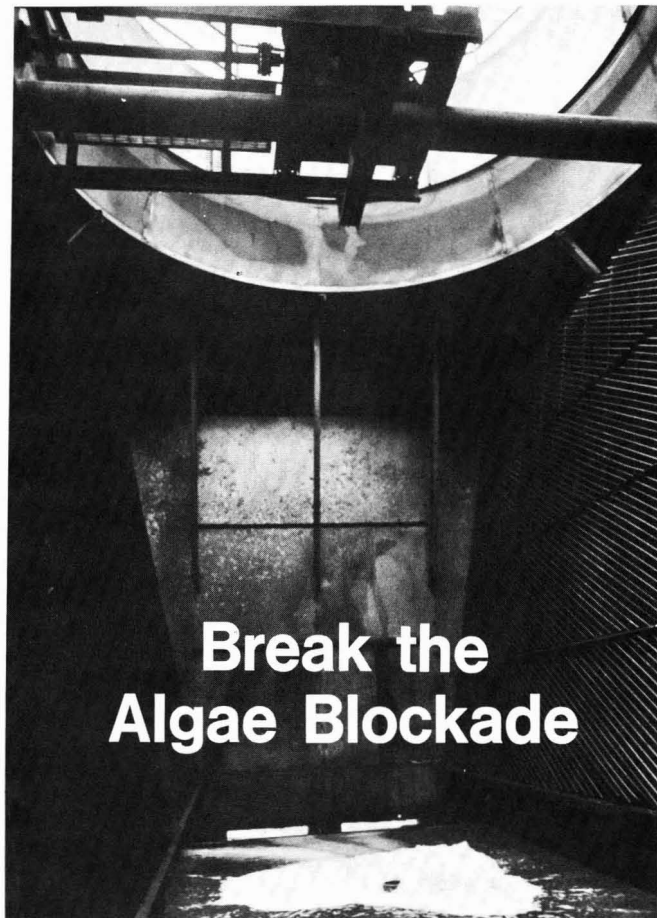
If the aeration period is increased to 5 hr:

$$F = \frac{240}{203(0.208) + 1} = 5.5 \text{ mg/l.}$$

Thus, 96-98% or greater removal of applied BOD is within the demonstrated capabilities of activated sludge systems. The failure of many activated sludge systems to achieve these levels of efficiency very often stems from a failure







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elsewhere, are urged. In terms of process efficiency, completely mixed activated sludge waste water treatment systems are capable of BOD removals of up to 99% even when loaded at rates considerably in excess of those generally permitted.

Adopting only the proposals presented here would result in substantially decreased waste water treatment capital and operating costs. Not considered here are further reductions in capital costs which would result from compatible and rational design of other portions of the total waste water treatment system. These economies would stem from the fact that a more rational aeration system design would yield an activated sludge possessing more desirable characteristics (increased solids settling rate, sludge density index, etc.) which would permit advantageous changes in the design criteria for other portions of the treatment system.

Also, exceptionally high-quality effluents can be obtained through addition of chemical and/or physical treatment processes to the basic biological process. Such combined treatment systems are in routine operation in many parts of the U.S. today.

In an era when required land area, capital costs, and operating costs are of such importance, the opportunity significantly to reduce these factors should not be overlooked. This is especially deserving of the most serious and immediate considerations since both land area requirements and costs can be very significantly reduced without sacrificing process efficiency.



**Brian L. Goodman** is presently head of the Process Control Section, Civil-Sanitary Division, Black & Veatch, Consulting Engineers. Mr. Goodman is experienced in administering all phases of comprehensive research, development, and design in areas of waste water treatment and transport.

## Recent Sedimentary History of Lake Mendota, Wis.

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■ The chemical composition of several sediment cores taken from Lake Mendota, Madison, Wis., has been investigated to determine changes in the flux of various chemicals to this lake. The uppermost sediments consist of approximately 1/2 meter of black gyttja. The chemical stratigraphy of a 9.9 meter-long core indicates that stable conditions existed in Lake Mendota and its watershed prior to the settlement of the area surrounding the lake by white man in the mid to late 1800s. Since that time, there has been an appreciable increase in the amounts of phosphorus, iron, manganese, aluminum, and potassium in the uppermost sediments. The organic carbon content of the sediments has fluctuated several times in the past with the most recent sediments showing slightly higher values than the older sediments. This study has demonstrated the feasibility of using the chemical composition of lake cores to estimate the influence of cultural activities of man on the rate of eutrophication of a lake.

Various human activities contribute to accelerated enrichment (cultural eutrophication) of waters. Among the symptoms of cultural eutrophication are nuisance blooms of algae, increased nutrient levels, depletion of hypolimnetic oxygen, increased turbidity, and changes in the species-composition of phytoplankton, invertebrates, and fishes. In most instances cultural eutrophication is an accomplished fact because there are few data to document changes that have occurred in precultural times. The information needed to trace changing limnological and watershed conditions must come from a record preserved in lake sediments. Although several chemical studies have been performed on postglacial sediments and interpreted on the basis of long-term historical trends (Brown, 1969; Gorham, 1961; Horie, 1966; Hutchinson and Wollack, 1940; Kendall, 1969; Livingstone and Boykin, 1962; Mackereth, 1966; Pennak, 1963), few investigators (Stockner and Benson, 1967; Shapiro et al., 1971) have examined the recent historical changes of lakes through the interpretation of chemical profiles of lake sediment cores.

Lake Mendota sediment cores were examined in this study. This lake is a hard-water eutrophic lake formed by morainic damming of the preglacial Yahara River Valley near Madison,

Wis. (Twenhofel, 1933). The lake currently receives domestic drainage from agricultural lands, urban runoff, and some municipal and industrial waste effluents contained in entering streams. For a survey of limnological information on the lake the reader should see Frey (1963).

*Experimental Procedures*

In October 1966, cores WC-84 and WC-89 were taken from Lake Mendota in 11.2, 18.3, and 23.2 meters of water, respectively, in line from University Bay to the center of the lake as shown in Figure 1. The main tributary to the lake, the Yahara River, enters from the north. The only surface outlet from the lake is located on the eastern shoreline. The outlet is actually a continuation of the Yahara River, which flows from Lake Mendota into Lake Monona and subsequently into two other lakes located toward the southeast. University Bay has two inlets; one coming from a pumping station of lowland drainage, and a small creek, University Creek, which serves as a storm sewer for urban Madison.

The sample drive through 1 meter of sediment was accomplished by a coring device consisting of a circular cutting head on the lower end, a clear acrylic plastic core barrel (3.5 in. in diam), a piston assembly, and a set of weights at the upper end. The design and operation of the piston corer was described in detail by Wentz (1967) and Bortleson (1968). A sampling platform and a winch were provided by a converted Army amphibious Dukw to facilitate raising the corer. The sample material after inspection for laminations was extruded and fractionated in the field into 5-cm intervals.

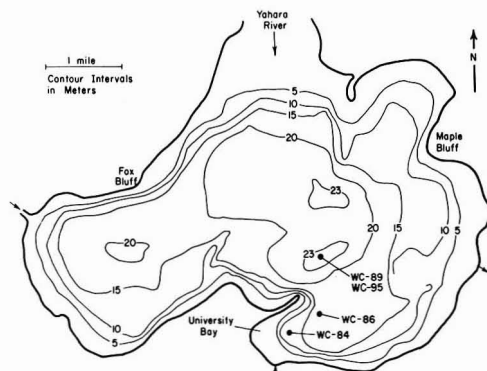


Figure 1. Bathymetry and coring locations for Lake Mendota

<sup>1</sup> To whom correspondence should be addressed.

**Table I. Precision of Analytical Methods**

| Element          | No. of replicates, <i>N</i> | Av value of <i>N</i> replicates, mg/g | Std dev, mg/g |
|------------------|-----------------------------|---------------------------------------|---------------|
| Iron             | 7                           | 23.6                                  | 0.6           |
| Phosphorus       | 5                           | 1.37                                  | 0.02          |
| Manganese        | 5                           | 0.622                                 | 0.012         |
| Magnesium        | 5                           | 13.1                                  | 0.4           |
| Potassium        | 5                           | 12.6                                  | 0.1           |
| Calcium          | 5                           | 110.0                                 | 2.0           |
| Aluminum         | 5                           | 31.3                                  | 0.28          |
| Organic nitrogen | 5                           | 7.08                                  | 0.36          |
| Total carbon     | 5                           | 128.0                                 | 7.0           |

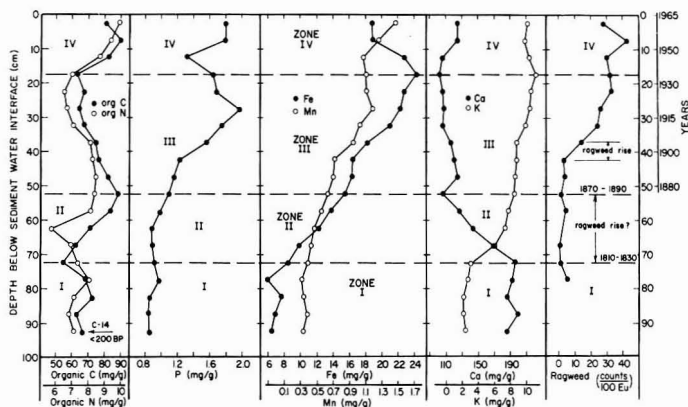
The samples brought to the laboratory were stored frozen at -20°C until commencement of analysis.

After thawing, the wet sediments were homogenized in a blender and air-dried. Prior to acid digestion, sediment sample aliquots were ground, passed through a 100-mesh screen, and heated to constant weight at 105°C. Acid digestion consisted of adding 5 ml of 48% HF to a 0.500-gram sample in a 50-ml polypropylene beaker. The sample was heated to about 100°C for 8 to 12 hr, after which only a dry

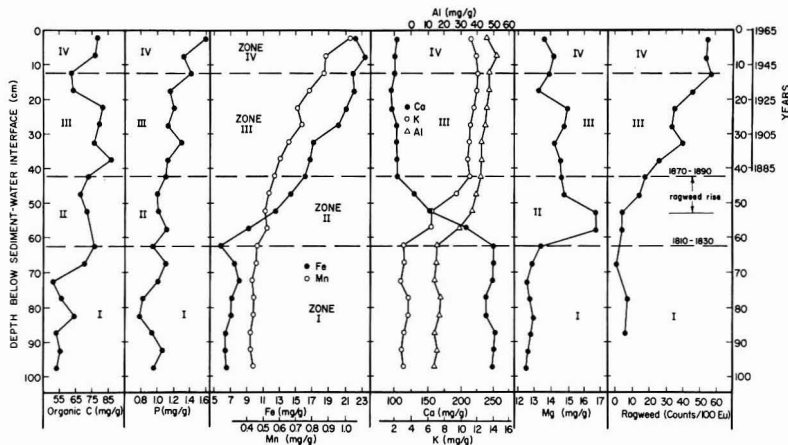
residue remained. The solid residue was removed from the beaker, transferred to a 100-ml Kjeldahl flask, and further digested for two hours to decompose the organic matter in the presence of 5 ml of concentrated HNO<sub>3</sub> and 60% HClO<sub>4</sub>. After this digestion, the sample was cooled, passed through a prerinsed Whatman No. 2 filter, and drained directly into a 100-ml volumetric flask. This solution, or an appropriate aliquot thereof, was used for total P, Fe, Mg, K, Ca, and Al determinations.

Iron was determined by the orthophenanthroline method (Olson, 1965) and P by the vanadomolybdophosphoric (VM) yellow colorimetric procedure (Jackson, 1958). Wentz and Lee (1969a) have discussed the sensitivity, minimum detectable concentration, precision, and working range for the VM yellow color procedure. Analyses for Mn, Al, Mg, K, and Ca were made by direct aspiration of the digestion solution, or diluted aliquots, into a Perkin-Elmer Model 303 atomic absorption spectrophotometer. Organic nitrogen was determined by semimicro Kjeldahl technique outlined by Bremner (1965). Total carbon was determined by a dry combustion technique using a LECO (Laboratory Equipment Corp.) low-carbon analyzer (Model 589-400) and LECO induction furnace. The CO<sub>2</sub> released by combustion of carbon compounds and decomposition of carbonate was measured by a thermal conductivity cell. With calcareous sediments, the choice is

**Figure 2. Chemical and Ambrosia pollen stratigraphy of Lake Mendota core WC-89**



**Figure 3. Chemical and Ambrosia pollen stratigraphy of Lake Mendota core WC-86**



between determining organic C on the sample after removal of carbonate C or computing organic C by subtracting carbonate C from total C. In this study the Ca dissolved by HF-HNO<sub>3</sub>-HClO<sub>4</sub> acid system was converted to carbonate C equivalents; this value was subtracted from total C to obtain organic C. Studies by Bortleson (1970) have shown a good correlation between measured and calculated inorganic C in Lake Mendota sediments.

Sediment sample aliquots (0.200-gram sample, 100-mesh, dried 105°C) for Ambrosia pollen analysis consisted of removal of carbonates with HCl, silicates with HF, solubilization of humic material with KOH, and removal of cellulose with acetolysis solution (Faegri and Iversen, 1950; Andersen, 1960; and Maher, 1969). Since a total pollen assemblage was not counted and identified—e.g., oak, pine, hickory, grass pollen—to obtain a percentage of ragweed pollen, it was necessary to add an internal standard. A suspension volume of 0.20 ml of internal standard (1 gram of pure Eucalyptus pollen in 500 ml of tertiary butyl alcohol) was pipetted while well-stirred and at constant temperature (27.5–0.5°C) and transferred to the sediment aliquot. The Eucalyptus pollens, which are exotic pollens, were easily identifiable triangular-shaped grains. Identification of Ambrosia-type pollen was made with high power magnification using a Bausch & Lomb microscope. No reference was given to a particular species of ragweed. Continuous sweeps were made across the entire width of the preparation; in each sample, 100 to 200 grains were counted. The abundance of ragweed found in the sediment cores was based on the average ragweed-to-Eucalyptus pollen ratio of duplicate or triplicate samples.

The results presented for the chemical analyses of each core are mean values of two or five replicate determinations. Data for the precision of the analysis are given in Table I. The relative standard error was less than 5% for 73% of the analyses performed in replicates of five. Duplicate pollen counts were made from each processed sample. In the transition zone (high or low ragweed) triplicate counts were made.

### Results and Discussion

The sediments laid down from the precultural period to the present day can be subdivided into four zones according to changes in ragweed pollen and chemical distribution patterns as shown in Figures 2–4. The main physical and historical features of the Lake Mendota cores are shown in Table II, and the mean concentrations of organic C, carbonate

C, P, Fe, K, and % solids are shown in Table III for each of the sediment zones.

No evidence of laminations or lenses, which could be used for dating purposes, was observed for any of the cores. To identify pre- and postcultural periods of deposition in the sedimentary column, Ambrosia pollen counts were performed; the appearance of these pollen grains provided a stratigraphic horizon which could be dated from historical records showing when man moved into southern Wisconsin and began modifying the environment. Ragweed pollen occurs in relatively high percentages (5–40%) in surface sediment samples from the deciduous forest region of the northeastern and north-central USA; the plant seems to have increased as a result of disturbance and creation of open habitats through forest clearance by European settlers (Ogden, 1967; Davis, 1967; Wright, 1968). For instance, a short core (50 cm) was taken from Frains Lake in Michigan by Davis (1968). The ragweed pollen increased from less than 1% to about 30% of the total from below to above 25 cm of sediment, respectively. According to Davis, the time of land settlement and forest clearance around Frains Lake occurred in 1830.

The lowermost sediments in Zone I consist of a buff marl containing 45–60% CaCO<sub>3</sub> or 190–255 mg/g Ca. The sedimentary concentrations of Fe, Mn, Al, K, Mg, P, and organic C show little or no change with depth in the buff marl. Minimum ragweed pollen counts were observed in Zone I. Presumably, the buff marl was laid down prior to any major disturbance by white settlers in the Lake Mendota drainage basin. Although most of the Lake Mendota cores observed by Murray (1956) showed a simple sequence of black gyttja (called sludge by Murray) over buff marl, other sequences were found in parts of the Lake Mendota basin, usually in the shallower regions. Among the sequences found with sediment depth by Murray (1956) were a sludge-marl-blue plastic marl, sandy sludge-blue plastic marl-pink clay with sand and pebbles, and a sludge-blue plastic marl-blue plastic clay.

The sediments in Zone II consist of gray-colored gyttja-marl which represents the transition zone between the buff marl and black gyttja. The reported (Murray, 1956) knife-sharp nature of the contact between gyttja and marl was not observed in any of the cores used in this study. In all the core sections examined, the buff marl passed gradually upward into a gyttja marked by a gradual darkening of color. Apparently, the false impression of a knife-sharp contact was

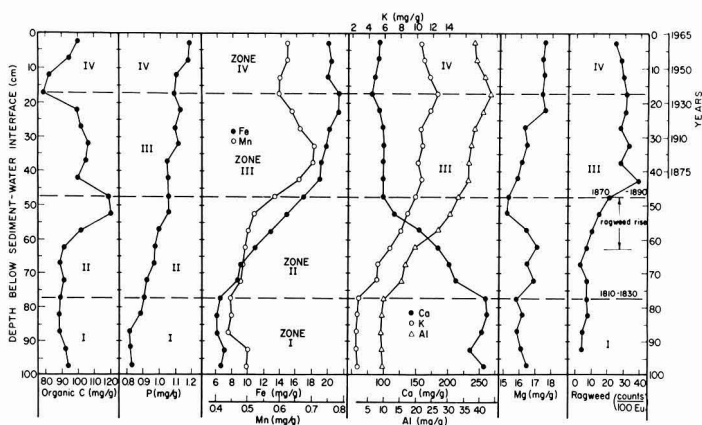


Figure 4. Chemical and Ambrosia pollen stratigraphy of Lake Mendota core WC-84

**Table II. Main Features of the Lake Mendota Cores and Corresponding Historical Events**

| Core No. | Sediment depth and thickness of zones, cm | Chemical zone | Type of deposit | Period   | Relevant historical events   |
|----------|---|---------------|-----------------|--|--|
| WC-89    | 0-15                                      | IV            | Black           | Late cultural  | Accelerated urbanization in Madison (pop. 67,000-158,000, 1940-1965)<br>"Detergent era"<br>Decline in cisco ( <i>Coregonus artedii</i> ) after 1940 (Frey, 1963)<br>Large decline in wetland from 1938 to 1950's<br>Sewage diversion around lake December 1971<br>Rapid urbanization of Madison (pop. 12,000-67,000, 1884-1940)<br>Rapid settlement in L. Mendota basin<br>L. Mendota received sewage effluent from Madison, 1884-1899 |
| WC-86    | 0-10                                      |               | gyttja          | 1940 to present  |  |
| WC-84    | 0-15                                      |               |                 |  |  |
| WC-89    | 15-50                                     | III           | Black           | Midcultural<br>1880 to 1940  | Rapid settlement in L. Mendota basin<br>L. Mendota received sewage effluent from Madison, 1884-1899<br>Early urbanization in Madison (pop. 2500-12,000, 1850-1884)<br>Raised lake level 5 ft by outlet dam in 1847<br>Early settlement in southern Wisconsin<br>Privies, cesspools, and direct drains to lake to dispose sewage<br>Presettlement in southern Wisconsin   |
| WC-86    | 10-40                                     |               | gyttja          |  |  |
| WC-84    | 15-45                                     |               |                 |  |  |
| WC-89    | 50-70                                     | II            | Gray-           | Early cultural<br>1820 to 1880   | Early urbanization in Madison (pop. 2500-12,000, 1850-1884)<br>Raised lake level 5 ft by outlet dam in 1847<br>Early settlement in southern Wisconsin<br>Privies, cesspools, and direct drains to lake to dispose sewage<br>Presettlement in southern Wisconsin  |
| WC-86    | 40-60                                     |               | colored         |  |  |
| WC-84    | 40-75                                     |               | gyttja-marl     |  |  |
| WC-89    | 70-95                                     | I             | Buff marl       | Precultural<br>before 1820<br><br>C-14 date, <200 yr B.P.<br>at 90-95 cm level of<br>WC-89 (Bender, 1969). |  |
| WC-86    | 60-100                                    |               |                 |  |  |
| WC-84    | 75-100                                    |               |                 |  |  |

created by either compression of the core sections during sampling or the manner of fractionating the core column. The increase in ragweed pollen begins in the middle of Zone II and increases upward throughout Zone III in cores WC-84 and WC-86. The ragweed pollen rise probably corresponds to the period of active settlement of southern Wisconsin and the Madison area in the decades following 1820. The population of Madison increased from 2000 in 1850 to 12,000 in 1884 and to 30,000 by 1918; the acreage devoted to crop production in southern Wisconsin increased from about 400,000 to 2,900,000 to 15,300,000 in 1830, 1850, and 1880, respectively (Curtis, 1959; Smith, 1929; Sarles, 1961). Thus, the time period for the early postcultural interval (Zone II) is estimated to have taken place from 1820-1880. During this period, concentrations of organic C, Fe, Mn, K, Al, and P show an initial upward rise, and Ca mostly in the form of CaCO<sub>3</sub> shows a rapid decrease in concentration. Selenium was found by Wiersma and Lee (1971) to increase from a background concentration of 0.8-1.4 mg/g in Zone I to 2.2 mg/g in Zone II.

The lower column of black gyttja is shown in Zone III; the interval thickness ranges from 40-50 to 10-15 cm depending on the core locations. During the midpostcultural interval, estimated to span the period 1880-1940, concentrations of P, Fe, Mn, Al, and K show a rapid upward increase. At the same time, Fe, Al, and K reach maximum concentrations in Zone III. Goldberg (1971), who used <sup>210</sup>Pb with a half-life of 22.4 years, has determined the sedimentation rate for core WC-89 for the past 100 years to be 5.8 mm/yr. This is in agreement with a mean sedimentation rate of 6.2 mm/yr and the time scale given for core WC-89. The mean sedimentation rates of cores WC-86 and WC-84 are 5.0 mm/yr and 5.6 mm/yr, respectively.

High counts of Ambrosia pollen are observed in all three cores in Zone III, but the distribution pattern of ragweed pollen in each of the cores is different. In core WC-89 the first increase in abundant ragweed pollen occurs at the 35-40 cm level in Zone III while in the other Lake Mendota cores, ragweed pollen first appears in abundance in Zone II and increases upward to reach a peak in Zone III. It seems, based on the chemical and ragweed pollen evidence from cores WC-84 and WC-86, that the ragweed horizon shown in Zone III for WC-89 is an anomaly.

Additional evidence supporting the above contention is given by sediment studies of Nriagu and Bowser (1970). They observed the presence of magnetic iron spherules beginning at the 35-40 cm horizon and continuing to the sediment-water interface in a deepwater Lake Mendota core. Nriagu and Bowser (1970) suggested the iron spherules are flue products derived from industrial and domestic activities supplied to the lake through the action of washing the atmosphere or as a detrital load from urban runoff. The depth of appearance in the magnetic iron spherules (Zone III) and ragweed pollen grains (Zone II) is in approximate agreement if it is assumed that extensive fossil fuel burning occurred approximately 50-80 years after the commencement of initial land clearance in the Mendota basin. No clear explanation for the late rise in ragweed pollen in profile WC-89 can be given. It is observed, however, that the relative counts of ragweed pollen against the Eucalyptus standard throughout the entire core for WC-89 are less than in WC-86, but in core WC-84 the relative ragweed count is about the same as WC-89.

These differences suggest that the final deposition of ragweed pollen may vary locally within the lake depending on sedimentation rate of the pollen grains and whole sediment



at different water depths or locations within the lake. Davis (1968) noted at Frains Lake, Mich., the pollen grains are deposited an average of two to four times before being buried deeply enough to escape further disturbance. Davis explains that "the sediments in shallow water are apparently stirred up and resuspended more frequently or more extensively than sediment in deep water. The net result of repeated resuspension, mainly from shallow water sediment, followed by redeposition over the entire basin, is movement of material from shallow to deep water."

The black gyttja in Zone IV (upper 10–15 cm) is characterized by high ragweed counts. Iron, Al, and K concentrations level off or decrease slightly from maximum concentrations in Zone III while P, Ca, organic C, and organic N concentrations increase upward to the sediment-water interface. This interval is estimated to cover the period 1940 to the present. Among the domestic changes taking place in the Lake Mendota basin during this time were the rapid urbanization of Madison, rapid growth of towns in the northern part of the drainage basin which contribute effluent to Lake Mendota tributaries, drainage of large acreages of wetlands in the Lake Mendota basin, and emergence of the "detergent era" as an additional P source. Since 1940, a decline in the cisco fish population has been noted (Frey, 1963). The changes in the catchment basin that have been responsible for the decline of this species are not known, but increasing quantities of domestic sewage and severe siltation are suspected offenders (Frey, 1963).

**Distribution of Carbon.** Several investigators have examined the distribution of organic C with sediment depth to measure trends in historical aquatic productivity (Mackereth, 1966; Gorham, 1961; Hutchinson and Wollack, 1940; Horie, 1966). Often the organic C profile has been used to explain lake succession from oligotrophic to eutrophic conditions.

The deepwater core and University Bay cores show similarities as well as differences in the organic C profiles. The fact that the three cores show such a degree of similarity indicates that they are reflecting general conditions of the lake, not just local conditions. Especially notable are the similarities in the organic C profile of cores WC-89 and WC-84 and the similarities of the organic C and organic N profiles in WC-89. In the case of organic C and organic N almost every irregularity of the former is reflected in the latter. However, sedimentary profiles of organic matter varied for three cores taken in Lake Washington at different locations (Shapiro et al., 1971). The authors concluded that the different rates of deposition of eroded inorganic material in various parts of the lake caused the observed changes in organic matter in the three cores. In soils and lake sediments organic N is the dominant N form usually ranging from 95 to 98% of the total N (Bremner, 1965; Keeney et al., 1970) and is a function of the amount of particulate organic matter deposited. The deposition of organic C is rather uniform during the precultural period, but in the early postcultural period the organic C concentration increases upward to a maximum near the junction of Zones II and III for cores WC-84 and WC-89. In all three cores there is a subsequent upward decline in organic C throughout Zone III which is followed by an increase in organic C in Zone IV.

To discuss the factors believed to be controlling the deposition of organic C, a review of various possible methods of organic C deposition in lakes is necessary. The primary factors controlling the abundance of organic C in the sediments are: (1) production of organic C of autochthonous origin, (2) sedimentation of allochthonous organic matter,

(3) destruction of organic material by organisms or nonbiological processes, and (4) variation in deposition rate of the whole sediment.

The trends in the organic C deposition may be due to variations in any of the four factors mentioned in controlling the organic C deposition. Belcher and Fogg (as quoted by Brown, 1969) reported that eutrophy and the associated hypolimnetic deoxygenation were considered as major factors in favoring the preservation of pigments in cores from Windermere and Ennerdale Water. A rapid rate of sedimentation would also favor the preservation of organic C, since the period of time during which the organic substance is in contact with the oxygen-bearing bottom water is reduced before being buried. Thus, a portion of the increase in organic matter in the Lake Mendota postcultural sediments may be the result of anaerobiosis favoring preservation of organic molecules and a more rapid rate of sediment accumulation.

However, there are some compounds, such as DDT, which only break down more rapidly under anaerobic conditions (Stalling, 1970); therefore, the overall effects of anaerobic conditions on the breakdown of organic compounds are not known. It is important to remember that the concentration and the rate of deposition of organic constituents in sediments are the result of differences between rates of formation and decomposition. Sediment trap studies by Kleerekoper (1953) show at least 70–90% of the organic matter synthesized in a column of lake water is decomposed prior to incorporation in surface sediments. Nevertheless, Mackereth (1966) and Hutchinson and Wollack (1940) believed that the organic matter which becomes incorporated below the biologically surface-active layers of the English Lakes and Linsley Pond reaches a state of considerable stability toward further oxidation shortly after burial.

The lignin content of the gyttja from several cores in Trout Lake was determined by Twenhofel et al. (1945). They had anticipated that bacterial decomposition would have led to a decrease in the nonligneous materials, and thus an increase in ligneous materials with depth. Twenhofel et al. (1945) concluded that the fact that such a decrease was not observed suggested that bacterial activity ceased in the organic sediments of Trout Lake shortly after burial. However, Shapiro et al. (1971) found organic matter, as measured by loss on ignition, increased in the upper 15 cm of sediment in a core taken from Lake Washington in 1958. Another core taken in the same location in 1970 revealed that the high values for organic matter found in 1958 had decayed. The authors concluded that diagenetic changes caused the decrease in organic matter after burial with newer sediments. Thus, the final concentration of organic C in the sediments will probably depend on all factors (1)–(4) mentioned above.

In all the Lake Mendota cores examined, the mean concentration of organic C was lowest in Zone I as shown in Table III. The observed increases in the mean concentrations of organic C in the postcultural muds may represent an increase in both an auto- and allochthonous organic C. Thus, an increase in a lake's own total production of organic C becomes mixed with and is indistinguishable from that of external origin. However, organic production of either internal or external origin may increase since the cultural period may result in increasing the hypolimnetic oxygen uptake rate. In Lake Mendota the oxygen is allowed to deplete without replenishment during stagnation, but the rate of change in hypolimnetic oxygen deficiency is not known since the cultural period began about 140 years ago. The increase in the organic C deposition in the recent sediments could be at-



tributed in part to increased biological productivity since the advent of domestic drainage. The observed variation in the organic C content in the cores from Lake Mendota may best be attributed to the combined influence in the rates of carbonate C, organic C, and inorganic sedimentation since the onset of extensive agricultural and urban activities in the Lake Mendota watershed.

Further insight into the relative importance of the variation in the sedimentation rates of carbonates and inorganic materials in controlling organic C deposition may be gained from Murray's (1956) studies on Lake Mendota. The relationship of gyttja to marl as suggested by Murray (1956) may be considered from the three possibilities: the gyttja is a diagenetic precursor of the marl, the gyttja is developed by leaching of the marl, and the gyttja and marl are separate sedimentary units developed under different limnologic conditions. Twenhofel (1933) postulated that the black gyttja was a diagenetic precursor of the marl and that the process of change was one of removal of organic matter by bacteria and precipitation of  $\text{CaCO}_3$  at depth in the gyttja, thereby the gyttja was converted to marl. Twenhofel based his conclusion that the gyttja was a preliminary product in the production of marl on the assumption that the color of the gyttja resulted from the disappearance of organic matter with depth to produce the light marl. Murray (1956) maintained the black color in the gyttja results from the presence of ferrous sulfides deposited under conditions of oxygen deficiency and not from the organic content. Berner (1964) found that recent sediments containing fine-grained black FeS, even in small concentrations, tend to be colored gray and black. Furthermore, Murray (1956) argues that it is doubtful the gyttja might have resulted from alteration of the marl by removal of carbonate since the deeper stagnated waters would be expected to develop leaching conditions first and thus to a greater degree retain a lower carbonate content. But in fact, the greater the carbonate content, the deeper the water. Murray thus concluded that the gyttja is simply the most recent sedimentary unit to be deposited in the lake postdating the buff marl. According to Murray, the fact that the gyttja is a universal deepwater sediment resting not only on marl but on other varied sediment types suggests that it is a unit in itself. The change in sedimentation from marl to gyttja was explained as being the result of increasing rates of clastic and organic matter sedimentation superimposed on a constant carbonate deposition pattern.

The variations in organic C shown for Zones II-IV can be explained by variations in the superimposed inorganic sedimentation rates. A pronounced increase in either auto- or allochthonous organic C early in Zone II is attributed to the simultaneous increase in inorganic and organic sedimentation. The net effect of the early cultural activities in the Lake Mendota basin appears to have been to produce an increase in organic C and inorganic materials in somewhat the same proportion. If the organic sedimentation rates were not high, it would be reflected as a decrease in the concentration depth diagram the same as  $\text{CaCO}_3$ . In Zone III, the inorganic sedimentation rate is probably occurring faster than the organic production rate which produces a decrease in the organic C profiles. In Zone IV, the organic C profiles show an increase toward the sediment-water interface indicating perhaps an accelerated rate of organic C production of either internal or external origin in the last 20-25 years.

