



ENVIRONMENTAL Science & Technology

Emphasizing

Water,

Air, &

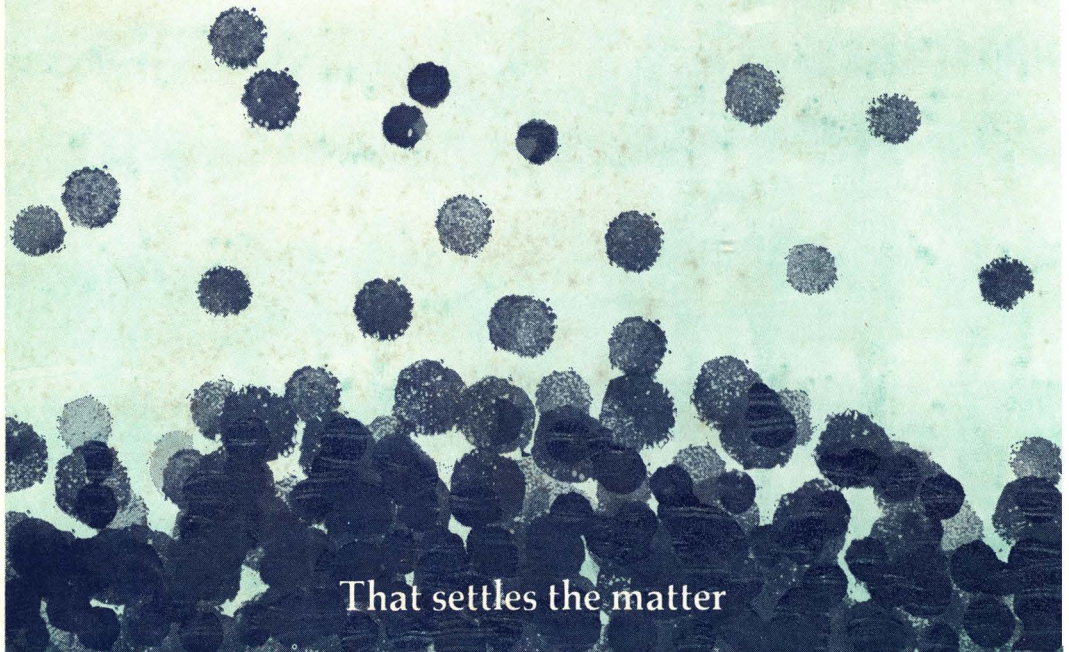
Waste

Chemistry

JANUARY 1970



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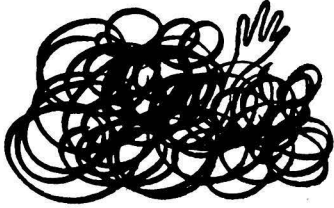
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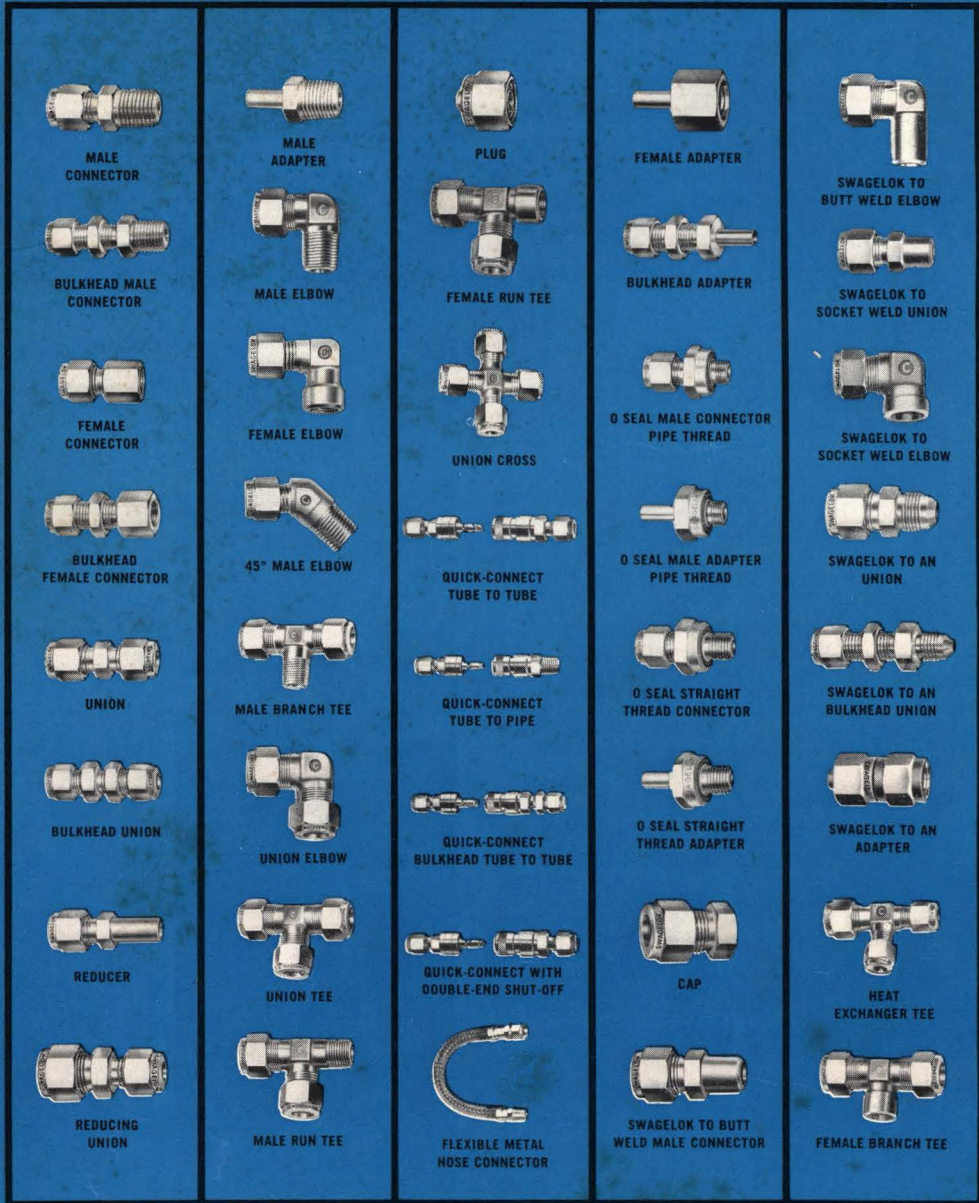
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Current research

- Inhibition of atmospheric photooxidation of hydrocarbons by nitric oxide** 37
W. A. Glasson and C. S. Tuesday

The presence of nitric oxide in such polluted atmospheres as that found in Los Angeles is necessary for the photooxidation inhibition of other pollutants such as hydrocarbons. Atmospheric concentrations of nitric oxide have been found to inhibit photooxidation of five hydrocarbons—propylene, ethylene, *trans*-2-butene, isobutene, and *m*-xylene. These data indicate that hydrocarbon emissions from automobiles should be controlled preferentially than those of oxides of nitrogen.

- Photochemical reactivities of aromatic hydrocarbon-nitrogen oxide and related systems** 44
A. P. Altshuller, S. L. Kopczynski, W. A. Lonneman, F. D. Sutterfield, and D. L. Wilson

Control of olefins and aromatic hydrocarbons effectively reduces the level of photochemical oxidants and decreases the eye irritation response from smoggy atmospheres. The results for toluene indicate that large decreases of nitrogen oxide can be ineffective in reducing oxidant yield. Although eye irritation is reduced with decreasing NO, it would appear that hydrocarbon emissions such as those from automobiles should be controlled preferentially to nitrogen oxides.

- Thermal neutron activation analysis of particulate matter in surface air of the Chicago metropolitan area. One minute irradiations** 50
S. S. Brar, D. M. Nelson, E. L. Kanabrocki, C. E. Moore, C. D. Burnham, and D. M. Hattori

Metals—such as aluminum, vanadium, manganese, and sodium—and halogens—such as chlorine and bromine—have been found in the urban metropolitan area of Chicago, Ill. There also is evidence of other atmospheric pollutants such as seven other metals, and calcium and/or sulfur, based on the analysis of 22 samples.

- Lead and other metal ions in United States precipitation** 55
A. L. Lazrus, E. Lorange, and J. P. Lodge

The concentration of lead in the atmosphere is correlated with the amount of gasoline consumed in the U.S., and the concentration patterns for lead and four other metals—zinc, copper, iron, and manganese—are engendered primarily by human activity. Six months average values collected during 1966–67 from a network of 32 stations reveal that the northwest portion of the U.S. is conspicuously low in contamination; the northeast is relatively high; and the southwest and southeast vary from low to moderate, depending on the metal.

- Kinetics of the reaction of SO₂ with calcined limestone** 59
R. H. Borgwardt

Processes for SO₂ removal from flue gases are of practical importance in achieving air quality standards. Involving the dissociation of calcium carbonate followed by reaction of calcium oxide with SO₂, the sorption of SO₂ by calcined limestone is dependent to a large extent upon the kinetics of the reaction which were found to be first order. And this rate of reaction predominates as the overall rate controlling reaction for conversion of at least the first 20% of the calcium oxide.

- Influence of pH on the adsorption of aromatic acids on activated carbon** 64
T. M. Ward and F. W. Getzen

The removal of acidic persistent chemicals from waste waters is made possible by controlling the pH of aqueous discharges. The three herbicides—2,4-D, Dicamba, and Amiben—are aromatic acids whose sorptions on activated carbon are pH dependent. At pH 3.0, approximately 50% of the herbicides in a 10⁻⁴ molar solution was adsorbed by 0.01 g. of activated carbon in four hours. At pH 7.0, the removal generally ranged from 8–22%, and at pH 11.0, from 2.5–15%, depending on the specific herbicide present.

Communication

- Automated variable flow for pilot plants** 68
W. K. Johnson

A new device has been developed which permits pilot plants at municipal waste water plants to vary the rate of input flow continuously and automatically. The device simulates flows from 13–3800 milliliters per minute and can be used on projects which involve an investigation of the effect of variable flow on the process such as those projects for nitrogen removal by denitrification and others.

Depending on your point of view

Environmental field needs open discussion and resolution of opposing points of view, just as it needs hard facts

Vice President Agnew's recent, well publicized attack on the news media for alleged lack of objectivity in news reporting did not generally strike any raw nerves on the staffs of technical publications, but, nevertheless, we took note of Mr. Agnew's complaints. For, although ES&T was not one of the particular objects of the vice president's displeasure, there have been occasions when it has been accused of being less than totally objective about events in the world of environmental control.

Occasionally, it has been suggested that ES&T has an inbuilt bias against industry, manifested in news stories that, in some people's eyes, carry a strong vein of criticism of "industrial polluters." On the other side of the coin—generally, the nonindustrial side—we have been told that certain stories concerning new technological processes were little more than pieces of free advertising for the companies involved. The reader might care to go over the content of this and other issues of ES&T and decide for himself whether such criticisms are justified.

What must be said immediately is that these criticisms are still rather few and far between, but, despite that fact, the central question of objectivity remains an important one. We tend to agree with news commentator David Brinkley's observation that it is not possible for intelligent human beings to be truly objective; what is possible—and necessary—is that they be fair. In staff written reporting for the Environmental Currents and Outlook departments, ES&T makes every effort to be fair and to present documented or documentable facts. But to scrupulously avoid including any comment which might be construed as biased would inevitably lead to such blandness as to make total unreadability a quite likely result. However, a legitimate desire to provide the reader with readable prose in no way absolves writers

and reporters from the responsibility of seeking out and presenting plain facts.

Having said this, we should make it clear that, as far as humanly possible, opinion will be kept out of the news portions of ES&T. Opinion will continue to appear on this page, and we hope that readers will continue to read our editorials and agree or disagree as they think fit. It should also be explained that opinions on the editorial page are those of the one person who signs them and not necessarily the view of the American Chemical Society or even of other ES&T staff members.

Of course, editors certainly have no monopoly on opinion, either in the field of environmental science and technology and its management or any other subject. In fact, diversity of ideas and freedom to express them are hallmarks of a free society. Presentation, discussion, and reconciliation of differing points of view about our environment are going to be absolutely necessary if we are ever to extricate ourselves from the mess which people, unrestrained technology, and urbanization have wrought.

Recognizing the need for discussion of varying opinions, ES&T is inaugurating a new, one page department (see page 7). Entitled "VIEWPOINT," the monthly page will carry the views of people who have responsibility or deep interest in how the environment can or should be controlled. It is most unlikely that you will agree with all the views to be presented over the months on the VIEWPOINT page—the contributors vary considerably in background and philosophy. If their ideas conflict with yours, you are invited to let us know your opinions, too.

D. H. Michael Bowen

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Kenneth M. Curtis
Governor of Maine

Toward a new environmental attitude

For some years now, it has been evident that Americans are slowly creating a national attitude toward the natural environment of our country. This new attitude may have been a long time in coming and its development still may be slow, but it must be measured against the time span of the three and a half centuries from the arrival of the Pilgrims upon the wilderness shores of North America.

The earliest American attitudes toward our environment were incubated in an atmosphere of unbounded available land, merely waiting to be tamed by axe and plow. The wilderness was the enemy to the early settlers. It was there to be conquered and subdued.

So, bred into the American consciousness right at the start was the idea of "development." This was soon abetted by the many groups of speculators who formed companies for the establishment of towns and communities.

Another part of the American attitude toward the environment was formed by the very abundance of the environment, the seemingly inexhaustible supplies of wildlife, of natural resources, and of public land that an undeveloped country was eager to have exploited for private use.

It was perhaps only at the beginning of this 20th century that we Americans felt our frontiers close in upon us. Gradually, the realization has come upon us that we are no longer the great wilderness and that nothing in nature is inexhaustible. Old attitudes die hard and, every day, we see vestiges of the old modes of thinking that still prevail, whether it is the industry head who cannot understand why he should not go on using a public river or the public air as his private waste ground, or the motorist flipping a cigarette out his window who does not consider that he is using the public roadway as his private ashtray.

Conservation has taken hold as an American ideal. The National Park is an American invention (along with the National Seashore and our system of State Parks), created in response to the need for setting aside areas of the wilderness we once thought would be endless. Now, at long last, we are waking up to the

menace of pollution and litter and the entire complicated process of befouling our own nest.

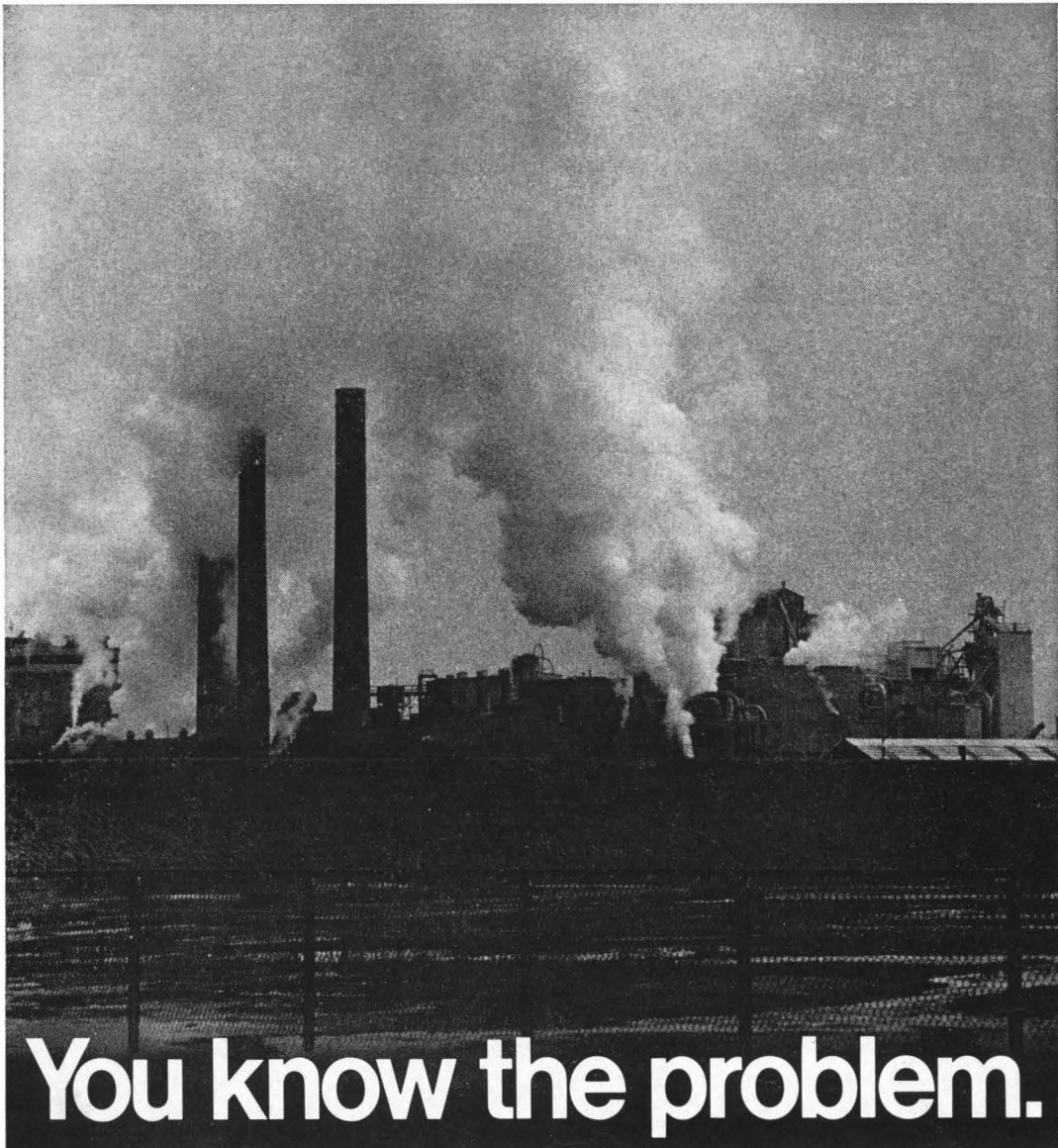
Yet, to a considerable degree, the concern about our environment has not produced, nationwide, the sense of a national obligation as great, say, as our devotion was to becoming the first nation to reach the moon. Our national attention and our national imagination still has not been focused effectively on the problems of our environment. Sufficient funding has not been forthcoming from Washington. And money, alone, is not the entire answer, although without sufficient funding, our environment can neither be cleansed nor protected.

The extension of the new attitude toward our environment must continue on all fronts. Industry has at last begun to see that research into the potential use of wastes has a profit potential, but basic research into pollution has only scratched the surface. Whole new ways of looking at the problem must be considered. One recommendation of my Committee on Pollution Abatement in Maine was for a dedicated anti-pollution fund, similar to the Highway Fund that was responsible for our Interstate Highway System, and this approach has merit. Another thing we have started is a coastal development plan, a comprehensive plan to map the future of our incomparable Maine coast.

On all environmental fronts, there must be this continual seeking of new thoughts and new solutions for both remedying and avoiding the desecration that we Americans have caused to our homeland and are still continuing to cause, even as I write, for the assaults on the American environment have grown worse, not better. The hopeful sign is that we now recognize that there is a problem. With this recognition, therefore, has come the obligation to act.



Kenneth M. Curtis was elected Governor of Maine in 1966, after serving as Secretary of State of Maine (1965-66)



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WASHINGTON **White House approves public works appropriations bill**

Before adjourning for the holiday recess, Congress forwarded to the White House its more than \$4.7 billion public works appropriations bill for fiscal year 1970. Signed by President Richard M. Nixon on Dec. 11, P.L. 91-144 permits expenditures of \$886,382,000 by the Federal Water Pollution Control Administration (FWPCA)—\$800 million for waste treatment construction grants (up from \$214 million in the budget request) and \$86,382,000 for operations and research. In fiscal year 1970, the following independent offices receive the following sums of money: Water Resources Council—\$3,925,000 (ES&T, February 1969, page 115); National Water Commission—\$1,050,000; Delaware River Basin Commission—\$200,000; and Interstate Commission on the Potomac River Basin—\$500,000. Recently, President Nixon announced the appointment of two new members of the National Water Commission—Roger C. Ernst (Phoenix, Ariz.) and Josiah Wheat (Woodville, Tex.), who replace DiLuzio and Wright (ES&T, November 1968, page 991).

White House task force on air pollution

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Harvard School of Public Health

White House names task force on air pollution

President Nixon recently announced the establishment of a task force on air pollution which will evaluate the effectiveness of present efforts to curtail air pollution and recommend further actions that may be necessary. Chaired by A. J. Haagen-Smit, chairman of the California Air Pollution Board, the task force will be making recommendations for 1970 and beyond.

Automobile manufacturers must label their products

The National Air Pollution Control Administration (NAPCA) regulation requiring automobile manufacturers to label all motor vehicles as conforming to federal emissions standards was published in the *Federal Register*, Dec. 10, and becomes effective in 90 days (ES&T, September 1969, page 791).

Estuarine and coastal findings trigger legislation

Awaiting action by the 91st Congress when it returns this month is a legislative proposal to amend the Federal Water Pollution Control Act. The National Estuarine and Coastal Zone Management Act of 1970—S. 3138 and companion bill H.R. 14845—would implement certain of the recommendations of Interior's estuarine study. The proposal initially calls for \$2 million authorization for fiscal year 1971 and specifies cooperative federal-state programs of matching grants with the federal share being up to 50% for developing a comprehensive management plan. The proposal stems from Interior's three volume report, "The National Estuarine Pollution Study."

Students, brush up your environment

Late last month, FWPCA held full one day seminars in its nine regions across the U.S. (ES&T, September 1969, page 804) in its attempt to involve the youth of the nation in the fight to prevent contamination of the environment. Senator Gaylord Nelson, who calls for an environmental teach-in on April 22, recently introduced the Environmental Quality Education Act to develop a national strategy on environmental education, at all levels from preschool through graduate training.

STATES Pennsylvania public officials fined for water discharge

Seven public officials of Allegheny County, including the mayor of West Elizabeth, each were fined \$500 and given suspended sentences for failing to halt the discharge of raw sewage into the Monongahela River. The penalty results from the first contempt proceeding against a municipality under the Commonwealth's Clean Streams Law; the sentence was handed down by Judge Carl B. Shelley. "The court's decision is a serious warning to Pennsylvania municipal officials who have not taken prompt steps to clean up pollution from municipal sewage systems," says Thomas W. Georges, acting state secretary of health.

California sets pace with new air pollution laws

The 1969 California legislature passed, and Governor Reagan signed, seven bills to reduce air pollution emissions in the state. In addition, resolutions were passed authorizing its Air Resources Board (ARB) to perform studies on fuel composition and low emission vehicles. The new laws include: • AB 896 permits conversion of vehicles from gasoline and diesel fuel to other types of fuel (such as liquid petroleum gas and natural gas) if emissions standards are not exceeded. • AB 1056 authorizes ARB to set exhaust emissions standards for used cars which are less strict than those for new cars. Under AB 1056, an exhaust control device can be accredited for used cars if the item doesn't cost more than \$65 and doesn't exceed the emission standards of 350 p.p.m. hydrocarbons, 2% carbon monoxide, and 800 p.p.m. oxides of nitrogen. • AB 1985 imposes a \$50 penalty on manufacturers whose vehicles fail to meet standards and test procedures in respect to assembly line emission tests authorized to begin this month.

Air quality regions purchase monitoring equipment

Philadelphia, core city in the fourth air quality region to be designated by the Secretary of Health, Education, and Welfare, is purchasing an aerometric system to monitor the city's air quality. Edward F. Wilson, assistant health commissioner for air management services, recently announced that the \$252,308 contract was awarded to Leeds & Northrup Co. (North Wales, Pa.) and that two thirds of the cost would be paid for by the federal government.

In another region, the Minnesota Air Pollution Control Agency recently awarded a contract to Beckman Instruments, Inc. (Fullerton, Calif.), for a trailer type air monitoring laboratory which is to be delivered this year.

New York City varies approaches for automobile pollutants

Beginning this month, New York City's Department of Air Resources will equip all eight of its new cars with catalytic mufflers. Department officials expect to reduce carbon monoxide emissions by about 70% of that emitted from 1968 and 1969 cars, but lead free gasoline must be used, according to commissioner Austin N. Heller. "If the combination proves successful, specifications to require it can be written for all 1971 cars," Heller says. The city's fleet of automobiles number 13,000. City officials also will monitor the air and noise levels at East River Drive, the first of 10 sites for such monitoring, and hope to be able to design highways, ultimately, to enhance the urban environment.

TECHNOLOGY

Leaner fuels cut emissions, but need new injection systems

Burning leaner fuel-air mixtures in auto engines would reduce the amount of exhaust pollutants emitted, but would require a new approach to fuel induction, according to a recent study by Battelle engineers, D. A. Trayser and F. A. Creswick. Lean mixtures would significantly reduce NO emissions and slightly improve hydrocarbon and CO emissions, but contribute to rougher operation in conventional engines. To resolve the dilemma, the engineers suggest three new injection systems to provide uniform fuel-air mixtures and precise injection cycle timing: Ultrasonic atomization, in which fuel droplets are formed from a liquid film flowing across a vibrating cylinder; spinning disk atomization in which the fuel droplets are generated by centrifugal force; and impinging jet atomization, in which pressurized air impinges on a fuel jet. Such devices would allow smooth operation on lean mixtures at all operating conditions, the engineers claim.

National Research Council asks more CO research

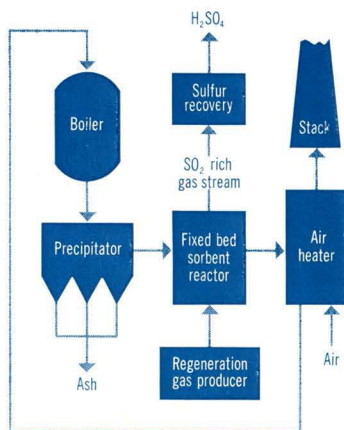
A National Research Council committee that has reviewed the health effects of carbon monoxide has concluded the facts must be firmly established by additional research before safe CO standards can be set. The committee found that, since there is no level of CO in ambient air that is known to be without effect, it is important to minimize exposure to CO. On the other hand, the study uncovered no evidence for the contention that urban air pollution produces any chronic health effects specific to CO. Chronic CO poisoning, characterized by fatigue, headaches, irritability, and dizziness, was not found, even in such high exposure groups as garage attendants and traffic tunnel personnel. However, the report notes that recent experiments show that CO exposure results in some impairment of mental functions, particularly judgment of time intervals; this may be a plausible explanation for some automobile accidents.