The carbonate profiles of the Lake Mendota cores indicate uniform deposition has occurred in the precultural period. The constant deposition is interrupted during the cultural

period to depress the carbonate C concentration. Calcium carbonate precipitation initiated by planktonic photosynthesis or physiochemical precipitation has probably not decreased in recent times as inferred directly by the concentration profile of Ca. If photosynthetic uptake of carbon dioxide is the dominant mechanism for carbonate precipitation, then an increase in  $\text{CaCO}_3$  precipitation in recent times might be slightly favored with increased productivity. However, increased biological respiration, bacterial activity, and chemical oxidation serve to decrease  $\text{CaCO}_3$  precipitation. Furthermore, Megard (1969) noted that it is unlikely the productivity during the history of lakes can be inferred from the concentration of carbonate in the sediment because a large proportion of the carbonate formed in the epilimnion of productive lakes is dissolved in deep water during periods of stratification. It appears that the most likely explanation for the post-cultural decrease in carbonate C concentration is the masking of a somewhat constant (or increasing) carbonate deposition by the increased inorganic sedimentation. The distribution of carbonate C in the marl increases with decreasing water depth. The distribution of carbonate C in the gyttja shows the opposite relationship. The content of carbonate C decreases with decreasing water depth. The same phenomenon was observed by Murray (1956). The basic change in carbonate C deposition may be the result of a relative increase in dilution of carbonate C by inorganic materials closer to the shore regions or to a relative increase in planktonic photosynthesis in the deeper water vs. the shallower water of Lake Mendota since the cultural period. However, Wetzel (1970) noted that the present-day deposition rates of littoral carbonate were much higher than those of the central portion of the allochthonous carbonates associated with warm, wet climatic conditions precipitating before entering the major volume of the lake.

**Distribution of Phosphorus.** The migration and precipitation of P into the bottom muds may take place both by P incorporation into plant and animal remains and by sorption or precipitation with inorganic components. The final concentration of P residing in the sediment depends primarily on the rates of supply of P in the form of inorganic and organic P from inflowing waters; the efficiency at which P is precipitated or sorbed with other chemical components such as Ca, Al, Fe, and Mn or sorbed onto particulate matter and carried into the sediment; the retentive capacity of the sediments for P; and the rate of accumulation of the whole sediment.

A period of constant P deposition (0.8-0.94 mg/g) occurs in Zone I of the Lake Mendota cores. During this time, the concentrations of Fe, Mn, Ca, Mg, K, Al, and ragweed pollen are all relatively constant. It probably can be assumed that all factors mentioned in controlling the distribution of P maintain a relatively constant ratio to each other during this period.

During the subsequent interval (Zone II), the P concentration steadily increases upward. There is a concomitant increase in Fe, Mn, and K concentrations in all the cores. The additional source of P provided to the lake during the early postcultural period may most likely be associated with increased erosional products, presumably, owing to man's first appearance in the watershed. An increased influx of Fe and Mn hydrous oxides, clay minerals, and oxides and hydroxides of Al from domestic drainage of urban and rural areas may have provided for increased efficiency for P precipitation. Phosphorus may be taken from solution by precipitated ferric and aluminum hydroxides or clay minerals (Carritt and Goodgal, 1954; Hsu, 1965); however, the mode of P

deposition which is favored in the calcareous lake system is sorption or precipitation with  $\text{CaCO}_3$  (Frink, 1969; Wentz and Lee, 1969b). An eroded colloidal soil, low in P, might remove considerable amounts of P from the water before final deposition. Wang and Brabec (1969) have shown that the turbidity in Illinois River water was related to particulate P, particulate Si, and particulate Fe(III). With the increase in runoff waters since the advent of agricultural practices in the Lake Mendota watershed, a particulate P-Fe-Si complex associated with clay minerals similar to that proposed by Wang and Brabec may have contributed to an increased depositional efficiency of P since the cultural period.

High concentrations of P are maintained in Zone III representing the period 1880–1940. Any of the observed increases in the concentration of sorbed or precipitated P in the sediment could be attributed to an increase in the supply of P to the waters as well as the increase in efficiency of P deposition. For example, from 1884 to 1899, Lake Mendota received the effluent from Madison's sewage treatment plant (Sawyer, 1947). In core WC-89 a reversal in P concentration is shown to occur in about 1920; however, no reversal in the trend of P concentration is shown for WC-86 and WC-84 in University Bay. Thus, it appears that a different interpretation for explaining the P profiles may be given for the two locations within the lake. An explanation for the minimum P value in the late postcultural interval may be due either to a decrease in P supply and/or P depositional efficiency or to an increase in inorganic or organic sedimentation diluting the P fraction. The latter alternative seems the most plausible considering all the additional sources of P which usually accompany urbanization of a watershed.

Maximum concentrations of P are found in Zone IV for WC-84 and WC-86, but in the deepwater core a maximum peak for P occurs in both Zones IV and III. Increases in P concentration in the recent sediment of Zone IV are only modest—i.e., 1.3–1.8 mg/g for WC-89—compared to the P increase in Zone III from 1.0–2.0 mg/g. If substantial P has been added to the lake waters from storm sewer runoff and domestic waste since the detergent era, then either the additional source of P is masked by increased sedimentation rate of the whole sediment throughout Zone IV or the P associated with agricultural runoff (Zones III and IV) overwhelms the P added from new sources since the detergent era (Zone IV).

The final concentration of P that resides in the sediment is also dependent on the P sorptive and retentive capacity of the sediment. If the chemical composition of the sediments has changed historically, presumably, the P sorptive and desorptive capacity of the sediment will also be influenced. Bortleson (1970) conducted a laboratory study to assess the P sorptive characteristics on selected strata representing pre- and postcultural sediments in WC-89. The sorption and desorption of added increments of P to the sediments indicated that the postcultural gyttja is a more favorable sorptive and less favorable desorptive environment for P than the precultural marl. In other words, the postcultural sediment which sorbed the most P during the sorption step released the least P during the subsequent desorption. The higher concentrations of Fe, Mn, Al, and K in the gyttja probably account for the greater P binding capacity. Thus, it appears during the precultural period the marl sediment was less capable of sorbing and retaining P, but in recent lake history the muds are capable of sorbing and retaining P which may be added to the lake. Livingstone and Boykin (1962) noted that the productivity in a lake could be inversely proportional to the sorptive capacity of the mud. They found the P

content was highest in the deeper-lying samples of the sedimentary column of Linsley Pond, which formed during the oligotrophic stage in the lake's history. In such a case, the P that had not been released from the mud during the early history of the lake would still be trapped in the sediment. Acid-soluble P concentration, as determined and reported by Wentz and Lee (1969a,b), provides additional evidence for a greater P binding capacity in the gyttja. The acid-soluble P concentration follows a similar trend to total P in core WC-89. The P released with 0.075N HCl– $\text{H}_2\text{SO}_4$  extractant is an operationally defined fraction of the total which is desorbed at 20°C at pH 1–2 (Wentz and Lee, 1969a). Presumably, the acid extractant would remove Ca-bound forms of P plus an undefined fraction of Fe-P and Al-P. The ratio of acid-soluble P to total P decreases above the 55–60-cm level indicating that the more recent sediments contain a greater fraction of P which is not acid extractable. Acid treatment probably would not extract organic P or occluded forms of Fe-P and Al-P (Shah et al., 1968). Williams et al. (1970) reported values indicating that 26% of the total P is organic P in Lake Mendota surface muds.

The mean P concentration in the precultural marl is about the same in cores WC-84, WC-86, and WC-89, but, for the same cores, the P concentration increases more in the postcultural sediment the deeper the water. It appears that the P concentration in the marl sediment was more uniform over the lake, but since the advent of domestic drainage, the influent materials have allowed fractionation of sediment particles with water depth which has complicated the sedimentation regime of the postcultural sediments. Based on surface sampling of 32 stations in Lake Mendota, P, Fe, and Mn concentrations show a positive statistical correlation with sample depth (Delfino et al., 1969); a linear correlation coefficient of 0.82, 0.74, and 0.81 was found for P, Fe, and Mn, respectively. Since higher concentrations of P, Fe, and Mn were found at deeper depths in Lake Mendota, and since these deeper depths are essentially in the middle or central part of the lake, a relatively simple particle fractionation of tributary-born suspended matter may have occurred (Delfino et al., 1969). Apparently, the P in the center of the lake is associated with the finer sediment fraction (see Table III). The differences in the thickness of the sedimentary Zones for cores WC-84, 86, and 89 can also be partially attributed to changes in percent solids in a given interval which is a function of the particle fractionation in the lake and consolidation after burial. Frink (1969) found in eutrophic Bantam Lake, Conn., that the center of the lake was enriched in clay, organic matter, and P when compared with the sediments around the lake edge. The Fe-P and Al-P fractions were always highest in the finer fractions toward the center of the lake, but Ca-P decreased with increasing water depth in Bantam Lake and was associated with the coarser fraction (Frink, 1969).

**Iron and Manganese Distribution.** Total Fe and Mn analyses were performed on all the cores investigated. The distribution of Fe and Mn in the sediments may depend primarily on the supply rate of particulate and dissolved Fe and Mn, the migration of Fe and Mn as influenced by redox conditions and the rate of accumulation of the whole sediment.

The Fe and Mn content increases by two- to fourfold in the postcultural over the precultural interval; the initial upward increase in Fe and Mn occurs in the early cultural period prior to an increase in P in WC-86 and WC-89. The increase in sedimentary Fe is probably associated with an increased Fe supply to the lakes from land runoff. Wang and Brabec

(1969) found the turbidity in Illinois River water to be related to the particulate P, Si, and Fe(III) concentrations. The molar ratio of Si to Fe(III) was 1.0:1.47. Carroll (1958) found that the association of Fe with clay minerals is an important means whereby Fe is transported by rivers to lakes. According to Carroll, Fe is associated with clay minerals as an essential constituent, as a minor constituent within the crystal lattice, and as iron oxide on the surface of mineral platelets. The close relationship between the Fe, K, and Al profiles in the calcareous lakes are further evidence that Fe is mainly associated with the clay mineral fraction. Analyses of the clay fractions of soils show that Fe is mainly associated with the finest fractions (the clay and silt grades), which have extremely large surface areas (Carroll, 1958). This may account for the high concentrations of Fe found in the center of Lake Mendota (Delfino et al., 1969).

Nriagu (1967) proposed from his studies of Fe and S in Lake Mendota cores that the progressive upward enrichment of Fe in the sediments may be due to the increased efficiency of precipitation and retention of ferrous iron in the sediments as sulfides. Nriagu (1967) found a positive relationship between Fe and sulfide in the cores. However, a feature shared by the gytja and marl is that the Fe content is greater than should be required to hold all the sulfur as FeS. Murray (1956) concluded that the black color of the gytja resulted from the presence of ferrous sulfides deposited under conditions of oxygen deficiency which occurred contemporaneously with increased clastic deposition as a consequence of farm and domestic drainage. However, Nriagu (1968) suggested prior to the change in sedimentation of Lake Mendota associated with human activity, the lake had developed an oxygen deficiency intense enough to cause reduction of sulfates to sulfides, but the lake was able to maintain its basin free of black muds by the process of self-purification.

#### Distribution of Aluminum, Potassium, Calcium, and Mag-

nesium. The distribution of Al, K, Mg, and Ca may depend primarily on the rate of supply of dissolved and particulate mineral matter, the biological or chemical precipitation of carbonates, and the variation in the accumulation of the whole sediment. Al, Mg, Ca, and K may occur in a large variety of mineral structures such as feldspars, clay minerals, and amorphous aluminosilicate gels. Mackereth (1966) noted that Na, K, and Mg were associated with the mineral fraction of the sediment of English lakes, but Ca was not so clearly associated with mineral erosion. Calcium was evidently more easily leached from the soil than Mg. According to Mackereth, the Ca is abundantly deposited into the English lake sediments only at times of very intense erosion when the rate of precipitation of clastic material is high enough to prevent removal by leaching of much Ca. In Lake Mendota the Ca concentration is controlled mainly by carbonate deposition (discussed previously), but Mg concentration is influenced by the rate of detrital inorganic sedimentation and Mg carbonate deposition. Processes other than Mg carbonate (or mixtures of Mg with CaCO<sub>3</sub>) sedimentation are dominant in Zones II-IV because the Mg concentration is not depressed in the recent muds as is CaCO<sub>3</sub>.

Al and K concentrations increase initially in Zone II and continue to increase throughout Zone III before leveling off in Zone IV. The K and Al concentration is enriched two to five times in the postcultural over the precultural sediments indicating erosional activity has increased since man moved into the Madison lake region. The construction of a dam at the Yahara outlet in 1847 led to raising the level of the lake 5 ft and has exposed new shoreline to erosion. There should, on the grounds discussed above, exist a direct relationship between Al and K content in the sediments and erosion intensity of the drainage basin.

**Lake Mendota Long Core.** In November 1968, a 990-cm core was taken from the center of Lake Mendota in 23 meters of water using a 1-1.5-in. piston-operated corer. The 9.9-meter core was fractionated in 20-cm intervals as shown in Figure 5. The zones shown in Figure 5 indicate approximate changes in chemical stratigraphy as described previously for the short cores WC-84, 86, and 89. The purpose of the sample probe was to determine the physical and chemical homogeneity of the precultural sediment during the late postglacial period. The top 62 cm of sediment consisted of a black gytja containing 98-111 mg/g Ca; below 62 cm to 990 cm (Zone I), the fine-grained, buff-marl deposits contain 183-226 mg/g Ca. There was no variation in appearance from 62 to 990 cm of sediment.

The marked increase in ragweed abundance occurs upward of the 42-62 cm stratum (Zone II). The low ragweed pollen deposited during the period represented by 920 cm of sediment below the recent muds supports the use of Ambrosia pollen as an indicator of the cultural base in a sedimentary sequence. A ragweed maximum in pollen diagrams may not necessarily be related to European-type settlement. At Silver Lake, Ohio, and at Rogers Lake, Conn., high ragweed pollen counts were found in core intervals dated 5000-8000 years B.P. (Ogden, 1966; Davis, 1967).

Organic C concentration varies from 59 to 77 mg/g over the core interval of 62-990 cm. This compares favorably with 55-73 mg/g organic C found in the marl sediment of WC-89, a short deepwater core. The postcultural sediment contains 87-92 mg/g organic C.

The enrichment of P in the postcultural sediments of Lake Mendota is of particular interest because the long core (9.9 meters) provides a background concentration of P that was

**Table III. Mean Concentrations of Phosphorus, Iron, Potassium, Organic Carbon, Carbonate Carbon, and % Solids in the Lake Mendota Cores<sup>a</sup>**

| Core  | Chemical component | Zone           |                        |                       |                       |
|-------|--------------------|----------------|------------------------|-----------------------|-----------------------|
|       |                    | Pre-cultural I | Early post-cultural II | Mid-post-cultural III | Late post-cultural IV |
| WC-89 | P                  | 0.90           | 0.96                   | 1.57                  | 1.63                  |
|       | Fe                 | 7.00           | 12.9                   | 20.2                  | 20.2                  |
|       | K                  | 2.43           | 7.45                   | 9.78                  | 10.2                  |
|       | Organic C          | 64.8           | 76.3                   | 70.5                  | 84.1                  |
|       | Carbonate C        | 57.6           | 41.3                   | 33.6                  | 35.6                  |
|       | % solids           | 13.4           | 12.6                   | 16.3                  | 15.5                  |
| WC-86 | P                  | 0.96           | 1.06                   | 1.23                  | 1.46                  |
|       | Fe                 | 6.90           | 13.1                   | 19.8                  | 22.9                  |
|       | K                  | 3.12           | 8.42                   | 11.5                  | 11.7                  |
|       | Organic C          | 59.8           | 70.0                   | 74.7                  | 77.4                  |
|       | Carbonate C        | 74.9           | 46.1                   | 30.5                  | 30.5                  |
|       | % solids           | 18.0           | 23.2                   | 24.4                  | 17.9                  |
| WC-84 | P                  | 0.85           | 0.997                  | 1.09                  | 1.16                  |
|       | Fe                 | 6.70           | 12.4                   | 20.2                  | 20.0                  |
|       | K                  | 2.71           | 7.34                   | 11.1                  | 11.1                  |
|       | Organic C          | 90.5           | 102                    | 98.6                  | 92.3                  |
|       | Carbonate C        | 76.1           | 48.4                   | 28.4                  | 27.4                  |
|       | % solids           | 26.2           | 27.7                   | 33.3                  | 28.9                  |

<sup>a</sup> All concentrations are mg element/g dry wt of solids.

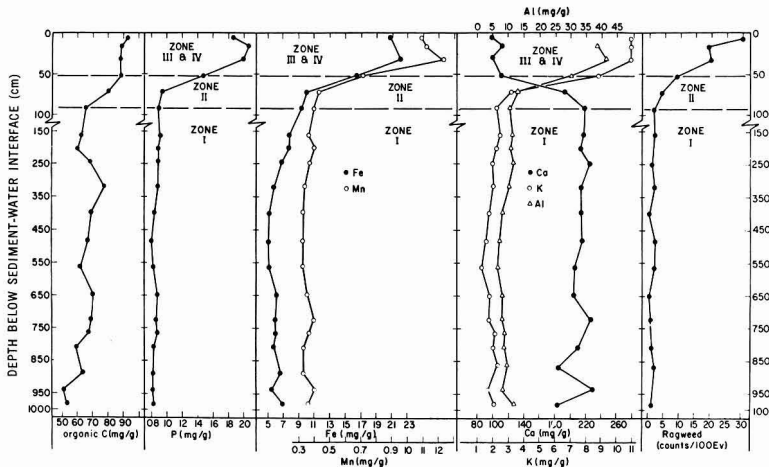


Figure 5. Chemical and Ambrosia pollen stratigraphy of Lake Mendota core WC-95

deposited for a long period historically. The P concentration remains constant at 0.8–0.94 mg/g throughout Zone I, then in Zones III and IV, the P concentration increases to 1.5–2.1 mg/g in the postcultural sediment.

The depth plot of Fe, Mn, K, and Al concentrations is remarkably uniform below the ragweed horizon to 990 cm, but the postcultural concentrations of these elements increases three–five times that found in the precultural sediment. For all the above elemental concentrations, a slight minimum inflection is observed in the zone of 400–650 cm.

Several species of ostracodes were described by Burrell (1971) for Lake Mendota core WC-95. Ostracodes were present throughout the 990-cm core length, but in the upper 60 cm (Zone III and IV) there was an increase in diversity of species and total ostracod numbers. Species reported as exclusive to the recent upper 60 cm of sediment were *Darwinula aurea*, *Candona caudata*, *Candona poseyensis*, and *Candona spinaensis* (Burrell, 1971).

In summary, the chemical stratigraphy of the 9.9-m core indicates that stable conditions existed in Lake Mendota and its watershed for a long historical period before the settlement period in Wisconsin.

#### Summary and Conclusions

The composition of the sediments with depth and, therefore with time, presents a pattern of change which documents the progressive increment of materials deposited to Lake Mendota. Thus, changes in the chemical stratigraphy can be traced to man's activities in the watershed. If it is assumed that the sedimentation rate throughout the period represented by the concentration-depth diagram is constant, a calculation can be made showing the incremental increase or decrease in concentration per unit thickness of sediment (or per year if time is estimated). However, this study has revealed that concentration-depth diagrams do not generally contain sufficient information to estimate an incremental rate change in nutrient concentration which accurately reflects changes in nutrient supply owing to man's activities in the watershed. The deposition rate of the whole sediment imposes a constraint on the system which necessitates an absolute time scale in the pre- and postcultural sediments.

A basic change in sedimentation is recorded in the Lake Mendota cores by a buff marl (Zone I) overlain by a gray-

colored gyttja-marl (Zone II) and a black gyttja (Zones III and IV). Initial increases in Fe, Mn, Al, K, and ragweed pollen occur in Zone II corresponding to the first active period of settlement in southern Wisconsin and the Lake Mendota basin (ca. 1820–1880) while carbonate C shows a rapid decrease in concentration during the same interval. The change in sedimentation is attributed to increased deposition of erosional material as a consequence of farm and urban activities in the drainage basin. Further increases in the deposition of Al-, K-, Fe-, and Mn-containing compounds in Zone III (ca. 1800–1940) are correlated to the increased runoff and leaching of the soils in the Lake Mendota basin. The overall trend in Lake Mendota has been to increase in the rate of deposition of the whole sediment from about 1820–1940. The core profiles indicate that the runoff of erosional products reached a peak and leveled off approximately 20–30 years ago. The enrichment of Fe appears to be caused by an increase in the rate of sedimentation of a detrital mineral or group of minerals that contain the element as a firmly bound major component or sorbed constituent. The marked ability of the postcultural sediments to retain inorganic P compared to the precultural marl is probably due to the higher Fe content in the black gyttja.

Analysis of past rates of change must be taken together with the detection and measurement of recent man-induced changes. Therefore, the chemical stratigraphy of lake sediment cores provides the understanding which is needed to detect a change as an acceleration; only by detecting accelerations is it possible to distinguish between normal and cultural processes. In the Lake Mendota cores, the normal rate of P change (before man's influence) with sediment depth is nearly zero. The chemical stratigraphy of precultural interval of the Lake Mendota long core indicates that stable limnological and watershed conditions existed in Lake Mendota and its basin prior to man's influence for a long period historically. The concentrations of P, organic C, Fe, Mn, Al, K, Ca, as well as ragweed pollen are all relatively constant in Zone I. In the midcultural period (Zone III) an accelerated upward increase in P occurs and reaches a first maximum (ca. 1920) in core WC-89; a second maximum in P concentration occurs in the most recent sediment (Zone IV). The enrichment of P in the postcultural sediments of Lake Mendota is due not only to an increase in supply of P from domestic drainage,

but to an increase in P retentive capacity of the postcultural sediment and to an increase of P depositional efficiency owing to the concomitant increase in Fe-, Mn-, K-, and Al-containing compounds. The P concentration in the marl sediment is more uniform over the lake, but since the advent of domestic drainage, the influent materials have allowed fractionation of sediment particles with water depth to produce higher concentrations of P toward the center of the lake.

Organic C concentrations in the Lake Mendota sediments have increased since the precultural period indicating an increase in biological productivity of the lake; however, it is difficult to determine what part of the increase is attributable to allo- or autochthonous organic production. In Zone IV organic C increases upward to the sediment-water interface perhaps indicating an accelerated increase in level of organic productivity since 1940. The increase in organic C concentration in Zone IV is accompanied by an increase in P and a slight increase in carbonate C.

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# A pH-Dependent Succession of Iron Bacteria

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■ The role of an acid-tolerant, filamentous iron bacterium in a succession of pH-dependent events affecting the rate of iron oxidation is identified. This organism significantly catalyzes iron oxidation in the pH range 4.5–3.5. At pH greater than 4.5, abiotic iron oxidation proceeds rapidly. At pH less than 3.5, *Thiobacillus ferrooxidans* significantly catalyzes iron oxidation. The activity of the filamentous iron bacteria in this succession of events may directly affect the rate of acidity production in coal mine waters.

The rate of acidity production from the degradation of iron pyrites found in coal deposits has been shown by Singer and Stumm (1970) to depend on the rate of ferrous iron oxidation. The rate of abiotic ferrous iron oxidation is directly related to solution pH (Stumm and Lee, 1961) with the relationship above pH 4.5 being:

$$\frac{-d[\text{Fe}^{2+}]}{dt} = k[\text{Fe}^{2+}]p[\text{O}_2][\text{OH}^{-}]^2$$

where  $k = 8.0 \times 10^{13} \text{ l. mol}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$  at 25°C. At pH between 4.5 and 3.5, chemical ferrous iron oxidation proceeds at a rate indirectly pH dependent (Singer and Stumm, 1970). The oxidation rate at pH less than 3.5 is approximately  $7 \times 10^{-3} \text{ mg/l. day}$  for an initial ferrous iron concentration of 250 mg/l. This rate remains relatively constant at lower pH. Table I shows the relationship between pH and the rate of abiotic ferrous iron oxidation over the meso-acidic pH range (pH 3.5–5.5). The ferric iron released can then oxidize iron pyrite even in the absence of oxygen. Singer (1969) showed that the half time of reaction between ferric iron and pyrite in the absence of oxygen is 25 min for a pyrite concentration of 5 gram/l. The chemical equations of the pyrite degradation reactions are shown in Table II. The acidity in coal mine drainage waters is produced either by the formation of ferric hydroxides (Equation 4) or by the oxidation of the sulfur moiety in pyrite degradation (Equation 3).

In a coal mine, pyrite degradation may occur in the self-accelerating cycle identified in Table II with pyrite being oxidized by ferric iron. Of the two ferric iron-producing equations shown in Table II (Equations 1 and 2), Singer and Stumm (1970) showed that only ferrous iron oxidation is a significant source of ferric iron. Assuming that influent mine waters have an average total iron concentration of 0.5 mg/l., that ferrous iron oxidation is the only ferric iron source, and that no ferric iron is hydrolyzed, 93 turns of the pyrite degradation cycle (Equations 2 and 3, Table II) must occur to result in the release of 300 mg/l. total iron commonly observed in mine drainage. If average mine water residence time is 10 months, each pyrite degradation cycle can thus take no longer than 3.2 days. Ferric iron hydrolysis and precipitation

(Equation 4) will naturally increase the number of cycles required and thus decrease the theoretical time available per cycle.

The iron oxidation-pyrite degradation cycle identified in Table II will proceed slowly at pH < 4.5 in the absence of catalysis. This is because at pH < 4.5, the cycle is rate-limited by the ferrous iron oxidation rate (Singer and Stumm, 1970). Catalysis of ferrous iron oxidation can be biologically or abiotically mediated. Singer (1969) examined the effect of chemical and physical catalysts on abiotic ferrous iron oxidation and he showed that their effect was a catalysis factor of less than 30. The iron bacterium, *Thiobacillus ferrooxidans*, significantly catalyzes iron oxidation with catalysis factors greater than 300 under laboratory conditions. (Schneitman, et al., 1969). However, optimal activity of this organism is at pH < 3.5 (Silverman, 1967). Thus, there is no mechanism for rapid catalysis of the iron oxidation-pyrite degradation cycle in the pH range 4.5–3.5. In this report, we describe the effect of a filamentous iron bacterium on catalyzing the formation of the environment necessary for optimal *T. ferrooxidans* activity and thus for pyrite degradation.

## Materials and Methods

Samples of sediment and mine water were obtained from five widely separated sources: a coal mine in Illinois, an iron-bearing stream in New Hampshire, a zinc mine in New Jersey, a coal mine in West Virginia, and an iron-bearing stream in Vermont. These samples were obtained during different seasons (August, September, December, May). From all of these samples we isolated an acid-tolerant filamentous iron bacterium of the genus *Metallogenium*, using a medium containing the following constituents:  $(\text{NH}_4)_2\text{SO}_4$ ,

Table I. Rate of Ferrous Iron Oxidation over the Meso-Acidic pH Range<sup>a</sup>

| pH  | Abiotic Fe <sup>2+</sup> oxidation rate, mg/l.-day <sup>b</sup> |
|-----|---|
| 3.5 | 0.007   |
| 4.0 | 0.25  |
| 4.5 | 0.70  |
| 5.0 | 5.76  |
| 5.5 | 57.6  |

<sup>a</sup> From Singer and Stumm, 1970.

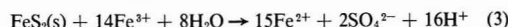
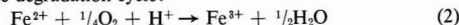
<sup>b</sup>  $[\text{Fe}^{2+}]_0 = 250 \text{ mg/l.}$

Table II. Chemical Reactions in Iron Pyrite Degradation

Pyrite oxidation:



Pyrite degradation cycle:



Ferric iron deposition:



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**Table III. Rate of Fe<sup>2+</sup> Oxidation in the Presence of the Iron-Oxidizing Metallogenium<sup>a,b</sup>**

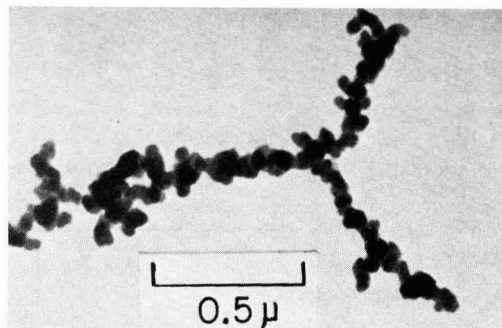
| Initial Fe <sup>2+</sup> concn, mg/l. | Fe <sup>2+</sup> oxidation, mg/l.-day |        |        |
|---------------------------------------|---------------------------------------|--------|--------|
|                                       | pH 3.6                                | pH 4.1 | pH 5.0 |
| 0                                     | 0                                     | 0      | 0      |
| 50                                    | 3                                     | 5      | 0      |
| 250                                   | 12                                    | 58     | 4      |
| 400                                   | 7                                     | 24     | 2      |
| 1,250                                 | 5                                     | 14     | 0      |

<sup>a</sup> Rates reported are differences between rates observed in inoculated and in control flasks.

<sup>b</sup> In the presence of 0.4% KH phthalate.

0.1%; CaCO<sub>3</sub>, 0.01%; MgSO<sub>4</sub>, 0.02%; KH<sub>2</sub>PO<sub>4</sub>, 0.001%; KH phthalate, 0.4%; and 250 ppm ferrous iron from an acidified FeSO<sub>4</sub>·7H<sub>2</sub>O solution (Walsh, 1971). Phthalate was used to buffer the growth medium in the pH 4 range. Initial isolation required addition of 0.4% formalin to 100 ml of the isolating medium in a 250-ml Erlenmeyer flask (Nunley and Krieg, 1968). After three transfers, each following four days of growth, pure cultures were obtained in nine of ten flasks. Culture purity was based on the absence of contaminant growth on solid and liquid media used to culture heterotrophs and other iron or sulfur bacteria (Walsh, 1971). The extent of iron oxidation catalysis by this acid-tolerant stalked iron bacterium was measured by comparing the change in the ferrous iron concentration in solution in an inoculated flask and in a control flask. Ferrous iron concentration was measured by acid permanganate titration of a 1-ml sample (diluted to 50 ml) using an *o*-phenanthroline indicator.

To identify the pH-dependent succession of iron bacteria, *T. ferrooxidans* and the iron-oxidizing *Metallogenium*, as well as eight heterotrophs isolated from acidic coal mine drainage, were inoculated into a 500-ml solution with ion concentrations similar to those observed in some influent mine waters [CaCO<sub>3</sub>, 50 mg/l.; MgSO<sub>4</sub>·7H<sub>2</sub>O, 25 mg/l.; MnSO<sub>4</sub>, 5 mg/l.; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 2 mg/l.; KH<sub>2</sub>PO<sub>4</sub>, 0.25 mg/l.]. Initial pH was adjusted to 5.0. Ferrous iron concentration was initially 20 mg/l. with an additional 20 mg/l. added every two weeks. Sterile distilled water was added weekly to maintain the initial volume of 500 ml. This medium was circulated in a 10-ft Tygon tube (3/8 in. diam) using a nitrogen gas lift pump. The total population of the heterotrophs in the medium was followed by colony counting on the eight solid media used to isolate the bacteria. *T. ferrooxidans* and *Metallogenium* populations were followed using a five-tube most probable



**Figure 1. Electron micrograph of the iron-oxidizing *Metallogenium* washed in 0.05% oxalic acid (×27,000)**

number (MPN) technique ("Standard Methods for the Examination of Water and Waste Water," 1965). *T. ferrooxidans* was tested on the 9 K medium (Dugan and Lundgren, 1964); the iron-oxidizing *Metallogenium* was tested on our liquid growth medium. Because of the unusual morphology of the *Metallogenium*, care was taken not to break the filaments during dilution in the MPN procedure. A wide-tipped pipet was used, and shaking of the dilution tubes was kept to a minimum.

A control system was run in which bacterial populations were also followed. The same liquid medium was used in this system, and it was inoculated with the heterotrophs and *T. ferrooxidans* but not with the *Metallogenium*. Again heterotrophic populations were counted on solid media and those of *T. ferrooxidans* by the MPN technique. A second control system was run which was buffered at pH 4.1 with phthalate. This system was inoculated with *T. ferrooxidans*, the *Metallogenium*, and the eight heterotrophs.

#### Experimental

Cultures of the filamentous iron bacterium were isolated from five widely separated sources and appeared morphologically to belong to a single species. The organism grew in multibranching colonies of interweaving ferric iron encrusted stalks (0.1–0.4 μ diam) without a conventional cell body. Macroscopically, these stalks appeared as a rusty precipitate, but when this precipitate was washed carefully with 0.05% oxalic acid, the stalks were visible under the electron microscope, still partially encrusted with iron (Figure 1). This organism is morphologically similar to the manganese-oxidizing bacterium *Metallogenium symbioticum* described by Zavarzin (1961, 1964) and Dubinina (1969, 1970). It differs from the stalked iron bacterium, *Gallionella ferruginia*, in the

**Table IV. Bacterial Populations Observed in the Mine Water System**

| Time, days | Mine water inoculated with <i>Metallogenium</i> |                                     |                                   |                           | No <i>Metallogenium</i> |                                     |                                   |                           |
|------------|---|-------------------------------------|-----------------------------------|---------------------------|-------------------------|-------------------------------------|-----------------------------------|---------------------------|
|            | pH  | <i>T. ferrooxidans</i> <sup>a</sup> | <i>Metallogenium</i> <sup>a</sup> | Heterotrophs <sup>a</sup> | pH                      | <i>T. ferrooxidans</i> <sup>a</sup> | <i>Metallogenium</i> <sup>a</sup> | Heterotrophs <sup>a</sup> |
| 2          | 5.0   | ...                                 | ...                               | 5.1                       | 5.0                     | ...                                 | ...                               | 4.0                       |
| 5          | 4.3   | ...                                 | 2.7                               | 7.8                       | 5.0                     | ...                                 | ...                               | 5.5                       |
| 10         | 4.3   | ...                                 | 4.1                               | 8.3                       | 4.9                     | ...                                 | ...                               | 7.1                       |
| 20         | 3.8   | ...                                 | 4.0                               | 8.5                       | 4.5                     | ...                                 | ...                               | 7.2                       |
| 30         | 3.2   | 2.0                                 | 1.2                               | 4.7                       | 4.1                     | ...                                 | ...                               | 7.0                       |
| 45         | 2.6   | 4.0                                 | ...                               | 2.7                       | 4.0                     | ...                                 | ...                               | 6.3                       |

<sup>a</sup> Log number of cells/ml.

absence of a conventional cell body and in its acid tolerance (Walsh, 1971). The iron bacterium we have isolated does not catalyze manganese oxidation but we consider it to be an acid-tolerant, iron-oxidizing strain of *Metallogenium*. This is based on morphological similarities and on the inhibition of both organism strains by high initial concentrations of their metal ion substrates (Walsh, 1971). Although we have measured a base pair ratio (gc) of 72–73% for the iron-oxidizing strain of *Metallogenium*, there are no similar data available in the literature for comparison with *Gallionella* or other *Metallogenium*.

Initial studies showed that the iron-oxidizing strain of *Metallogenium* is active in the pH 3.5–5.0 range with an activity optimum at pH 4.1 (Walsh, 1971). Initial ferrous iron concentration directly affected activity. Concentrations over 40 mg/l. increasingly inhibited growth with an upper tolerance limit of 150 mg/l. ferrous iron. The phthalate buffer in the growth medium permitted growth in a medium of higher initial ferrous iron content (Table III). This effect was probably the result of the formation of a ferrous iron phthalate complex.

We investigated the changes in populations of acid mine drainage heterotrophs, of *T. ferrooxidans*, and of the iron-oxidizing *Metallogenium* in a synthetic mine water system. Table IV shows the changes in bacterial populations in the test system. As the pH decreased from 5.0 to 3.3, the *Metallogenium* population increased from less than  $10^3/100$  ml at pH 5 to almost  $10^7/100$  ml at pH 4.2 and then decreased again to less than  $10^3/100$  ml at pH 3.5. There was heavy bacterial growth on the tube surface when the pH declined to 4.3. When the pH decreased from 3.5 to 2.5, the *T. ferrooxidans* population increased from less than  $10^3$  cells/100 ml to almost  $10^6$  cells/100 ml.

Table IV also shows a comparison of populations between the test and a control tube system. This control system had not been inoculated with the *Metallogenium*. The pH of the control system remained above 4.0. The population of *T. ferrooxidans* remained below  $10^3$  cells/100 ml and only a minor decline in the heterotrophic population was observed after 35 days. This decrease was significantly less than that observed in the test system. The final characteristics of the test system after 45 days are very similar to those reported by Tuttle et al., (1968) for a gob pile drainage. Table V shows that the final characteristics of the control system are not similar to those of the gob pile or the test system.

A second control system was run to further demonstrate the effect of pH on the distribution of iron bacteria populations in the column. In this control, the pH was buffered at 4 with phthalate. No decline in the *Metallogenium* population and no increase in the *T. ferrooxidans* population was observed after 45 days. The heterotrophic population again remained high as in the previous control system.

Table V. Comparison of Characteristics of Gob Pile Drainage<sup>a</sup> with Test or Control Mine Water Systems<sup>b</sup>

|                   | [Fe] <sub>T</sub> , mg/l. | <i>T. ferrooxidans</i> , cells/ml | Heterotrophs, cells/ml |
|-------------------|---------------------------|-----------------------------------|------------------------|
| Gob pile drainage | 2.5–3.0                   | 100–500                           | 30–3,500               |
| Test system       | 2.6                       | 80                                | 10,000                 |
| Control system    | 4.0                       | 80                                | <10                    |

<sup>a</sup> From Tuttle et al. (1968).

<sup>b</sup> After 45 days.

## Discussion

The groundwaters influent into a coal mine are generally weakly buffered in the pH 5.5–7.5 range; they leave a coal mine at pH less than 3.0. This decrease in pH and increase in acidity has been reported to be the result of ferric iron degradation of iron pyrites and to be rate-limited by the rate of ferrous iron oxidation (Singer and Stumm, 1970). Our research has suggested a mechanism by which bacterial catalysis of iron oxidation can occur throughout the meso-acidic pH range (4.5–2.5) in which abiotic ferrous iron oxidation is extremely slow. Abiotic ferrous iron oxidation rates in the pH range 3.5–4.5 are not sufficient to produce the ferric iron required to react with pyrite so that sufficient hydrogen ion is released to lower mine water pH to 3.5 from pH 4.5 during the average 10-month water residence time in coal mines. The acid-tolerant *Metallogenium* increases ferrous iron oxidation rates and resultant acidity production by a factor greater than 200 in the pH range 3.5–4.5 (Walsh, 1971). This is an environmentally significant increase because the activity of this iron bacterium can create the pH environment necessary for *T. ferrooxidans* during a short portion of the 10-month mine water residence time.

The population differences in the test and the control column in the laboratory suggest the ecological importance of the iron-oxidizing *Metallogenium*. Although it was pH sensitive outside the pH range 3.5–5.0, within the range, *Metallogenium* was active in catalyzing iron oxidation. Hydration of the ferric iron in this laboratory simulation of the mine water system produced the acidity. The potential ecological significance of this iron-oxidizing strain of *Metallogenium* is that in a coal mine it may catalyze the creation of the acidic environment necessary for high activity of *T. ferrooxidans*. The resultant decrease in pH in the mine water, as it flows through the mine, may bring about a rapid decrease in the *Metallogenium* population and an increase in the *T. ferrooxidans* population. Thus, in regions near where groundwaters enter the mine, the *Metallogenium* should be the predominant iron bacterium. In water flowing from the mine, *T. ferrooxidans* should predominate.

The existence of this pH-dependent iron bacteria succession has interesting implications in the formation of acidity in coal mine drainage. The acid-tolerant *Metallogenium* may significantly catalyze the rate of formation of ferric iron in a coal mine in the pH range 4.5–3.5. As such, its activity would affect the rate of pyrite degradation under these meso-acidic conditions. In addition, the activity of *Metallogenium* may result in the creation of a pH environment in the mine suitable for the growth of a large *T. ferrooxidans* population. In the absence of the *Metallogenium*, the rate of acidity formation resulting from abiotic pyrite degradation in the short residence time of water in the mine may not be sufficient to create the environment necessary for significant *T. ferrooxidans* growth. An acid mine pollution control measure based on breaking the pH-dependent iron bacterium succession may be possible based on inhibiting the growth of the *Metallogenium*. Stopping the bacterial succession at this point should result eventually in effluent mine waters at pH greater than 3.5 and with iron concentrations less than 75 mg/l.

## Summary

Isolates of an acid-tolerant filamentous iron bacterium of the genus *Metallogenium* were obtained from a number of geographically separated neutral and acidic iron-bearing streams. This stalked iron bacterium catalyzed ferrous iron oxidation in the pH 3.5–5.0 range with an optimum at pH 4.1.

An examination of the ecological role of this filamentous iron bacterium showed it to be a member of a pH-dependent iron bacteria succession. Growth of *T. ferrooxidans*, an acid-tolerant iron bacterium, was shown to be dependent on the growth of the filamentous iron bacterium to lower solution pH through acidity production from the ferric iron reaction following catalysis of ferrous iron oxidation.

This iron bacteria succession has ecological and pollution control implications. The existence of this succession suggests an ecological mechanism by which neutral groundwaters become acidic coal mine drainage. Acid mine drainage pollution may be controlled by breaking the iron bacteria succession in the 4.0–4.5 range at which solely abiotic acidity and iron releases will be less significant.

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## Effect of Inhomogeneous Mixing on Atmospheric Photochemical Reactions

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■ The conventional assumption of local uniform mixing of reactive chemical species is reexamined by derivation of the chemical reaction equations to include the effect of locally inhomogeneous mixtures on the reaction rates. Preliminary solutions of a simplified version of these equations show that inhomogeneities in reactant concentration generally tend to slow the reaction rate. Estimates of the relative roles of local diffusive mixing and chemical reactions in inhomogeneous mixtures show that there are several relatively fast photochemical reactions which may be limited by local diffusive mixing. In these cases, the reaction proceeds much more slowly than would be predicted if the reactants were uniformly mixed.

In developing either mathematical simulation models or laboratory chambers for the study of chemical reactions in the atmosphere, it has been generally assumed that the reacting materials are uniformly mixed. However, observations of the time history of concentrations of trace materials show quite clearly that uniformly mixed materials are the exception rather than the rule in both air and water (Nickola et al., 1970; Singer et al., 1963; Csanady and Murthy, 1971). Local fluctuations of concentration are particularly significant during the early stages of atmospheric mixing, immediately following discharge of trace materials into the atmosphere, and when there are multiple point sources of pollutants. Our purpose here is to make a preliminary estimate of the importance of these fluctuations on atmospheric chemical reaction rates and determine, at least approximately, the relative roles of reaction rates and diffusive mixing in the control of atmospheric chemical reactions.

The importance of chemical reactions in the atmosphere has been increasingly recognized in the problems of air pollution. These are probably most acute in dealing with photochemical smog formation (Worley, 1971). We have, therefore, drawn our examples from photochemistry, but we have not attempted to go beyond an examination of the possible importance of inhomogeneous mixing in these processes.

#### Basic Chemistry Model

We assume a bimolecular reaction



where  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  denote chemical species and that the reaction of  $\alpha$  with  $\beta$  to form  $\gamma$  and  $\delta$  is stoichiometric and is governed by equations of the form

$$\frac{\partial[\alpha]}{\partial t} = -K[\alpha][\beta] \quad (2)$$

$$\frac{\partial[\beta]}{\partial t} = -K[\alpha][\beta]$$

$[i]$  denotes the molar concentration of the  $i$ th chemical species and  $K$  is the reaction rate constant in units of (sec mol/cm<sup>3</sup>)<sup>-1</sup>. It is convenient to transform the concentration terms in Equations 2 to dimensionless mass fractions,  $C_i$ , by

$$\rho_0 C_i = M_i [i] \quad (3)$$

where  $\rho_0$  is the density of the mixture (g/cm<sup>3</sup>) and  $M_i$  is the molecular weight of the  $i$ th chemical species. Then the depletion rates for the  $\alpha$  and  $\beta$  species may be written

$$\frac{\partial C_\alpha}{\partial t} = -K_\alpha C_\alpha C_\beta \quad (4)$$

and

$$\frac{\partial C_\beta}{\partial t} = -\frac{K_\alpha M_\beta}{M_\alpha} C_\alpha C_\beta \quad (5)$$

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where  $K_\alpha = K_{p0}/M_\beta$  and has dimensions  $(\text{sec}\cdot\text{ppm})^{-1}$  when  $C_\alpha$  and  $C_\beta$  are expressed in parts per million (ppm) by wt.

We may now examine the relative contributions of the means and fluctuations of  $C_\alpha$  and  $C_\beta$  to the chemical reaction rate by assuming the time history of these quantities at a fixed point constitutes a stationary time series and that

$$\left. \begin{aligned} C_\alpha &= \bar{C}_\alpha + C_\alpha' \\ C_\beta &= \bar{C}_\beta + C_\beta' \end{aligned} \right\} \quad (6)$$

where the overbar indicates a time average and the prime indicates the instantaneous fluctuation about the average. Noting that  $\overline{C_\alpha'} = \overline{C_\beta'} = 0$  and that

$$\frac{\partial C_i}{\partial t} = \frac{\partial \bar{C}_i}{\partial t} + \frac{\partial C_i'}{\partial t} \quad (7)$$

we obtain directly from Equations 4-6

$$\frac{\partial \bar{C}_\alpha}{\partial t} = -K_\alpha (\bar{C}_\alpha \bar{C}_\beta + \overline{C_\alpha' C_\beta'}) \quad (8)$$

and

$$\frac{\partial \bar{C}_\beta}{\partial t} = -\frac{K_\alpha M_\beta}{M_\alpha} (\bar{C}_\alpha \bar{C}_\beta + \overline{C_\alpha' C_\beta'}) \quad (9)$$

where we have suppressed the dependence of  $K_\alpha$  on the temperature and pressure. (This analysis can be extended to include the fluctuations of  $K_\alpha$  owing to significant fluctuations of temperature and pressure. For our present purposes, we shall assume an isothermal reaction at ambient pressure.)

The role of concentration fluctuations in chemical reactions is immediately evident from Equations 8 or 9. The second-order correlation in the joint fluctuations of  $C_\alpha$  and  $C_\beta$  either enhances the reaction rate (when the correlation is positive) or suppresses the reaction when  $\overline{C_\alpha' C_\beta'}$  is negative. *Only when these fluctuations either do not exist or are uncorrelated is the average reaction rate governed by the average concentrations.* As a simple example of the importance of this correlation term, imagine that the materials  $\alpha$  and  $\beta$  pass the point of observation at different times—i.e., they are never in contact with each other. Values of  $\bar{C}_\alpha$  and  $\bar{C}_\beta$  would be observed, but it is readily seen that  $\bar{C}_\alpha \bar{C}_\beta = -\overline{C_\alpha' C_\beta'}$  in this case, a result which correctly predicts no chemical reaction.

If we assume no diffusive mixing of the reacting materials, we may model the chemical reactions by noting that

$$\frac{\partial C_i'^2}{\partial t} = 2 C_i' \frac{\partial C_i'}{\partial t} \quad (10)$$

$$\frac{\partial C_i'}{\partial t} = \frac{\partial C}{\partial t} - \frac{\partial \bar{C}}{\partial t} \quad (11)$$

and

$$\frac{\partial C_\alpha' C_\beta'}{\partial t} = C_\alpha' \frac{\partial C_\beta'}{\partial t} + C_\beta' \frac{\partial C_\alpha'}{\partial t} \quad (12)$$

Performing the necessary operations and time-averaging, we get, repeating Equations 8 and 9,

$$\frac{\partial \bar{C}_\alpha}{\partial t} = -K_\alpha (\bar{C}_\alpha \bar{C}_\beta + \overline{C_\alpha' C_\beta'}) \quad (13)$$

$$\frac{\partial \bar{C}_\beta}{\partial t} = -\frac{K_\alpha M_\beta}{M_\alpha} (\bar{C}_\alpha \bar{C}_\beta + \overline{C_\alpha' C_\beta'}) \quad (14)$$

$$\frac{\partial \overline{C_\alpha' C_\beta'}}{\partial t} = -K_\alpha \left[ \frac{M_\beta}{M_\alpha} (\bar{C}_\alpha \overline{C_\alpha' C_\beta'} + \overline{C_\beta C_\alpha'^2} + \overline{C_\alpha'^2 C_\beta'}) + (\overline{C_\beta C_\alpha' C_\beta'} + \overline{C_\alpha C_\beta'^2} + \overline{C_\alpha'^2 C_\beta'^2}) \right] \quad (15)$$

$$\frac{\partial \overline{C_\alpha'^2}}{\partial t} = -2 K_\alpha (\bar{C}_\alpha \overline{C_\alpha' C_\beta'} + \overline{C_\beta C_\alpha'^2} + \overline{C_\beta'^2 C_\alpha'^2}) \quad (16)$$

$$\frac{\partial \overline{C_\beta'^2}}{\partial t} = -\frac{2 K_\alpha M_\beta}{M_\alpha} \overline{C_\beta C_\alpha' C_\beta'} + \overline{C_\alpha C_\beta'^2} + \overline{C_\alpha'^2 C_\beta'^2} \quad (17)$$

Equations 13-17 provide a closed set, except for the third-order correlation terms  $\overline{C_\alpha' C_\beta'^2}$  and  $\overline{C_\beta'^2 C_\alpha'^2}$ .

The appearance of the third-order correlations complicates the modeling problem very considerably since the statistical description now requires consideration of the distribution functions for  $C_\alpha$  and  $C_\beta$ . In an independent study, O'Brien (1971) has proceeded from Equations 13-17 by assuming the form of these distribution functions. Another approach, which we are pursuing, is to model the third-order correlations in terms of the second-order correlations. However, for our present purpose of determining whether or not the effects of inhomogeneous mixtures on chemical reactions may be significant, we may neglect the third-order correlations by assuming  $C_\alpha'$  and  $C_\beta'$  are symmetrically distributed about  $\bar{C}_\alpha$  and  $\bar{C}_\beta$ , respectively. This assumption is, of course, untenable for more general cases but it does permit a solution of Equations 13-17 by numerical techniques.

For an initial test of the significance of inhomogeneities in chemical reactions, we assume a reaction box in which the initial concentration distributions of  $\alpha$  and  $\beta$  are arbitrarily specified by  $\bar{C}_\alpha$ ,  $\bar{C}_\beta$ ,  $\overline{C_\alpha'^2}$ ,  $\overline{C_\beta'^2}$ , and  $\overline{C_\alpha' C_\beta'}$ . As a further constraint which isolates the chemical reaction process, we assume there is no mixing in the reaction vessel and no wall effects.

As a reference case, let us assume a completely uniform

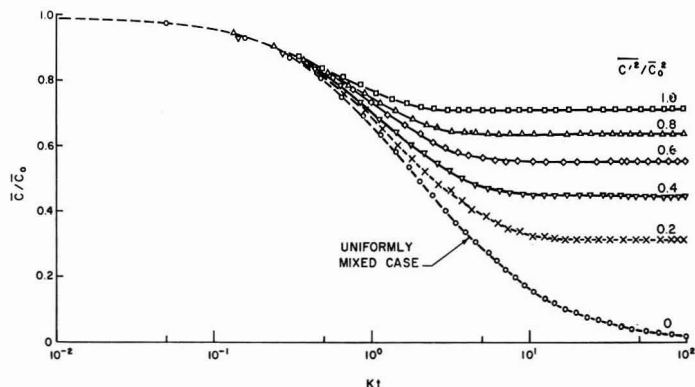
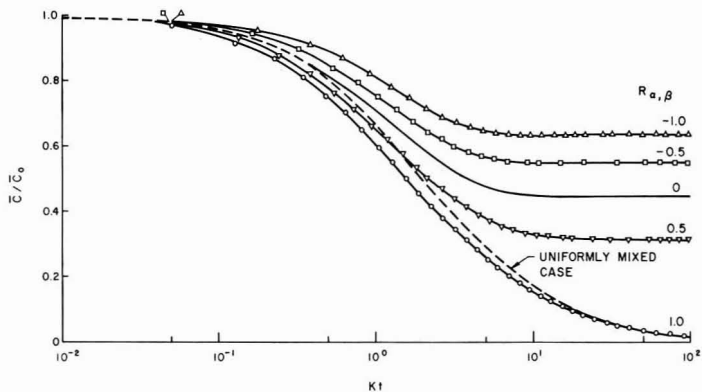


Figure 1. Chemical depletion of randomly mixed reactants ( $\overline{C_\alpha' C_\beta'} = 0$ ) for various initial degrees of inhomogeneity, as measured by  $\overline{C'^2}/C_0^2$ .



**Figure 2. Chemical depletion of initially inhomogeneously mixed reactants ( $C_i^2/C_0^2 = 0.40$ ) for various degrees of initial correlation between  $C_{\alpha'}$  and  $C_{\beta'}$ , as measured by**

$$R_{\alpha,\beta} = \frac{\overline{C_{\alpha'} C_{\beta'}}}{(\overline{C_{\alpha'}^2} \overline{C_{\beta'}^2})^{1/2}}$$



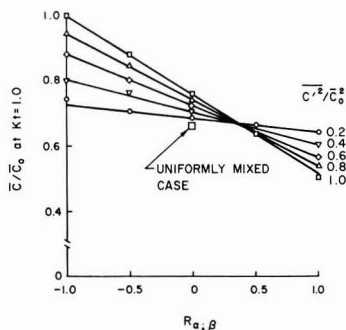
mixture of  $\alpha$  and  $\beta$ —i.e., no fluctuations in concentration,  $M_{\alpha} \simeq M_{\beta}$ , and initially  $C_{\alpha} = \overline{C_{\beta}} = \overline{C_0}$ . The predicted values of  $C_{\alpha}$  are shown in Figure 1 as a function of time normalized by the reaction rate constant. As can be seen, the reaction proceeds to exhaustion of the reacting materials.

Now let us assume that  $\alpha$  and  $\beta$  are initially inhomogeneously mixed but that there is no initial correlation between  $C_{\alpha'}$  and  $C_{\beta'}$ —i.e., initially  $\overline{C_{\alpha'} C_{\beta'}} \equiv 0$ . As a measure of these fluctuations, we take  $\overline{C_i'^2}/\overline{C_i^2} = 0.2, 0.4, 0.6, 0.8,$  and  $1.0$ . The results of these calculations are also shown in Figure 1, and it is immediately evident that any inhomogeneities operate to suppress the chemical reaction rate and to stop it completely before the reacting materials are exhausted. Mathematically, the model predicts that, in the absence of mixing, initial inhomogeneities operate to produce values of  $\overline{C_{\alpha'} C_{\beta'}}$  which eventually become equal to  $-\overline{C_{\alpha}} \overline{C_{\beta}}$  and the reaction ceases. Physically, the local reactions have everywhere proceeded to exhaustion of one of the reactants, leaving a residue of the other reactant and products at that site.

It is of special interest to note, from Equation 15, that the suppression of the reaction rate by  $C_{\alpha'} C_{\beta'}$  depends only on one of the reactants being nonuniformly distributed initially. A negative rate of change of  $C_{\alpha'} C_{\beta'}$  can be generated by nonzero values of either  $\overline{C_{\alpha'}^2}$  or  $\overline{C_{\beta'}^2}$ , since the terms  $\overline{C_{\beta}} C_{\alpha'}^2$  and  $C_{\alpha} \overline{C_{\beta'}^2}$  are positive definite. The presence of concentration inhomogeneities in one of the reactants generates inhomogeneities in the other.

The effect of an initial correlation between  $C_{\alpha'}$  and  $C_{\beta'}$  may now be examined by assigning initial nonzero values to  $\overline{C_{\alpha'} C_{\beta'}}$ ,  $\overline{C_{\alpha'}^2}$ , and  $\overline{C_{\beta'}^2}$ . To illustrate this effect, we have chosen  $\overline{C_{\alpha'}^2}/\overline{C_0^2} = \overline{C_{\beta'}^2}/\overline{C_0^2} = 0.4$  and  $\overline{C_{\alpha'} C_{\beta'}}/(\overline{C_{\alpha'}^2} \overline{C_{\beta'}^2})^{1/2} = +1.0, +0.5, 0.0, -0.5,$  and  $-1.0$  where  $\overline{C_{\alpha'} C_{\beta'}}/(\overline{C_{\alpha'}^2} \overline{C_{\beta'}^2})^{1/2} \equiv R_{\alpha,\beta}$ , the ordinary correlation coefficient. The resulting predictions of  $C/C_0$  are shown in Figure 2 and are again compared with the uniformly mixed case. As might have been expected, initial positive correlation accelerated the reaction rate, but only when this initial positive correlation was perfect did the reaction go to exhaustion of the reacting materials. In this case, although there were concentration fluctuations, stoichiometrically equal amounts of  $\alpha$  and  $\beta$  were initially placed in each local volume. In all other cases, the reaction was again halted when one of the reactants was exhausted locally, leaving a residue of the other reactants and products of the reaction.

The combined effects of initial inhomogeneities and correlations between the fluctuations are summarized in Figure 3 by plotting the depletion of  $\overline{C}$  during the first normalized time step as a function of  $R_{\alpha,\beta}$  and  $\overline{C_i'^2}/\overline{C_0^2}$ . The effect of the mag-



**Figure 3. Joint effect of initial correlation and inhomogeneity on depletion of reacting materials at  $Kt = 1.0$**

nitude of the fluctuations, as measured by  $\overline{C_i'^2}$ , reverses as one goes from large positive toward small positive and negative values of  $\overline{C_{\alpha'} C_{\beta'}}$ .

These results point toward an important role for fluctuations of concentration in controlling chemical reaction rates. For example, if two reacting materials are discharged simultaneously from a point source, during their initial mixing with the atmosphere their concentration fluctuations should be large and positively correlated. We would then expect, on the basis of this effect, that their reaction rate would be considerably faster than if they were uniformly mixed from the start. The emission of hydrocarbon and  $\text{NO}_x$  from auto exhausts is a case in point. Discharge of  $\text{SO}_2$  and particulate matter from power plant stacks is another.

On the other hand, if reacting materials are randomly mixed or if positive fluctuations in one are associated with negative fluctuations in the other, the reaction should be suppressed, compared to the uniformly mixed case. Both of these cases could be important, but their true importance depends critically on the rate at which atmospheric diffusion tends to mix chemical species and, hence, to diminish these fluctuations, as compared with the rate of chemical reaction produced by the concentration fluctuations.

#### Estimates of Local Mixing Rates in the Atmosphere

The only way in which the correlation  $\overline{C_{\alpha'} C_{\beta'}}$  can be eliminated, if it exists, in given flow situations is by the process of molecular diffusion. To estimate the rate at which this can occur, we may write the expressions for the contribution of

molecular diffusion to the time rate of change of  $C_{\alpha'}$  and  $C_{\beta'}$ . They are

$$\left(\frac{\partial C_{\alpha'}}{\partial t}\right)_{\text{diff}} = D_{\alpha} \nabla^2 C_{\alpha'} = D_{\alpha} \frac{\partial^2 C_{\alpha'}}{\partial y_i \partial y_i} \quad (18)$$

$$\left(\frac{\partial C_{\beta'}}{\partial t}\right)_{\text{diff}} = D_{\beta} \frac{\partial^2 C_{\beta'}}{\partial y_i \partial y_i} \quad (19)$$

Multiplying Equations 18 and 19 by  $C_{\beta'}$  and  $C_{\alpha'}$ , respectively, adding, and time-averaging gives

$$\left(\frac{\partial \overline{C_{\alpha'} C_{\beta'}}}{\partial t}\right)_{\text{diff}} = D \frac{\partial^2 \overline{C_{\alpha'} C_{\beta'}}}{\partial y_i^2} - 2 D \frac{\partial \overline{C_{\alpha'}}}{\partial y_i} \frac{\partial \overline{C_{\beta'}}}{\partial y_i} \quad (20)$$

(We have assumed  $D_{\alpha} \approx D_{\beta} = D$ , consistent with the assumption  $M_{\alpha} \approx M_{\beta}$ . See O'Brien (1971) for a discussion of this assumption.) The first term on the right-hand side of Equation 20 is nondissipative—i.e., it measures the transfer of the  $\overline{C_{\alpha'} C_{\beta'}}$  correlation by gradients in the value of this correlation within the field. The second term is dissipative—i.e., it measures the local diminution of  $\overline{C_{\alpha'} C_{\beta'}}$  by the action of molecular diffusion. The appropriate expression for this term is

$$2 D \frac{\partial \overline{C_{\alpha'}}}{\partial y} \frac{\partial \overline{C_{\beta'}}}{\partial y} = \frac{2 D \overline{C_{\alpha'} C_{\beta'}}}{\lambda^2} \quad (21)$$

In this expression, the dissipative scale length  $\lambda$  must be chosen as it is chosen for the calculation of other turbulent correlations when performing calculations of the structure of turbulence (Donaldson, 1969).

For such calculations,  $1/\lambda^2$  is given approximately by

$$\frac{1}{\lambda^2} \approx \frac{0.05 \rho_o q}{\mu_o \Lambda}$$

where  $\rho_o$  is the atmospheric density,  $q^2 = \overline{u'^2} + \overline{v'^2} + \overline{w'^2}$ ,  $\mu_o$  is the molecular viscosity of air, and  $\Lambda$  is a length scale related to the integral scale of the atmosphere, and is of the order of 1000 cm in the earth's boundary layer.

If we choose typical values of the parameters involved in evaluating the magnitude of the expression for  $(\partial \overline{C_{\alpha'} C_{\beta'}} / \partial t)_{\text{diff}}$  given in Equation 20, we have

$$\begin{aligned} \Lambda &= 1000 \text{ cm} \\ \rho_o &= 10^{-3} \text{ g/cm}^3 \\ \mu_o &= 1.7 \times 10^{-4} \text{ g/cm-sec} \\ D &= 1.7 \times 10^{-1} \text{ cm}^2/\text{sec} \\ q &= 30 \text{ cm/sec} \end{aligned}$$

These numbers give for the magnitude of the dissipative scale

$$\lambda = 10 \text{ cm}$$

From this result, we obtain, finally,

$$\frac{2 D}{\lambda^2} = 3.4 \times 10^{-3} \text{ sec}^{-1}$$

The rate of destruction of  $\overline{C_{\alpha'} C_{\beta'}}$  by molecular diffusion is of the order of magnitude of  $3.4 \times 10^{-3} \overline{C_{\alpha'} C_{\beta'}}$  and is tending to drive  $\overline{C_{\alpha'} C_{\beta'}}$  to zero. If this diffusion dissipation of  $\overline{C_{\alpha'} C_{\beta'}}$  is dominant,  $\overline{C_{\alpha'} C_{\beta'}}$  will remain close to zero and the chemical reaction will proceed according to the product of the mean concentrations. In this case, the chemical reaction rate is controlled by the reaction rate constant and the mean concentrations in the traditional way.

On the other hand, if the change of  $\overline{C_{\alpha'} C_{\beta'}}$  is dominated by chemical reactions—i.e., the reaction proceeds more rapidly than species diffusion,  $\overline{C_{\alpha'} C_{\beta'}}$  will tend to the value  $-\overline{C_{\alpha} C_{\beta}}$

**Table I. Reaction Rate Constant  $K_{\alpha}$  for Various Photochemical Reactions and Associated Estimates of  $N$  Using  $\overline{C_{\alpha}} = 1 \text{ ppm}$**

| Reaction  | $K$ (ppm-sec) <sup>-1</sup> | $N$                |
|---|-----------------------------|--------------------|
| 1. $\text{O}_3 + \text{NO} = \text{NO}_2 + \text{O}_2$  | $8.3 \times 10^{-4}$        | 4                  |
| 2. $\text{NO}_2 + \text{O}_3 = \text{NO}_3 + \text{O}_2$  | $1.7 \times 10^{-5}$        | $2 \times 10^2$    |
| 3. $\text{NO}_3 + \text{NO} = 2\text{NO}_2$   | 4.8                         | $7 \times 10^{-4}$ |
| 4. $\text{NO} + \text{HO}_2 = \text{NO}_2 + \text{OH}$  | $1.7 \times 10^{-1}$        | $2 \times 10^{-2}$ |
| 5. $\text{OH} + \text{O}_3 = \text{HO}_2 + \text{O}_2$  | 1.7                         | $2 \times 10^{-3}$ |
| 6. $\text{OH} + \text{CO} = \text{H} + \text{CO}_2$   | $5.0 \times 10^{-2}$        | $7 \times 10^{-3}$ |
| 7. $\text{CH}_3\text{O}_2 + \text{NO} = \text{CH}_3\text{O} + \text{NO}_2$                        | 1.7                         | $2 \times 10^{-3}$ |
| 8. $\text{C}_2\text{H}_3\text{O}_2 + \text{NO} =$<br>$\text{C}_2\text{H}_3\text{O} + \text{NO}_2$ | 1.7                         | $2 \times 10^{-3}$ |
| 9. $\text{C}_2\text{H}_4\text{O}_2 + \text{NO} =$<br>$\text{CH}_3\text{CHO} + \text{NO}_2$        | 1.7                         | $2 \times 10^{-3}$ |
| 10. $\text{CH}_3\text{O} + \text{O}_2 = \text{HCHO} + \text{HO}_2$                                | 1.7                         | $2 \times 10^{-3}$ |
| 11. $\text{C}_3\text{H}_6 + \text{O} = \text{CH}_3 + \text{C}_2\text{H}_3\text{O}$                | $6.0 \times 10^{-1}$        | $6 \times 10^{-3}$ |
| 12. $\text{C}_3\text{H}_6 + \text{O}_3 =$<br>$\text{HCHO} + \text{C}_2\text{H}_4\text{O}_2$       | $8.3 \times 10^{-3}$        | $4 \times 10^{-1}$ |
| 13. $\text{C}_3\text{H}_6 + \text{O}_2 = \text{CH}_3\text{O} + \text{C}_2\text{H}_3\text{O}$      | $1.7 \times 10^{-2}$        | $2 \times 10^{-1}$ |
| 14. $\text{C}_3\text{H}_6 + \text{HO}_2 =$<br>$\text{CH}_3\text{O} + \text{CH}_3\text{CHO}$       | $3.4 \times 10^{-2}$        | $10^{-1}$          |
| 15. $\text{C}_2\text{H}_3\text{O} + \text{M} =$<br>$\text{CH}_3 + \text{CO} + \text{M}$           | $1.7 \times 10^{-1}$        | $2 \times 10^{-2}$ |

and the reaction rate will be suppressed. In this case, the reaction is controlled by the rate of species mixing and will depend on parameters other than  $K_{\alpha}$  and  $\overline{C_{\alpha} C_{\beta}}$ .