Utilities to fund study of new SO₂ process . . .

Sixteen electric utilities will support an evaluation of a new flue gas desulfurization process developed by Esso Research & Engineering and Babcock & Wilcox. The process features absorption of SO₂ on a unique but undisclosed sorbent that can be readily regenerated, and recovery of marketable sulfuric acid. Because the process uses a dry sorbent, the system avoids water pollution problems and moisture laden plumes that fall rapidly to the ground. First step in the \$7 million evaluation will be pilot testing at a plant of Indiana Michigan & Electric, a subsidiary of one of the cooperating utilities, which, if successful, could lead to a commercial process by 1973.

. . . and NAPCA contract will optimize existing one

Another separate development in SO₂ control is a NAPCA contract to Stone & Webster Corp. to evaluate and select optimum absorber units for the flue gas scrubbing process it has developed jointly with Ionics, Inc. (ES&T, November 1968, page 994). The S&W-Ionics process uses absorption by SO₂ by caustic solution, with recovery of sulfuric acid by stripping and electrolysis of the absorbant solution to regenerate the caustic. Other byproducts of the electrolysis are dilute sulfuric acid, oxygen, and hydrogen. The process has been field tested, at Gannon Station of Tampa (Fla.) Electric Co.



Babcock & Wilson-Esso process

INDUSTRY Waste water needs through 1980 will cost \$66 billion

The New York market research firm of Frost and Sullivan, Inc., has published a report which predicts that the U.S. will have to spend \$66.3 billion on water and waste water facilities between now and 1980, just to keep up with the country's need for clean water. The report also estimates that water pollution currently is costing the U.S. \$12 billion every year. The research firm's prediction is that, by 1977, federal and local governments will be spending \$270 million on research and development alone. The report, entitled "The Water Resources and Pollution Control Equipment Market," draws together much data from the U.S. government and elsewhere, and can be purchased from Frost and Sullivan.

Steel companies up spending for environmental controls . . .

American Iron and Steel Institute reports that, as of late 1969, companies representing 98% of the nation's steel making capacity had authorized more than \$327 million for air and water pollution control projects—\$100 million more than had been authorized for similar projects a year earlier. Of the total amount, \$172 million will be spent on water pollution control. (In recent years, actual expenditures for pollution control have risen strongly: In 1968, steel companies spent \$61 million on clean water, versus \$54 million in 1967, and \$40 million on clean air, versus \$39 million in 1967.) The institute emphasizes that the figures do not include funds for research or operating expenses.

. . . and API budgets for air and water conservation research

The board of directors of the American Petroleum Institute (API) has approved a budget of \$3.7 million for research and development projects on air and water pollution control—\$1 million more than authorized for 1969. Almost \$2 million of the 1970 funds will be used for a continuing research program on automotive emissions (sponsored jointly by the Department of Health, Education and Welfare and the Automobile Manufacturers Assn.). \$650,000 is slated for use on the API oil spill cleanup research program, and another \$1 million will support assorted research projects, many of them to be undertaken jointly with other industries and federal agencies. Costs of research and full-scale pollution control projects undertaken by individual API member companies are not included.

Industries invest in air and water pollution controls

• **Armstrong Cork Co.** will construct a \$1 million, 3.5 million g.p.d. treatment plant at its building products plant (Macon, Ga.) to remove solids and organic matter from waste process water. • **American Cement Corp.'s** Peerless Division will install 26 Research-Cottrell fabric filter units at its Forman Ave. plant (Detroit, Mich.). Fourteen of the units will control dust from process operations and materials storage and the other 12 will trap dusts from handling systems and storage silos. • **Bethlehem Steel Corp.** is spending \$5.5 million on a baghouse dust collection system for five electric furnaces in Bethlehem, Pa. The system will treat 1.3 million c.f.m. of exhaust gases. • **General Electric Co.'s** Semiconductor Products Department has installed two roof-mounted reinforced plastic scrubber assemblies to control corrosive mists and gases at its integrated electronic circuit plant (Syracuse, N.Y.).



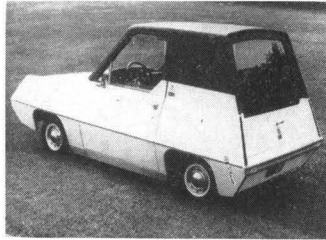
Scrubber unit installed at GE plant

Whatever happened to the electric car?

Remember the electric automobile? Not the 1895 Carpenter, the 1907 Boston, the 1926 Berwick, or any of the other dozens of electric powered passenger vehicles that had their heyday in the early years of this century. Even the under-thirty age group can recall the Mars II, developed in 1967 by the Electric Fuel Propulsion Co; or the Markette, a prototype electric auto developed by Westinghouse Electric Corp. three years ago; or the Amitron exhibited in 1967 by American Motors. These were just a few of the many new concepts in electric vehicles that were announced in 1966-67, a period when many observers both in and out of the auto industry sensed an imminent renaissance of the electric car.

Setting the mood for this optimism was a sense of public dissatisfaction over efforts to curb air pollution resulting from auto exhaust emissions. Progress in programs on control of exhausts from internal combustion engines was painfully slow, at least to those who felt that a radically new approach to urban transportation was needed. A revival of the emission-free electric cars which dominated the auto industry in its early days seemed a workable idea.

Symptomatic of the mood of that period, and perhaps partly responsible for it, was the formation of the U.S. Department of Commerce Committee to study potential electric vehicle development. The findings of the com-



Delta. Three door compact is a test vehicle built by the General Electric Co.

mittee were somewhat equivocal—the electric car would be a major advance in the fight for cleaner air, but because of strong technical, social, and economic factors, its development was not likely within a decade. Nevertheless, several bills introduced in Congress called for direct federal subsidy of electric vehicle development, and one after another, several manufacturing firms—among them Ford, General Dynamics, Electrochima, and American Motors—announced “breakthroughs” in vehicle battery technology. Even General Motors, which was generally pessimistic about the future of electric vehicles, acknowledged that it had conducted an extensive evaluation program. The most optimistic prediction at that time, made in 1966, was that electric vehicle production could begin in as little as five years, given sufficient expenditures of money and effort.

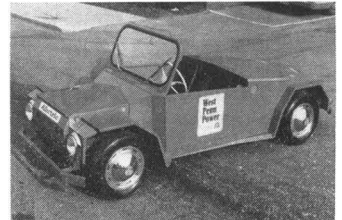
Electric vehicle developments do not now garner headlines the way they once did. The concept of a mass produced electric vehicle is not quite dead; vehicle development programs continue, but the prospect seems scarcely brighter than a few years ago.

One indication that the electric car is still a viable concept is the growth of the Electric Vehicle Council (EVC), formed in March, 1968. EVC, sponsored by the nation's investor-owned electric power companies through the Edison Electric Institution, has as its objective “the advancement of the art and acceptance of electricity as a form of motive power,” and seeks to “coordinate and

disseminate information on the technology of electric vehicle transportation, including current and proposed research.”

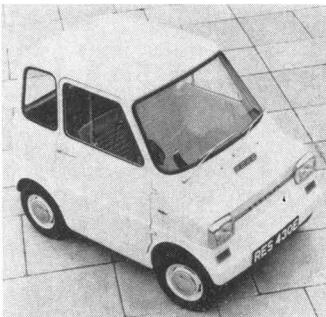
Last November, EVC—whose associate memberships now include more than 60 manufacturing companies—held its first International Electric Vehicle Symposium. In addition to a series of far ranging technical papers, the conference featured an exhibit of about a dozen prototype electric vehicles. Although some of these were impressive—a streamlined prototype that has achieved a top speed of 138 miles per hour, and a \$1000 British subcompact said to be already in production—the development of a competitive electric car that would satisfy the vagaries of the U.S. market still seems to be some time away.

The main stumbling block is, of

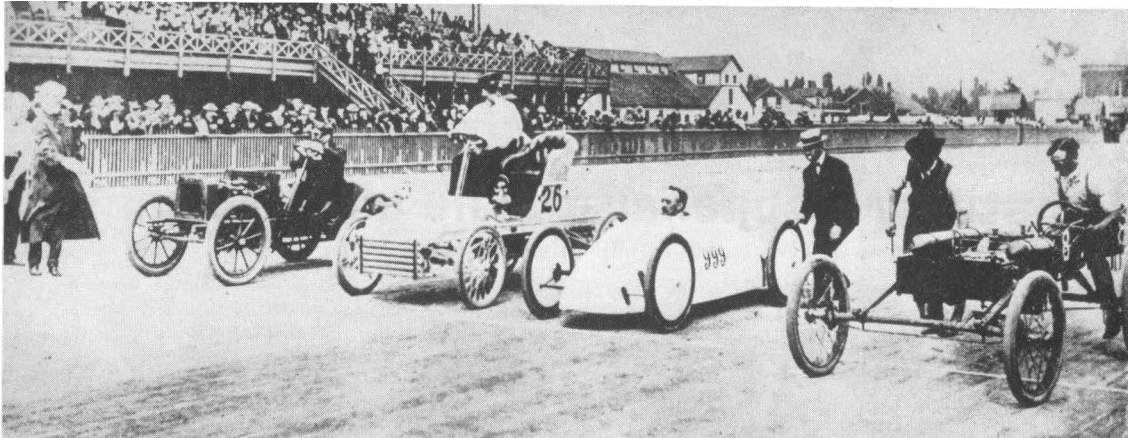


Alleric. Two-passenger electric was built by Allegheny Power subsidiary

course, the development of a high energy source to provide motive power at a performance level comparable to that of conventional internal combustion vehicles. Conventional lead acid batteries, of the general type that are used for starter, ignition, and accessory power on conventional autos—and which power most of the prototype electric cars—have a theoretical energy density of 40 watt hours per pound. However, the bulk and weight of such battery components as electrodes, grids, separators, etc., limit the practical energy density of lead-acid batteries to about 12-15 watt hours per pound, a figure generally regarded as too low for a practical electric vehicle power source. For example, at the recent



Commuta. Ford experimental car studied power needs for urban driving



Record. Way back in 1902, battery-powered Baker Torpedo amazed spectators by hitting 104 mph in speed trials

EVC symposium, W. H. Koch, of Ford's scientific research laboratory, presented the results of a Ford study on power requirements for electric vehicles. Among the results were figures that showed a maximum range without recharging for a lead-acid battery powered car of 35 miles, at a steady speed of 25 miles per hour; stop and start driving under typical urban conditions cut the time maximum range to about 15 miles.

For this reason, Koch feels that "future electric vehicles are expected to remain restricted to operations in suburbs and cities. One can conclude that high energy and power densities will be needed to obtain metropolitan driving ranges of 160 miles."

High energy

Energy densities somewhat higher than that of lead acid batteries are obtained in other battery systems, such as nickel-cadmium, nickel-zinc, and silver-zinc, but the cost of these batteries is too high for such large-scale applications as vehicle propulsion. Besides, even these cells fall short of the 100-150 watt hour per pound capacity which is probably a minimum requirement for any electric auto to be widely accepted. Such high energy density battery systems have been developed, though none has progressed beyond a laboratory scale prototype. Among the most promising designs are:

- The **zinc-air battery**, originally developed by General Dynamics. This battery system is based on the zinc-zinc oxide couple which has a theoretical energy density of 400 watt hours per pound; air bubbled through a nickel electrode serves as the cathode for the couple. A promising feature of this system is the possibility

of designing it for instantaneous mechanical recharging by replacement of the zinc anode.

- The **sodium-sulfur battery**, announced by Ford more than three years ago. This high-temperature battery uses a liquid sodium anode and a molten sulfur cathode, separated by a solid electrolyte of aluminum oxide. Based on the theoretical energy density of the sodium-sodium polysulfide couple, Ford extrapolates 150 watt hours per pound as an attainable level. One drawback to the system is that the electrodes must be heated to 300° C. when started up from ambient temperature.

- The **lithium-nickel halide** system, developed by Gulton Industries. The lithium-nickel fluoride version of this battery has a theoretical energy of 720 watt hours per pound, due to the high reactivities of its electrode materials. However, because of the high sensitivity to water of the lithium anode, the battery uses an organic electrolyte of propylene carbonate.

Gulton has entered a joint venture with American Motors on the development of electric vehicles. But, like Ford, Gulton has yet to build a high-energy density battery large enough to power an automobile. Both companies' programs have consisted of using conventional batteries for testing vehicle designs and nonbattery components. Robert C. Shair, Gulton's director of R&D, says the company has converted an American Motors' Rambler station wagon for operation with nickel-cadmium batteries. The test vehicle contains some relatively sophisticated solid-state control circuitry, as well as a regenerative braking system—two non-battery items vital to electric auto de-

velopment. Regenerative braking, in addition to providing braking characteristics similar to conventional vehicles, serves the more practical purpose of using the vehicle's momentum to recharge the batteries when decelerating, thereby extending the vehicle range per charge by 25%.

Lead time

There is no doubt that development of a practical electric car is somewhat problematic. The auto industry thinks in terms of five years or more of lead time for major changes in conventional auto designs; for a radically new concept such as an electric car, the necessary lead time would be much more, even if the basic technology—in the form of a practical high-energy battery—suddenly became available.