We may estimate which two-body reactions will proceed as though  $\overline{C_{\alpha'} C_{\beta'}} \approx 0$ —i.e., in the usual manner, and which will be modified by having values of  $|\overline{C_{\alpha'} C_{\beta'}}|$  of the same order as  $|\overline{C_{\alpha} C_{\beta}}|$  by forming the ratio

$$N = \frac{\left(\frac{\partial \overline{C_{\alpha'} C_{\beta'}}}{\partial t}\right)_{\text{diff}}}{\left(\frac{\partial \overline{C_{\alpha'} C_{\beta'}}}{\partial t}\right)_{\text{ch}}} = \frac{2 D}{\lambda^2 K_{\alpha} \overline{C_{\alpha}}} = \frac{3.4 \times 10^{-3}}{K_{\alpha} \overline{C_{\alpha}}} \quad (22)$$

When  $N \gg 1.0$ ,  $\overline{C_{\alpha'} C_{\beta'}}$  will tend to zero and the reaction will be controlled by the reaction rate constant and the mean concentrations; when  $N \ll 1.0$ ,  $\overline{C_{\alpha'} C_{\beta'}}$  will tend to and remain close to  $-\overline{C_{\alpha} C_{\beta}}$  and the reaction will proceed at a rate determined largely by the rate at which one reactant can be mixed with another and will depend on the scale of the patches of unmixed reactants.

Typical values of  $K_{\alpha}$  for various reactions which enter into the photochemical chains are listed in Table I along with estimates of  $N$ . For these two-body reactions, only the first and second are sufficiently slow for conventional kinetic models to apply. The propylene reactions with  $\text{O}_3$ ,  $\text{O}_2$ , and  $\text{HO}_2$  (numbers 12, 13, and 14 in Table I) tend to represent a transition stage between diffusive mixing control and chemical reaction control of the reaction rate. The remaining reactions are all clearly diffusion-limited in inhomogeneous mixtures and should proceed at a rate which is much slower than conventional chemical kinetics would predict.

### Conclusion

These results indicate there are clearly reactions in the photochemical chain which will be suppressed by the inability of the atmosphere to mix the reacting materials rapidly enough to prevent serious local depletion of one of the reacting materials. In these cases, conventional models of the reaction will tend to

seriously overestimate the reaction rate, and, therefore, the production rate of the chemical species which enters into the next reaction in the photochemical chain. On the other hand, the enhancement of the reaction rate for two materials emanating from a common source and, therefore, occupying the same volume of the atmosphere, during the initial period of incomplete mixing, may also represent a significant departure from conventional simulation models.

It is hoped that this brief and necessarily incomplete discussion will serve to demonstrate the importance of turbulent fluctuations of concentrations in atmospheric chemical reactions. Consideration of these effects in refining simulation models of these reactions appears to be important.

#### Nomenclature

- $C_i$  = mass fraction of  $i$ th chemical species, ppm  
 $D_i$  = molecular diffusion coefficient for  $i$ th chemical species,  $\text{cm}^2/\text{sec}$   
 $K$  = chemical reaction rate constant,  $\text{cm}^3/\text{sec-mol}$   
 $K_\alpha, K_\beta$  = chemical reaction rate constants,  $1/\text{ppm-sec}$   
 $M_i$  = molecular weight of  $i$ th chemical species, g/mol  
 $N$  = nondimensional ratio of characteristic times  
 $q^2 = \overline{u'^2} + \overline{v'^2} + \overline{w'^2}$ ,  $\text{cm}^2/\text{sec}^2$   
 $R_{\alpha\beta}$  = ordinary second-order correlation coefficient  
 $t$  = time, sec  
 $u', v', w'$  = orthogonal components of turbulent fluid motion,  $\text{cm}/\text{sec}$   
 $y_i$  = length along  $i$ th direction of a cartesian coordinate system, cm

[ ],  $\bar{\quad}$  = averaged quantity

' = departure from the average of the primed quantity

#### GREEK LETTERS

- $\alpha, \beta, \gamma, \delta$  = chemical species  
 $\lambda$  = dissipation scale length, cm  
 $\Lambda$  = macroscale of atmospheric turbulence, cm  
 $\mu_0$  = dynamic viscosity for air,  $\text{g}/\text{cm-sec}$   
 $\rho_0$  = fluid density,  $\text{g}/\text{cm}^3$

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## Hydrogen Peroxide Formation from Formaldehyde Photooxidation and Its Presence in Urban Atmospheres

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■ Hydrogen peroxide has been observed both in laboratory studies involving the photooxidation of formaldehyde and in urban atmospheres. In the laboratory studies, the  $\text{H}_2\text{O}_2$  yield was nonlinear with formaldehyde consumption and decreased in the presence of oxides of nitrogen. The urban atmosphere at Hoboken, N.J., contained 4 ppbm of  $\text{H}_2\text{O}_2$  under moderate smog conditions. Under severe smog conditions, the Riverside, Calif. atmosphere contained 18 ppbm of  $\text{H}_2\text{O}_2$ .

In the study of Purcell and Cohen (1967), hydrogen peroxide was found as a photooxidation product of formaldehyde. This observation contrasts with the earlier work of Carruthers and Norrish (1936) as well as that of Horner and Style (1954) who observed no  $\text{H}_2\text{O}_2$ . The differences in results obtained by these investigators may arise from the concentrations employed in the laboratory irradiations. Purcell and Cohen worked with very low concentrations, ranging from 1 to 30 ppm (v/v), whereas the earlier workers used millimeter

partial pressures of formaldehyde. This difference suggests that the mechanism for the photooxidation of formaldehyde may be significantly altered at low concentrations.

The purpose of this investigation was to extend the work of Purcell and Cohen by observing the  $\text{H}_2\text{O}_2$  and all of the carbon fragments resulting from the photooxidation of formaldehyde at two different wavelength regions (maxima near 3100 and 3600Å, respectively) and in the presence and absence of oxides of nitrogen. Also, since our laboratory studies have detected  $\text{H}_2\text{O}_2$  in irradiated systems containing oxides of nitrogen and such hydrocarbons as 1,3,5-trimethylbenzene, ethylene, propylene, 1-butene, as well as irradiated auto exhaust, we concluded that  $\text{H}_2\text{O}_2$  may also be present in polluted urban atmospheres.

#### Experimental

Formaldehyde in air was irradiated either in a 72-l. borosilicate flask or in 160-l. plastic bags made from fluorinated ethylene-propylene copolymer (Du Pont FEP Teflon). The bags were constructed of Tedlar plastic in the Hoboken, N.J., study. The irradiations were carried out in a thermostatted irradiation chamber described elsewhere (Altshuler and Cohen, 1964) at a temperature of  $23^\circ \pm 1^\circ\text{C}$  and at ambient pressure. The irradiation chamber was fitted with either 24

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GE F-40-BLB blacklights with maximum intensity at 3600 Å or with 28 Westinghouse FS-40 sunlamps with maximum intensity at about 3100 Å. The irradiation container was filled by injecting either or both nitrogen dioxide and formaldehyde solution through a rubber septum onto the inner wall of a glass tube through which a gas, usually air, was passing. The glass was then heated gently to ensure complete evaporation of the reactants.

Analysis for formaldehyde was performed by the chromotropic acid method (Altshuller et al., 1961), nitrogen dioxide concentration was measured by the method of Saltzman (1954), and nitrate as nitrite by reduction with hydrazine in a hot alkaline solution. The nitrate (as nitrite) was then diazotized with sulfanilamide and *N*(1-naphthyl)-ethylenediamine dihydrochloride (Mullin and Riley, 1955).

Carbon monoxide and carbon dioxide were measured by gas chromatography with a catalytic converter of the type originally developed by Schwenk et al. (1961) to convert the CO to methane for easy detection with the flame ionization detector. The formic acid analyses were made with 1-ethylquinaldinium iodide reagent (Sawicki et al., 1962). H<sub>2</sub>O<sub>2</sub> was determined by using the specific method developed by Cohen and Purcell (1967). This method involves the reaction of titanium IV and 8-quinolinol with H<sub>2</sub>O<sub>2</sub> to form a colored complex. Possible interferences from various atmospheric pollutants (SO<sub>2</sub>, O<sub>3</sub>, NO<sub>2</sub>, NO, and olefins) were investigated. Only SO<sub>2</sub> at high concentrations was found to give a negative interference of 0.7% at a SO<sub>2</sub> concentration of 20 ppm. Other compounds such as peracetic acid, ethyl hydroperoxide, *n*-butyl hydroperoxide, acetyl peroxide, and peroxyacetyl nitrate (PAN) were tested by Cohen and Purcell and found to give a very slight negative interference at high concentrations. Since no one has reported any of these compounds, aside from PAN, as being present in the atmosphere, one can assume that interferences are minimal. The concentrations of PAN in urban atmosphere are usually quite low (~4 ppb). Thus, no PAN interference with the H<sub>2</sub>O<sub>2</sub> determinations is possible.

Singlet oxygen (O<sub>2</sub> <sup>1</sup>Δg) was not tested as a possible interference for H<sub>2</sub>O<sub>2</sub> determinations in the atmosphere, but it is doubtful that O<sub>2</sub> <sup>1</sup>Δg is present at sufficiently high concentrations to make its interference important.

The formaldehyde solution was Matheson, Coleman and Bell reagent grade 36–38% in water with 10–15% methanol added as a preservative. This solution was used without further purification. Baker dry air and prepurified nitrogen and nitrogen dioxide (Matheson, 99.5% pure) were used.

The stability of H<sub>2</sub>O<sub>2</sub> in FEP Teflon bags was investigated by injecting microliter quantities of a standardized 22.9% H<sub>2</sub>O<sub>2</sub> solution into a metered airstream while filling the bag. The theoretical concentration of peroxide was calculated from the amount of liquid injected and the volume of air used. The actual concentration in the bag was determined by both the titanium IV reagent and the catalyzed 1% potassium iodide method (Cohen et al., 1967).

Ozone at the New Jersey site was monitored with a Regenerative instrument (Regener, 1960) while total oxidant was measured with the neutral κ<sub>1</sub> procedure. Laboratory measurements employed the chemiluminescence from the ethylene-ozone reaction (Nederbraght, 1965) and the Beckman Mark IV uv photometer. Total oxidant readings in California were obtained on a Mast ozone instrument. H<sub>2</sub>O<sub>2</sub> gives a 7% slow response with the Mast (Bufalini, 1968).

Light intensity of the irradiation chamber was determined by measuring the initial rate of disappearance of NO<sub>2</sub> in an inert atmosphere, as described by Tuesday (1961). This *k<sub>d</sub>*

value was all that was needed for our studies, but the absolute light intensity (photons cm<sup>-2</sup>sec<sup>-1</sup>) can be obtained by using the absorption cross section for NO<sub>2</sub> and the quantum yield. The first-order dissociation constants *k<sub>d</sub>* for the chamber were 0.32 min<sup>-1</sup> and 0.14 min<sup>-1</sup> for 24 blacklights and 28 sunlamps, respectively.

During the summer of 1970, the Environmental Protection Agency had one of its mobile instrument trailers stationed in Hoboken, N.J. Air was collected in large plastic Tedlar bags during the early morning hours of heavy traffic at the New Jersey entrance to the Lincoln Tunnel. These bags of polluted air were protected from sunlight and returned to the instrument trailer for irradiation and analyses. The collected air samples were irradiated by exposing the bags to sunlight on the roof of the trailer.

## Results

During the early stages of this work, we were uncertain about the suitability of formalin solution because of the presence of methanol. We compared the formaldehyde consumption and H<sub>2</sub>O<sub>2</sub> production of formalin and paraformaldehyde. The results showed that the presence of methanol had very little, if any, effect on the photooxidation of formaldehyde. In further tests, methanol was irradiated with NO<sub>2</sub>; these data are shown in Table I. Apparently some methanol reacts, since CO and formaldehyde are observed as products. The yield is small, however. Also, since the concentration of methanol present during the formaldehyde irradiations is three times lower than that shown in Table I, we concluded that methanol interference is minimal. We were not able to measure the methanol concentration directly. The retention time for the methanol on the gas chromatograph was extremely dependent on the relative humidity of the air employed for the irradiations. Since FEP Teflon is extremely permeable to water vapor, we found that the sensitivity of the gas chromatograph to methanol increased with increasing time. This phenomenon was apparently a result of column conditioning with water vapor.

The stability of H<sub>2</sub>O<sub>2</sub> in FEP Teflon bags was also investigated. The concentrations observed experimentally were lower than the calculated theoretical concentration. This discrepancy is probably owing to the destruction of H<sub>2</sub>O<sub>2</sub> in the metal needle of the syringe and the destruction of H<sub>2</sub>O<sub>2</sub> on the bag walls. An initial increase in H<sub>2</sub>O<sub>2</sub> was observed. This phenomenon was reproduced in replicate runs and was probably due to desorption of H<sub>2</sub>O<sub>2</sub> from the walls. In filling the bag initially, the surface-to-volume ratio was very large and some H<sub>2</sub>O<sub>2</sub> apparently condensed on the walls. As the bag filled, the surface-to-volume ratio decreased, and H<sub>2</sub>O<sub>2</sub> came off the walls and into the gas phase. The decomposition was linear at a rate of 10<sup>-3</sup> ppm/min at 2 ppm H<sub>2</sub>O<sub>2</sub> level. The data presented in the figures and tables were not corrected for decomposition.

Data from the photooxidation of formaldehyde in the presence and absence of NO<sub>2</sub> with sunlight fluorescent lights

**Table I. Photooxidation of Methanol with Nitrogen Dioxide and Blacklights**

| MeOH, ppm | NO <sub>2</sub> , ppm | Irradn time, min | Products formed, ppm |                   |
|-----------|-----------------------|------------------|----------------------|-------------------|
|           |                       |                  | CO                   | CH <sub>2</sub> O |
| 12.0      | 1.3                   | 60               | 0.253                | 0                 |
| 12.3      | 0.27                  | 120              | 0.153                | 0.280             |
| 12.8      | 0.20                  | 120              | 0.109                | 0.242             |

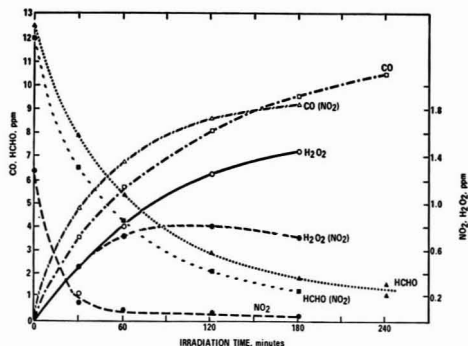


Figure 1. Formaldehyde irradiated with and without NO<sub>2</sub> in the presence of sunlight

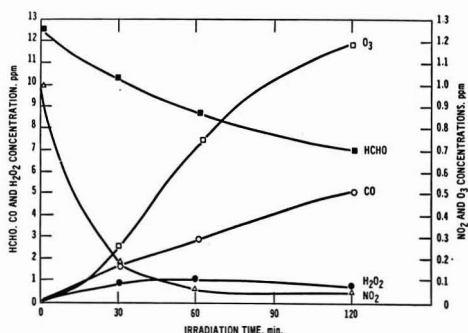


Figure 2. Formaldehyde irradiated with blacklights and NO<sub>2</sub>

Table II. Formaldehyde (12.5 ppm) in Air Irradiated with Sunlamps

| Irradn time, min | (HCHO)<br>(HCHO) <sub>i</sub> | (CO)<br>(HCHO) <sub>r</sub> | (H <sub>2</sub> O <sub>2</sub> )<br>(HCHO) <sub>r</sub> |
|------------------|-------------------------------|-----------------------------|---|
| 30               | 0.633                         | 0.732                       | 0.052   |
| 60               | 0.400                         | 0.724                       | 0.115   |
| 120              | 0.224                         | 0.796                       | 0.127   |
| 180              | 0.156                         | 0.836                       | 0.140   |
| 240              | 0.106                         | 0.833                       | 0.090   |

(wavelength maximum at 3100Å) are shown in Figure 1. Results from the photooxidation of formaldehyde again in the presence and absence of NO<sub>2</sub> but with blacklight fluorescent lights (wavelength maximum at 3600Å) are shown in Figures 2 and 3. The reduced data are shown in Tables II-V for the various conditions.

Gas chromatographic analyses indicated CO as the major product. As shown in the tables, this product accounted for as much as 90% of the total carbon. Limited data from two experiments with a closed glass system indicated that between 12 and 20% of the carbon appears as CO<sub>2</sub>. The remaining carbon appeared as CO.

Various techniques were employed to test whether any oxidant other than H<sub>2</sub>O<sub>2</sub> was formed in the photooxidation of formaldehyde. These tests were performed by the titanium-8-

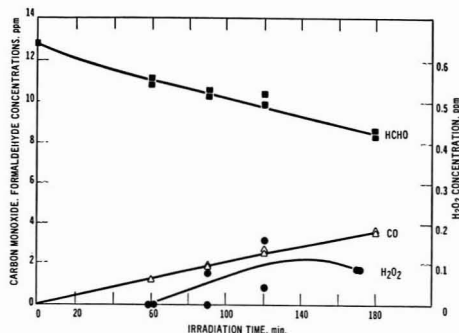


Figure 3. Formaldehyde irradiated with blacklights

Table III. Formaldehyde (12 ppm) Irradiated with 1.2 ppm NO<sub>2</sub> in Air and Sunlamps

| Irradn time, min | (HCHO)<br>(HCHO) <sub>i</sub> | (CO)<br>(HCHO) <sub>r</sub> | (H <sub>2</sub> O <sub>2</sub> )<br>(HCHO) <sub>r</sub> | (NO <sub>2</sub> )<br>(NO <sub>2</sub> ) <sub>i</sub> | O <sub>3</sub> , ppm |
|------------------|-------------------------------|-----------------------------|---|---|----------------------|
| 30               | 0.503                         | 0.771                       | 0.073   | 0.133   | ...                  |
| 60               | 0.336                         | 0.824                       | 0.0867  | 0.080   | 0.68                 |
| 120              | 0.190                         | 0.896                       | 0.0871  | 0.039   | 0.93                 |
| 180              | 0.118                         | 0.881                       | 0.0713  | 0.030   | 0.81                 |

Table IV. Formaldehyde (12.9 ppm) in Air Irradiated with Blacklights<sup>a</sup>

| Irradn time, min | (HCHO)<br>(HCHO) <sub>i</sub> | (CO)<br>(HCHO) <sub>r</sub> | (H <sub>2</sub> O <sub>2</sub> )<br>(HCHO) <sub>r</sub> |
|------------------|-------------------------------|-----------------------------|---|
| 60               | 0.861                         | 0.717                       | 0   |
| 90               | 0.813                         | 0.814                       | 0.018   |
| 120              | 0.759                         | 0.861                       | 0.035   |
| 180              | 0.669                         | 0.883                       | 0.021   |

<sup>a</sup> Ozone <0.1 ppm after 180 min. This was not observed with a clean Teflon chamber.

Table V. Formaldehyde (12.7 ppm) Irradiated with 1.01 ppm of NO<sub>2</sub> in Air and Blacklights

| Irradn time, min | (HCHO)<br>(HCHO) <sub>i</sub> | (CO)<br>(HCHO) <sub>r</sub> | (H <sub>2</sub> O <sub>2</sub> )<br>(HCHO) <sub>r</sub> | (NO <sub>2</sub> )<br>(NO <sub>2</sub> ) <sub>i</sub> | O <sub>3</sub> , ppm |
|------------------|-------------------------------|-----------------------------|---|---|----------------------|
| 30               | 0.814                         | 0.819                       | 0.050   | 0.152   | 0.27                 |
| 60               | 0.714                         | 0.864                       | 0.020   | 0.064   | 0.75                 |
| 120              | 0.527                         | 0.825                       | 0.028   | 0.089   | 1.19                 |

quinolinol method for H<sub>2</sub>O<sub>2</sub> with neutral potassium iodide reagent, the molybdate-catalyzed potassium iodide reagent. Most instrument equipped with an olefin titration system, and a Beckman Mark IV uv photometer. After obtaining some contradictory results, we found that formaldehyde interfered with the molybdate-catalyzed potassium iodide reagent giving more oxidant than is actually present. No other oxidants, such as performic or peroxyformyl nitrate, were observed as products. Some ozone (~0.1 ppm) was observed in the photooxidation of formaldehyde in the presence of blacklights and in the absence of oxides of nitrogen. However, this phenomenon was dependent on the history of the Teflon container. A container that had not been previously employed in irradiations involving oxides of nitrogen did not produce ozone. This suggests that very small concentrations of NO<sub>x</sub> (ppb range) can



be responsible for significant concentrations of ozone. The  $H_2O_2$  yield was lower when formaldehyde was irradiated with sunlamps in the presence of oxides of nitrogen.

Analyses for formic acid were performed on several experiments under the various conditions of these studies. The formic acid data were inconclusive, probably because of the difficulty of the analytical method. In one experiment, no formic acid was observed when formaldehyde was reacted with  $NO_2$  and sunlight for 30 and 60 min. At 120 min, when 9.69 ppm formaldehyde had reacted, 0.73 ppm formic acid was observed. At 180 min, when 10.16 ppm formaldehyde had reacted, 0.64 ppm formic acid was observed.

Since most if not all of the carbon from formaldehyde can be accounted for, it was necessary to determine the fate of  $NO_2$ . We (Gay and Bufalini, 1971) showed recently that when hydrocarbons are photooxidized in the presence of oxides of nitrogen, much of the nitrogen oxide is oxidized to nitric acid on the walls of the reaction vessel. Since Teflon bags could not be used for this study, we repeated some of the work with a large borosilicate flask. Two experiments were performed with the large flask for this purpose. Formaldehyde (6 ppm) was irradiated for 6 hr with 2.3 ppm of  $NO_2$ . After the irradiation, 2.25 ppm of nitrogen was recovered; 1.79 ppm appeared as nitrate on the walls; and 0.46 ppm appeared as nitrate in the gas phase. The alkaline hydrolysis product of  $NO_2$  at low ppm concentrations is a nitrite. This experiment was repeated with 6 ppm formaldehyde and 1.9 ppm  $NO_2$ . After 17 hr irradiation, no nitrate or nitrite were observed in the gas phase but 0.18 ppm of nitrite and 1.8 ppm of nitrate were observed on the walls of the reaction vessel.

The results from irradiating a bag of air collected at Hoboken are shown in Figure 4. The bag contained 6.0 ppm of  $CO$ , 4.1 ppm of methane, and 1.9 ppmC of nonmethane hydrocarbons. The total oxides of nitrogen were 36 ppb with 29.5 ppb as nitric oxide. After 1 hr exposure to sunlight, the  $NO_2$  maximum was reached, and after 2 hr all of the nitric oxide and most of the  $NO_2$  had disappeared. Total oxidant maximum and  $H_2O_2$  maximum were observed after  $3\frac{3}{4}$  hr exposure.

The atmosphere in the vicinity of the mobile instrument trailer in Hoboken, N.J., contained concentrations up to 4 ppb of  $H_2O_2$ . This concentration was measured on a day of high solar radiation and moderate smog formation. On days when solar radiation was low owing to cloud cover, no  $H_2O_2$  was observed.

In August 1970, the urban atmosphere at Riverside, Calif., was sampled for  $H_2O_2$  during days of photochemical smog

formation. On August 6, during a severe smog episode, concentrations of oxidant as high as 0.65 ppm were observed with the Mast ozone meter (Figure 5).  $H_2O_2$  reached a maximum of 18 ppb during the episode. This maximum appeared at the same time the total oxidant maximized.

The time at which the oxidant maximum for Riverside occurred was later in the afternoon than is usually observed in downtown Los Angeles. This difference can be explained by meteorological factors relating to the transport of air masses from west to east. Movements of polluted air mass and changes in photochemical smog formation are reflected in the observed changes in  $H_2O_2$  concentrations. Figure 6 shows the  $H_2O_2$  concentration as a function of time of day for various days at the Riverside site. On August 7, moderate to heavy smog buildup was observed for the air mass which moved eastwardly over Riverside. Maximum total oxidant observed was about 0.3 ppm between 2:00 and 3:00 P.M. A maximum concentration of 6 ppb of  $H_2O_2$  was observed. The polluted air mass which formed west of Riverside on August 11 never reached the sampling site owing to a change in wind direction. Less photochemical smog on August 10 was exhibited by increased visibility and lower oxidant readings. The maximum oxidant was observed at about 3:00 P.M. when 1 ppb of  $H_2O_2$  was measured.

### Discussion

The formation of  $H_2O_2$  can be explained by a sequence of reactions involving either the photolysis of formaldehyde, nitrous acid, or nitrogen dioxide. The photolysis of formaldehyde has been reported (Calvert and Pitts, 1966) in terms of two primary processes:

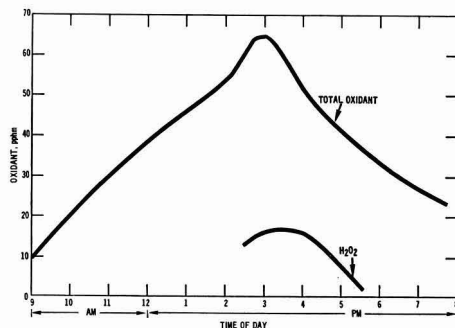


Figure 5. Measured oxidant at Riverside, Calif., August 6, 1970

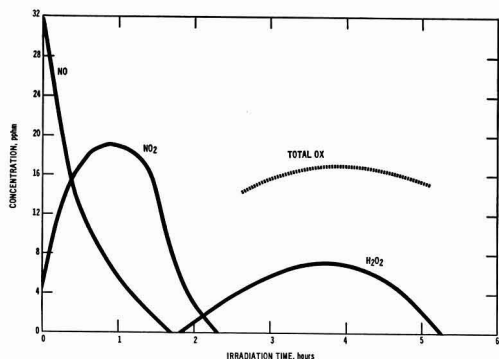


Figure 4. Lincoln Tunnel air sample irradiated with natural sunlight

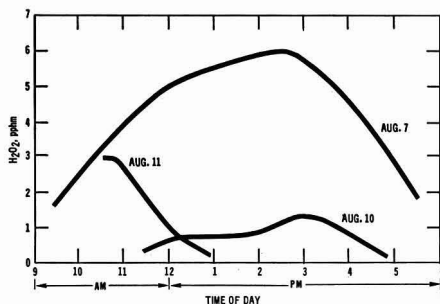
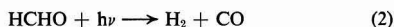
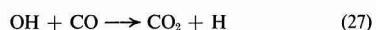
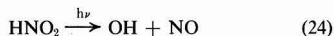
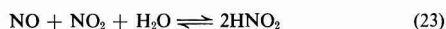
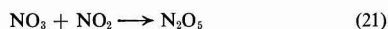
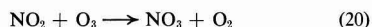
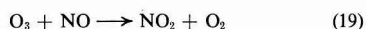
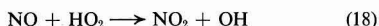
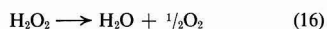
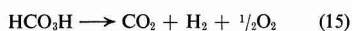
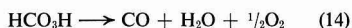
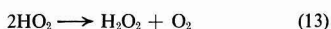
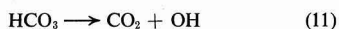
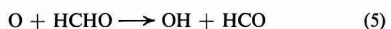


Figure 6.  $H_2O_2$  concentrations at Riverside, Calif., in August 1970



The importance of both processes at different wavelengths has been discussed recently by McQuigg and Calvert (1969) and by DeGraff and Calvert (1967). When CO, oxides of nitrogen, water vapor, and high partial pressures of oxygen are present, the following sequence of reactions can also occur:



From the sequence of reactions as written, it isn't obvious how formic acid can be produced in the absence of nitrogen oxides. In their presence, Reactions 28 and 29 can occur



This mechanism shows that formaldehyde participates in  $\text{H}_2\text{O}_2$  formation (Reaction 8). However, formaldehyde is not necessarily needed for the production of  $\text{H}_2\text{O}_2$ . If a hydrocarbon containing a weak C—H bond is replaced for formaldehyde in Reaction 8 and any hydrocarbon in Reaction 5, then as long as atomic hydrogen is formed (by Reaction 27 when CO is present),  $\text{H}_2\text{O}_2$  can be produced. Since polluted urban atmospheres contain  $\text{NO}_2$ , CO,  $\text{H}_2\text{O}$ , and various hydrocarbons,  $\text{H}_2\text{O}_2$  has a number of ways of being generated. However, the photolysis of formaldehyde is probably the pre-

dominant source of  $\text{H}_2\text{O}_2$  in the atmosphere.

In this work, as in the work of Purcell and Cohen (1967), the molecular balance between peroxide formed and aldehyde consumed is clearly lacking. This is especially true for prolonged irradiations, as shown in Figures 1 and 2. This discrepancy can be explained by Reactions 12 and 16 in the absence of nitrogen oxides. In the presence of nitrogen oxides, the amount of  $\text{H}_2\text{O}_2$  produced is significantly lower. This suggests that Reaction 18 is important. It is doubtful that Reaction 9 occurs, since no oxidants other than  $\text{H}_2\text{O}_2$  and ozone have been observed. It is also probable that peroxyformyl radical (Reaction 7) is not formed at all and that the HCO radical decomposes directly after combining with oxygen to form the products of Reactions 10 and 11. Evidence for this is found in the recent work of Dimitriades (1969) who was unable to produce peroxyformyl nitrate.

In one respect, the data shown in the tables do not fit the reaction scheme shown. In Tables II and III, the third columns show the CO/HCHO ratios for various irradiation times in the absence and presence of oxides of nitrogen. The ratios are higher in the presence of nitrogen oxides and with increasing irradiation time. Reaction 27 shows OH radicals reacting with CO. If this reaction were important, there should be a relative decrease in CO concentration after prolonged irradiation. The ratio should also be lower when oxides of nitrogen are present. Unless the rate constant for OH and HCHO is much greater than  $2 \times 10^{-13}$  cc molecule<sup>-1</sup> sec<sup>-1</sup> (Dixon-Lewis et al., 1966), which is the OH-CO rate constant, it would appear that OH radicals are unimportant in this system. However, comparison of Figures 1 and 2 shows that the rate of disappearance of formaldehyde is 50 to 200 times greater than the rate that can be explained by just the atomic oxygen reaction (Herron and Penzhorn, 1969; Niki, 1966). Since the  $\text{H}_2\text{O}_2$  yield is low in the presence of  $\text{NO}_2$ , and since little if any formic acid was formed and no peracid was observed, the types of free radicals operative in this system are clearly limited. Therefore, it must be concluded that OH radicals are the most important free radicals in this system and that the OH-HCHO rate constant is much greater than that for CO and OH. This conclusion is not in agreement with the work of Avramenko and Lorentzo (1949) but seems compatible with the observations of Herron and Penzhorn (1969). The former found a rate constant of  $10^{-13}$  cc molecule<sup>-1</sup> sec<sup>-1</sup> for the OH-HCHO reaction while the latter group found a lower limit of  $6 \times 10^{-12}$  cc molecule<sup>-1</sup> sec<sup>-1</sup>. This observation is also compatible with the recent work of Morris and Niki (1971). These investigators observed a rate constant of  $1.5 \times 10^{-11}$  cc molecule<sup>-1</sup> sec<sup>-1</sup>.

A possible explanation for the increase in the CO/HCHO ratio arises from the reaction of methanol. In Table I with 12 ppm of MeOH and 1.3 ppm of  $\text{NO}_2$ , approximately 2% CO arose from the photooxidation in only 60 min. Since 4 ppm of methanol are present in all of the formaldehyde experiments, it is reasonable to assume that the amount of methanol reacting should increase with increasing irradiation time. The CO concentration should increase thus making the CO/HCHO larger.

Reactions 22 and 26 are included in the reaction scheme as a possible source of nitrate formation. However, since no nitrate was observed in the gas phase, the reactions either occur on the walls of the reaction vessel or they are of little importance.

The data shown in Tables II and IV indicate that more  $\text{H}_2\text{O}_2$  is formed when formaldehyde is irradiated with sunlamps ( $\lambda = 3100\text{\AA}$ ) than when irradiated with blacklights ( $\lambda =$

3600Å). This suggests that Reaction 1 is less important at the longer wavelength, an observation that is compatible with the work of McQuigg and Calvert (1969) and earlier investigators and incompatible with the observations of DeGraff and Calvert (1967). This observation is also in qualitative agreement with the recent work of Calvert et al. (1972).

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## Aerosol Filtration by Fibrous Filter Mats

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■ The physical properties and aerosol filtration characteristics of U.S. Army Types 5, 6, 7, and 8 filter mats were studied. Filter bulk densities ranged from 0.197 to 0.243 g/cm<sup>3</sup>, and the fractional void volumes from 0.845 to 0.883. Pressure drops of the filters were expressed as a function of the product of the mat thickness and the superficial linear velocity in a simple polynomial in conformity with Darcy's law for fluid flow through porous media. Filtration by the filter mats of 0.3 μ diam dioctylphthalate (DOP) aerosols was expressed both by the long-standing equation relating DOP penetration to the filter pressure drop at any discrete flow velocity and by the more recent Dorman equations. The Dorman flow regimes were found consistent with the experimental data, and the parametric relationships confirmed the concept of a discrete velocity at which maximum aerosol penetration of a filter occurred.

Much current interest is centered at the control and reduction of air pollution. One of the means of accomplishing this is the removal of fine aerosol particles from the air by fibrous filter mats.

The published literature in the general field of aerosol filtration is exceedingly voluminous, and the problem existing with

the new experimentalist is how to limit the references in order not to stagger the reader without slighting the important contributions of many workers in this field. Excellent background in aerosol filtration can be found in the work of First and Silverman (1953), Chen (1955), Green and Lane (1957), Fuks (1964), Werner and Clarenburg (1965), Pich (1965), Dorman (1966), and Torgeson (1968).

In addition to the generalized studies of aerosol filtration, a body of literature ("Handbook on Aerosols," 1950; "Handbook on Air Cleaning," 1952) had accumulated on methods of generating aerosols, measuring their particle size distribution, the choice of solid or liquid aerosol, instrumentation for the detection of aerosol penetration of filters, and on the underlying theories based on which the instrumental methods were developed.

#### Purpose

The purpose of this study was to determine the penetration characteristics of a 0.3-μ-diam liquid dioctylphthalate (DOP) aerosol through four types of U.S. Army mask filter mats as a function of variables such as flow velocity, filter thickness, and pressure drop, and to develop those mathematical relationships in accord with present theory which quantitatively expresses the experimental data.

#### Theory

Dorman (1960a, 1966) has developed a means of analyzing aerosol filtration data in terms of a semiempirical formulation

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which takes into account the relative contributions of inertial, diffusional, and interception mechanisms. Implicit to his work is the assumption that these three mechanisms contribute additively. Hence, the percentage penetration may be related to physical parameters of the system by the expression:

$$\log \text{DOP } \% \text{ penetration} = -(k_R \lambda V_L^x + k_D \lambda V_L^{-y} + k_I \lambda) + 2 \quad (1)$$

where  $k_R$ ,  $k_D$ , and  $k_I$  are, respectively, the inertial, diffusional, and interception parameters;  $V_L$  is the superficial linear velocity; and  $\lambda$  is the thickness of the filter. Dorman reported that  $x$  and  $y$  are found empirically to range up to 2 and  $2/3$ , respectively.

As demonstrated experimentally, a plot of  $\log \text{DOP } \% \text{ penetration}$  vs.  $V_L$  exhibits a maximum for the velocity equal to, say,  $\bar{V}_L$ . Knowing this we find the analytic maximum for Equation 1 by taking the derivative with respect to  $V_L$  and setting it equal to zero. From this we obtain the relationship

$$k_D = k_R \left( \frac{x}{y} \right) \bar{V}_L^{(x+y)} \quad (2)$$

with which Equation 1 can be reduced to the form

$$\log \text{DOP } \% \text{ penetration} = -k_R \lambda \left[ V_L^x + \left( \frac{x}{y} \right) \bar{V}_L^{(x+y)} V_L^{-y} \right] - k_I \lambda + 2 \quad (3)$$

Plots of  $[2 - \log \text{DOP } \% \text{ penetration}]$  vs.  $[V_L^x + (x/y) \bar{V}_L^{(x+y)} V_L^{-y}]$  being straight lines enable  $k_R$  and  $k_D$  to be calculated from the slope and  $k_I$  from the intercept.

Darcy's law (Collins, 1961) for flow of an incompressible fluid through a porous material of length  $\lambda$ , cross-sectional area  $A$ , volumetric flow rate  $q$ , fluid viscosity  $\mu$ , and material permeability  $K$  expresses the pressure drop  $\Delta P$  as

$$\Delta P = \frac{\mu q}{KA/\lambda} = \frac{\mu}{K} \lambda V_L = k_2 \lambda V_L \quad (4)$$

where  $k_2$  is the ratio  $\mu/K$ . In these relationships cognizance has been taken of the facts that  $V_L = q/A$  by definition and that both  $\mu$  and  $K$  are constants of the fluid flow and porous material under study.

A simplistic aerosol filtration equation can be derived by assuming that filtration is a first-order removal process. Thus,

$$\frac{-dn}{d\lambda} = kn \quad (5)$$

where  $n$  is the number density of aerosol particles (no./cm<sup>3</sup>),  $\lambda$  is the filter thickness, and  $k$  the constant of proportionality. Integrating over appropriate limits we get:

$$-\int_{n_1}^{n_2} \frac{dn}{n} = k \int_{\lambda_1}^{\lambda_2} d\lambda \quad (6)$$

or

$$-\ln \frac{n_2}{n_1} = k\lambda \quad (7)$$

since  $\lambda_2 - \lambda_1$  constitutes the boundaries of the filter thickness and therefore  $\lambda_1$  can be set as zero. From Darcy's law, Equation 4, we see that pressure drop  $\Delta P$  is a linear function of filter thickness for a fixed velocity, then

$$\Delta P = k_2 \lambda \quad (8)$$

and

$$-\ln \frac{n_2}{n_1} = k_3 \Delta P \quad (9)$$

where  $k_3$  is equal to  $k/k_2$  and  $n_2/n_1$  is the fractional density of DOP particles penetrating the filter. It follows, therefore, that

$$\frac{n_2}{n_1} = \frac{\text{DOP } \% \text{ penetration}}{100} \quad (10)$$

and

$$-\ln \left( \frac{\text{DOP } \% \text{ penetration}}{100} \right) = k_3 \Delta P \quad (11)$$

from which, by defining

$$\alpha = k_3 / (2.303 \times 10^{-2}) \quad (12)$$

we obtain

$$\log \text{DOP } \% \text{ penetration} = -0.01 \alpha \Delta P + 2 \quad (13)$$

From Equations 4 and 13 we form the expression:

$$\log \text{DOP } \% \text{ penetration} = -0.01 k_2 \lambda \alpha V_L + 2 \quad (14)$$

Comparisons of the right-hand sides of Equations 3 and 14 yield, after logarithms are taken, the equation

$$\log \alpha = -\log V_L + \log \left\{ k_R \left[ V_L^x + \left( \frac{x}{y} \right) \bar{V}_L^{(x+y)} V_L^{-y} \right] + k_I \right\} - \log (0.01 k_2) \quad (15)$$

The above set of equations form the basis for analysis of our experimental data.

#### Equipment

The equipment used to test the filtration characteristics of the filter mats was a DOP aerosol test apparatus. The apparatus, assembled on a laboratory bench and occupying a space 2 ft deep, 3 ft high, and 8 ft wide, consisted of three functional parts: a generator for the test aerosol, a holder for exposure of the filter mat to the aerosol, and a detector for measurement of that fraction of the challenge aerosol penetrating the filter. The aerosol was produced by a MIT-EIR9 generator at 100 l./min (lpm), 20 lpm of which was preheated (150°C) and passed over DOP liquid at 168–170°C picking up existing vapor. The remaining 80-lpm air (room temperature) quenched the vapor to the aerosol (mean diam, 0.3  $\mu$ ) by virtue of the temperature gradient in the flows. A concentration of aerosol between 80 and 120  $\mu\text{g/l.}$  of air was formed by regulation of the temperature of the DOP liquid. The particle size of the aerosol was adjusted, as desired, by the temperature of a small filament heater in the 80-lpm quenching airstream which altered the temperature gradient. The 0.3  $\mu$  diam corresponded to a reading of 29° ( $\pm 1^\circ$ ) on the MIT-EIR2 particle size meter, referred to as the Owl. The newly formed aerosol was next directed into a 5-gal. reservoir which served to age or store the DOP aerosol, and from which aerosol was drawn by vacuum through the remaining portions of the test apparatus when required. Excess aerosol generated was vented to a laboratory hood.

The sample filter mats were conditioned in the laboratory at the temperature (25°C) and r.h. (50%) of the room. The mats were positioned in a cast iron mat holder which held them in place by a pressure seal and exposed an area of 100 cm<sup>2</sup> to the challenge DOP aerosol.

**Table I. Composition of Fibrous Filter Mats**

| Fiber Type           | Density, g/cm <sup>3</sup> | % Composition of filter types |      |      |      |
|----------------------|----------------------------|-------------------------------|------|------|------|
|                      |                            | 5                             | 6    | 7    | 8    |
| Cotton floc          | 1.52                       | 58.2                          | 25.6 | ...  | ...  |
| Viscose rayon        | 1.51                       | 34.0                          | ...  | 42.0 | 46.3 |
| Manila hemp          | 1.48                       | 4.9                           | 6.4  | 4.3  | 9.8  |
| Bl. Bol. crocidolite |                            |                               |      |      |      |
| asbestos             | 3.2-3.3                    | 2.9                           | 20.0 | 11.7 | ...  |
| Duralba wood pulp    | 1.15                       | ...                           | ...  | 42.0 | 23.9 |
| AAA glass            | 1.25                       | ...                           | ...  | ...  | 20.0 |
| Causticized esparto  | 1.33                       | ...                           | 48.0 | ...  | ...  |

The detection and measurement of that fraction of the challenge DOP aerosol penetrating the filter mat was accomplished with a NRL-E2R1 Smoke Penetration Meter which employed small-angle forward light scattering to measure the DOP aerosol. The meter was capable of detecting aerosol particles over a range of 0.001-100% penetrating the filter mats.

#### Procedure

The generator cup was filled with liquid DOP to a depth of 2 in. All electrical and heater switches were activated including an auxiliary heater, which in a 15-min period aided in attaining the operating temperature (168-170°C) for the DOP. When operating temperature was obtained, the air pressure valves were opened to generate the DOP aerosol. The aerosol particle size was checked with the Owl and the temperature gradient adjusted until a mean 0.3- $\mu$ -diam aerosol was being formed.

The concentration range of 80-120  $\mu$ g DOP/l. of air was determined as follows: A 5<sup>1</sup>/<sub>4</sub> × 5<sup>1</sup>/<sub>2</sub> in. cut of Type 6 filter mat, having reached equilibrium at the temperature and relative humidity of the room, was placed in the filter mat holder and exposed to air without DOP for 15 min at a flow of 32 lpm. The mat was removed from the holder and, after an additional 10-min waiting period, the initial weight of the mat was obtained to the nearest tenth of a milligram on an analytical balance. The same mat was then replaced in the holder and exposed to the DOP aerosol concentration for 15 min at 32 lpm. After another 10-min waiting period the final weight was determined. The mean concentration was calculated by dividing the net increase in filter weight due to DOP by the volume of air passed through the filter. After the desired concentration range was obtained, the system was purged with pure air prior to actual testing of filter mats.

Pressure drop and DOP % penetration were determined in the following manner for one-six layers of Type 5 filter material over a linear velocity range of 50-797 cm/min and for one layer of Types 6-8 filter materials over a linear velocity range of 80-850 cm/min.

The filter mat was placed in the pad holder and the pressure

drop across the filter mat at the specific flow velocity was noted from a pressure manometer. Next the mat was exposed to the predetermined DOP aerosol concentration by drawing the aerosol through the mat at the same flow velocity. The DOP % penetration was read directly as the maximum deflection of the microammeter needle on the NRL penetrometer. The system was again purged before each pressure drop and DOP penetration determination.

#### Results and Discussion

The four filter mats studied, namely Types 5-8, were each composed of both aerosol filtering fibers and coarse matrix fibers. The fine filtering fibers in Types 5-7 were blue Bolivian Crocidolite asbestos beaten to separate the mineral clusters; in Type 8 AAA glass fibers having a range of diameters between 0.50 and 0.74  $\mu$ . Matrix fibers in the various filter mats consisted of mixtures of fibers such as cotton, rayon, hemp, and wood pulp. Density values for the various fibers ranged from 1.15 to 3.25 g/cm<sup>3</sup> (Hall, 1965). The compositions used for the formation of the filter mats are shown in Table I. The specification governing the composition and performance of these mats is MIL-F-13785A, Amendment 2, July 25, 1958, and formed the basis for their manufacture on commercial size Fourdrinier equipment by various industrial paper-making companies. The filters are widely used in industrial and government laboratories.

Weight per unit area and mat thickness values were determined for each of the four filter types. From these data physical properties such as the bulk density, mean fiber density, volume fiber fraction, and porosity (volume void fraction) were calculated. The mean fiber density for the filter was calculated as the weighted mean in accord with

$$\bar{d}_f = \sum_1^n (d_{\text{fiber}} \times \text{fiber fractional composition}) \quad (16)$$

where  $n$  was the number of different fibers in the composition of the filter. The porosity  $\epsilon$  of the filter mat was calculated from the relationship

$$\epsilon = \frac{\frac{1}{\text{bulk density}} - \frac{1}{\bar{d}_f}}{\frac{1}{\text{bulk density}}} \quad (17)$$

since the reciprocal of the bulk density represented the specific volume (cm<sup>3</sup>/g) of the filter mat which included both the specific volume of the filter fibers and their interfiber space volumes. The fraction of a total filter volume filled by fibers ( $\sigma$ ) was:

$$\sigma = 1 - \epsilon \quad (18)$$

The physical properties of the filter mats are shown in Table II.

The pressure drop across the filter, resulting from forced air-flow through the filter, was determined as a function of both the number of layers and the superficial linear velocity for

**Table II. Filter Mat Physical Properties**

| Filter type | Wt/area, g/cm <sup>2</sup> | Thickness, <sup>a</sup> cm | Bulk density, g/cm <sup>3</sup> | Weighted mean fiber density, g/cm <sup>3</sup> | Fiber fraction, $\sigma$ | Porosity (vol. void fraction) |
|-------------|----------------------------|----------------------------|---------------------------------|--|--------------------------|-------------------------------|
| 5           | 0.0128                     | 0.062                      | 0.206                           | 1.565  | 0.131                    | 0.869                         |
| 6           | 0.0214                     | 0.103                      | 0.208                           | 1.772  | 0.117                    | 0.883                         |
| 7           | 0.0245                     | 0.101                      | 0.243                           | 1.561  | 0.155                    | 0.845                         |
| 8           | 0.0203                     | 0.103                      | 0.197                           | 1.369  | 0.144                    | 0.856                         |

<sup>a</sup> Measured with Randall & Stickney thickness gauge.



**Table III. DOP % Penetration of Type 5 Filter Mats as a Function of Layers and Linear Flow Velocity**

| Linear velocity,<br>cm/min | DOP % penetration through |                       |                       |                       |                       |                       |
|----------------------------|---------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                            | 1 Layer<br>0.0619 cm      | 2 Layers<br>0.1238 cm | 3 Layers<br>0.1857 cm | 4 Layers<br>0.2476 cm | 5 Layers<br>0.3095 cm | 6 Layers<br>0.3714 cm |
| 50                         | 17.000                    | 2.390                 | 0.330                 | 0.055                 | 0.006                 | ...                   |
| 100                        | 18.000                    | 3.150                 | 0.462                 | 0.070                 | 0.013                 | 0.001                 |
| 150                        | 19.000                    | 3.360                 | 0.798                 | 0.170                 | 0.029                 | 0.006                 |
| 200                        | 19.000                    | 4.116                 | 0.756                 | 0.210                 | 0.033                 | 0.007                 |
| 300                        | 21.000                    | 3.990                 | 0.819                 | 0.200                 | 0.041                 | 0.008                 |
| 400                        | 26.000                    | 5.000                 | 1.092                 | 0.240                 | 0.059                 | 0.007                 |
| 500                        | 25.000                    | 5.500                 | 1.071                 | 0.200                 | 0.043                 | 0.006                 |
| 600                        | 24.500                    | 5.000                 | 1.176                 | 0.255                 | 0.065                 | 0.015                 |
| 700                        | 24.500                    | 5.000                 | 1.197                 | 0.245                 | 0.057                 | 0.012                 |
| 797                        | 22.000                    | 5.000                 | 1.008                 | 0.235                 | 0.040                 | 0.009                 |

Type 5 filter mats. Because of the high-pressure drop across one layer of the Types 6-8 filters, pressure drop was determined only as a function of linear velocity. Pressure drop measurements in millimeters of water were made for as many as six layers of Type 5 filters. For the Type 5 filter, the superficial linear velocity range tested was 50-2983 cm/min; for Types 6-8, 80-850 cm/min. The data, if plotted as pressure drop vs. mat thickness for each velocity or vs. velocity for each mat layer, would result in a family of straight line curves for each filter type. However, by plotting the pressure drop vs. the product of the superficial linear velocity and mat thickness, one straight line curve was obtained for each of the four filter types in accord with Darcy's law, as expressed in Equation 4.

The curves are shown in Figure 1, the smooth lines being the Univac 1108 computer regression lines and the points some of the experimental data used in the regression analyses. The coefficient of correlation *R* for each of the lines was greater than 0.998, indicating an extremely high confidence that the regression lines accurately represented the experimental data. The regression line equations obtained were as follows:

For Type 5:  $\Delta P$  (mm water) = 0.268  $\lambda V_L$  (*R* = 0.99840)

For Type 6:  $\Delta P$  (mm water) = 1.297  $\lambda V_L$  (*R* = 0.99856)

For Type 7:  $\Delta P$  (mm water) = 1.335  $\lambda V_L$  (*R* = 0.99829)

For Type 8:  $\Delta P$  (mm water) = 0.883  $\lambda V_L$  (*R* = 0.99815)

In these equations, the product  $\lambda V_L$  was in  $\text{cm}^2/\text{min}$  and the slope of the  $\Delta P$  vs.  $\lambda V_L$  was equal to  $\mu/K$  of Equation 4 in (min) (mm water/ $\text{cm}^2$ ). To convert to centime gram sec (cgs) units, the  $\Delta P$  values would be multiplied by 98.03 to obtain  $\Delta P$

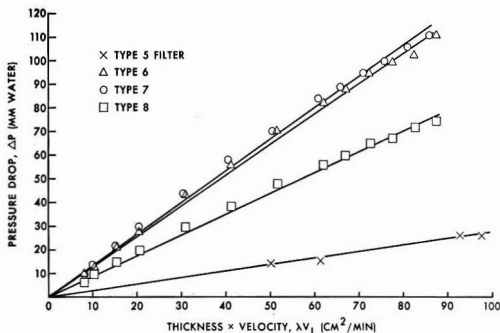


Figure 1. Pressure drop as a function of thickness × velocity

in dynes/ $\text{cm}^2$  which, if the product  $\lambda V_L$  were converted to  $\text{cm}^2/\text{sec}$ , would result in slopes ( $\mu/K$  values) in  $\text{g}/\text{cm}^3 \cdot \text{sec}$ . These equations show that the slope ( $\mu/K$ ) of Darcy's equation varies for each filter. Since the fluid viscosity  $\mu$  was constant, the variations in slope were attributable to differences in the material permeability factor *K* for each of the filters studied.

The aerosol filtration characteristics of the various filter mats were studied using DOP aerosols with a mean diameter of 0.3  $\mu$  and measuring the % penetration of the DOP through the mats. The penetration of Type 5 mats was tested as a function of pressure drop by using multilayers of mats at any one flow velocity, and then separately by varying the velocity. These data are shown in Table III. Figure 2 shows that for these data a plot of the log DOP % penetration is an inverse linear function of pressure drop and results in a family of straight line curves for the various flow velocities. The equations of these straight line curves for the six linear velocities plotted (ranging from 50 to 797 cm/min) are shown in Table IV in accordance with the form of Equation 13 where the slope of the log DOP % penetration vs.  $\Delta P$  plot is equal to  $-0.01 \alpha$ . Figure 3 shows that a plot of the log DOP % penetration vs. velocity has a maximum for each of the six layers displayed, the maxima being 450, 550, 580, 540, 520, and 570 cm/min for the one to six layers, respectively.

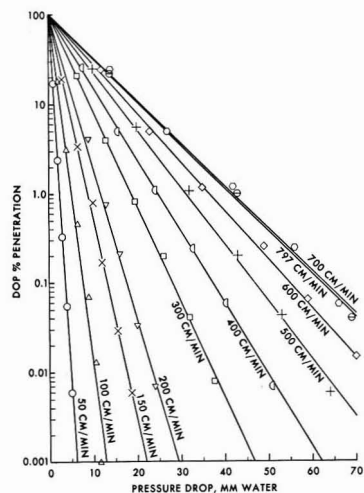


Figure 2. DOP penetration as a function of pressure drop at various velocities for Type 5 filter

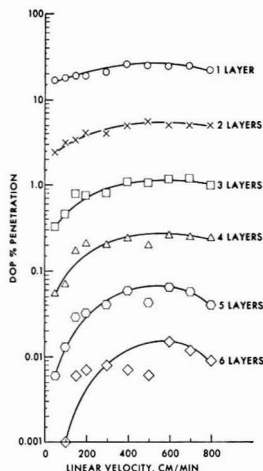


Figure 3. DOP penetration as a function of linear velocity for various layers of Type 5 filter.

Figure 3. DOP penetration as a function of linear velocity for various layers of Type 5 filter

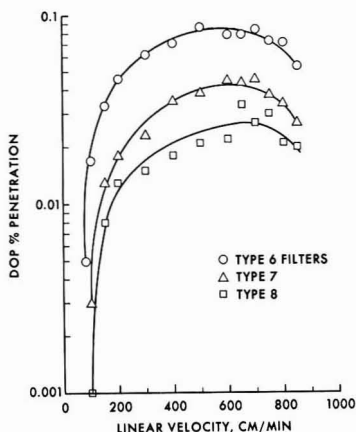


Figure 4. DOP penetration as a function of linear velocity

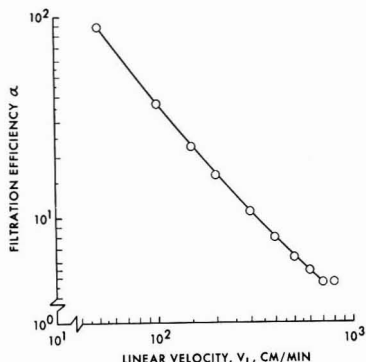


Figure 5. Filtration efficiency as a function of velocity for Type 5 filter mat

Table IV. Filtration Efficiency as a Function of Velocity for Type 5 Mats

| Linear velocity ( $V_L$ ), cm/min | Aerosol penetration equation                              | Filtration efficiency, $\alpha$ |
|-----------------------------------|---|---------------------------------|
| 50                                | $\log \text{DOP } \% \text{ pen.} = -0.8807 \Delta P + 2$ | 88.1                            |
| 100                               | $\log \text{DOP } \% \text{ pen.} = -0.3651 \Delta P + 2$ | 36.5                            |
| 150                               | $\log \text{DOP } \% \text{ pen.} = -0.2276 \Delta P + 2$ | 22.8                            |
| 200                               | $\log \text{DOP } \% \text{ pen.} = -0.1676 \Delta P + 2$ | 16.8                            |
| 300                               | $\log \text{DOP } \% \text{ pen.} = -0.1059 \Delta P + 2$ | 10.6                            |
| 400                               | $\log \text{DOP } \% \text{ pen.} = -0.0797 \Delta P + 2$ | 7.97                            |
| 500                               | $\log \text{DOP } \% \text{ pen.} = -0.0628 \Delta P + 2$ | 6.28                            |
| 600                               | $\log \text{DOP } \% \text{ pen.} = -0.0544 \Delta P + 2$ | 5.44                            |
| 700                               | $\log \text{DOP } \% \text{ pen.} = -0.0475 \Delta P + 2$ | 4.75                            |
| 797                               | $\log \text{DOP } \% \text{ pen.} = -0.0483 \Delta P + 2$ | 4.83                            |

Table V. DOP % Penetration of Filter Mats as a Function of Linear Flow Velocity

| Linear velocity, cm/min | DOP % penetration through |        |        |
|-------------------------|---------------------------|--------|--------|
|                         | Type 6                    | Type 7 | Type 8 |
| 80                      | 0.005                     | 0.000  | 0.000  |
| 100                     | 0.017                     | 0.003  | 0.001  |
| 150                     | 0.033                     | 0.013  | 0.008  |
| 200                     | 0.046                     | 0.018  | 0.013  |
| 300                     | 0.062                     | 0.023  | 0.015  |
| 400                     | 0.071                     | 0.035  | 0.018  |
| 500                     | 0.087                     | 0.039  | 0.021  |
| 600                     | 0.079                     | 0.045  | 0.022  |
| 650                     | 0.079                     | 0.044  | 0.034  |
| 700                     | 0.084                     | 0.046  | 0.027  |
| 750                     | 0.073                     | 0.038  | 0.030  |
| 800                     | 0.072                     | 0.034  | 0.021  |
| 850                     | 0.054                     | 0.027  | 0.020  |

Because of the high aerosol filtration per layer, the Types 6-8 mats were only studied by varying the flow velocity through single layers. These data are shown in Table V and plotted in Figure 4. Again the plot shows the characteristic maxima in the penetration of DOP aerosols as a function of velocity, the maxima occurring at 560, 640, and 670 cm/min for Types 6-8 mats, respectively. The velocity at which the maximum DOP % penetration occurs was indicated by  $\bar{V}_L$  and obtained by direct inspection of the log DOP penetration vs. velocity plots.

Should the plot of log DOP penetration vs. velocity for some filters show either an apparent absence of a maximum or a broad plateau which prevents unique determination of  $\bar{V}_L$  by inspection, the following alternative method for determination of  $\bar{V}_L$  was devised. Using the values  $x = 2$  and  $y = 2/3$  in Equation 15 and differentiating, we obtain

$$\frac{d \log \alpha}{d \log V_L} = -1 + \frac{2 k_R (V_L^2 - \bar{V}_L^{8/3} V_L^{-2/3})}{[k_R (V_L^2 + 3 \bar{V}_L^{8/3} V_L^{-2/3}) + k_I]} \quad (19)$$

with the second term  $>0$  if  $V_L > \bar{V}_L$ ,  $=0$  if  $V_L = \bar{V}_L$ , and  $<0$  if  $V_L < \bar{V}_L$ . Thus, the magnitude of the slope—i.e.,  $(d \log \alpha) / (d \log V_L)$ , decreases as  $V_L$  increases. The experimental results in Table IV are plotted as  $\log \alpha$  vs.  $\log V_L$  in Figure 5 and demonstrate this decreasing magnitude of slope with increasing  $V_L$ . The value of  $\bar{V}_L$  is the abscissa value for the point of

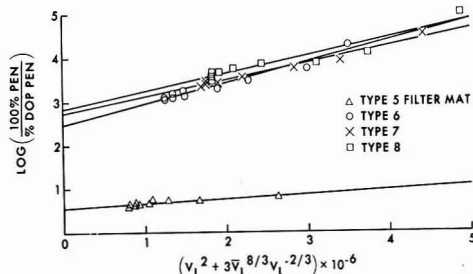


Figure 6. Log (100% pen./% DOP pen.) vs.  $(V_L^2 + 3 \bar{V}_L^{8/3} V_L^{-2/3})$  for various filter mats

**Table VI. Dorman Parameters for Aerosol Filter Mats**

| Dorman parameter   | Filter mat type       |                       |                       |                       |
|--------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                    | 5                     | 6                     | 7                     | 8                     |
| Inertial $k_R$     | $1.51 \times 10^{-6}$ | $4.67 \times 10^{-6}$ | $3.72 \times 10^{-6}$ | $3.82 \times 10^{-6}$ |
| Diffusional $k_D$  | 53.9                  | 298                   | 354                   | 402                   |
| Interception $k_I$ | 8.99                  | 24.0                  | 27.3                  | 27.8                  |

tangency of this curve with a straight line with slope equal to minus unity. This uniquely determines  $\bar{V}_L$  as seen from Equation 19.

The filtration data shown in Tables III and V were replotted in Figure 6 according to the Dorman procedure as expressed in Equation 3 with  $x = 2$  and  $y = 2/3$ . These values are chosen for a best fit and, as stated by Dorman (1960b), with some theoretical justification for the latter value. Straight line curves were obtained for the Types 5-8 filter mats. Since the slope of these lines equals  $\lambda k_R$ , the  $y$ -axis intercept equals  $\lambda k_I$ , and  $k_D = 3 k_R \bar{V}_L^{2/3}$  (from Equation 2), the three Dorman parameters were calculated for the various filter mats and are shown in Table VI.

It should be noted that these Dorman parameters apply to aerosol penetration of a filter, as shown in Equations 1-3, and therefore some reciprocal function of the parameters would apply to aerosol filtration. It is of interest that the Dorman penetration parameters for Types 6-8 filters are in the same order of magnitude, and are, in general, 2.8 times higher for  $k_R$  and  $k_I$  and 6.5 times higher for  $k_D$  than the corresponding values of the Type 5 filter.

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## Decontamination of Noncombustible Agricultural Pesticide Containers by Removal of Emulsifiable Parathion

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■ Large quantities of noncombustible containers have resulted from years of widespread use of agricultural pesticides, an ingredient of which has been parathion in an emulsifiable form. The used containers all show residues, in significant amounts, of the original solution. The formulation can be effectively removed from the containers by repeated rinsings with small volumes of water or alkaline detergent solution. The parathion in the resulting wash liquids undergoes slow degradation and its toxicity persists for months. Ethanol, however, strongly enhances the rate of hydrolysis of parathion in alkaline solutions.

A pressing problem associated with the widespread use of pesticides is the disposal of used agricultural pesticide containers. A survey by the California Department of Public Health shows that 3.87 million agricultural pesticide containers were used in California during 1969. These and the hundreds of thousands of containers accumulated from previous years all contain significant amounts of residual pesticides (Wolfe et al., 1961) and have become a serious threat to the public health quality of the environment.

These used pesticide containers, particularly the noncombustible ones such as glass bottles and metal drums,

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cannot easily or inexpensively be disposed of by incineration; they must either be decontaminated and then disposed of as conventional solid wastes, or be received by landfill sites capable of absorbing toxic wastes. Many agricultural areas do not have the necessary special disposal sites; therefore, it is mandatory that these containers be decontaminated for proper disposal. The easiest and most inexpensive way of decontaminating these containers appears to be by solvent washing of the pesticide residues from the container surfaces and subsequent detoxification of the residues in the washes. The procedure recommended by the National Agricultural Chemicals Association (1965) is to wash with 1N NaOH in a 1.4% detergent solution. This solution is added to the empty container in a volume equal to one fifth of the container's volume; the container is sealed, shaken, and allowed to stand 20 min or longer; the mixture is then poured out and buried, and the container disposed of as usual nontoxic waste.

In the above procedure, the pesticide residues are assumed to undergo hydrolysis and detoxification in the strong alkali mixture. However, laboratory studies (Kennedy et al., 1969) have shown that the rate of decomposition of most pesticides in the alkaline mixture is rather low and that detoxification of the residues is unlikely to be complete during the alkaline exposure.

In the present study, the efficiency of removal of a parathion emulsifiable concentrate by washing various types of containers with different solvent systems was determined as well as the rate of decomposition of the parathion in various decontamination liquids in order to assess the effectiveness of existing decontamination procedures and to select specific areas for further study and improvement.

#### Experimental

**Chemicals.** The parathion formulation used throughout this study was a 4-lb emulsifiable concentrate (47.6% active ingredient) obtained from Niagara Chemical Co., Richmond, Calif. A technical parathion containing 98.76% active ingredient (City Chemical Corp., New York, N.Y.) dissolved in benzene was used as a standard in the gas chromatographic assays. Sodium hypochlorite was obtained from a commercial chlorine disinfectant (Georgia Pacific Corp., Durate, Calif.) which contained 5.25% active ingredient. All solvents used were double distilled, and the chemicals were reagent grade.

**Containers.** All containers except the 125-ml and 1-gal. glass bottles were obtained from Niagara Chemical Co. and represented the types of containers commonly used for agricultural pesticides.

**Wash Solvent Systems.** Three solvent systems were used in the parathion removal studies. These were distilled water; DIAS (a mixture originally developed in Russia) containing in 1 liter 250 grams of disodium dioctylsulfosuccinate, 50 grams of sodium valerate, 50 grams of sodium caprylate, 90 ml of ethylene glycol, 80 grams of sodium carbonate, and 8 grams of sodium silicate, diluted twentyfold (pH 9.88); and an alkaline detergent mixture containing in 1 liter 40 grams of sodium hydroxide and 14 grams of laboratory detergent (Glis-N, Perf Co.) diluted tenfold (pH 12.45).

**Determination of Residual Parathion in Containers.** Ample parathion formulation was added to empty, weighed containers to completely wet the containers' inner walls. The containers were closed, shaken, and swirled so that the entire surfaces were wetted by the formulation. The containers were then opened, inverted, and allowed to drain (at least 5 min) until dripping stopped, and were either reweighed or the formulation net volume retention was determined. The residual

formulation in the container was determined by the difference in weights or volume or both.