A further question surrounding development work in electric cars is the size of the potential market. At best, electric cars would be confined (at least initially) to the second car market, with use limited to short haul, urban driving conditions; whether this market is large enough to attract a major manufacturer is still not clear.

Recent federal legislation has taken the form of an attempt to guarantee at least a limited market for low emission vehicles such as electric cars. Companion bills introduced into both houses of Congress would allow developers of low emission vehicles—whether steam, electric, or turbine—to seek certification by a board set up under the Secretary of Transportation. If the vehicle met suitable exhaust standards, it would be eligible for purchase by the General Services Administration (GSA), if its cost did not exceed 125% of that for a comparable conventional vehicle.

Scrubber promises reduced power costs

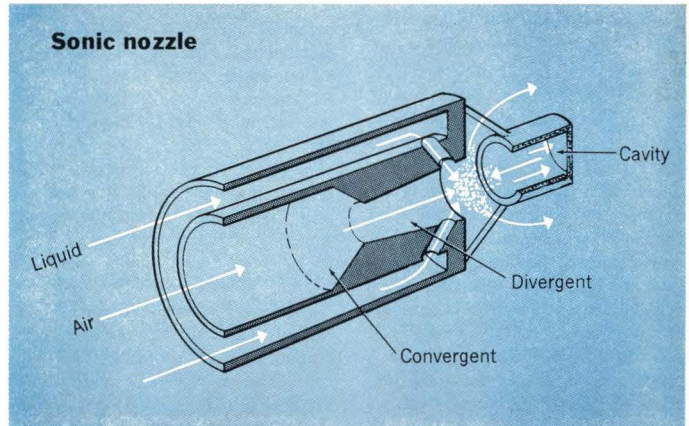
A new type of wet scrubber being developed by Standard Havens Systems (Glasgow, Mo.) is claimed by its manufacturer to show promise of cutting power costs sharply. While various types of wet scrubbers—packed towers, centrifugal spray scrubbers, venturi scrubbers, and many others—are in common industrial use, most require expenditure of large amounts of energy to ensure good contact between the particulate matter and the scrubbing liquid (generally water or an aqueous slurry). In general, scrubber design is arranged so that relative velocity between liquid and solid is as high as possible; but the price that must be paid for high velocities is a small but significant gas-stream pressure drop across the constricting section where gas velocity is increased. For instance, a pressure drop of six inches of water is quite usual in a commercial scrubber installation.

Nozzle principle

Standard Havens' approach is based on the capabilities of sonic nozzles developed by Sonic Development Corp. of America (Yonkers, N.Y.). These nozzles have successfully atomized viscous liquid fuels used in oil-burning furnaces. They have no moving parts: Sonic Development's original design involved passing air through a convergent-divergent section and focusing the resulting high frequency pressure wave into an open cavity. Liquid drawn into the acoustic wave is immediately atomized.

In early tests conducted by Standard Havens, engineers used recycled water from a pond in which most of the dust particles were allowed to settle—a common water conservation practice with scrubbers whose nozzles can handle slurries. However, they discovered that particles in the water tended to clog the holes feeding the shockwave area in the nozzles. They then reversed the gas and liquid streams to the nozzles, merely as an experiment. To their surprise and delight, when slurry was fed through the convergent-divergent section and air passed around this section, it still was possible to effect atomization. Further, because the narrowest part of the inner section of the nozzle is $\frac{5}{16}$ inch

More efficient contact between gas and scrubbing liquid is reason for optimism about new type of dust control device



Atomization. *Scrubbing liquid forms drops in acoustic wave produced by gas flow*

in diameter, no clogging problems were experienced.

Application

Standard Havens has tested a scrubber system employing the sonic nozzles on a 20,000 c.f.m. asphalt plant rotary rock dryer (owned and operated by Rein-Schultz & Dahl, Inc., Madison, Wis.). Dust loadings in the dryer exhaust gases delivered to the scrubber were around five grains per cubic foot. Water was supplied to the nozzles (18 in all) at a pressure of 60 p.s.i. and a rate of 200 g.p.m.; 32 p.s.i. compressed air at a rate of 350 c.f.m. provided the atomization capability. The dust-liquid contact took place in a 10 foot long vertical chamber. Under these conditions, Standard Havens reports that the scrubber trapped 97.8% of the particles between 3-15 microns in size; efficiency was 80.3% for particles of less than 3 microns. In this asphalt plant application, 40 horsepower was required to run the air compressor. Pressure drop across the contacting section was less than $\frac{3}{4}$ inch of water.

Potential advantages

Admittedly, no one would rush out and buy a Standard Havens scrubbing

system on the basis of the data given here; many more tests are needed and are being planned. But the use of sonic nozzles promises several potential advantages over more conventional systems. Chief among these, company president Lamson Rheinfrank, Jr., points out:

- The system is not sensitive to large changes in gas throughput.
- Low pressure drop on the gas side eliminates the need for careful balancing of the total system.
- Low water requirements, due to ability to reuse water in the slurry leaving the contacting unit (after settling).
- Good possibility that waste steam could be used in the nozzles, rather than compressed air.

Rheinfrank is particularly optimistic about prospects for replacing air with steam as the atomizing fluid. He intends to focus future efforts at installations where steam is readily and cheaply available. Since much of the operating cost on a regular wet scrubber is due to the need for powerful fans, Rheinfrank hopes that use of his company's system may be able to save customers as much as 50% of their operating costs. Time will tell whether his optimism is well founded.

Firm offers broad environmental services

Weston stands ready to help industrial and municipal clients meet pollution abatement deadlines

Last October, the engineering consulting firm of Roy F. Weston, Inc. (West Chester, Pa.), went public. Running the gamut of environmental areas, the firm offers an integrated and comprehensive service in water supply and treatment, waste water treatment and disposal, air pollution control, solid waste management, industrial hygiene (including noise control), and community planning. Weston's announcement serves as one indicator that consulting firms stand ready to help industrial and municipal planners with their mounting pollution abatement problems, requirements, and deadlines.

With more than 200 currently active projects in its business operation, the firm showed \$2.8 million in sales in 1968, expected \$3.5 million in last year's sales, and looks forward to \$5.0 million in sales this year. "The upsurge in our activities occurred three years ago and is largely attributable to federal water pollution legislation," says Roy F. Weston, founder and president of the firm. With the Nixon administration's mandate for a clean environment, Weston feels assured of continuing company activity.

"It is true that water—treatment, resources, and planning—is our forte," Weston elaborates, and this is due largely to the founder's background. Prior to entering the consulting field in 1951 and founding his own company in 1955, corporate president Weston spent more than 16 years in charge of pollution control activities with the Atlantic Refining Co. (now Atlantic-Richfield Co.). "Admittedly, the term pollution control engineer was not in vogue then," he explains. He goes on to note that in-plant control for industrial processes is an area where, in his work experience, much has been done and where small changes in process can result in considerable and notable improvement

in the control of waste discharges.

The firm's activities are not isolated in any geographical area. Already, Weston, Inc., has regional offices in Atlanta (Ga.), Wilmette (Ill.), Houston (Tex.), and Roslyn (N.Y.). The company also conducted an air and water pollution study for the government of Israel. In this case, the study assessed the feasibility of locating an oil refinery at Eilat.

"The active projects can be split into two main groups—industrial projects and public works projects," says Harry H. Curtin, vice president for corporate planning. "It's a 60-40 split, 60% industrial and 40% public works."

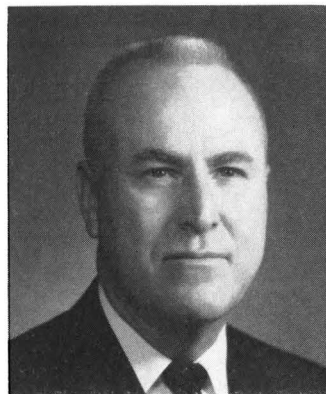
Industrial

Many U.S. industrial giants have availed themselves of Weston services at one time or another. The pulp and paper industry is one of the firm's largest clients to date. Weston, Inc., has provided engineering services in the construction of waste water treatment facilities for U.S. Plywood-Champion at its mills (Pasadena, Tex.; Canton, S.C.; and Calhoun, Ala.).

Petrochemicals and refining come next, and most of these activities have been in the Gulf area, mainly Texas and Louisiana. Chemical and plastic manufacturing industries rank third; included in these projects are studies and constructions for such notable chemical giants as Dow, Atlas, Monsanto, and Olin. Steel ranks fourth, and textiles, pharmaceuticals, foods, and the plating industry round out the firm's broad category of industrial clients.

Municipal

The firm's municipal clients range in size from the largest, New York City, to smaller communities of less than 1000 people. Ongoing projects illustrate the type of integrated planning available from Weston, Inc. Perhaps, the comprehensive type of water planning best illustrated by Weston's engineers and scientists is a study they conducted for the Neshaminy Creek Basin (Bucks County, Pa.). Last June, the firm recommended advanced waste treatment for the area. In 1969, the population of



Roy F. Weston

the area was 103,000; by 1985, the number is projected to be 289,000.

Another client—Onondaga County Department of Public Works (Syracuse, N.Y.)—contracted Weston, Inc., for a master plan for waste water treatment facilities that would combine the discharges from 130 industries with domestic sewage from a population of 40,000. With the financial aid of a \$300,000 grant from the Federal Water Pollution Control Administration, Weston, Inc., advised that the industrial flows from the multicommunity area could be treated in a single industrial waste water treatment plant, combined with the municipal sewage.

In these studies and consultations with municipalities, the firm is routinely kept on a retainer basis for any construction that is necessary based on their findings. (This practice is similar to the operating procedures of other consulting firms.)

Ranking

Some indication of Weston, Inc.'s ranking with respect to other engineering consulting firms is afforded by glancing at the *Engineering News Record's* annual rating of the top 500 independent general engineering firms headquartered in the U.S. Prior to 1964, Weston, Inc., was not included in the listing. But the move upward has been significant over the past few years. In last year's rating, the firm ranked 152 out of 500, having ascended from the positions of 211 in 1968 and 272 in 1967.

Auto hulk disposal—a growing business

The most conspicuous part of a typical junked or scrapped automobile is the body, but the body constitutes only about one third the total weight of the junked vehicle and much less than one third its scrap value. In addition, 28% of the scrap value of such vehicles comes from the nonferrous scrap which by weight makes up an insignificant part. And 10% by weight of the vehicle is solid waste material, including scrap tires and glass.

Regardless, the auto wrecking/dismantling industry is an important sector of the U.S. economy. In 1968, the industry took in 9 million cars and trucks for an estimated overall gross revenue of approximately \$5 billion. In that year, an estimated 15,600 companies with 98,500 workers were actively engaged in this business.

More than half of the firms employ from 2-5 workers; 17% are one man operations. The firms are located throughout the U.S.: California leads with 2000 companies; New York is second with 1250; and Texas ranks third with 1200. The average company showed a \$300,000 gross revenue in 1968.

Such are the findings of the Department of Commerce report, "The Auto Wrecking/Dismantling Industry," which is based on questionnaire data of a representative 7% of these companies. "Although the above numbers are not official Business and Defense Services Administration (BDSA) estimates, the report describes some industry problems and their impact upon national programs for environmental quality," says Edward W. Hassell, program manager for BDSA's Office of Business Programs. The information was voluntarily furnished to BDSA by such industry trade associations as the National Auto and Truck Wreckers Assn. (San Mateo, Calif.) and the Institute of Scrap Iron and Steel (Washington, D.C.), and by individual statements from more than 1100 companies.

The activities of this industry can be placed into four categories:

- Acquiring damaged, junked, or abandoned automobiles.
- Stripping these autos of useful parts.

In the early 1970's, the majority of auto hulks will be processed by shredders; most urban areas will have at least one

- Selling the useful parts.
- Disposing of the scrap metal residue (usually, of secondary importance).

"There is hardly a community in the country that does not have one or more companies devoted to this activity," Hassell indicates. "If the used parts inventory of the auto wreckers/dismantlers were not available, millions of our automobiles would soon become inoperable because of the lack of repair parts for older model vehicles."

A number of factors determine the rate of acquisition of junked cars. These include junk rate, prices for auto scrap, used parts prices, state safety inspection laws, and availability of labor. Other factors which influence the rate of take-in by the industry include:

- Vehicle inspection laws or lack thereof.
- Restrictions on open burning.
- Location of auto wrecker.

Many dealers report that a \$500-1000 expenditure is not unusual for a late model junked vehicle with many salable used parts. Dealers acquire some vehicles for little or nothing. But the average revenue for all vehicles junked in 1968 is about \$500, according to BDSA data. The report also notes that there did not appear to be any major price variation due to geographic factors.