**Determination of Washing Efficiency.** The parathion formulation was added to the empty containers in the amounts equal to their predetermined retention volumes. The containers were shaken and swirled to wet the internal surfaces completely. Predetermined volumes of wash solvents were then used to repeatedly rinse the specific sized containers. The wash volume aliquot for the various sized containers was as follows: 125-ml glass bottle, 25 ml; 1-gal. glass jug, 75 ml; and 1-gal. flat head steel drum, 150 ml. The parathion in each wash was extracted three times with equal volumes of a solvent system composed of 16 parts isopropanol, 22 parts diethyl ether, and 20 parts mixed pentanes, added in the order described with mixing between the addition of each solvent. The extracts were analyzed by gas-liquid chromatography.

**Degradation of Parathion.** Appropriate amounts of the parathion formulation were added to various degradative solvent systems to prepare reaction mixtures which contained 10-10,000 ppm of parathion. Twenty-five milliliters of each reaction mixture was contained each in a 25-ml volumetric flask. The flasks were stoppered and shaken periodically during the reaction period. Samples (1 ml) were taken at different times of incubation and each was extracted three times with 6 ml of the extracting solvent mixture. For the samples with different ethanol content, dilution was made such that the final ethanol concentrations were equal for all the samples before solvent extraction.

**Measurement of Parathion.** Both the spectrophotometric and gas chromatographic methods were used. The optical density of the parathion in benzene at 280 nm was measured on a Hitachi Perkin-Elmer UV-vis spectrophotometer. Although the cutoff value for benzene is 280 nm, using the same solvent as reference, a good linear relationship between optical density and parathion concentration was observed in the range 0.2-2 ppm. Aliquots of the extracts were also injected into a 4 ft  $\times$  1/8 in. i.d. glass column packed with 3% SE-30 on Chromosorb G, 60/80 mesh, with a column temperature of 190°C and a nitrogen carrier-gas flow rate of 20 ml/min in a Varian Aerograph 1700 gas chromatograph equipped with a flame ionization detector coupled with a Rb<sub>2</sub>SO<sub>4</sub> salt pellet which significantly enhances the specificity and sensitivity for phosphorus detection. The analytical data by both methods were in close agreement.

#### Results and Discussion

Parathion residues in containers of various types after complete draining are shown in Table I. The parathion residue in

Table I. Container Retention Volume of Parathion Emulsifiable Concentrate (EC)<sup>a</sup>

| Container type       | Inner surface area, in. <sup>2</sup> | Residual EC, ml | Unit vol retention, ml/l. | Unit Surface area residue, mg/in. <sup>2</sup> |
|----------------------|--------------------------------------|-----------------|---------------------------|--|
| Glass bottle, 125 ml | 22                                   | 0.3             | 2.4                       | 13.6   |
| Glass bottle, 1 gal. | 222                                  | 0.6             | 0.2                       | 2.7  |
| Metal can            |                                      |                 |                           |  |
| Flat top 1 gal.      | 244                                  | 14.0            | 3.7                       | 57.3   |
| Flat top 5 gal.      | 658                                  | 40.0            | 2.1                       | 60.8   |
| Flat top 55 gal.     | 3040                                 | 90.0            | 0.4                       | 29.6   |

<sup>a</sup> Four-pound emulsifiable concentrate, 47.6% active parathion.

**Table II. Efficiency of Parathion Removal from Drained Containers by Three Wash Solvents**

| Wash solvent       | Container type                  | Cumulative parathion removal, % <sup>a</sup> |       |       |       |       |       |
|--------------------|---------------------------------|--|-------|-------|-------|-------|-------|
|                    |                                 | 1 <sup>b</sup>                               | 2     | 3     | 4     | 5     | 6     |
| Water              | Glass bottle, 125 ml            | 98.80  | 99.81 | 99.86 | 99.94 | 100.0 | 100.0 |
|                    | Glass bottle, 1 gal.            | 99.20  | 99.90 | 99.98 | 99.99 | 100.0 | 100.0 |
|                    | Metal drum, <sup>c</sup> 1 gal. | 88.00  | 96.90 | 98.12 | 98.15 | 98.18 | 98.20 |
| Dias               | Glass bottle, 125 ml            | 98.20  | 99.45 | 99.95 | 99.97 | 100.0 | 100.0 |
| Alkaline detergent | Glass bottle, 125 ml            | 98.95  | 99.90 | 99.98 | 99.99 | 100.0 | 100.0 |

<sup>a</sup> For the volume of solvent per wash, see experiment.

<sup>b</sup> Number of washes.

<sup>c</sup> Steel epoxy coated, 1-gal. flat head drum.

completely drained containers ranged from 150 to 45,000 mg. If we consider the LD<sub>50</sub> of parathion which is 3 mg/kg body weight for the rat, the residual toxicity present in the emptied containers cannot be overemphasized. The variation in the unit volume and unit surface area residues suggests that the important factor in determining how much formulation remains in a container is the geometry and location of the container's spout. This may also account for the much greater retention found with metal drums than glass containers.

The efficiency of removal of parathion residues by repeated rinsing with three types of solvents is shown in Table II. In all runs with glass bottles the amounts of parathion added to the containers as residues were totally removed in the washes regardless of the chemical properties of the wash solutions. About 99.9% of the residues could be removed by two or three washings with the volumes of the solvents used. Removal from steel drums was less efficient and about 2% of the residue remained unremovable by the aqueous solvents. Subsequent rinsing with benzene, however, recovered all the parathion originally added into the drums. This washing efficiency represents the maximum efficiency attainable in the laboratory; however, in the field where rinsing and draining are usually less thorough and complete, the efficiency could possibly decrease.

From the above residue and washing data, we can say efficient removal of the residues occurred in the first three washings. The volumes of the three washes used with three types of containers and the parathion concentrations in the resultant wash liquids are shown in Table III. At these volumes of washes, the concentration of parathion in the resultant liquids is alarmingly high, suggesting that the fate of parathion in the wash liquids needs to be closely examined.

The degradation of parathion in different alkali concentrations is shown in Figure 1. The rate of degradation is dependent on the alkali concentration. As an ester of phosphorothioic acid, parathion contains an electrophilic phosphorus atom and reacts readily with nucleophilic agents by direct displacement at the phosphorus atom (O'Brien, 1960).

**Table III. Parathion Concentrations in Resultant Wash Liquids**

| Container type       | Residues in emptied container, mg | Total wash volume, ml <sup>a</sup> | Parathion concn in wash, ppm |
|----------------------|-----------------------------------|------------------------------------|------------------------------|
| Glass bottle, 125 ml | 142                               | 75                                 | 1,900                        |
| Glass bottle, 1 gal. | 285                               | 150                                | 1,900                        |
| Metal drum, 1 gal.   | 666                               | 450                                | 14,800                       |

<sup>a</sup> Volume for three washes.

Thus, the reaction can be represented by a second-order rate equation

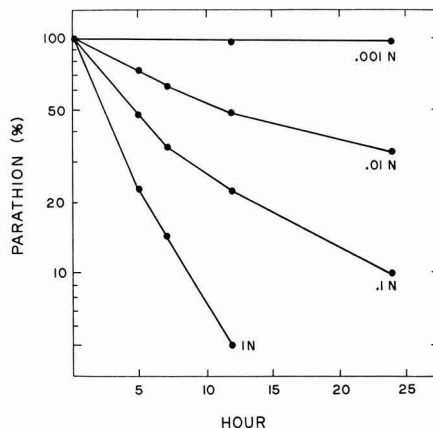
$$\frac{dC_1}{dt} = -kC_1C_2 \quad (1)$$

where  $C_1$  and  $C_2$  are the concentrations of parathion and OH<sup>-</sup>, respectively. Since in this experiment, the concentration of OH<sup>-</sup> is much greater than that of parathion—i.e.,  $C_2 \gg C_1$ — $C_2$  can be considered a constant, and the integrated form of Equation 1 can be shown to reduce to

$$\ln \frac{C_1(\text{init})}{C_1(\text{at time } t)} = C_2kt$$

It follows that a plot of  $C$  vs. time (hr) on a semilogarithmic scale should yield a straight line with its slope equal to  $C_2k/2.303$ . The semilogarithmic plot as shown in Figure 1, however, did not give straight lines. Significant tailing is observed with all the OH<sup>-</sup> concentrations. Moreover, the  $k$  values evaluated from the initial phase of the different curves vary from 0.3 to 6.5  $m^{-1} \text{ hr}^{-1}$ . Therefore, the widely used pseudo first-order reaction model does not adequately describe the hydrolysis of parathion in alkali under our experimental conditions.

To simulate the degradation of parathion in washes, different quantities of emulsifiable parathion were subjected to decomposition by 1N NaOH solution. Figure 2 shows a plot of residual parathion in the alkaline solution vs. time on a semilogarithmic scale. Instead of a single curve, a family of curves resulted, again showing that the pseudo first-order re-



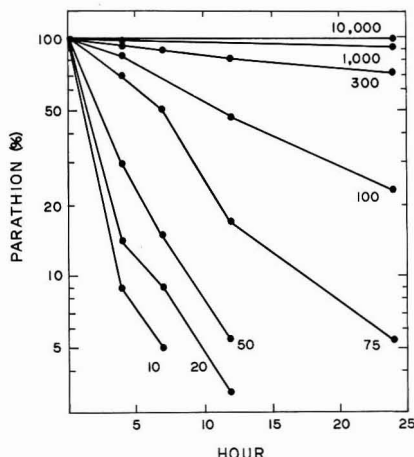
**Figure 1. Degradation of 50 ppm emulsifiable parathion in NaOH solutions**



**Table IV. Effect of Ethanol and Hypochlorite on the Hydrolysis of Parathion in 1N NaOH Solutions**

| Additive            | Concn, % | Residual parathion, ppm/hr |            |                 |            |            |
|---------------------|----------|----------------------------|------------|-----------------|------------|------------|
|                     |          | 0                          | 5          | 10              | 15         | 26         |
| None                | 0        | 927 (100) <sup>a</sup>     | 880 (94.9) | 840 (90.6)      | 798 (86.1) | 785 (84.7) |
| Ethanol             | 10       | 927 (100)                  | 829 (89.4) | 782 (84.4)      | 776 (82.6) | 751 (81.0) |
|                     | 25       | 938 (100)                  | 740 (78.9) | 553 (59.0)      | 467 (49.8) | 207 (32.7) |
|                     | 50       | 966 (100)                  | 87 (9.0)   | ND <sup>b</sup> | ND         | ND         |
| Sodium hypochlorite | 0.525    | 903 (100)                  | 778 (86.2) | 710 (78.6)      | 636 (70.4) | 518 (57.4) |
|                     | 1.31     | 906 (100)                  | 704 (77.7) | 569 (62.8)      | 460 (50.8) | 256 (28.2) |
|                     | 2.62     | 982 (100)                  | 652 (66.4) | 605 (61.6)      | 523 (53.2) | 344 (35.0) |

<sup>a</sup> Figures in parentheses are percentages.  
<sup>b</sup> Not detectable.



**Figure 2. Degradation of different quantities of emulsifiable parathion in 1N NaOH (Numbers with curves show initial ppm of parathion)**

action model does not adequately describe the actual reactions. The reaction mechanism in this experiment was probably complicated by the presence of emulsifiers and the concentration and solubility of parathion. (Parathion must first be dissolved into the aqueous phase before the nucleophilic attack can occur.) At concentrations higher than saturation, which occurs at approximately 20 ppm (Heath, 1961), the degradation rate of parathion is not proportional to the concentration, and the highest rate found at the initial phase of the reaction was only 5 ppm per hr. Therefore, at levels of parathion found in washes (ranging from 2000 to 15,000 ppm), very little change could be expected in 24 hr of alkaline exposure, and the toxicity would persist for months.

Two approaches were made to increase the solubility of parathion in water. Ethanol was added to the mixture as a mediator. Also, sodium hypochlorite was used to oxidize parathion to paraoxon which is considerably more water soluble (Heath, 1961). Table IV summarizes the effect of ethanol and sodium hypochlorite on the degradation of parathion in 1N NaOH solutions. Addition of ethanol to the reaction mixture strongly enhanced the rate of hydrolysis of parathion. In the presence of 25 and 50% ethanol, the rate increased four- and eighteenfold, respectively. The total parathion disappeared in 5 hr from the solution containing 50% ethanol. It should be noted that the experiment was run for a system containing more than 900 ppm of parathion

initially. Therefore, use of ethanol in the washing solvents for pesticide containers deserves special considerations. Use of 1.3% sodium hypochlorite along with the sodium hydroxide yielded a degradation capacity similar to that of the 25% alkaline ethanol solution. Additional amounts of bleach did not show increased degradative effectiveness. Although bleach has been used along with sodium hydroxide to detoxify waste water from the production of parathion (Mel'nikov et al., 1958; Libman and Fuks, 1967), in the case of decontamination of pesticide containers its effectiveness seems to be limited.

Recently, a solvent system composed of dipropylene glycol monomethyl ether and monoethanolamine has been developed for decontamination of organophosphorus insecticides on and around aircraft and spray equipment (Wolverton et al., 1970). This solvent is effective in neutralizing high concentrations of *O,O*-dimethyl-*s*-bis(carboxy) ethyl phosphorodithioate (malathion) and 1,2-dibromo-2,2-dichloroethyl dimethyl phosphate (naled) and has low toxicity to fish and is noncorrosive to aluminum. Its applicability to the decontamination of used pesticide containers deserves further evaluation.

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## Distribution of Cadmium and Nickel of Tobacco During Cigarette Smoking

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■ Analyses of wet- and dry-ashed cigarettes, cigars, and pipe tobacco revealed that these products contained appreciable amounts of cadmium and nickel. Our results indicate values of 1.56–1.96  $\mu\text{g}$  Cd and 4.25–7.55  $\mu\text{g}$  Ni per cigarette, and 0.93–1.86  $\mu\text{g}$  Cd/gram of cigar and pipe tobacco. Only 7–10% of the Cd and 0.4–2.4% of the Ni in the smoked portion of the cigarettes appeared in the particulate phase of the mainstream smoke (rsc); the remainder is present in the ash, trapped in the butt or lost in the sidestream. These data suggest that 38–50% of the Cd and 11–33% of the Ni in the smoked portion of cigarettes are present in the sidestream. Thus Cd and Ni in the sidestream smoke of cigarettes may present a health hazard to nonsmokers as well as smokers.

Cadmium and nickel are toxic metals which are present in our environment because of certain industrial uses and because of their widespread occurrence in foods, fuels, and many industrial products (Stokinger, 1963; Mastro-matteo, 1967; Smith et al., 1960; Schroeder et al., 1961).

Several investigators (Nandi et al., 1969; Szadkowski et al., 1969) have attempted to assess the fate of heavy metals including cadmium during the smoking of cigarettes. Nandi et al. (1969) assumed that 69% of the cadmium in the unsmoked cigarette entered the mainstream. However, Szadkowski et al. (1969) reported that only 13% of the cadmium in the unsmoked cigarette was found in the inhalable mainstream smoke.

To delineate the cadmium and nickel distribution during smoking of nonfilter cigarettes in a more exact manner, we reinvestigated this problem with the particular intent of confirming suspicions that the sidestream smoke might contain significant amounts of these trace metals, which could be detrimental to the health of the smoker as well as the non-smoker.

**Materials and Methods.** Tobacco products: Reference cigarettes (KR) prepared for research purposes by the University of Kentucky Institute for Research on Tobacco were used in the main part of our study, and were from one lot. A popular commercial brand (CB), purchased on the market, consisting of two different lots was also tested for comparisons. All cigarettes were of the nonfilter type, measuring 85 mm in length, and weighing about 1.12 grams each.

For comparison, we determined the metal content of one brand of cigar and one brand of pipe tobacco, which were purchased on the market.

**Smoking Procedure.** Cigarettes were smoked on a Mason Mark III, 24-port smoker which was adjusted to provide a 35-ml puff in a 2-sec interval during each minute of smoking per cigarette. During the nonsmoking interval, the mouth-piece was exposed to the air. The cigarettes were smoked to a 23-mm butt (73% of total length).

The ash from the cigarettes used in each experiment was collected directly in metal-free beakers utilized for the wet-ashing procedure. Tobacco smoke condensate (rsc), which is the particulate phase of the mainstream smoke, was collected in cold acetone traps as previously described (Michael et al., 1971). The acetone was removed by evaporation at reduced pressure and the residue was ashed as described below. The butts remaining after the cigarettes had been smoked to the prescribed length were extinguished with deionized water and analyzed as indicated below.

**Preparation of Analytical Samples.** The samples of tobacco, ash, or rsc were either wet ashed or dry ashed. The two methods were used as convenience dictated, since no evident difference in results could be associated with these procedures. Wet ashing of smoked or non-smoked tobacco products was accomplished by heating these materials with concentrated  $\text{HNO}_3$  until liquefaction and oxidation occurred. The resultant solutions and reagent blanks were reduced by evaporation to approximately 1 ml prior to dilution with hot 10%  $\text{HNO}_3$  for analysis.

Dry ashing was accomplished in a muffle furnace at 400–450°C after moistening the sample with concentrated nitric acid. The residue from the dry-ashing procedure was dissolved in 2 ml of concentrated  $\text{HNO}_3$ , which was evaporated and the residue taken up in hot 10%  $\text{HNO}_3$  for analysis.

**Analytical Determinations.** Analyses for cadmium, nickel, zinc, and lead by atomic absorption spectroscopy were made on the 10% nitric acid solution of the digested or ashed samples by aspirating these directly into a Perkin-Elmer Model 303 unit equipped with a Belling burner and recorder readout.

Values for each metal were determined by comparison with standard absorption curves using certified Fisher standards. It was found that recovery of added standard solution to samples was 92% for cadmium, 95% for nickel, 95% for zinc, and 98% for lead, using external standards.

### Results

**Metal Content of Tobacco Products.** The cadmium, nickel, and zinc contents of several tobacco products are listed in Table I. The standard deviations for cadmium, nickel, and zinc mostly reflect the variability of metal levels in the samples and in different batches of the cigarettes.

The data show that cadmium occurs in all of the tobacco products at 1–2  $\mu\text{g/g}$  levels. Nickel was determined in KR and CB cigarettes only, giving 4.5 and 7.5  $\mu\text{g/cigarette}$ , respectively.

The values for nickel in KR and CB cigarettes were two and

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**Table I. Metal Content of Tobacco Products**

| Sample   | Metal concn, <sup>a</sup> $\mu\text{g}$    |                               |                              |
|--|--|-------------------------------|------------------------------|
|  | Cd   | Ni                            | Zn                           |
| Kentucky reference <sup>b</sup><br>cigarettes (KR) | 1.56 $\pm$<br>0.19/cig<br>(6) <sup>c</sup> | 4.25 $\pm$<br>0.18/cig<br>(2) | 33.4 $\pm$<br>2.4/cig<br>(7) |
| Commercial brand <sup>b</sup><br>cigarettes (CB)   |  |                               |                              |
| Batch 1  | 1.90 $\pm$<br>0.14/cig<br>(4)              | ...                           | 38.9 $\pm$<br>9.0/cig<br>(4) |
| Batch 2  | 1.96 $\pm$<br>0.11/cig<br>(4)              | 7.55 $\pm$<br>0.50/cig<br>(4) | 20.0 $\pm$<br>0.8/cig<br>(4) |
| Cigar (commercial)                                 | 1.86/g                                     | ...                           | 51.4/g                       |
| Pipe tobacco<br>(commercial)                       | 0.93/g                                     | ...                           | 33.0/g                       |

<sup>a</sup> Values are mean  $\pm$  S.D.  
<sup>b</sup> KR cigarettes weighed 1.12  $\pm$  0.04 grams and CB cigarettes weighed 1.12  $\pm$  0.10 grams.  
<sup>c</sup> Digit in parentheses denotes number of samples.

three times as large, respectively, as that reported for German cigarettes (Szadkowski et al., 1969).

The zinc determinations in Table I, in conjunction with those in Table II, served as an analytical control. All types of tobacco products show high concentrations of zinc (Cogbill and Hobbs, 1957; Nadkarni and Ehmman, 1969, 1970; Nadkarni et al., 1970), ranging from 20  $\mu\text{g}$ /cigarette in CB to 51.4  $\mu\text{g}$ /g in a cigar.

**Metal Content of Smoked Cigarettes.** The metal contents of the smoked portion of cigarettes are listed in Table II. These include determined values for ash, tsc, and smoked butt, and calculated values for the smoked portion, and the sidestream. The sidestream Cd, Ni, and Zn were calculated as that part of the smoked portion which could not be accounted for by summing up the levels of each metal in the ash, tsc, and smoked butt.

The sidestream percentages in Table II are given in terms of the amount of cadmium, nickel, and zinc originally in the smoked portion of a cigarette.

**CADMIUM.** The results show that only a small percentage (10.1 and 7.0%) of the cadmium in the smoked portion of either the KR or CB cigarettes appears in the tsc and so would be directly available for pulmonary absorption by the smoker (Lewis et al., 1972). The amount of cadmium in tsc per cigarette is 0.12 and 0.10  $\mu\text{g}$  for KR and CB cigarettes respectively, or about 2.4 and 2.0  $\mu\text{g}$  per pack of 20 cigarettes. This amount is less than the amount in mainstream smoke found by Szadkowski et al. (1969). Nevertheless, depending on the chemical form of the cadmium, it may be a source of cadmium as well as a health hazard to the smoker (Schroeder et al., 1961; Lewis et al., 1972).

The total mainstream smoke consists of the tsc and what is trapped by the tobacco in the butt during smoking, designated butt enrichment. Thus the total mainstream cadmium of KR and CB cigarettes is 22 and 17%, respectively. The ash and mainstream cadmium constitute the readily measurable amounts, and in both types of cigarettes these sums are only 62 and 50% of the cadmium in the smoked portion. Thus, there remain 38 and 50% of original smoked portion cadmium to be accounted for.

This cadmium has been assumed as being present in the sidestream smoke—i.e., the smoke which drifts off the burning end of a cigarette between puffs. A preliminary result obtained in our laboratory (Hoegg et al., 1972) on directly collected sidestream smoke has indicated the presence of cadmium in an amount which was similar to the calculated values given here (0.43 and 0.72  $\mu\text{g}$  cadmium per KR and CB cigarette, respectively); this is taken to be indicative of the logic of our method of estimating sidestream Cd. These amounts are equal to 8.6 and 14.4  $\mu\text{g}$  for a pack of 20 KR and CB cigarettes, respectively.

The importance of the sidestream cadmium is that it represents a large amount of this toxic metal which is available for inhalation by both the smoker (Lewis et al., 1972) and anyone in his vicinity. It thus becomes a possible general indoor air contaminant.

**NICKEL.** Nickel has recently become a toxic metal of concern to environmental scientists. The data in Tables I and II show that it is present in considerable amounts in cigarettes, and like cadmium, a large portion is lost during smoking presumably as part of the sidestream smoke. The apparent loss of Ni during smoking of the KR and CB cigarettes (computed by subtracting the sum of Ni in tsc, ash, and butt from the total Ni in the whole cigarette) amounted to 1.03  $\mu\text{g}$  per KR and 0.62  $\mu\text{g}$  per CB cigarette. Thus, quantities of nickel, equivalent to 33% (KR) and 11% (CB) of the initial amount present in the smoked portion, were unaccounted for and are

**Table II. Trace Metal Content of Cigarette Fractions**

| Fraction   | Metal content <sup>a</sup> |                        |                        |
|--|----------------------------|------------------------|------------------------|
|  | Cd                         | Ni                     | Zn                     |
| KR cigarettes                                      |                            |                        |                        |
| Smoked portion<br>(73% of total)                   | 1.14                       | 3.10                   | 24.3                   |
| Smoked butt  | 0.56 $\pm$                 | 1.33 $\pm$             | 12.4 $\pm$             |
|  | 0.03 (6)                   | 0.07 (2)               | 1.9 (6)                |
| tsc <sup>b</sup> (mainstream<br>particulate phase) | 0.12 $\pm$<br>0.03 (5)     | 0.08                   | 0.36                   |
|  | 10.1%                      | 2.6%                   | 1.5%                   |
| Ash <sup>b</sup>                                   | 0.45 $\pm$<br>0.03 (4)     | 1.81 $\pm$<br>0.16 (2) | 21.3 $\pm$<br>4.7 (5)  |
|  | 39.4%                      | 58.4%                  | 87.6%                  |
| Sidestream <sup>b,c</sup>                          | 0.43<br>38%                | 1.03<br>33%            | -0.66<br>3%            |
| CB cigarettes                                      |                            |                        |                        |
| Smoked portion<br>(73%)                            | 1.43                       | 5.51                   | 14.6                   |
| Smoked butt  | 0.67 $\pm$                 | 2.64 $\pm$             | 7.6 $\pm$              |
|  | 0.02 (4)                   | 0.17 (4)               | 0.8 (4)                |
| tsc <sup>b</sup> (mainstream<br>particulate phase) | 0.10 $\pm$<br>0.01 (2)     | 0.02 $\pm$<br>0.01 (2) | 0.06 $\pm$<br>0.01 (2) |
|  | 7%                         | 0.4%                   | 0.4%                   |
| Ash <sup>b</sup>                                   | 0.48 $\pm$<br>0.02 (4)     | 4.27 $\pm$<br>0.20 (4) | 11.9 $\pm$<br>0.5 (4)  |
|  | 33.5%                      | 77.5%                  | 81.5%                  |
| Sidestream <sup>b,c</sup>                          | 0.72<br>50%                | 0.62<br>11%            | 0.40<br>3%             |

<sup>a</sup> Concentrations are in  $\mu\text{g}$  per fraction listed. Values are means  $\pm$  S.D. or calculated values. Parentheses indicate the number of samples.

<sup>b</sup> Percentages were calculated on basis of smoked portion.  
<sup>c</sup> Sidestream was calculated by subtracting the values of smoked butt, tsc, and ash from the total cigarette value given in Table I. (Butt enrichment can be estimated by subtracting the calculated value for unsmoked butt from the experimental value given.)

assumed to have entered the sidestream smoke. This results in 20.6  $\mu\text{g}/\text{pack}$  of KR and 12.4  $\mu\text{g}/\text{pack}$  of CB cigarettes, which is lost to the atmospheric environment of the smoker. The TSC nickel levels were 0.08 and 0.02  $\mu\text{g}$  per KR and CB cigarettes respectively, indicating that only a very small amount of this metal is directly inhaled by the smoker.

**ZINC.** The data for zinc were obtained as a control on the analytical procedures, since its presence in the sidestream smoke was not expected to be significant. The values for zinc given in Table II show that 87.6 and 81.5% of the zinc in the smoked portions of KR and CB cigarettes respectively were found in the ash. The remainder of the zinc was mainly found in the mainstream smoke absorbed by the butt. Very little zinc was found in TSC and probably none was actually present in the sidestream. Thus, the fate of zinc is quite different from that of cadmium and nickel, a difference which emphasizes the importance of these metals in sidestream smoke.

**LEAD.** Untabulated values obtained for lead show a fate similar to that for zinc. Most of the lead was found in the ash and only 1.8–1.9% of the initial smoked portion was found in the TSC. It appears unlikely that the sidestream contained an appreciable amount of lead.

#### Discussion

These results not only lend support to the suggestion of Schroeder et al. (1961) and Lewis et al. (1972) that cadmium in tobacco represents a contributory source to the total body burden of the smoker, but also indicate that the presence of cadmium and nickel in the sidestream smoke may affect the health of both the smoker and anyone breathing the air in the general vicinity of the smoker.

From our data, it appears that 38–50% of the cadmium and 11–33% of the nickel of the smoked portion of cigarettes was released into the sidestream smoke. The TSC data suggest that a pack of 20 cigarettes would provide about 2  $\mu\text{g}$  of cadmium and from 0.4 to 1.6  $\mu\text{g}$  of nickel in the TSC which is inhaled by the smoker; the sidestream smoke, on the other hand, would put into the general environment 8.6–12.8  $\mu\text{g}$  of Cd and 12.4–20.6  $\mu\text{g}$  of nickel per pack. These amounts of Cd and Ni constitute a considerably greater environmental contamination than is found in ambient air. Although the smoker is the most exposed individual to the smoke, nevertheless, it could

be a hazard also to the nonsmoker in the vicinity of the smoker.

In addition, since there is considerable sidestream smoke derived from the smoking of cigars and pipe tobacco, the presence of cadmium in both of these products suggests that such sidestream smoke could also contain cadmium.

Since both cadmium and nickel are known to be harmful in occupational situations (Szadkowski et al., 1969; Friberg, 1957; Smith et al., 1960; Mastromatteo, 1967; Stokinger, 1963), and since smoking exposes a very large number of people to these toxic metals, the presence of cadmium and nickel in tobacco products (especially cigarettes) needs to be carefully considered in evaluating the health effects of tobacco smoking (Anderson et al., 1964; Lewis et al., 1972).

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## NOTES

# Infrared Estimation of Oil Content in Sediments in Presence of Biological Matter

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■ The crude oil content of marine sediments was determined by ir spectrometry from the magnitude of  $2925\text{ cm}^{-1}$  ( $-\text{CH}_2-$  stretching band) absorbance. Biological materials also absorb at  $2925\text{ cm}^{-1}$  and have a well-defined absorbance band at  $1650\text{ cm}^{-1}$  (the  $-\text{NH}-$  band characteristic of proteins) whereas, crude oils do not exhibit an amide band. The relative contributions of oil and organic material of recent biological origin in marine sediments were determined from measurements of these two absorbance bands, and a correction applied which enables the calculation of the oil content in the presence of these biological materials.

In a recent study of the effects of the winter 1969 oil blow-out at Platform A in the Santa Barbara Channel, analytical procedures for the rapid determination of the oil content of the channel bottom sediments using both transmission and internal reflectance ir spectrometry were reported (Mattson et al., 1970b; Kolpack et al., 1971; Yu et al., 1971). In these analyses, the oil content of the sediment was considered to be related to the magnitude of the  $2925\text{ cm}^{-1}$  ( $-\text{CH}_2-$  stretching band) absorbance.

Those analyses were made primarily on bottom sediments which were deposited following a major flood. The rate of sedimentation of this highly oxidized detrital flood material was very rapid and in most samples there were no significant amounts of organic material of recent biological origin present. However, some of the samples were obtained from the central part of the Santa Barbara Channel up to 18 months after the flood. The rate of detrital sedimentation in this area is much slower, and the surficial sediments often were mixed with organic debris of biological origin. The presence of biological material interfered with the determination of the oil content as the  $-\text{CH}_2-$  groups of such biological matter also absorb at  $2925\text{ cm}^{-1}$ . This ir band is identical for any  $-\text{CH}_2-$ -containing compound, and the relative contributions of oil and biological matter to the observed absorbance cannot be determined by a simple measurement of the  $2925\text{ cm}^{-1}$  band. This paper reports a simple extension of the above ir procedure which permits estimation of the concentration of biological materials. This provides a method for correcting the  $2925\text{ cm}^{-1}$  absorbance band to enable the estimation of the oil contribution alone.

## Experimental

The experimental procedures and the instrumentation employed in this study are described in detail in previous publications (Mattson et al., 1970b; Kolpack et al., 1971; Yu and Mark, 1971; Mattson et al., 1970c). A Beckman IR-12 infrared spectrometer was employed for all measurements described in this paper.

## Results and Discussions

The complete ir spectrum of a large number of different crude oils (Mattson, 1971) and of different biological materials was examined. All materials of biological origin exhibited a large, well-defined absorbance band at  $1650\text{ cm}^{-1}$  (the  $-\text{NH}-$  band characteristic of proteins) while crude oils and sediments had no observable  $1650\text{ cm}^{-1}$  band (Figure 1). The ir spectra of a variety of finely ground biological materials in sediment were measured in the region from  $4000$  to  $1200\text{ cm}^{-1}$ . Similar spectra results were obtained for both transmission and internal reflectance modes of measurement. In each sample the peak absorbances of the  $-\text{CH}_2-$  band at  $2925\text{ cm}^{-1}$  and of the secondary amide band at  $1650\text{ cm}^{-1}$  were measured and the  $-\text{CH}_2-/-\text{NH}-$  ratio calculated from the absorbance bands. It was found that this  $-\text{CH}_2-/-\text{NH}-$  band ratio was relatively constant (varying from 1.24 to 1.42 for transmission ir measurement) for all of the biological materials examined (see Table I) and also was independent of the concentration of

Table I. Comparison of the  $-\text{CH}_2-/-\text{NH}-$  Peak Ratios for Various Biological Materials

|  | $-\text{NH}-$<br>( $1650\text{ cm}^{-1}$ )<br>(transmission,<br>peak length) | $-\text{CH}_2-$<br>( $2925\text{ cm}^{-1}$ )<br>(transmission<br>peak length) | $-\text{CH}_2-/-$<br>$-\text{NH}-$<br>(transmission<br>length<br>ratio) <sup>a,b</sup> |
|--|--|---|--|
| Plankton   | 12   | 7   | 1.26   |
| Algae  | 12   | 6   | 1.39   |
| Seaweed  | 9.5  | 6   | 1.26   |
| Shrimp   | 9.5  | 6   | 1.26   |
| Kelp   | 10   | 5   | 1.43   |
| Equal mixture of<br>plankton, algae,<br>seaweed, shrimp,<br>kelp | 11   | 7   | 1.24   |

<sup>a</sup> Ratio values given here are those obtained for transmission mode ir measurement. Ratio values obtained for internal reflectance mode are larger as expected (Mattson et al. 1970c) with a similar variation of values.

<sup>b</sup> Peak lengths converted to absorbance before calculation of band ratio.

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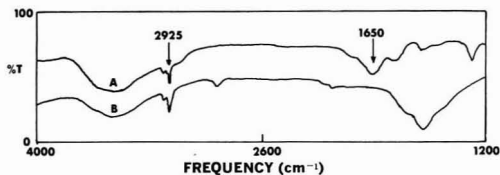


Figure 1. Typical transmission ir spectra

A, Oil-containing sediment sample containing biological (protein) material; B, oil-containing sediment sample containing no biological material

the material in the sediment. Thus, it is possible to correct for the contribution of the biological materials to the 2925  $\text{cm}^{-1}$  band by measuring the 1650  $\text{cm}^{-1}$  transmission band, converting percent transmission to absorbance units (so that a linear correction can be made) multiplying the 1650  $\text{cm}^{-1}$  band height by 1.3 (the average of all  $-\text{CH}_2-/-\text{NH}-$  band ratios which was arbitrarily chosen as the correction factor), and subtracting the resulting number from the total 2925  $\text{cm}^{-1}$  band height (also converted to absorbance). Results for a few examples of the determination of the oil content in some Santa Barbara Channel sediments which contain biological matter are shown in Table II. It is apparent that the accuracy of the estimation of the oil content decreases as the concentration of the biological matter increases. This decrease in accuracy arises from the uncertainty or variations of the  $-\text{CH}_2-/-\text{NH}-$  band ratios for various biological materials. The precision of the measurements themselves were better than  $\pm 10\%$ , and, thus any correction of the  $-\text{CH}_2-$  absorbance which shows that the oil content is only 10% or less of the total  $-\text{CH}_2-$ -containing material is a meaningless number. For example, the value of 0.6 ppt oil content for sample 12973 in Table II should be considered to be zero detectable oil content. However, for most applications in ecological and/or geological studies, this sensitivity limitation should not present a significant problem.

It should be pointed out that this method must be used with caution as it is absolutely necessary for the analyst to know the chemical nature of organic material present in the sediment samples. For example, an organic material which does not contain  $-\text{NH}-$  groups, such as cellulose, could be present in sediments from some areas. If the analyst were not aware of its presence, it would be analyzed as part of a fossil fuel hydrocarbon in the sediment. Thus, it is recommended that the total ir spectra of the sediment sample be examined for other organic functional group bands which would suggest other  $-\text{CH}_2-$ -containing species were also present in significant amounts to cause significant error in the hydrocarbon content estimate. It is further suggested that, as a precaution, random sediment samples from the series being studied be analyzed by a separate means which can qualitatively identify the various organic species present to determine if a potential source of error is common to the area. Extraction and gas

Table II. Example Analyses of Sediment Samples Containing Oil and Biological Material

| Sediment sample no. <sup>a</sup> | C—H (2925 $\text{cm}^{-1}$ ) transmission peak length | N—H (1650 $\text{cm}^{-1}$ ) transmission peak length | Oil concn <sup>b</sup> after correction, ppt |
|----------------------------------|---|---|--|
| 12,888                           | 14  | 8   | 4.3  |
| 12,889                           | 16  | 11  | 4.6  |
| 12,929                           | 16  | 9   | 5.1  |
| 12,930                           | 14  | 3   | 5.5  |
| 12,932                           | 19  | 4   | 7.5  |
| 12,934                           | 15  | 3   | 6.1  |
| 12,935                           | 24  | 5   | 9.8  |
| 12,972                           | 13  | 12  | 2.9  |
| 12,973                           | 9   | 14  | 0.6  |
| 12,981                           | 7   | 4   | 2.4  |
| 13,027                           | 49  | 10  | 19.5   |

<sup>a</sup> See Kolpack et al. (1971).

<sup>b</sup> Resultant  $-\text{CH}_2-$  peak length converted to concentration by means of a calibration curve (Mattson et al., 1970a).

chromatograph were actually used in the Santa Barbara Channel study to determine if other types of organics were generally present in the sediments of this area in sufficient concentration to cause interference in the ir estimation of the hydrocarbon content. In this particular study, no other measurable interferents were found.

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# Brucine Analysis for High Nitrate Concentrations

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■ The validity of the brucine method for the determination of nitrate concentration in groundwaters was examined when it was found that some samples yielded higher concentrations of nitrate upon dilution. A detailed study of the relationship of brucine to nitrate stoichiometry and reaction time in color development to the shape of the absorbance vs. nitrate concentration curve was made in the 550–350  $\mu$  range. The shape of the absorbance curve at 410  $\mu$  is totally dependent on brucine-to-nitrate stoichiometry, thus necessitating at least an approximate knowledge of nitrate ion concentration in the sample prior to analysis if gross errors in calculations are to be avoided.

Conformity to accepted methods of quantitative wet chemical analysis is good practice for any analytical laboratory. However, using the brucine method (tentative) described in Standard Methods for the Examination of Water and Wastewater (1971) has led to discrepancies in our analyses of nitrates in well waters. The procedure is one used by the Environmental Protection Agency (Training Manual, 1969).

Inconsistent results were obtained when samples known to be high in nitrates were diluted according to the procedure referred to. For example, when a water sample of unknown  $\text{NO}_3^-$  concentration was successively diluted with distilled water in a 1:1, 1:3 and 1:10 ratio (Sample:  $\text{H}_2\text{O}$ , vol/vol), and the intensity of the developed color measured on a uv spectrophotometer at 410  $\mu$  (1-cm cells), absorbances increased with increased dilution instead of decreasing as would be expected. On other occasions, a well water sample with an absorbance above that of the standards was diluted until it absorbed within the proper range. However, on further dilution the sample again exhibited an absorbance in excess of the standard curve. Literature on the much beleaguered brucine method (Greenburg et al., 1958; Jenkins and Medsker, 1964) did not provide an answer to this anomaly: an increase in color intensity and absorption at 410  $\mu$  as the sample was further diluted. Also, these observations were not thought to be caused by the interferences discussed in Standard Methods.

Although the color of the brucine-nitrate complex does not follow Beer's law, a good standard curve from 0.1 to 2 mg/l.  $\text{NO}_3^-$ -N can be achieved with little difficulty. If we assume the absorbing complex measured at 410  $\mu$  adheres to a 1:1 brucine:nitrate stoichiometry, excess brucine would be exhausted at about 7 mg/l.  $\text{NO}_3^-$ -N. Above such a concentration of nitrate, absorbance at 410  $\mu$  would not be expected to change. This we found to be false.

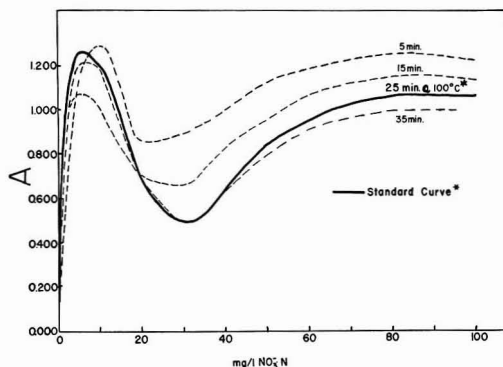


Figure 1. Absorbance vs.  $\text{NO}_3^-$ -N concentration as a function of color development time

## Experimental Results

To identify the reason for the observed discrepancy, a standard curve was constructed following Standard Methods except that nitrate concentrations ran up to 100 mg/l.  $\text{NO}_3^-$ -N. The standard curve obtained for absorbance measured at 410  $\mu$  is shown in Figure 1.

Absorbance did not level off at the point of 1:1 stoichiometry, but in fact dropped to absorbance levels within the range of the 0.1–2 mg/l. of  $\text{NO}_3^-$ -N standard curve before increasing again. This can lead to instances where absorbance determined at 410  $\mu$  seems to be well within the range of the standards, but the sample may be 50 times as concentrated in nitrate. Thus, an absorbance reading of 0.6 could actually be obtained from a sample containing 0.8, 23, or 38 mg/l. of  $\text{NO}_3^-$ -N. The concentration at which this curve reaches maximum absorbance at 410  $\mu$  corresponds closely to the depletion of excess brucine, assuming a 1:1 stoichiometry. With higher concentrations, the unusually rapid drop in absorbance down to  $\sim 0.5$  is followed by a gradual rise which reaches a plateau at  $\sim 1.0$  as the  $\text{NO}_3^-$ -N concentration continued to increase.

Similar curves were developed using different times for color development to determine if inadvertent changes in development time would result in mistaking high nitrate concentrations for lower concentrations. Plots were made of standards heated at 100°C for 5, 15, 25, and 35 min to determine dependence of the shape of the absorbance curve on color development time. Results showed (Figure 1) that in all cases the analyst could be misled by the absorbance minima dropping within the range of standards. The shorter color development time minimized the chance of this occurring to a certain extent.

To examine the drop in absorbance with increasing con-

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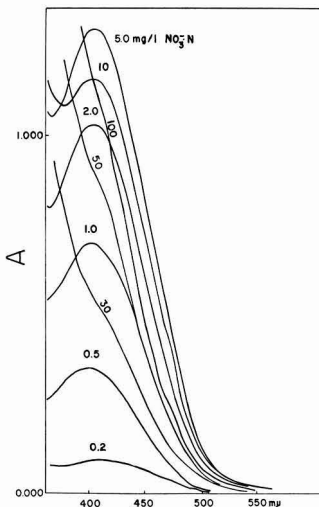


Figure 2. Absorption vs. wavelength curves for nitrate standards from 0-100 mg/l. N

centration, the spectra of the color developed from standard samples were scanned from 550  $m\mu$  down to 350  $m\mu$ . The results are shown in Figure 2. The absorbance peak at 410  $m\mu$  increased through 5 mg/l.  $NO_3^-N$ , then declined in the manner already shown in Figure 1. As the 410- $m\mu$  peak began to disappear, background absorbance increased at the higher wavelengths until at 80-100 mg/l. of  $NO_3^-N$  little change in absorbance was observed at 410  $m\mu$ .

Additional scans were made using two sets of standards run with 1:1 and 1:2 nitrate:brucine stoichiometry, respectively (Figure 3). This was to show the effect of a constant ratio of nitrate and brucine. The procedure was otherwise identical to that described in Standard Methods. With increasing concentrations of nitrate, absorbance at 410  $m\mu$  continued to increase until it reached opacity (1-cm cells). The scans of absorbance vs. wavelength indicated all standards had peaks at 410  $m\mu$  even as background absorbance increased.

Standard curves were also run with enough excess brucine to prevent a higher concentration of nitrate from being mistaken for a concentration within the standard range. This procedure required sufficient brucine to cause absorbance to approach opacity (in 1-cm cells) with increasing nitrate concentrations. It would also indicate whether excess brucine would increase background absorbance and jeopardize the sensitivity of the method. To show this, two more sets of standards were developed, one using 7 and the other 21 mg of brucine  $SO_4^{2-}$  in each standard. Standard Methods requires 5 mg brucine  $SO_4^{2-}$  in its procedure. Twenty-one milligrams of brucine was the minimum required to produce opacity at 410  $m\mu$  in 1-cm cells. This was enough for 1:1 brucine:nitrate stoichiometry to about 20 mg/l. of  $NO_3^-N$ . The standard (Figure 4) seemed to have less precision at lower concentrations as indicated by the greater deviation from a smooth curve.

The samples treated with brucine approached opacity at 5 mg/l. of  $NO_3^-N$  with 21 mg of brucine  $SO_4^{2-}$ . This is well above the 2-mg/l. limit of the standard procedure.

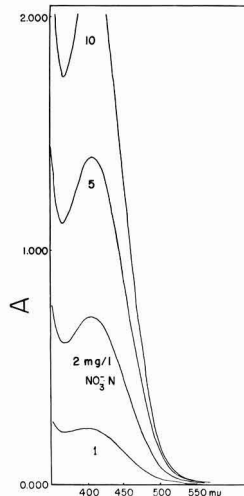


Figure 3. Absorption vs. wavelength curves of nitrate standards from 0-10 mg/l. N, with a 1:2 stoichiometric ratio of nitrate to brucine

#### Discussion

The results of these experiments show that without a stoichiometric equivalent or an excess of brucine over nitrate, the brucine method can lead to erroneous results. If a brucine:nitrate procedure does not produce a standard absorbance curve which goes to opacity with increasing nitrate concentration (or levels off at constant absorbance), then it will be subject to undetected error. A procedure which uses sufficient brucine to avoid this problem sacrifices the low-end sensitivity of the method, and as the absorbance of low concentrations approaches that of the blank, it degrades in both precision and accuracy. Therefore, as Standard Methods implies, one must know the approximate concentration of nitrate in a sample before analysis.

To use this procedure without the risk of having a high concentration of  $NO_3^-N$  mistaken for falling within the

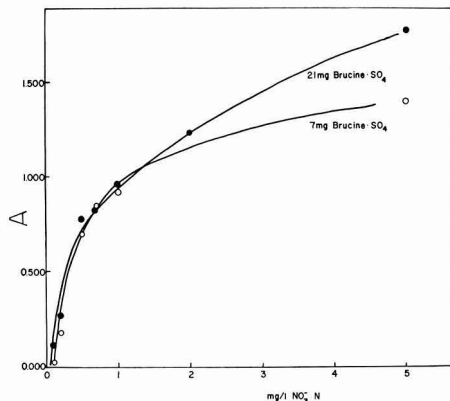


Figure 4. Standard curves, absorbance vs. concentration, developed with slight excess brucine (410  $m\mu$ )

range of standards, the analyst has a choice of three approaches. He may use a selective ion electrode for preliminary screening, and from the results obtained, determine the required dilution. A second alternative is to employ a systematic dilution strategy in which either a specified absorbance—i.e., 0.5 (in 1-cm cells) is not to be exceeded—or the absorbance of two dilutions of the same sample must lie on the standard curve, one of which should not exceed a specified absorbance. Additional effort is required to analyze samples by this method and makes this second technique undesirable. A third and less time-consuming alternative is to add enough extra brucine to prevent the absorbance curve from decreasing with higher concentrations of  $\text{NO}_3^-N$ . If a particular circumstance prevents the addition of excess brucine, it is recommended that

a specific ion electrode be used for preliminary screening to determine the required dilution.

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## CORRESPONDENCE

### Singlet $\text{O}_2$ Production from Photoexcited $\text{NO}_2$

SIR: In the recent article by Frankiewicz and Berry [ENVIRON. SCI. TECHNOL., **6**, 365 (1972)], it is stated that a paper by Altshuller and Bufalini [ENVIRON. SCI. TECHNOL., **1**, 133 (1967)] indicates that the rate of hydrocarbon oxidation can be explained solely on the basis of O-atom oxidation. The authors have not only misquoted our findings but have missed the basic theme of the paper—i.e., that O-atom and ozone reactions could not explain the hydrocarbon oxidation. Our manuscript went into great detail explaining that free radicals must be introduced to explain the "excess rate."

I would also like to point out that all of the evidence strongly suggests that  $\text{O}_2(^1\Delta_g)$  is not important in smog formation. If the concentration of  $\text{O}_2(^1\Delta_g)$  is indeed  $10^7$  to  $10^8 \text{ cm}^{-3}$ , while the  $\text{O}(^3P)$  is of the order of  $\sim 5 \times 10^5 \text{ cm}^{-3}$  as the authors state, the  $\text{O}_2(^1\Delta_g)$  will only exceed the O-atom concentration by  $10^2$  to  $10^3$ . Since the ratio of  $k(\text{O}^3P)/k(\text{O}_2^1\Delta_g)$  is usually  $10^4$  to  $>10^6$  [J. T. Herron, R. E. Huie, ENVIRON. SCI. TECHNOL., **4**, 685 (1970)] then the singlet oxygen-hydrocarbon reaction rate is  $10^{-1}$  to  $10^{-4}$  times that of the O-atom-hydrocarbon reaction. When hydrocarbons are photooxidized in the presence of nitrogen dioxide, the O-atom reaction is most important in the initial stages of reaction. Its importance decreases with

irradiation time. If the best fit is taken between the calculated and observed rates of reaction for 1-butene [Figure 5 in ENVIRON. SCI. TECHNOL., **1**, 133 (1967)], the O-atom reaction is responsible for only 50% of the total reaction. Since the  $k(\text{O}^3P)/k(\text{O}_2^1\Delta_g)$  is  $\geq 2.4 \times 10^5$  for 1-butene (Herron and Huie, 1970), the contribution of the  $\text{O}_2(^1\Delta_g)$  reaction at best is less than  $10^{-2}$  that of atomic oxygen. We do not feel that this is a significant contributor to smog formation as the authors suggest.

There have been a large number of papers published on the role of singlet oxygen in smog formation. However, to date, there is still no experimental proof either in the laboratory or in situ to suggest that singlet oxygen is important in the photooxidation of hydrocarbons at realistic atmospheric concentrations.

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SIR: Apparently the wording of our note (Frankiewicz and Berry, 1972) has caused some confusion, at least for some readers, as Bufalini's comment indicates. It is perhaps worth clarifying how the misinterpretation has arisen.

It was not our intent to imply that direct reactions of oxygen atoms were considered by Bufalini and Altshuller to account for all the oxidation of hydrocarbons; they were almost surely quite right in their statement in 1967 that chain reactions are responsible for the "missing" factor, as several recent studies have shown (Levy, 1971; McConnell et al., 1971; Weinstock, 1972). Second, it was hardly the intent of our note to argue that metastable  $\text{O}_2$  is a major contributor to smog formation, but rather, that is one contributor and that its contribution can be estimated and measured. The numbers presented in our note surely make it clear that the contribution is of the order 0.1–5%, depending on the class of compounds

being considered and not of an overall order of 50%, which would be required to make the species a major contributor.

#### Literature Cited

- Frankiewicz, T. C., Berry, R. S., ENVIRON. SCI. TECHNOL. **6**, 365 (1972).  
Levy, H., *Science*, **173**, 141 (1971).  
McConnell, J. C., McElroy, M. B., Wofsy, S. C., *Nature*, **233**, 187 (1971).  
Weinstock, B., *Science*, **176**, 290 (1972).

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# industry trends

**Ionics, Inc.** and **Stone & Webster Engineering Corp.** have signed an agreement with EPA and Wisconsin Electric Co. for a full-scale demonstration of the sulfur dioxide removal system developed jointly by the two firms (August 1972, p 688). The system will be installed on one boiler at Wisconsin Electric's Valley Plant in Milwaukee. The agreement commits the electric utility and EPA to a total expenditure of \$7 million over a period of three years or more.

**California Filter Co.** (Burlingame, Calif.) will design, fabricate, and install a waste water treatment plant for a paper mill owned by American Forest Product Corp. in Newark, Calif. The plant will include a flash mixer, clarifier, and sludge thickener. The 150-gpm plant will be fully automatic. The Newark mill uses 100% recycled material to make corrugating medium.

**Keene Corp. Water Pollution Control Division** (Aurora, Ill.) has licensed one Italian and one Japanese company to manufacture and sell its line of standard waste treatment process equipment in Italy and Southeast Asia, respectively. The foreign concerns are Fenwick S.p.a. (Milan, Italy) and Daido Steel Co. Ltd. (Nagoya, Japan).

**Landis & Assoc.** (Auburn, Calif.) has purchased California Analytical Laboratories (Sacramento, Calif.). Details of the transaction were not announced. Landis is a civil and sanitary engineering firm. California Analytical Laboratories has capabilities in water analysis, pesticide residue analysis, and toxicology.

**North American Rockwell's Information Systems Co.** has received a contract from the Louisiana state legislature to develop a comprehensive statewide environmental management system. The system, first of its kind, is jointly funded by EPA and the state.

**SCA Service Inc.,** (Boston, Mass.) will acquire seven more privately owned solid waste management companies in several southern, eastern, and south-

western states, with combined annual revenues in excess of \$11 million. Acquisitions were for an undisclosed amount of common stock and followed a similar acquisition of seven firms announced last June.

**The National Association of Secondary Material Industries, Inc.** has formed a Solid Waste Recycling Information Service to provide guidance to state, municipal, and county officials involved in solid waste management or related environmental problems.

**Chemical Construction Corp.** (Chemico) has announced the successful startup and continuous operation of a full-scale calcium oxide additive SO<sub>2</sub>-fly ash scrubbing system in Japan. Startup of the unit at the Ohmuta power plant of the Mitsui Aluminum Co. was last March.

**Grumman Ecosystems Corp.** has formed a subsidiary, Puritech Industries, Inc., which will serve as a general contractor and construction project manager for waste and sewage treatment systems.

**American Housing Systems** (Cleveland, Ohio) has announced an agreement in principle to acquire Robert Bossow, Inc. (Garrettsville, Ohio) for an undisclosed amount of cash. Robert Bossow builds sewage treatment plants and water purification and distribution plants.

**Combustion Equipment Associates, Inc.** (New York, N.Y.) and **Arthur D. Little, Inc.** (Cambridge, Mass.) announce that they have joined forces to provide air pollution control systems for municipal waste disposal.

**Rex Chainbelt's Ecology Division** has received an \$83,333 contract from the National Environmental Research Center of EPA to develop and demonstrate a method for removal of spilled materials from the bottom of the Little Menomonee River in Milwaukee, Wis.

**Georgia-Pacific** is expanding its new continuous-process panel manufacturing program which converts formerly

wasted wood fiber into an endless hard-board sheet of multipurpose resin-bonded wood. G-P has three such plants in operation and will build a fourth at Crosett, Ark. Cost is about \$3 million.

**The National Society of Professional Engineers** has signed a six-month, \$21,000 contract with EPA's Office of Air Programs to conduct a salary analysis of air pollution control personnel in the private business sector.

**Compaktion Engineering** (Miami, Fla.) has appointed Tepco of Florida, Inc. (Miami, Fla.) and Environmental Control of Illinois (Carterville, Ill.) as distributors of the firm's heavy-duty compaction equipment.

**Houston Research, Inc.** will be acquired by a group of investors headed by Arthur E. Nall from its present owner, sci systems, Inc. (Huntsville, Ala.). Nall will be president of the firm which is expanding its current activities in water desalination, oil cleanup, and development of waste treatment processes.

**Peabody Engineering Corp.** will design and furnish a wet-scrubbing system to remove fly ash from the 630-MW unit No. 4 of Potomac Electric's Chalk Point generating station in Prince George's County, Md. The system will cost in excess of \$2 million.

**Dow Chemical Co.** has announced licensing of its automatic phosphate analyzer to Ionics, Inc. (Watertown, Mass.). The instrument is designed to analyze phosphate content of municipal waste water.

**American Cyanamid Co.** will build a new acrylamide plant at its Frontier complex in New Orleans, La. Acrylamide is used in the production of polymers to aid flocculation and sludge dewatering.

**Research-Cottrell** will supply a counter-flow natural draft cooling tower for Arkansas Power and Light Co.'s Arkansas Nuclear One plant. The multi-million dollar tower is designed for a flow rate of 404,000 gpm.



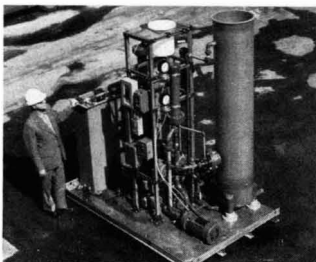


## Phenols test kit

Simplified version of "Standard Methods" colorimetric test for phenols uses patented vacuum-reagent ampuls to eliminate usual problems of reagent handling and stability. Reliable results can be obtained by nontechnical personnel in less than a minute. CHEMetrics, Inc. **61**

## Recorder

Portable battery-operated unit employs sonar to measure and record the level of any liquid waste without actually contacting the waste stream. Corrosion resistant PVC sensor is not subject to buildup. C. W. Stevens, Inc. **62**



## Clarifier

Compact waste water treatment system provides economical separation of emulsified oils from industrial and commercial process discharges. Unit adapts chemical coagulation and air flotation principles to clarify water at rates of less than 20,000 gpd. Tenco Hydro/Aerosciences, Inc. **63**

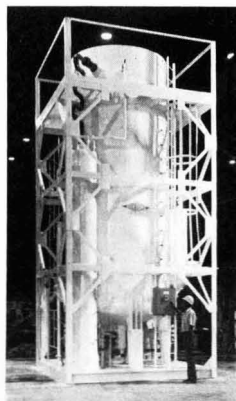
## Velocity meter

Air velocity meter boasts newly designed probe that features small diameter noncorrosive tubing as sensing element instead of delicate wires. Meter

with probe is available in several velocity ranges with logarithmic scale to permit expansion for lower velocities. Can be used for other gases as well as air. Hastings-Raydist **64**

## Cooling systems

Modular evaporative cooling system uses sonic atomizing nozzles to inject a fog of ultrafine water droplets into hot gaseous effluents. Typical applications include smelters, waste incinerators, generating stations, and kilns. Sonic Development Corp. **65**



## Ion exchanger

Commercial size fluidized bed ion exchange unit can continuously treat 600 gpm industrial liquid waste. Water can be recycled or safely vented to public waterways. Liquitech, Inc. **66**

## Oil/water separator

Separator is designed to remove oil from water where oil content is greater than 25 ppm. Unit uses system of regulated compartmentation, leveling gates, and controlled flow to separate liquids. Flow rates from 10-1000 gpm available. Automatic Filter Systems, Inc. **67**

## BOD instrument

Electronic instrument measures BOD of waste water by measuring pressure decrease in head space as microorganisms deplete oxygen supply in test flask. Mechanical sensor activates a cell which generates oxygen electrolytically until pressure is restored to equilibrium value. Ecological Controls, Inc. **68**



## Visible emissions monitor

Low-maintenance visible emissions monitor has electronic components housed in weatherproof case and yields readout in percent opacity on a meter or, if desired, on a recorder for permanent records. Finds application in stack monitoring. Leeds & Northrup **69**

## Combustible gas monitor

Compact instrument will detect gasoline, propane, methane, smoke, carbon monoxide, and most common industrial solvents with solid state sensor that will not burn out in high gas concentration. Remote sensor activates alarm, and meter indicates concentration levels. International Sensor Technology **70**

## Organic carbon analyzer

Direct reading instrument gives rapid measurement of total organic carbon and total carbon in water. Instrument determines carbon content directly, not by difference, from single sample. Uses chemical oxidation followed by nickel/hydrogen reduction and hydrogen flame detection of methane produced. Envirotech Corp., Dohrmann Div. **71**

## Airport pollution monitor

Mobile monitoring system aids in developing program for dealing with noise and air pollution generated by airport traffic and aircraft emissions. Instrument Systems Corp. **72**

*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

**Oxygen analysis.** Four-page brochure describes company's flue gas and industrial oxygen analyzers working on paramagnetic principle. Includes typical applications and detailed specifications. Taylor-Analytical Instrument Div. **91**

**Microscopy.** New publication outlines various techniques using optical microscopy for detection and measurement of pollutants in air, water, and food products. Bausch & Lomb **92**

**Flocculants.** Wide range of industrial flocculants and water treatment chemicals are described in booklet. Lists applications for paper and steel mills, chemical plants, refineries, and sewage treatment plants. American Cyanamid Co. **93**

**Chelant information.** Technical paper answers questions about chelant properties—effects on economizer operation, boiler corrosion, relation to oil contamination, effects on steam blanketing situations, and more. Betz. **94**

**Lift station.** Brochure describes operation of packaged lift station for handling small flows with solids up to 3½ in. Capacity is from 20–75 gpm with heads to 150 ft TDH. Marolf, Inc. **95**

**Turbine silencer.** Reprint of magazine article tells how company silenced aircraft turbines on converted floating power plant with acoustical package. Industrial Acoustics Co., Inc. **96**

**Anticorrosion agents.** Bulletin describes use of additives to solve a wide range of corrosion problems affecting utility power stations such as fireside fouling, air heater corrosion, acid smut, and waterside condenser corrosion. Apollo Chemical Co. **97**

**Chromatography catalog.** New pocket-sized comprehensive catalog lists offering of firm in gas chromatography. Carle Instruments, Inc. **98**

**Pollution control.** Illustrated booklet describes company's specialty chemical

offerings and details consulting services available for combating all forms of pollution. Nalco Chemical Co. **99**

**Ultrafiltration.** Buyers guide and catalog provides comprehensive information about ultrafiltration membranes and equipment for desalting, concentration, and fractionation uses. Includes price list. Amicon Corp. **100**

**Data Sheet.** Leaflet describes company's proprietary coagulation/sedimentation package for water treatment/industrial effluent treatment. Andoc Environmental Processes, Inc. **101**

**Newsletter.** Hydromike is a quarterly publication distributed free to those interested in water and fluid waste measurement and instrumentation. Current issue is devoted to articles on digital recording and telemetry. Leupold & Stevens, Inc. **102**

**Fasteners.** Booklet gives details of operating experience with nickel stainless steel components in water and waste treatment plants. International Nickel Co. **103**

**Sampling techniques.** Bulletin describes principles of sampling effluent streams and tells how to tailor sampling techniques to characteristics of the stream to be sampled. Denver Equipment Div., Joy Mfg. Co. **104**

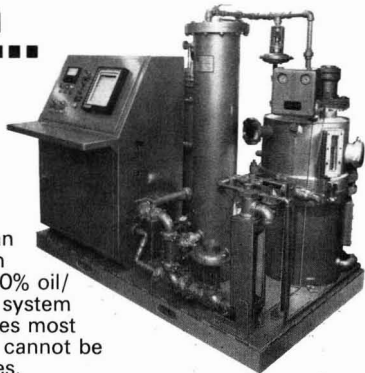
**Spectra.** Literature describes collection of newly obtained infrared reference spectra for coating chemicals and specialty water treatment chemicals. Sadtler Research Laboratories, Inc. **105**

**Reverse osmosis.** Booklet tells of company's reverse osmosis system and details applications of system in demineralization, removal of organics, purification, and concentration. Illinois Water Treatment Co. **106**

**Silencer.** Bulletin describes operation of silencer that reduces sound caused by gas streams by exhausting to the atmosphere at sonic velocities. King Tool, Inc. **107**

**Film list.** Brochure describes loan films available for free viewing which deal with issues of social concern, including pollution. Modern Talking Picture Service, 2323 New Hyde Park Road, New Hyde Park, N.Y. 11040. (Write direct.)

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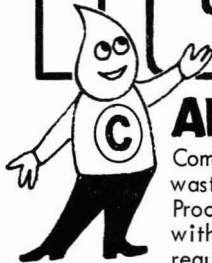


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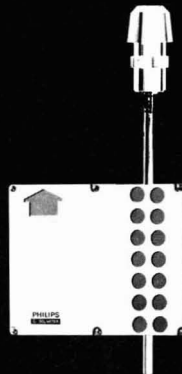
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# bookshelf

**Electret Devices for Air Pollution Control.** Thomas Kallard, Ed. vii + 126 pages. Optosonic Press, Box 883, Ansonia Station, New York, N.Y. 10023. 1972. \$9.95, paper.

This volume relates generally to the various methods of producing electrets—a permanently polarized dielectric that can be used as a source of an electrostatic field and, more particularly, to their applications in air pollution control. Twenty-one patents are fully described. ■

**Lead: Airborne Lead in Perspective.** xi + 330 pages. National Academy of Sciences, 2101 Constitution Ave., Washington, D.C. 20418. 1972. \$6.50, paper.

National Academy of Sciences report of current knowledge of airborne lead to serve as a background for preparation of criteria documents and EPA decisions and to make recommendations for research where sound information is lacking. Discusses strictly biological aspects thoroughly and nonbiological effects of lead in brief. ■

**Environmental Law, Vol. 2, No. 1.** Cary V. Abbott, Ed. x + 312 pages. Lewis and Clark College, 10015 S.W. Terwilliger Blvd., Portland, Ore. 97219. 1972. \$6.00 per volume of 2, paper.

Published twice annually by students of the Northwestern School of Law of Lewis and Clark College. Devoted primarily to the problems of man and his environment with emphasis on workable solutions. Contains both legal and scientific articles. ■

**Air Pollution, Part A: Analysis.** Joe O. Ledbetter. xii + 424 pages. Marcel Dekker, Inc., 95 Madison Ave., New York, N.Y. 10016. 1972. \$11.95, paper.

Discusses the measurement of the air pollutant and the evaluation of the problem presented by the pollutant. Since engineers have an important role in informing decision-makers in pollution control as well as carrying out the control, Dr. Ledbetter hopes "that this book will aid the engineer in his job." ■

**Upper Mississippi River Comprehensive Basin Study.** Division Engineer, U.S. Army Engineer Division, North Central, 536 S. Clark St., Chicago, Ill. 60605. 1972. \$33.