In preparing auto hulks for scrap processors, the auto wrecking/dismantling dealer first must remove all usable parts from the vehicles. Normally, the dealer follows one of three procedures:

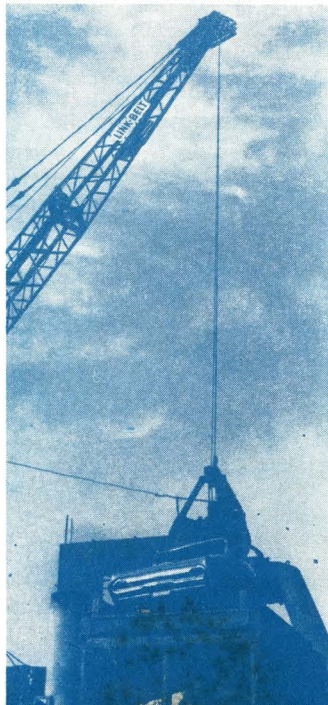
- Finds a scrap processor or shredder operator who will take the hulk as it stands, with upholstery, seats, and other solid waste materials.
- Strips the hulk by hand at a usual cost of from \$3-5 per vehicle.
- Burns the hulk to clean it.

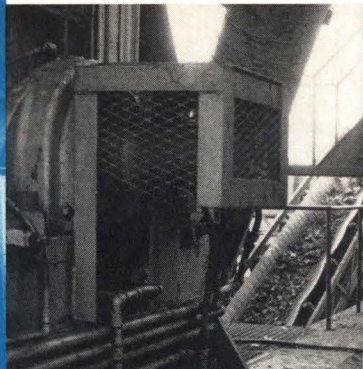
Processing equipment

Shredders, balers, flatteners, shears, and incinerators are used to ready auto hulks for scrap processors. Of these, shredders are the newest; balers are used by the majority of dealers; shears offer certain advantages over the other two, but are too new for positive evaluation; and incinerators do not appear promising. The impact of these new handling and preparation techniques could stimulate more effective use of auto scrap.

Shredders, one of the most significant developments in scrap processing in recent years, can rip whole automobile bodies and frames into small pieces of metal at rates to 120 cars per hour. The shredded scrap is separated magnetically or by hand, and the resulting ferrous material is a relatively clean, easy to handle scrap, relatively free of copper and other non-ferrous contamination.

Automobiles. Recovery of metal from autos is important for U.S. economy





Shredder input-output. A junked automobile (left) is being processed by new shredder; after being cut into sections, these sections are fed into the hammer-mill type shredder (center), which then shreds the hulk into fine pieces of metal (right)

Last April, about 65 shredder plants were in operation throughout the U.S., with an estimated production of 3-4 million tons of scrap annually. Many shredders are equipped with after-burner devices to incinerate such combustible trash as upholstery materials, insulation, and rubber remaining in the junk body.

However, shredders are not inexpensive. This equipment can cost from \$500,000 for small units to more than \$3 million for units capable of handling more than 100 tons of scrap per hour. Nevertheless, shredder advantages far outweigh the disadvantages which include:

- High investment cost for the equipment.
- High maintenance costs.
- Product of lower density than the conventional bundle of sheared automotive slab.

More often, **balers** are used today to process automotive hulks. In fact,

the majority of hulks presently processed are done so with this type of equipment. Although accurate data are not available for the number and location of balers throughout the U.S., there are at least 800 balers in operation, and some companies have more than one baler.

Compared with the shredder, the baler is a relatively simple piece of equipment. In this operation, the hulk is stripped, either by hand or incineration, to varying degrees of contamination, and then compressed into a cube weighing approximately 1200 pounds. Referred to as a No. 2 bundle, the cube is a basic item in auto scrap.

One problem with these cubes is that many steel industries and foundries have discontinued use of No. 2 bundles in steel manufacture. In 1967, about one quarter of the total purchases by domestic steel mills and foundries was auto scraps. In fact, the auto scrap processor made avail-

able 8.6 tons of scrap of a total 35.2 million net tons scrap in that year. Last March, the price paid to scrap processors by steel mills and foundries for No. 2 bundles ranged from a high of \$23 in Pittsburgh to a low of \$17 in Detroit, the report notes.

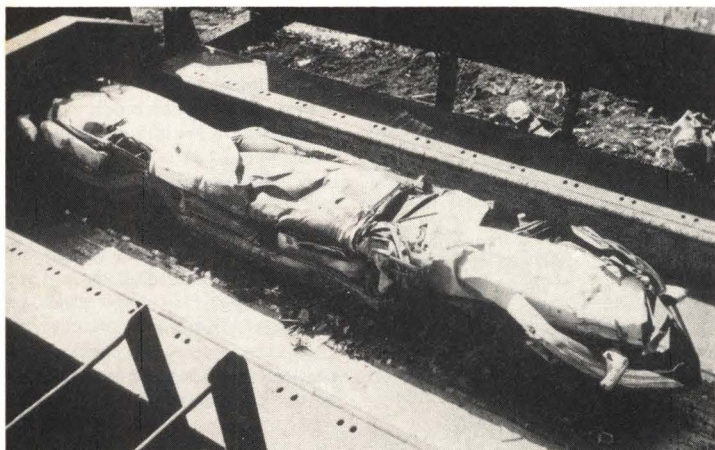
Shears, a relatively new development in the scrap industry, first processes the hulk into a scrap log. The 2 x 2 x 20 foot rectangle then is fed into a guillotine shear. Here, the shears cut and compress the log into predetermined lengths, so that the resulting sheared slab is a pillow-shaped, uniform piece of very high density melting scrap. As such, the scrap is easy to inspect and transport by railroad or truck. Total time required for the complete shear operation is roughly 40-60 man-minutes for each ton of product.

Last, few **incinerators** are operated by dealers in this industry. In view of cost, technical problems, and increasing number of air pollution regulations, the auto wrecking industry probably will not develop such equipment for its use, the report says.

Scrap value

The nonferrous scrap metals—lead, copper, aluminum, and zinc—are economically important factors in the total value of the scrap metal in junked vehicles, although they constitute a very insignificant part of the metallic scrap weight.

Copper, even in small quantities, is a serious contaminant of finished steel ingot. So, scrap processors are reluctant to accept shipment from auto wreckers unless they can be sure of the probable contaminant level. The copper problem is pinpointed by the fact that a typical auto body, including the engine, transmission, radiator,



Balers. Processing the majority of junked automobiles, more than 800 balers are in operation throughout the U.S. today; some companies have more than one

and heater core, weighs about 1200 pounds and contains nearly four pounds of copper wiring, primarily in inaccessible locations.

Almost 10% by weight of a junked automobile is solid waste material with no presently recoverable value. In 1968, the wrecking industry accounted for 1.2 million tons of solid waste. Scrap tires, the largest single item, accounted for 24.4% of such waste materials, and scrap glass, for 17.6% of the total.

Scrap tires create particularly annoying problems for the dealer. Although many junked tires now are burned haphazardly in open air dumps, this practice should cease with enforcement of more stringent air pollution codes. Most cities refuse to incinerate scrap tires because they burn so fiercely as to burn out the grates of ordinary incinerators.

At least seven British manufacturers have announced that they can provide suitable equipment for disposal of scrap rubber by incineration, according to BDSA's findings. Hennan & Froude (Worcester) has made an installation for the Watts Tyre Rubber Co. (Gloucestershire) which disposes of 840 pounds of scrap tires per hour.

The report notes that the value of a typical 20 pound, old passenger car tire is from 7-12 cents at collection points, hardly worth the cost of handling. Scrap tires have been considered for use as an asphalt additive for road beds, as soil conditioners, and as a source of chemicals and materials (ES&T, February 1969, page 119).

But no really good solution is evident at this time, the report notes.

Industry problems

Three main problems face the dealers in the auto wrecking/dismantling industry:

- Yard screening.
- Restrictions on open burning.
- Location of processing equipment.

The majority of auto wrecking yards are not located on the interstate or federal highway systems. BDSA estimates that no more than one third of the companies in the industry are affected by federal controls. But a vast majority of yards are controlled by state and local zoning regulations and other statutory provisions.

Increasingly strict requirements for screening of auto wrecking facilities are being placed on the dealers so that their operations will be less visible from the street or highway. So, dealers report that meeting the zoning and fencing standards of their community has cost them thousands of dollars. A cost of \$5000-10,000 for yard enclosures is not at all unusual.

During the period 1966-69 restrictions on outdoor burning have increased sharply; 89 of the 115 locations surveyed either forbid open burning or impose restrictions.

Many auto wrecking dealers are too far away from the equipment that is available. For example, 35% of the vehicles handled by the auto wrecking/dismantling industry in 1968 were more than 100 miles from the nearest shredder.

Recommendations of Business and Defense Services Administration report

- The federal government should consider a program of guaranteed loans and technical research and development grants to assist private industry to construct scrap shredders, balers, and incinerators for processing auto scrap.

- The auto wrecking/dismantling industry, the scrap metal industry, and the steel industry should join efforts, as appropriate, to study ways to lower freight costs for transport of metal scrap.

- States are encouraged to enact uniform motor vehicle titling legislation and adopt other administrative procedures as necessary to protect auto wreckers and scrap yards from legal action or harassment resulting from picking up or accepting motor vehicles presumed to be abandoned or disposed of by owner.

- The auto wrecking industry, in cooperation with the Department of Transportation, should analyze the situation to determine the need and type of action required to solve this problem.

- States should consider establishment of special funds for facilitating movement of abandoned motor vehicles from streets and other areas as appropriate to auto wrecker yards and scrap metal yards.

- The federal government should study the technical, economic, and national defense benefits which might result from stockpiling of motor vehicle scrap. A review of the need, benefits and cost of stockpiling auto scrap should be undertaken jointly by industry and interested government agencies.

- Federal agencies should accelerate and expand research devoted to increased use of auto metal scrap.

- Federal and private industry research directed toward increased utilization and/or disposal of junk or scrapped auto tires should be significantly expanded.

- Federal agencies and private research agencies should expand their current efforts to develop improved techniques and facilities for disposal of the nonmetallic solid waste other than tires created by the operations of the auto wrecking industry.

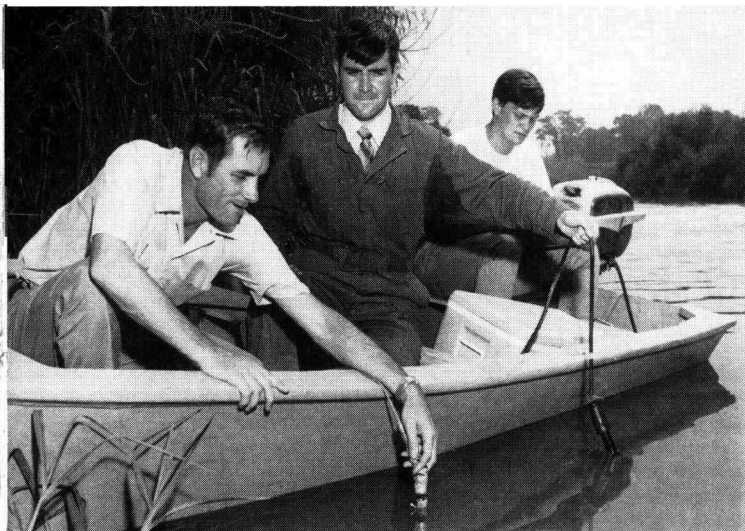
- Federal and state agencies and private industry should join in a study devoted to developing better statistics on the number and location of junked and abandoned motor vehicles.



No. 2 bundles. Weighing about 1200 pounds each, this basic auto scrap item accounted for one quarter of domestic steel mills and foundries' purchases in 1967

Grass roots pollution control

Texas engineers show local efforts really work



Testing. Don Vacker, Ron Lees and John Rife measure water quality in bayou

Stung by the charge of a leading engineering educator that engineers' lack of positive action on pollution problems is their "greatest failure," a group of chemical engineers in Texas has started a program that looks like a model of effective grass roots action for technical people. The Pollution Solution group of the South Texas section of the American Institute of Chemical Engineers (AIChE) is less than two years old, but already has attracted such attention and has had such success that the AIChE is actively encouraging the formation of similar groups in other parts of the nation.

The challenge

At a meeting of the South Texas AIChE section in 1967, John J. McKetta, then Dean of Engineering at the University of Texas, challenged the engineers present to take the initiative in solving pollution problems. McKetta urged engineers to participate at state and local levels, where their special skills could be used to best effect. "I challenge you as an organized group to think, to plan, and to act," said the educator.

McKetta's challenge soon was taken up; but, at first, things misfired. At a workshop meeting with the Houston League of Women Voters (October

1967), engineers who had intended to educate the ladies in the complexities of pollution control instead were themselves educated in the public's increased impatience with slow progress. One lady present berated the engineers: "How would you feel if you came home from work to find the house in a shambles, the beds unmade, and your dinner not prepared, to be greeted with your wife's sanguine remark, 'It's a complex problem, dear; I'm studying it?'"

The hostile female reaction gave local engineers further incentive for action. At the request of the local section executive committee, A. Roy Price, of Merichem Co., prepared recommendations for action, which were adopted formally by the section in March 1968. From the start, the keyword was action—40 members stepped forward and pledged themselves ready to help apply existing technology to local pollution problems. The Pollution Solution group was born.

Goals

Roy Price, who has been one of the main driving forces behind the group's activities, outlined the immediate goals:

- Acquaint local section members with Texas pollution laws and regulations.

- Set up a clearinghouse of available services and case history solutions to industrial pollution problems.

- Formulate a professional anti-pollution code (incorporating state standards).

- Maintain close liaison with state and local government agencies to aid in applying existing standards and in formulating new ones.

- Maintain contact with other groups active in the anti-pollution field.

- Set up an action committee to implement plans.

Since the formation of Pollution Solution in South Texas, many of these goals have been met: Through their regular meetings, members of the local AIChE section learned from invited speakers about Texas pollution laws; subcommittees of the group have assisted state legislators through expert advice on proposed legislation and have provided control officials with the group's opinion on proposed regulations.

Civic efforts

But, perhaps, the most impressive achievement of the Texas engineers—at any rate, the one that has generated the most outside interest and much favorable press coverage—is a civic project undertaken jointly with the Houston Chamber of Commerce.

The Pollution Solution group's civic target was the Buffalo Bayou, a stream that flows through Houston, and becomes the Houston Ship Channel. Buffalo Bayou was heavily polluted and filled with silt, and the engineers felt that cleaning it up would be a real contribution to the city, especially since no efforts previously had been made to do so. With hard work from group members, cooperation from city officials, and continuing support from the local news media, the project proved highly successful. The group was able to pinpoint a major source of pollution (untreated effluent from a laundry, entering the bayou because of a sewer stoppage) and, later, to demonstrate how silt could be settled in the flowing stream through the use of Hercules polyelectrolyte flocculating agents and electrostatic charge neutralizing compounds (the latter were supplied in the form of an aluminum chloride containing waste material from a nearby Sinclair-Koppers chemical plant!).

State officials speak out on air quality standards

Views and experiences in two of the first half dozen air quality control regions may prove useful to officials in other regions



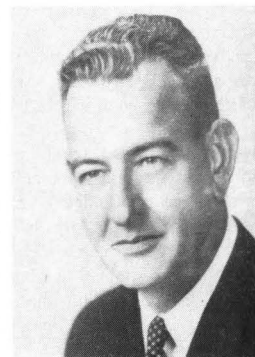
Palomba



Arey



Schueneman



Hope

The year 1970 promises to be a busy one for air pollution control officials. The Department of Health, Education, and Welfare's (HEW) air quality standards clock is ticking off the days until the following:

- Submission of standards from state officials in designated air quality control regions.

- Submission of implementation plans.

- Issuing of criteria and technology documents for additional pollutants (other than SO₂ and particulates).

- Designation of other regions (all 57 by midyear).

Last Nov. 10, standards were due from the first six regions—which include the District of Columbia and 12 states. This month, standards are due from another half dozen regions. Six months from these dates, implementation plans will be due from the first dozen regions. Next month, criteria and technology documents will be issued for carbon monoxide, hydrocarbons, and photochemical oxidants. So, another set of time schedules will be set into motion.

Designated by HEW as the first region, the National Capital Interstate Air Quality Control Region comprises the District of Columbia and sectors of the neighboring states of Maryland and Virginia. The problems and goals experienced here by control officials

in formulating their standards for submission illustrate the problems of an interstate region. On the other hand, the experiences of the Denver Region official illustrates, to some extent, the problems met in intrastate regions.

Two states—Illinois and Pennsylvania—submitted their standards for the St. Louis and Pittsburgh Air Quality Control Regions, respectively, on Nov. 3, earlier than required by law. Even so, all 13 areas in the first six regions did not meet their Nov. 10 deadlines. HEW Secretary Robert H. Finch granted an extension to three regions—Denver, Los Angeles, and New York City. These deadline extensions do not compromise the fight for clean air, and were granted because of technical difficulty. In fact, the additional time granted will be made up in the 180 day period before implementation plans are due, according to a National Air Pollution Control Administration (NAPCA) spokesman. The problems of the National Capital Region are complex because of the three jurisdictions involved. Three sets of standards have been submitted for this region—one from D.C., another from Maryland, and a third from Virginia. Although the numerical values for SO₂ and particulate levels are not identical in all cases, the levels are essentially the same and are consistent with the criteria documents.

District of Columbia

“One D.C. problem is that there are 2700 single chamber flue bed incinerators whose use must be discontinued after three years,” explains Malcolm C. Hope, associate director for environmental health in the District of Columbia Department of Health.

Washington, D.C., has set forth two goals for air pollution levels—a short-term goal to be attained in three years and a long-term goal to be reached within seven years. “With these goals in our standard, the present level of SO₂ concentrations will be reduced 40% within three years and 50% within seven years,” Hope says.

Already, the SO₂ level in Washington, D.C., is on the decrease, due to the regulation requiring the burning of less than 1.5% sulfur fuel. “During fiscal 1969, the annual arithmetic average of SO₂ was 117 µg./m.³ (0.041 p.p.m.), whereas, the previous fiscal year, the value was 146 µg./m.³ (0.051 p.p.m.),” Hope stated at the D.C. public hearing (Oct. 24).

The requirement for burning 1.5% sulfur fuel in the District became effective July 1, 1968, and was further reduced to 1% on July 1, 1969. In going from 2.5% to 1.0% sulfur fuel, 33,000 tons of SO₂ will be prevented from entering the atmosphere this heating season, Hope notes.

Similar to the nondegradation policy on water, an antidegradation air

policy is another item that has come up, and this item certainly stirs controversy. "Before the public hearing, District of Columbia officials saw no need for such a statement," Hope says. "But the public insisted on its insertion, and such antidegradation language went forth in the D.C. standard that was submitted to HEW," Hope notes. "Much interest was generated in our hearing; approximately 50-60 organizations testified," he continues. "In some cases, the public is over-responding, but I will buy that in preference to no response."

Six months, actually 180 days, from last Nov. 10, D.C. will be required to submit its implementation plan on what steps Washington, D.C., will take to achieve the level of air pollution specified in their standard.

"Although public hearings on an area's implementation plan are not required by the Air Quality Act of 1967, D.C. plans to hold hearings on this phase, too," Hope explains. "And then, later, when other HEW documents on air pollutants are issued, D.C. will hold other public hearings for the criteria setting phase for them."

Virginia

"The first state to submit its standard to HEW for its sector of the National Capital Interstate Air Quality Control Region, Virginia passed its state air pollution law in 1966, so we anticipated some of the requirements of the Air Quality Act of 1967," says Richard W. Arey, executive secretary of the Virginia Air Pollution Control Board. "Obviously, the National Capital area was designated first, not because of any serious air pollution threat, but because this area is a convenient showplace for the nation."

"The Virginia Air Pollution Control Board is a completely independent agency in the executive department of the state," Arey explains. "It is not a division or part of the Department of Health, and the board has full powers to perform its duties."

"Our law made it easy for Virginia to jump right into doing this sort of thing—standards setting and the like," he adds. "When the necessity arose for standards for the Virginia sector of the first air quality region—four counties (Arlington, Fairfax, Prince William, and Loudoun) and three cities (Alexandria, Fairfax, and Falls Church)—the public already knew what the board was planning and considering statewide."

"There is a tremendous effort today to say what is good enough for California is good enough for every other part of the U.S.," Arey complains. "But this is not necessarily true. The entire Commonwealth of Virginia has about the same number of vehicles as Los Angeles County, but Virginia does not have the persistent day after day thermal inversions that are common in L.A. County." Arey acknowledges that Virginia has certain inversions at night in the mountainous regions of the state, but that these inversions break up the next morning. "Obviously, we do not have the buildup of photochemical smog constituents," he concludes.

An avid proponent of states' rights, Arey stresses that Virginia problems should be handled in a way best for the Commonwealth. "The same applies to other states and regions," he adds. "All regions have different situations; so, officials in state regulatory agencies must do their homework, get everything well organized and planned, comply with each requirement under the federal act of 1967, and then stand their ground."

"I'm afraid that there are places where the intent of Congress is being stretched to many things that Congress did not intend," Arey says and cites the public's demand for an antidegradation clause in the District of Columbia standard as an example. "An antidegradation statement, in the form that I have seen, is a meaningless exercise in futility of words," he notes. "If you really wanted to enforce such a policy, there would not be another baby born or another car driven, and the status quo would be maintained so that nothing changes."

"If state officials have done what the act requires and the Congress intended, there should be no troubles. We don't expect any problem with our standard," Arey concludes.

Maryland

"The Maryland standard for its sector of the National Capital Region—Montgomery and Prince George's Counties—was submitted several days late," says Jean J. Schueneman, chief of the air pollution control division of the Maryland State Department of Health. "Although the language in Maryland's standard makes it difficult to compare with that of the Virginia standard, it is consistent with the HEW documents," he adds. But Schueneman personally regrets that

the standard and implementation plans did not go forth simultaneously, because the real test for achieving whatever degree of air pollution control is specified in the standard will have to be faced in that plan.

"The participatory democracy—the conservation groups, the citizens for clean air, the public—opt for the lowest level of pollution but haven't adequately considered how or what this means in the course of a normal day of operation," he adds. "So, in the implementation plan, we will be concerned with the actual cost that the public will be willing to pay for cleaner air, and the degree of social upheaval that the public is willing to tolerate."

"For the Maryland sector of the National Capital Region, all electric power companies are on the way to 90% control of SO₂ emissions from coal burning electric utilities. We have achieved a 60% reduction of emissions from residual oil burning installations, and 97% particulate controls generally are in effect. Fuel with no more than 1% sulfur is being burned in the area."

The Dickerson electric generating station (Montgomery County) will be reducing its level of SO₂ emissions by 90% in the coming years, from 53,000 tons in 1971 to 5500 tons in 1973. "But all of this depends on the success of the stack gas desulfurization processes still in the pilot plant today," Schueneman says. "By the end of this year, control officials will know better where they stand on this problem."

Last January, another Maryland regulation became effective which specifies Ringelmann No. 1 for all incinerators and new industrial processes. "Eventually, all small incinerators will be eliminated in this air quality region, but the public must realize that waste compactors in apartment houses may cost about \$4000 each, and then, there will be the hauling problem and expense."

"The public is in for a rude awakening when officials start to implement standards for 65 µg./m.³ air," the Maryland official says. "For the Maryland sector, implementation will be a considerable problem, but for the Baltimore Air Quality Control Region, whose standard is due May 13, implementation may be impossible."

In Baltimore, the ambient air contains from 130-140 µg./m.³ of particulate material, and a number of cities have this level of dirty air. "Maryland has made some preliminary calcula-

57 Air quality control regions

▲ Standard due Nov. 10, 1969

- 1 Washington, D.C.
- 2 New York
- 3 Chicago
- 4 Philadelphia
- 5 Denver
- 6 Los Angeles

▼ Standard due this month

- 7 St. Louis
- 8 Boston
- 9 Cincinnati
- 10 San Francisco
- 12 Pittsburgh
- 13 Buffalo

■ Officially designated region

- 11 Cleveland
- 14 Kansas City
- 15 Detroit
- 16 Baltimore
- 17 Hartford
- 18 Indianapolis
- 19 Minneapolis-St. Paul
- 20 Milwaukee
- 21 Providence
- 22 Seattle-Tacoma

◆ Designation imminent

- 23 Louisville
- 24 Dayton
- 25 Phoenix
- 26 Houston-Galveston
- 27 Dallas-Ft. Worth

● To be designated

- 28 San Antonio
- 29 Birmingham
- 30 Toledo
- 31 Steubenville
- 32 Chattanooga
- 33 Atlanta
- 34 Memphis
- 35 Portland
- 36 Salt Lake City
- 37 New Orleans
- 38 Miami
- 39 Oklahoma City
- 40 Omaha
- 41 Honolulu
- 42 Beaumont-Port Arthur
- 43 Charlotte
- 44 Portland
- 45 Albuquerque
- 46 Lawrence-Lowell-Manchester
- 47 El Paso
- 48 Las Vegas
- 49 Fargo-Moorhead
- 50 Boise
- 51 Billings
- 52 Sioux Falls
- 53 Cheyenne
- 54 Anchorage
- 55 Burlington
- 56 San Juan, P. R.
- 57 Virgin Islands



tions on how to meet, for example, 65 $\mu\text{g}/\text{m}^3$ air," he says. "We find that the only way to achieve such clean air for the heavily industrialized Baltimore region is simply to stop burning coal, oil, and refuse. Ninety-nine percent control will not be enough.

"Eventually, Baltimore may need an all gas city," Schueneman says. "We don't have any idea of the cost, but I am not too timid to propose it. There is some danger if we set standards down in the 65 $\mu\text{g}/\text{m}^3$ range. Such a level may be impossible to achieve in the Baltimore area, and perhaps many people would not pay any attention to it, because they would consider it too unrealistic.

"Although the Maryland standard does not contain an out and out anti-degradation clause, it does contain a minimization of pollution clause," Schueneman says. "Inherent in this clause is language which gives us a license to adopt emission regulations which would make the air cleaner than the numerical levels specified.

"For the Maryland sector, the short-term three year and the long-term seven year goals, in my judgment, are nearly impossible," he concludes. "We will do our level best, but are less than optimistic of our ability to deliver that kind of air to Baltimore."

Colorado

Denver's standard did not make the Nov. 10 deadline, and this region has been granted an extension because of a technical difficulty. "Denver's experience to date is not anything unusual, but our situation is unique in that we are working on a state law which puts us in technical violation of the federal law," says Joseph Palomba, chief of the air pollution control section of the Colorado Department of Health.

"The only people who adopt standards are the state legislature," he explains. "Denver had no legal way to adopt its standard for submission because the legislature does not meet until Jan 7. But Governor John A. Love did designate the Department of Health to hold public hearings (Oct. 15), and we were completely satisfied and pleasantly surprised with the response.