Designed to develop a framework for the best use, or combination of uses, of water and related land resources to meet the future needs of the Upper Mississippi river basin. ■

**Environmental Conservation, 3rd ed.** Raymond F. Dasmann. xi + 473 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1972. \$10.50, hard cover.

Looks at environmental and human problems from an ecological viewpoint. Attempts to provide a factual basis on which action to improve the environment can be taken. Each chapter is well illustrated. ■

**Proceedings of the Third Mineral Waste Utilization Symposium.** Murray A. Schwartz, Ed., vi + 445 pages. IIR Research Institute, 10 W. 35th St., Chicago, Ill. 60616. 1972. \$17.50, hard cover.

Reports on the current state-of-the-art in solving mineral waste disposal problems and recycling to useful products. Contains over 60 papers reporting on such subjects as mining and mineral wastes, industrial wastes, scrap metals, and municipal refuse. ■

**Waste Heat Utilization.** Marvin M. Yarosh, Ed. viii + 348 pages. National Technical Information Service, U.S. Department of Commerce, Springfield, Va. 22151. 1972. \$6.00, paper.

"It was the intent of the conference," says Editor Yarosh, "not only to present a status of technology and technical applications of heat use but also to explore the often less tractable problems of implementation of heat use." Individuals experienced in marketing, regulation, legal and industrial problems, and financial aspects participated. ■

**Determination of Air Quality.** Gleb Mamantov, W. D. Shults, Eds. xii + 197 pages. Plenum Publishing Corp., 227 W. 17th St., New York, N.Y. 10011. 1972. \$13.50, hard cover.

Introduction to air pollution control. Composed of data submitted by chemists, physicians, engineers, administrators, and systems analysts. The Proceedings of an ACS symposium held in Los Angeles, Calif., April 1-2, 1971. Considered a contribution to the present state of science and technology. ■

**Methods of Air Sampling and Analysis.** xvii + 480 pages. American Public Health Association, 1015 Eighteenth St., N.W., Washington, D.C. 1972. \$12.50, hard cover.

First published volume of methods for air sampling and analysis adopted as "tentative" by the Intersociety Committee for a Manual of Methods of Air Sampling and Analysis. The Intersociety Committee was organized in 1963 and consists of 10 organizations. ■

**Detergency: Theory and Test Methods, Part 1.** W. G. Cutler, R. C. Davis. ix + 451 pages. Marcel Dekker, Inc., 95 Madison Ave., New York, N.Y. 10016. 1972. \$28.50, hard cover. ■

Presents a compilation of detergency test methods in use as well as the theoretical basis of these tests. Includes the relationship of detergents to the environment. Reference for academic and industrial researchers or students in the textiles, soap, coatings, lubricants, petroleum, drug, and food industries. ■

**Biology of Brackish Water.** Adolf Remane, Carl Schlieper. viii + 372 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1972. \$21.75, hard cover.

Translation of earlier German works but revised and covering a broader field of knowledge. The authors, editors, and publisher hope that this English edition will stimulate international research on brackish water and enlarge the general scientific interest in this field. ■

**The Saving of San Francisco Bay.** Rice Odell. xii + 115 pages. Conservation Foundation, 1717 Massachusetts Ave., N.W., Washington, D.C. 20036. 1972. \$3.00, paper.

Book is about the functioning of a regional governmental agency. Traces citizen's movement to save the Bay from excessive encroachment by developers and then describes the function of the San Francisco Bay Development and Conservation Commission. ■

**Environmental Measurement and Interpretation.** Robert B. Platt, John F. Griffiths. xii + 235 pages. Robert E. Krieger Publishing Co. Inc., Box 542, Huntington, N.Y. 11743. 1972. \$12.50, hard cover.

Textbook and reference manual designed to meet the need for gathering literature on the instrumentation and analysis of environmentally oriented research. Concerned primarily with the terrestrial environment. Intended for botanists, zoologists, scientists, engineers, and others in the environmental field. ■

**UCSB Oil Spill Index Catalog.** Robert W. Holmes, Ed. Four Vols. Oil Spill Information Center, Marine Science Institute, University of California at Santa Barbara, Santa Barbara, Calif. 93106. 1972. \$275.

Key to information on oil spills around the world. Contains maps, photographs, unpublished manuscripts, patents, pamphlets and letters, and collections of journalistic works providing a framework of oil spill incidents, public reaction, government legislation, and court action. ■

**The Economic Impact of Pollution Control.** 332 pages. U.S. Department of Commerce, National Industrial Pollution Control Council, Washington, D.C. 20230. 1972. \$2.50, paper.

Purpose is to put into perspective studies which were conducted to assess the economic impacts of air and water pollution abatement requirements on a

number of industrial activities. Report was prepared for the Council on Environmental Quality, Department of Commerce, and federal Environmental Protection Agency. ■

**Nitrogen Metabolism and the Environment.** J. W. Campbell, L. Goldstein, Eds. xi + 318 pages. Academic Press, 111 Fifth Ave., New York, N.Y. 10003. 1972. \$13.95, hard cover.

Covers the regulation of nitrogen metabolism in animals. Discusses both biochemical and physiological regulatory mechanisms relative to their function in the adaption of animals to different environmental situations. Water restriction in the terrestrial and marine environment and environmental pollution are investigated at different biological levels. ■

**Chemosphere.** Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, N.Y. 10523. 1972. \$35 annually.

Interdisciplinary journal designed for publication of articles related to environmental affairs and reporting scientific investigations in the fields of chemistry, physics, and biology. Emphasis placed on evaluation of changes in the atmosphere, in water, and on land in relation to plants, animals, and man. Published bimonthly. ■

**Conflicts in Water Resources Planning.** Earnest F. Gloyna and William S. Butler, Eds. x + 172 pages. Center for Research in Water Resources, The University of Texas at Austin, Austin, Tex. 78757. 1972. \$15, hard cover.

Contains lectures that examine the conflicts in water resources planning in the belief that understanding the issues is essential if basic conflicts are to be resolved. Deals with such important issues as conservation of resources and the relation of water resources planning to land use policy, the government's role in resources planning, and ecology. ■

(Continued on p 844)

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**Pollution Analyzing and Monitoring Instruments.** vii + 354 pages. Noyes Data Corp., Noyes Bldg., Park Ridge, N.J. 07656. 1972. \$36, paper.

Gives basic technical information on "step one" in a systems approach to total war on pollution. Descriptions of what is available in ready-made, on-the-line commercial equipment for sampling, measuring, and analyzing pollutants found in the air, in water, in soil and food or foodstuffs, or noise and radiation. ■

**SOS Books.** 244 pages. Snyder Oceanography Services, P.O. Box 98, Jupiter, Fla. 33458. 1972. \$2.35, paper.

Catalog of environmental science and technology books. Lists over 3000 books in print from the U.S. and abroad. Organized into six major categories—environmental sciences, engineering & technology, commerce, natural resources, glossaries, and juvenile books. ■

**ASCATOPICS.** Institute for Scientific Information, 325 Chestnut St., Philadelphia, Pa. 19106. Begun 1972. Usually \$95 annually.

Information alerting service that provides subscribers with weekly bibliographies of literature published in the areas of environmental science, medicine, biology, and chemistry. Emphasis on the adverse effects of pollutants, food additives, pesticides, and drugs. ■

**The Domination of Nature.** William Leiss. xii + 242 pages. George Braziller, Inc., One Park Ave., New York, N.Y. 10016. 1972. \$6.95, hard cover.

Historical and critical approach describing the circumstances in which the modern versions of the idea of the domination of nature first arose, how it became associated with science and technology achievements, and why it became a powerful ideology in society. ■

**Salinity and Water Use.** T. Talsma, J. R. Philip, Eds. viii + 296 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1972. \$17.95, hard cover.

Papers from the second National Symposium on Hydrology. Offers up-to-date review of the scientific and, to some extent, social backgrounds, both

of which are problems of natural and man-made salinity. Papers range from geochemistry, soil physics, hydraulics, and biology of salinity to legal and administrative aspects. ■

**The Air Pollution Control Market.** 150 pages. Frost & Sullivan, Inc., 106 Fulton St., New York, N.Y. 10038. 1972. \$345.

Identifies and projects industrial and government markets for pollution control equipment and services. Contains technical information which defines gaseous and particulate pollutants, gives the state of development of major pollutant control equipment classifications, discusses sulfur dioxide, and provides profiles of 13 leading pollution control companies. ■

**The Careless Technology: Ecology and International Development.** M. Taghi Farvar, John P. Milton, xxix + 1030 pages. The Natural History Press, Garden City, Long Island, N.Y. 11530. 1972. \$25, hard cover.

Explores the relationships between technological development in the Third World nations and the ecological strains that "progress" creates. Contains 50 case studies. Follows the theme that too often science and technology are used to conquer the world rather than help people live better in it. ■

**Ecological Aspects of the Nuclear Age: Selected Readings in Radiation Ecology.** Vincent Schultz. 588 pages. National Technical Information Service, U.S. Dept. of Commerce, Springfield, Va. 22151. \$6.00, paper.

Scientific literature compiled to bring together summary papers, ecosystems studies, and historical background papers around which the radiation ecology developed. Covers terrestrial and marine and freshwater environments. Intended for concerned individuals and groups outside the radiation ecology community. ■

**Handbook of Environmental Management, Vol. 1: Fundamentals.** Charles J. Hilado. xi + 113 pages. Technomic Publishing Co., Inc., 265 W. State St., Westport, Conn. 06880. 1972. \$25, paper.

Synthesis of up-to-date information on population, food, water, air, materials, and energy. Each section is supplemented by data tables and references. Designed for both the general reader and

the professional. Provides information on the environment, environmental problems, and remedies. Also useful for study programs, reference, and bibliography. ■

**Journal of Environmental Quality.** American Society of Agronomy, 677 S. Segoe Rd., Madison, Wis. 53711. \$10 annually, paper.

Brings together reviews and technical reports on all aspects of the environment (not limited to agricultural practices). Includes effects of practices and chemicals on ecosystems, pest control programs, waste disposal, and land use development. Four issues annually. ■

**Air Pollution Control, Part 2.** Werner Strauss, Ed. xi + 300 pages, John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1972. \$14.95, hard cover.

Provides reviews in areas of current importance in air pollution control. Each article is aimed to completely cover theory, experimentation, and practice in the field discussed. Especially valuable to those planning research in the areas reviewed. ■

#### Films

**Environmental Pollution.** Environmental Communications, 62 Windward Ave., Venice, Calif. 90291. \$50.

Set of 40 color slides. Visual survey of sea, air, and land pollution in urban and rural areas of California. ■

**The 1st Pollution.** Stuart Finley Inc., 3428 Mansfield Rd., Falls Church, Va. 22041. 1972. \$300.

Film about water pollution problems: what they are, who produces them, what's being done about them, and what'll happen in the future. Reports on current efforts to clean up U.S. waters. Cites comparison between earlier pollution problems and conditions today. Excellent photography. ■

#### Record

**Spaceship Earth.** Addison-Wesley, Menlo Park, Calif. 94025. 1972. \$5.95.

Songs by Pete Seeger, vignettes of American life, and straight talk from people knowledgeable in the environment. Based on broadcasts from CBS News and the CBS *News Magazine of the Air*. Originally produced for distribution in schools. ■

# meeting guide

## September 24-27

### U.S. EPA

National Environmental Information Symposium  
Cincinnati, Ohio

Forum for producers and handlers of environmental data to identify and explain resources and methods. To bring together groups and organizations to share objectives and interests related to the production, use, and dissemination of environmental information. Contact: Gilbert M. Gigliotti, Director, Public Affairs Office, National Environmental Research Center, U.S. EPA, Cincinnati, Ohio 45268

## September 27-29

### Western Canada Section, American Water Works Association

24th Annual Western Canada Water and Sewage Conference and Operator's School

Regina, Saskatchewan, Canada

Contact: D. A. Shillabeer, c/o Division of Pollution Control, 6th Floor Milner Bldg., 10040-104th St., Edmonton, Alta., Canada

## September 28-29

### Paper Technology Foundation, Inc.

Thirteenth Annual Meeting  
Kalamazoo, Mich.

Contact: Paul W. Bartholomew, Executive Secretary, Paper Technology Foundation, Inc., Western Michigan Univ., Kalamazoo, Mich. 49001

## September 28-30

### American Assoc. of Textile Chemicals & Colorists

National Technical Conference  
Philadelphia, Pa.

Contact: George P. Paine, AATCC, P.O. Box 12215, Research Triangle Park, N.C. 27709

## October 2-3

### American Medical Association

1972 Air Pollution Medical Research Conference

Chicago, Ill.

Sessions on familial and inherited response to air pollution, air pollution and human illness, health effects research, and epidemiology. Write: Department of Environmental, Public, and Occupational Health, American Medical Association, 535 N. Dearborn St., Chicago, Ill. 60610

## October 4

### American Society for Testing and Materials

Committee on Toxic Materials and Harmful Physical Agents Organizational Meeting

Philadelphia, Pa.

For additional information, B. J. Corrigan or R. D. Bauer, ASTM, 1916 Race St., Philadelphia, Pa. 19103

## October 4-6

### Institute of Noise Control Engineering and others

International Noise Control Engineering Conference and Equipment Exposition  
Washington, D.C.

Comprehensive technical program and product display in fields of noise/vibration/shock control and hearing conservation. Contact: INTER-NOISE 72, c/o Applied Acoustics Section, Mechanics Div., National Bureau of Standards, Washington, D.C. 20234

## October 8-13

### Water Pollution Control Federation

WPCF Conference

Atlanta, Ga.

Write: Robert A. Canham, WPCF, 3900 Wisconsin Ave., Washington, D.C. 20016

## October 9-12

### Association of Official Analytical Chemists

86th Annual Meeting

Washington, D.C.

Papers on analysis of feeds, fertilizers, food additives, pesticides, and related subjects. Contact: L. G. Ensminger, Executive Secretary, AOAC, Box 540, Benjamin Franklin Station, Washington, D.C. 20044

## October 9-12

### Instrument Society of America

27th Annual ISA Conference

New York, N.Y.

Includes papers on major sectors of instrumentation and automatic control including pollution control. Write: R. I. Gray, ISA Conference Program Chairman, 400 Stanwix St., Philadelphia, Pa. 15222

## October 10-11

### Industrial Health Foundation

37th Annual Meeting

Pittsburgh, Pa.

Discussions will cover standards for OSHA, toxicology, industrial hygiene engineering, and other related topics. Contact: IHF, 5231 Centre Ave., Pittsburgh, Pa. 15232

## October 11-12

### Society of Plastics Engineers

Regional Technical Conference

Chicago, Ill.

Theme "PlastEcology—1972" includes 17 speakers dealing with plastics and ecology. Contact: Robert N. Bose, CO<sub>2</sub> Consultants Co., 303 E. Elm St., Wheaton, Ill. 60187

## October 11-19

### Institute of Sanitation Management

15th Annual ISM National Conference and Exposition

Philadelphia, Pa.

Will cover federal environmental standards, planning, and assistance; economics; and education. Write: ISM, 1710 Drew St., Clearwater, Fla. 33515

## October 15-17

### Virginia Polytech Institute and State University

The Environment—Conflicts, Costs, Action Conference  
Blacksburg, Va.

Proposes to give editors and reporters covering the environment concentrated background in ecology. Write: Mary Ann Johnson, Burruss 400, Virginia Tech, Blacksburg, Va. 24061

## October 15-18

### Institute of Sanitation Management

National Environmental Sanitation & Maintenance Management Educational Conference

Philadelphia, Pa.

Aimed at environmental sanitation maintenance management personnel as well as supervisors, foremen, and related personnel. Write: ISM, 1710 Drew St., Clearwater, Fla. 33515

## October 18-20

### National Automatic Laundry and Cleaning Council and National Carwash Council

1972 National Convention-Exposition  
Chicago, Ill.

Features problems and possible solutions to pollution, waste water, and recycling. Write: NALCC-NCC, 7 S. Dearborn St., Chicago, Ill. 60603

## October 24-26

### Engineers Society of Western Pa.

33rd International Water Conference  
Pittsburgh, Pa.

Write: W. M. Porter, Secretary, Engineers Society of Western Pennsylvania, William Penn Hotel, Pittsburgh, Pa. 15219

## October 24-28

### Federation of Societies for Paint Technology

50th Annual Meeting

Atlantic City, N.J.

Includes topics on air pollution control, water pollution control, and solid waste disposal. Contact: Federation of Societies for Paint Technology, 121 S. Broad St., Philadelphia, Pa. 19107

## October 25-26

### New York State Action for Clean Air Committee

Eighteenth Annual Symposium on the Environment and Health  
Syracuse, N.Y.

Theme "Environmental Education for the Adult Public." Write: New York State Action for Clean Air Committee, 105 E. 22nd St., New York, N.Y. 10010

(Continued on p 846)

**October 25-28**

**Clackamas Community College**

Environmental Technology Show  
Oregon City, Ore.

Will focus on new technological equipment and research. For information: Marvin Weiss, Community Services Office, 19600 S. Molalla Ave., Oregon City, Ore. 97045

**Courses**

**September 25-29**

**University of Texas at Austin**

Advanced Water Pollution Control: Biological Waste Treatment Short Course  
Austin, Tex.

Contact: Engineering Institutes, P.O. Box K, University of Texas at Austin, Austin, Tex. 78712

**September 27-28**

**George Washington University**

Air Pollution Control Short Course  
Washington, D.C.

State-of-the-art information on air pollution control for engineers and technical personnel working in this field. Fee: \$145. Contact: Continuing Engineering Education Program, George Washington Univ., Washington, D.C. 20006.

**September 28-29**

**University of Wisconsin**

Structural Design of Sanitary Engineering Facilities Short Course  
Milwaukee, Wis.

Based on improving and maintaining environmental quality. Fee: \$95. Write: University of Wisconsin—Milwaukee Civic Center Campus, 600 W. Kilbourn Ave., Milwaukee, Wis. 53203

**October 2-5**

**B&K Instruments, Inc.**

Industrial Noise Control Seminar  
Cleveland, Ohio

Objective is to provide information necessary successfully to implement industrial noise control programs. Fee: \$135. Contact: B&K Instruments, Inc., 5111 W. 164th St., Cleveland, Ohio 44142

**October 5-6**

**International Association on Water Pollution Research**

Toward a Unified Concept of Biological Waste Treatment Design Seminar  
Atlanta, Ga.

Will discuss mathematical models in present use and factors affecting their use and applications. Registration: \$125. Contact: Fred G. Pohland, Civil Engineering Department, Georgia Institute of Technology, Atlanta, Ga. 30300

**October 5-6**

**University of Wisconsin—Extension**

Applications of Remote Sensing to Urban and Regional Planning Institute  
Madison, Wis.

Will present a picture of how various remote sensing devices can be used and should be used to study urban problems. Fee: \$100. Contact: Donald E. Baxa, Program Director, Dept. of Engineering, University of Wisconsin—Extension, 432 N. Lake St., Madison, Wis. 53706

**International**

**September 25-27**

**Water Research Association**

Groundwater Pollution Conference  
Reading, England

Contact: The Water Research Association, Medmenham, Marlow, Buckinghamshire, SL7 2HD, England

**October 2-6**

**Commission of the European Communities and U.S. EPA**

International Symposium on Environmental Health Aspects of Lead  
Amsterdam, The Netherlands

Program will cover uptake and metabolism, subclinical effects, epidemiological studies, sources, and monitoring. Write: J. Smeets, Secretary, Health Protection Directorate, Commission of the European Communities, 29 Rue Aldringen, Luxembourg

**October 3-4**

**Office of Civil Engineers**

Management of National and Regional Water Resources Conference  
London, England

Contact: Conference Office, Institution of Civil Engineers, Great George St., Westminster, London, SW1P 3AA, England

**October 4-9**

**Japan Management Association**

International Ocean Development Conference  
Tokyo, Japan

Information from Secretariat, International Ocean Development Conference, Japan Management Assoc., No. 25, Shiba Park, Minato-ku, Tokyo, Japan

**October 10-14**

**Society of Chemical Engineers (Japan) and AIChE**

First Pacific Chemical Engineering Congress  
Kyoto, Japan

Includes sessions on air pollution control and water pollution control. Write: American Institute of Chemical Engineers, Japan Meeting, 345 E. 47 St., New York, N.Y. 10017

**October 16-20**

**National Society for Clean Air**

39th Annual Conference  
Scarborough, England

Contact: National Society for Clean Air, 134-137, North St., Brighton, BN1 1RG, England

**October 26, 1972-September 7, 1973**

**UNESCO**

International Course in Environmental Science and Technology  
Delft, The Netherlands

Postgraduate course is related to inter-governmental research program on "Man and the Biosphere" focusing on causes, implications, and solutions of environmental problems. Contact: Netherlands Universities Foundation for International Cooperation, 27 Molenstraat, The Hague, The Netherlands

**November 3-9**

**Sewage Engineering Association of the German Federal Republic and others**

International Sewage and Refuse Engineering Exhibition and European Sewage and Refuse Symposium

Munich, Germany

Address Inquiries to: Wissenschaftlicher Leiter des EAS 73 Munchen, Gunter Muller-Neuhaus, Technische Universität Munchen, D-8000 Munchen 2, Arcisstrasse 21, West Germany

**November 15-19**

**U.S. Trade Center and ANTINQUINAMENTO '72**

PURAU—PURARIA '72

Milan, Italy

Contact: Don Johnson, Project Officer, Bureau of International Commerce (Ref: 948), U.S. Dept. of Commerce, Washington, D.C. 20230

**December 4-8**

**Ministry of Water Resources (Mexico) and International Association of Hydrological Sciences**

International Symposium on the Planning of Water Resources

Mexico City, Mexico

International experts will compile methodologies and experiences of many countries toward enhancement of international cooperation. Contact: Ing. Gerardo Cruickshank G., Subsecretario de Planeación, Secretaría de Recursos Hídricos, Reforma No. 69-11° Piso, Mexico, D.F.

**June 4-9, 1973**

**UNESCO and others**

International Symposium on the Development of Water Resources Projects with Inadequate Data

Madrid, Spain

Write: David R. Dawdy, U.S. Geological Survey, Engineering Research Center, Colorado State Univ., Foothills Campus, Fort Collins, Colo. 80521

**July 1973**

**AAAS and National Council of Science and Technology of Mexico**

1973 Inter-American Scientific Meeting

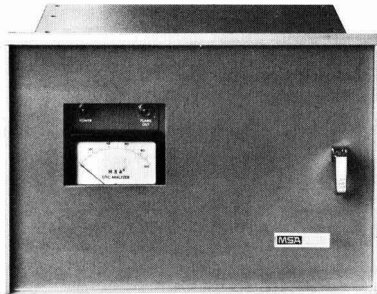
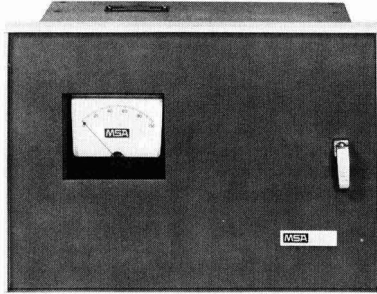
Mexico City, Mexico

Includes air and water pollution discussions. Contact: American Association for the Advancement of Science, 1515 Massachusetts Ave., N.W., Washington, D.C. 20005

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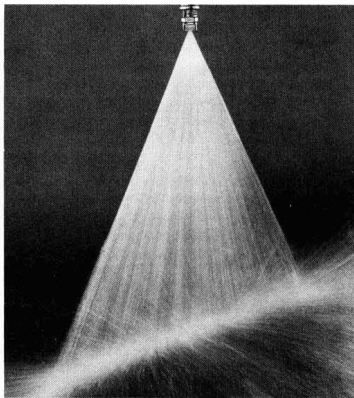
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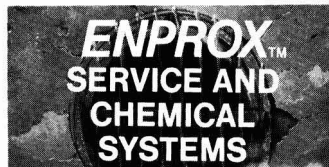
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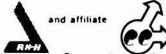
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142 East Ave.,  
Norwalk, Conn. 06851  
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Various state laws against discrimination and the Federal Civil Rights Act of 1964 prohibit discrimination in employment because of sex unless based on a bona fide occupational qualification. Help wanted and situations wanted advertisements on these pages are for readers' convenience and are not to be construed as instruments leading to unlawful discrimination.

## DESIGN ENGINEER

A well known consulting environmental engineering firm needs a Senior Associate Engineer for the St. Louis Office. P.E. registration and capable of being licensed in Missouri, Tennessee and Illinois, plus 8-12 years experience. Will design varied size wastewater treatment plants up to 10 MGD, manage design teams, write specs, develop standard cost and design packages. Salary \$15,000-\$22,000. Send resume in confidence to Box #972-3, Environmental Science & Technology, Easton, Pa. 18042.  
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## ENVIRONMENTAL ENGINEERS

We have many position openings in U.S. for professionals experienced in the design, application and/or sale of air, water or waste pollution control equipment, chemicals and systems. Client companies pay fees. Send resume & salary history in confidence to Roger M. Hoffman.

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You will be involved with environmental impact statements, plant location studies, plus consultation on applications for pollution permits, and interpretation of current regulations and design methods to achieve compliance and secure Federal and State permits for your respective areas.

**WATER POLLUTION (Civil or Sanitary)** Responsibilities will include organization and supervision of preparation and presentation of applications for Federal and State permits for water discharges, dredging, water front construction, wells, sewage treatment and discharge, solid waste disposal, blasting, road access, and building construction.

**AIR POLLUTION (M.E. or Ch.E.)** You will be responsible for securing permits as regards to air and noise pollution, personnel and safety standards and compliance, aviation obstruction, and other waste discharges. Experience in safety engineering or analysis desirable but not mandatory.

**WASTE TREATMENT (Ch.E.)** Your responsibilities will include treatment and discharge of sanitary sewage and industrial gas, liquid, and solid wastes.

These positions offer unusual opportunities to grow professionally while still permitting enough time to enjoy your families and the pleasant, rustic environment of our Berks County, Pennsylvania Headquarters. We provide excellent salaries to match the responsibilities we'll expect you to assume, plus comprehensive benefits and advancement potential and relocation expenses. You can trust us with your resumes. For prompt consideration, please send them including references and requirements to the personal attention of Carl Mycoff.



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# CLASSIFIED SECTION

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## MISCELLANEOUS

### Business Opportunity

Profitable, financially responsible sanitary maintenance chemical product manufacturer wishes to purchase or merge with knowledgeable and profitable analytical and consulting laboratories in air, water pollution and environmental protection field. Eventual aim—going public. All inquiries will be held confidential. BOX 972-4, ENVIRONMENTAL SCIENCE & TECHNOLOGY, EASTON, PA. 18042

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| 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 |

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| 106 | 107 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 | 119 | 120 |

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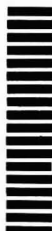
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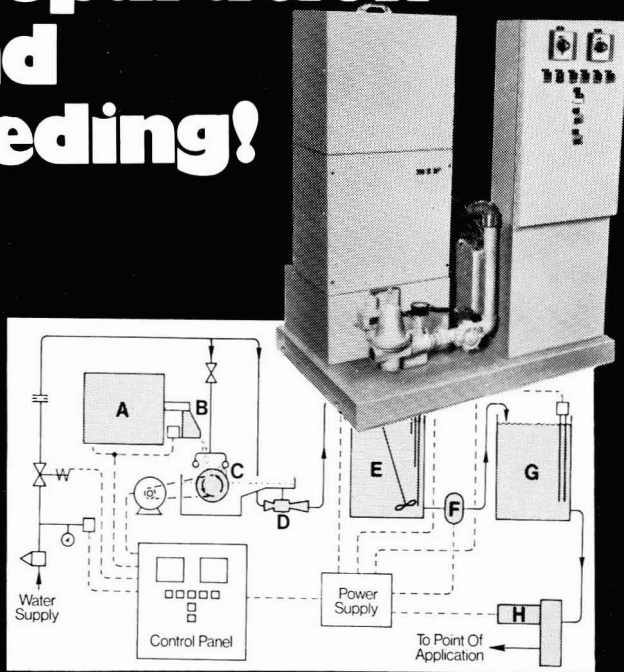
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# A pack of savings for polyelectrolyte preparation and feeding!



**Complete, pre-assembled system includes: Phase I Control panel and (A) Volumetric feeder. (B & C) Conditioning and wetting device. (D) Eductor; Phase II (optional) (E) Mixer and mixing tank. (F) Transfer pump. (G) Feed tank. (H) Metering pump.**

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skids saves assembly time. Find out how Polypak can work for you. Write or call BIF, a unit of General Signal, 326 Harris Ave., Providence, R.I. 02901. Tel: 401-421-4301.

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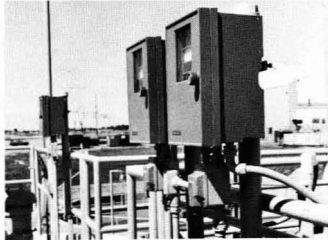
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# WATER AND WASTE CONTROL NEWS

## Air Base Waste Controls Installed

McClellan Air Force Base (California) recently started up its new industrial waste treatment facility under centralized control by a Honeywell automation system.

McClellan is a key base in the Air Force Logistic Command network. A "city" of more than 24,000 persons, its large service and repair shops provide worldwide day and night logistic support for combat jets like the F-111, F-100, and F-105. The 1.2 - 2.4 MGD flow of wastewater from



*Model 54 water management analyzer instruments measure pH and ORP values in neutralizing and chrome reduction tanks at McClellan Air Force Base industrial waste treatment facility and transmit signals to central control panel. Design of Model 54 instruments suits them for outdoor application, with minimum maintenance attention.*

the shop complex contains free and emulsified oils, chrome and acid-bearing solutions, and heavy metal "dragout" from plating operations.

Oils are separated, heavy metals precipitated, chrome reduced, and acids neutralized in the treatment plant. The effluent from the facility is further processed through aeration tanks and a chlorine contact stage before discharge into Magpie Creek which leads into the Sacramento River.

System instrumentation — including the latest Class 54 Analyzer-Transmitters and *VutroniK* electric recording and indicating controllers — was furnished and installed by Honeywell and started up with technical assistance by Honeywell. The facility and control system was designed by the San Francisco consulting firm of Kennedy Engineers.

## Improved Parts Service for Honeywell Customers

Industrial Division's new parts depot at Indianapolis, Ind., is now ready for business to serve needs of customers with 24-48 hour delivery of parts, charts, thermocouples, wire, and stock instruments. 20,000 square feet of floor space provide storage for approximately 12,000 items. The depot is located in Park Fletcher Industrial Park within a short distance of the Indianapolis airport and major through highways.

The Indianapolis depot complements Fort Washington as a centralized source of spare parts for the U.S.

## Inspect our Pollution Control Capabilities at Atlanta Conference

At the Water Pollution Control Federation Conference, to be held at the Municipal Auditorium in Atlanta, Ga., October 8-12, you can get a good feel for the overall water and wastes control capabilities of Honeywell's Industrial Division.

Visit booths 329-331-333. Among the many products on display will be: field-mountable analyzer-transmitters for pH, ORP, conductivity and DO; chlorinator; chemical feeder; residual chlorine analyzer; and miniature, intermediate-size and conventional-size instruments.



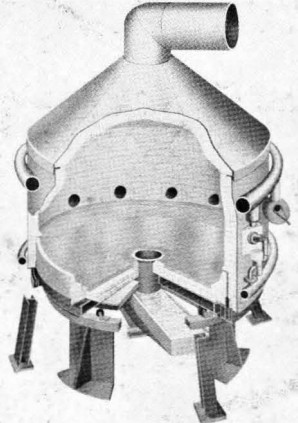
**Honeywell**  
The Automation Company  
INDUSTRIAL DIVISION, M 436,  
FORT WASHINGTON, PA. 19034

Control Instrumentation since 1860

Circle No. 7 on Readers' Service Card

## Old Tires Fuel New Furnace

A new, smokeless, odorless Tire Destruction Furnace, controlled by Honeywell instrumentation, will use old tires as fuel to generate heat feeding a steam boiler for new tire production at The Goodyear Tire & Rubber Company plant in Jackson, Mich.



*Cross-section diagram shows basic configuration of Lucas Tire Destruction Furnace of the type soon to go into operation to generate steam power at The Goodyear Tire & Rubber Company plant in Jackson, Mich. First of its kind in the U. S., the unit will consume about 3,000 old tires a day.*

The unit, to be built and installed by Lucas American Recyclers, Inc., of South San Francisco, will burn whole tires without any shredding to a sterile, inert ash. Tires are fed by conveyor to the outer edge of the furnace's rotating hearth. From there they travel in a spiral to the center where the intense heat—up to 2400 degrees Fahrenheit—is sufficient to oxidize even the wire bead.

*VutroniK* miniature indicating proportional controllers automatically regulate furnace temperatures to achieve optimum combustion conditions.

Completion date for the project, first of its kind in the U. S., is scheduled for late summer. Several Lucas Tire Destruction Furnaces are being operated successfully in England.