"HEW criteria documents talk in terms of ranges," Palomba observes. "Denver's standard for SO_2 and particulate levels is toward the restrictive side of the range.

A mild complaint was registered from commerce and industry at the hearing, according to this Denver official. Speaking collectively for their interests, a spokesman for the Colorado

Association of Commerce and Industry (CACI) complained that the standard could not be seen until two days prior to the hearing. Although the CACI spokesman noted that commerce and industry heartily endorse the protection of health and welfare of the people, they did not necessarily favor the more restrictive values in proposed standard.

Another problem in the Denver region is that NAPCA, under present state law, cannot support maintenance grants for its air pollution efforts.

So, the advice that Palomba would pass along to other officials is to release, as early as possible, any proposed standards to all interested parties before the hearing. Although the short-term session of the Colorado legislature is expected only to last two months, the authority to set air quality standards hopefully will be taken up, and Department of Health personnel plan to attend and stand ready to assume some responsibility.

"In the future, the Denver Region looks forward to an expansive air monitoring network," Palomba concludes. "We look forward to a minimum of six stations in the Denver Region with data from these stations telemetered to the Denver Air Pollution Control headquarters."

Panel appraises progress on air quality

Industry, government speakers see immediate effects of 1967 Act, but some problems still remain

With the federal Air Quality Act of 1967 already two years old, the inevitable process of evaluating its effect is beginning to occur. At a recent meeting of the American Institute of Chemical Engineers, the evaluation took the form of a panel discussion among the federal and state officials and representatives of three industries directly involved—coal, chemicals, and autos. If any consensus was reached, it was that the Air Quality Act has become a formidable social force, but many pitfalls lie in the way of further progress.

R&D funds

To lead off the discussion, the National Air Pollution Control Administration's (NAPCA) J. H. Ludwig summarized the federal air pollution control activities under the 1967 act. He pointed out that federal research and development spending on air pollution abatement is now more than \$40 million per year. Spending on SO₂ control (the largest single item) is \$14 million; motor vehicle emissions, \$4 million; industrial sources, \$21.5 million; research on effects, \$10.6 million; miscellaneous programs, \$13 million.

Richard J. Sullivan, head of New Jersey's Department of Health, pointed out that the act, like most remedial legislation, is a compromise, but, in general, he commented, "I like the compromise, in that it will involve a consensus." But the compromise may lead to oversimplification and senseless delays, said Sullivan, stemming from two serious defects of the act. For one thing, the system proceeds from the false premise that technology is available to make things happen on schedule, and then assumes that we are able to draw hard and fast lines to define the threshold of harmful effects. "In actuality, none of us has enough precision on our side to draw such a line," he said, and added that the standards which must be drawn are not inarguable.

The second defect is that the standards, although conceptually sound, infer that pollution is okay if the air is not seriously polluted—in other words, correct the problem after pollution has built up past the threshold. "That's how we got where we are today," Sullivan said.

The problem of how much control cost can be afforded was tackled by Stauffer Chemical's M. V. Anthony. He pointed to considerable progress that has been made in the chemical processing industry, and agreed with the assumption that health protection can not be compromised. But neglecting cost benefit considerations in control measures often leads to restrictive

legislation that can only be viewed as "control for control's sake." This has the effect of diverting financial resources from other pressing needs.

Unduly restrictive legislation has also posed technical problems in the chemical process industries for which there are at present no known solutions, according to Anthony. A few examples he cited:

- Control and measurement of sub-micron sized particles.
- Control of organic vapors that are emitted at levels too low to be economically recoverable and do not have the necessary fuel value for destruction by combustion.
- Control of odor causing materials, such as phenols, which are objectionable at low concentrations.

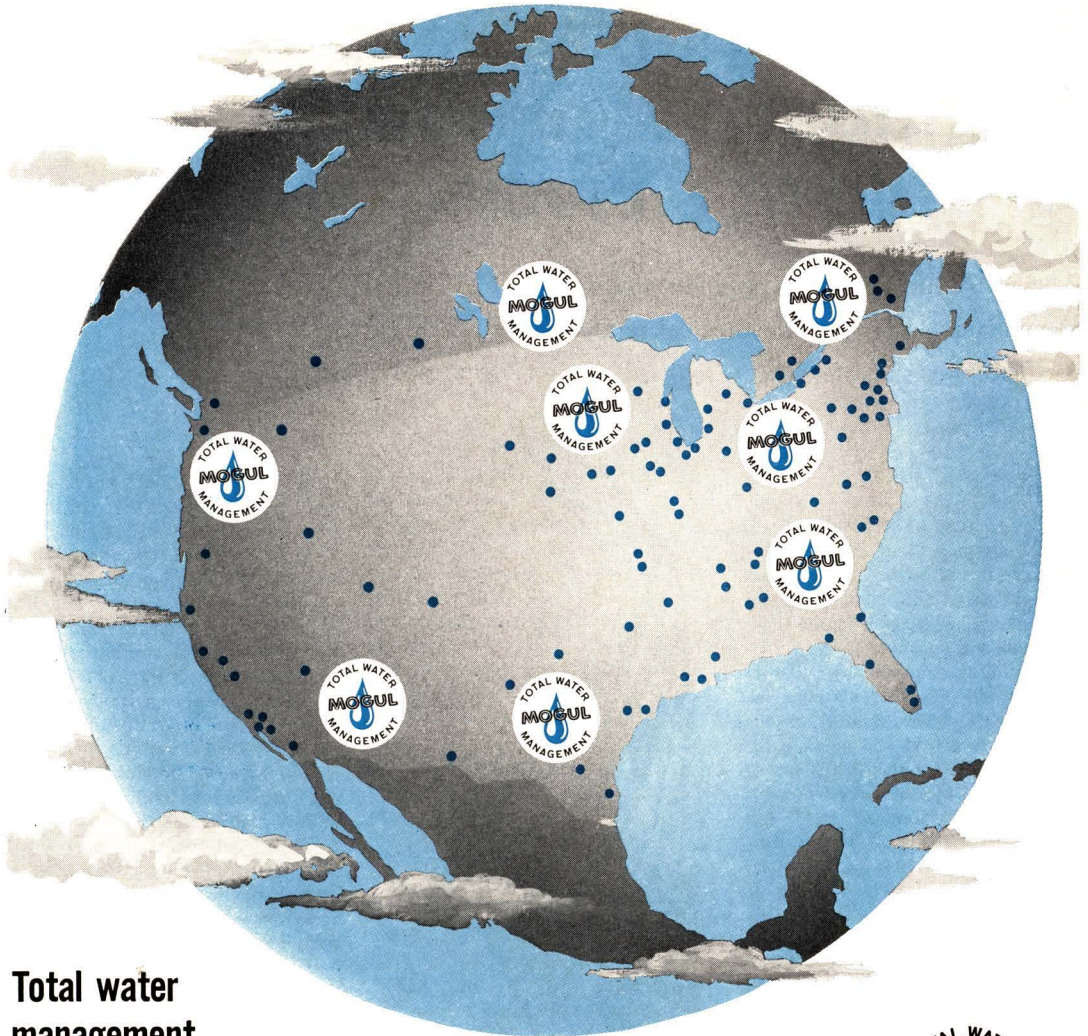
Coal and autos

Speaking for the coal industry, James R. Garvey, of Bituminous Coal Research, Inc., said that the full effect of the Air Quality Act has not yet been felt because of the changing situation regarding atomic energy. Orders for nuclear power plants climbed dramatically between 1964-68, but lately, for a number of reasons, many utilities are now going back to fossil fueled plants. With insufficient supplies of low sulfur fuels available to meet demands, increased emphasis should be placed on methods for removal of SO₂ from stacks of boilers that must, of necessity, use high sulfur coals. Garvey feels that NAPCA should take the initiative in this regard and build, operate, and maintain full-scale control processes that have been demonstrated in pilot plants.

The effect of the Air Quality Act on the automobile industry has been immediate and direct, said Frank W. Bowditch, speaking for the Automobile Manufacturers' Assn. He presented data to support his contention that, since the advent of emission control devices on the 1968 model autos, levels of hydrocarbons and carbon monoxide in urban atmospheres have dropped considerably. In fact, concentrations of these pollutants have already passed a peak, and by 1980, even without additional controls, concentrations will have dropped to 1940 levels. He concludes that before additional controls are asked for, some justification for the increased expenses be forthcoming.



Assessment. NAPCA's J. H. Ludwig opens AIChE panel discussion on air quality act



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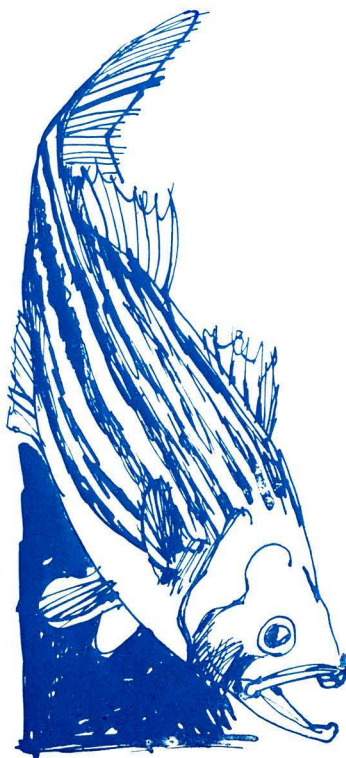
Water quality in industrial areas: profile of a river

The lower Hudson, like most tidal areas, must serve many needs, and its biological status is a direct measure of its ability to do so

The Hudson River drainage area, one of the major watersheds of eastern North America, encompasses about 12,400-14,500 square miles, and supports a human population of about 10.5 million. The flow in the southerly portion is controlled by a dam at Troy, about 155 miles north of the river mouth. The channel of the river can be traced well out into the Atlantic, and, at the northern limit of the tide at Troy, the river bottom is still four feet below sea level. The physical characteristics of the river bed indicate that it is a "drowned river."

The lower Hudson is a major transportation artery and, at the same time, a source of water for industrial and domestic purposes, an unsurpassed recreational resource in an area of great natural beauty and important historical associations, and serves as a drain for industrial and domestic wastes. The economic, industrial, and recreational potential of the river can hardly be overemphasized, yet, regrettably, little is known about its hydrology, biology, or chemistry. At a time when there is a need to predict the impact of projected developments, much basic data still are unavailable or controversial.

Part or all of the lower Hudson can be defined as estuary. The more seaward stretches are mesohaline (from two thirds to one third seawater), an intermediate zone is oligohaline (one third to one tenth seawater), and there is a final limnetic (or fresh water) stretch. The extent of these zones in the lower Hudson is closely dependent on fresh water runoff from the drain age area, and,



consequently, the saltfront—or the intrusion of seawater—varies from year to year, and with the seasons.

Hydrology

The average annual fresh water inflow into the lower Hudson at Green Island has been estimated at between 12,000-23,000 cubic feet per second (c.f.s.). This flow is uneven, with spring maxima as high as 40,000 c.f.s. (as in April 1967), and summer minima as low as 2000 c.f.s. The summer low flow period lasts from four to seven months each year. As the fresh water flow diminishes, the salt water

front pushes upstream from its spring limit near Tappan Zee (30 miles from Battery Park, Manhattan), reaching Newburgh (59 miles), Poughkeepsie (74 miles), or even Kingston (88 miles) in the summer and fall, depending on the annual rainfall. At any station on the river, the salinity increases progressively from May to November. There is generally a minor additional flow of fresh water before the cold temperatures of mid-winter reduce the flow. Although salinity is reduced somewhat (and the salt front pushed southwards), it remains relatively high throughout the winter, until the spring thaw brings about a massive dilution in March or April.

As seawater pushes up a river at flood tide, it tends to form a wedge of more dense saline water at the bottom of the river bed. Since the Hudson River is more than 100 feet deep in places, this saline water might be expected to remain near the bottom. In fact, only relatively slight differences have been seen between the surface and the bottom, indicating that the water gets fairly well mixed, at least north of the Tappan Zee.

The northward motion of the tides at some periods apparently reverses the river flow; since the tidal flow is massive—approximately 300,000 c.f.s.—it dwarfs the summer fresh water flows. Upstream flows of 19,000 c.f.s. have been measured at Governor's Island, 5000 c.f.s. at Riverdale, and even 2100 c.f.s. at West Point. The Federal Water Pollution Control Administration's Hudson-Champlain project, using dye marking studies, showed virtually no flow during the summer of 1965, when dyes added to the river at different sites were followed for 14 tidal cycles. At the head

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of the tidal influence at Troy, the tidal excursion was only three miles, but the velocity of net movement of the dye mass downstream was a mile and a half for each tidal cycle, or about 20 miles in a week. At Kingston and further south, while tidal excursions were greater, there was no net movement of the dye downstream.

The overwhelming effect of the tidal flux appears to produce a seiche-like movement of the brackish water, but little effective exchange. The implication for pollution and eutrophication effects are clear. The large volume of water (150 miles long with an average cross section of 150,000 feet) behaves as a brackish lake rocked north and south by the tide. The inflow is sufficient to exchange only 0.3-2% each day, assuming the simplest model of a single compartment, no evaporation or withdrawal, and no rain or additional inflow. The mean life of pollutants that remain in solution or suspension thus ranges from 40 days to more than 300 days, depending on the flow. Effluents and nutrients discharged into this brackish lake will, as in a true lake, be recirculated during dry summers between water, sediments, and biota. Only the high spring flows provide a flushing volume of water necessary to prevent an accumulation of pollutants and eventual eutrophication.

Too little is known about the physical hydrology of estuaries generally, and of the complex Hudson River system in particular. Without detailed knowledge of the self-purifying capacity of a river or an estuary, we cannot make a reasonable forecast of the effects that will follow a polluting load. A British study of pollution in

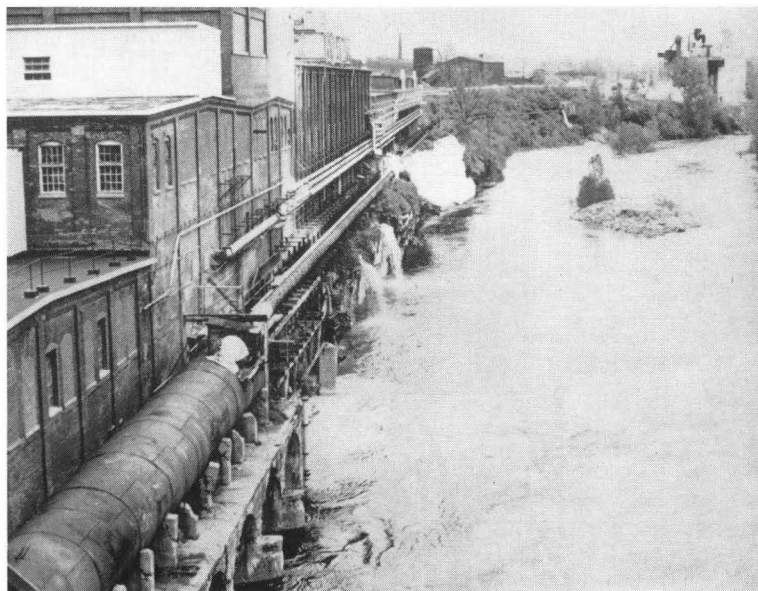
the River Thames demonstrated that the narrow parts of estuaries have a comparatively limited capacity to purify polluting material. The water flowing to and fro is substantially the same water from one day to the next, and, at times of low fresh water flow, pollutants may remain within the system for several months, building up in concentration. The narrow tidal stretches of the Hudson, then, are most vulnerable to pollution, with a limited surface area and mud-water interface available as either a source or a sink for pollutants.

Hudson ecology

The Laboratory for Environmental Studies, part of New York University Medical Center's Institute of Environmental Medicine, has been studying

aspects of Hudson River biology and chemistry since 1963. The study, financially supported in part by the New York State Health Department and the Consolidated Edison Co., developed initially from an interest in environmental radioactivity problems, and has broadened into a wider ecological study of the effects of various pollutants on the biota. We are accumulating survey data from the river, and trying to relate our information to that from other studies, especially those of water flow and industrial use of the river.

Those who have been actively engaged in this study (aside from the authors) are A. Perlmutter and H. Hirshfield of the biology department, and A. McCrone of the geology department at the Washington Square



Campus of New York University, and Dale Bath at the Lanza Laboratory.

Investigators pursued several lines of study:

- Considerable knowledge was acquired about the abundance, distribution, and variety of animals and plants in the river, from microscopic forms to fish.

- Seasonal changes in the nutrient anions as well as trace cations were followed.

- A long, continuing study was made of levels of radioactivity—both natural and man-made—in the water and biota.

- A study was made of levels of organo-chlorine pesticides in the river water and mud, and their accumulation in selected species of the biota.

- Present and future effects of heat additions to the river from industrial cooling and processes are being evaluated.

We are trying to see how the ef-

fects of varying fresh water flow and tidal cycle influence the distribution of inorganic pollutants, nutrients, pesticides, and heat, and how these affect the biota of the river. In short, we are trying to predict the future of the river in terms of eutrophication, in the face of increasing industrial and domestic utilization.

Nutrient loads

The sparsely populated agricultural Mohawk watershed, stocked with farm animals and supplied with fertilizers, provides significant nutrient input. This is seen in the relatively high nutrient levels of Mohawk river water (0.85 mg. nitrogen/l.) compared with other northeastern American rivers. About 17% of this could be attributed to natural runoff, and the remainder to artificial sources.

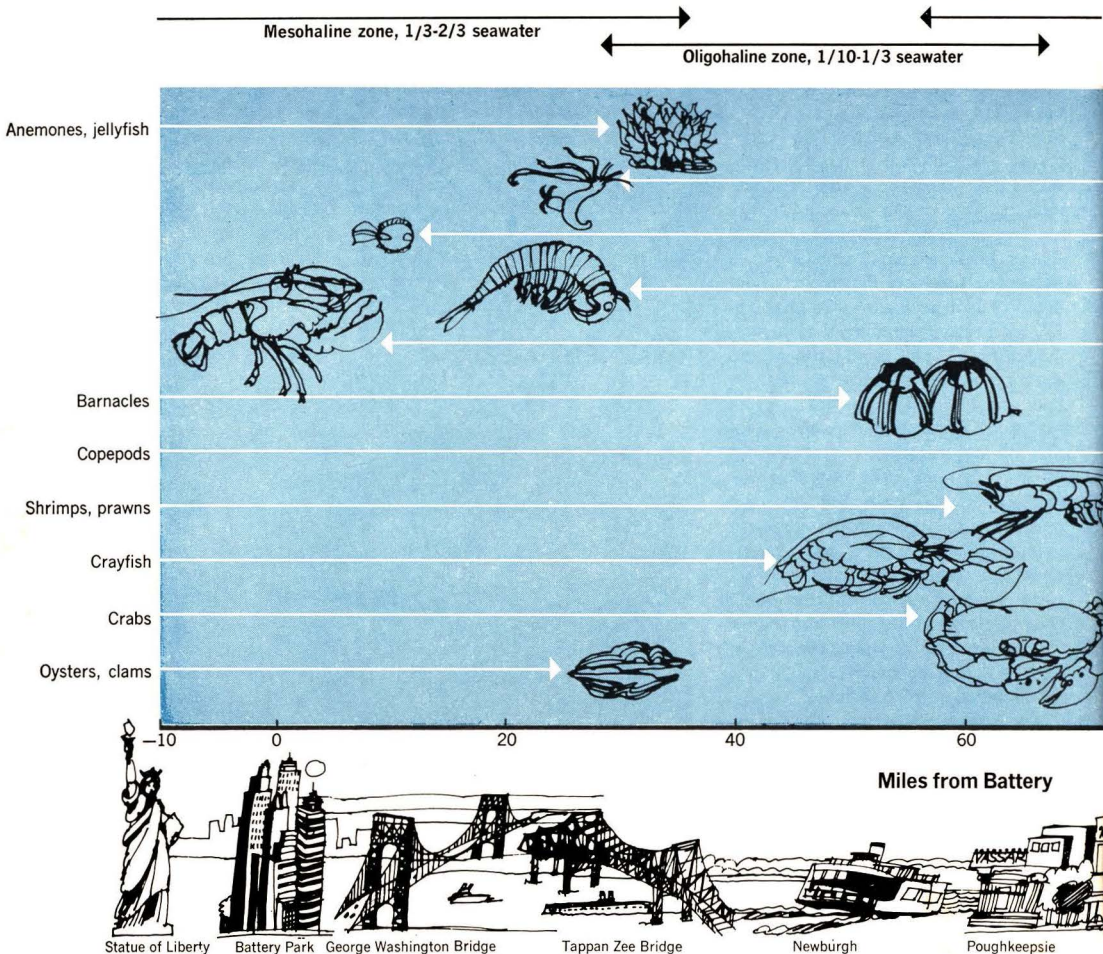
The 10.5 million population of the Hudson watershed produces 61 million kg. of nitrogen and 5.5 million

kg. of phosphorus as domestic waste in a year, much of which ultimately will be carried seawards by the river. Other wastes such as domestic detergents (contributing two thirds of total phosphate in one municipal discharge), and wastes from meat and dairy industries, yeast production, and paper manufacture, also contribute to the nutrient load.

Present municipal waste discharges north of Yonkers provide 1.6% of the spring volume of river flow, and 16% in the summer. At the Verrazano Narrows (Brooklyn), the proportions are much greater, because of the population density of the New York City area. The use of some rivers as sewage conduits has led to deoxygenation and conditions impossible for fish life, especially when sewage disposal is coupled with other industrial uses.

The nutrient content of the river water reflects its use. At Indian Point (43 miles from the Battery), the phos-

Distribution of common



phorus content of the water ranges from 9.5-2.5 μg -atoms/l. and, at the southern tip of Manhattan, a maximum of 12 μg -atoms/l. was recorded. (Seawater has about 2 μg -atoms/l.) Most of the phosphorus (70%) is present as inorganic phosphate, available for immediate plant assimilation and growth, while the remainder is dissolved organic phosphorus or particulate material. In general, phosphorus in river water usually is higher than in lakes, but these values are high by any measure—2.8 μg -atom/l. is the approximate upper limit of unpolluted water. Lake Washington (Seattle, Wash.), where eutrophication is slowly being reversed by a costly sewage diversion, has a phosphorus concentration of 7.5 μg -atoms/l.

Ketchum deduced a theoretical relationship that oxygen demand is equivalent to the oxygen supply from photosynthesis at concentrations of about 2 μg -atoms of phosphorus/l.

At higher phosphorus concentrations, the net oxygen demand during darkness will deplete the dissolved oxygen levels in the water. On this basis, we might expect that south of Albany, and around Manhattan, there will be net oxygen depletion. This has been shown to be true by monitoring studies of dissolved oxygen and biological oxygen demand levels. However, at many sites on the river, the dissolved oxygen level is adequate to maintain a healthy fauna in spite of the high phosphorus content.

Nitrate nitrogen concentrations in the mid-Hudson range from 0.2 mg. to as much as 1 mg. N/l., and are somewhat related to the tidal incursion. Inflowing water from the upper Mohawk watershed has a concentration of about 0.85 mg. N/l. These levels may be compared with values of 10 mg. total N/l. in the Thames River in England, and values around 1 mg. or less in relatively un-

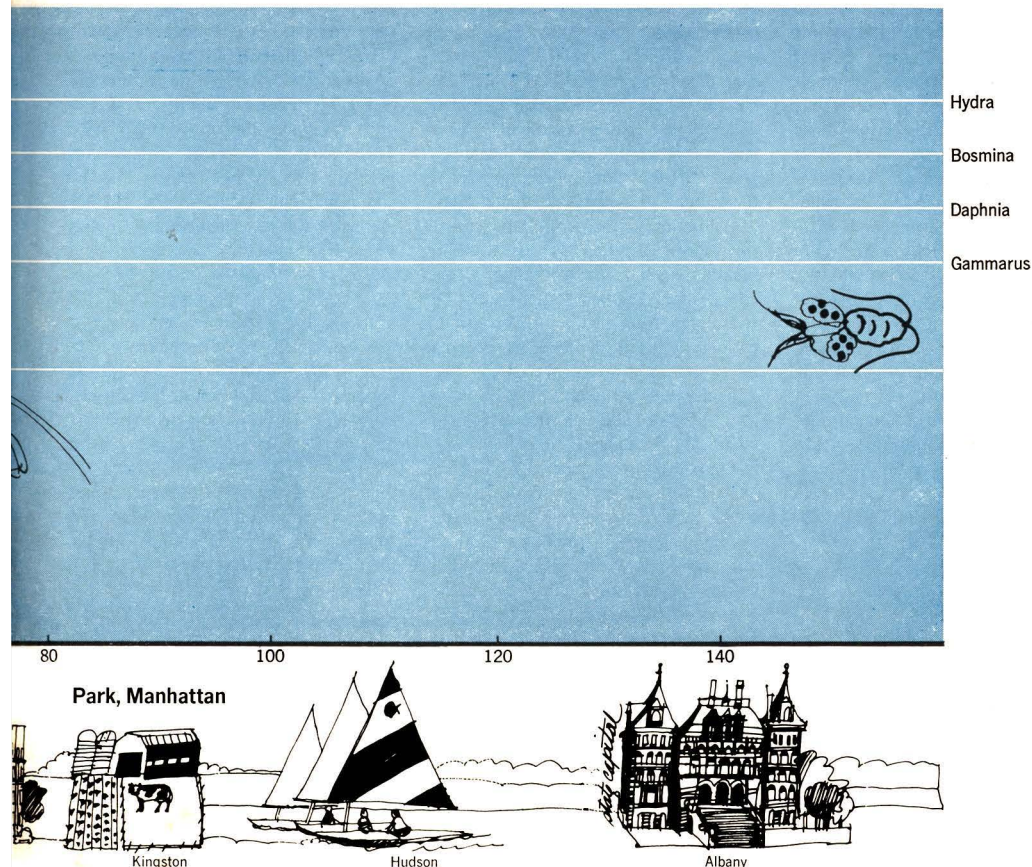
polluted lakes. A seasonal fall in nitrate concentrations, such as that seen in the late spring of 1968 at Indian Point, could be a limiting factor in phytoplankton growth in this region, although many other factors may be implicated. Nitrates can act as an important reserve of oxygen, even with appreciable concentrations of dissolved oxygen, but, in anaerobic conditions, nitrogen compounds are reduced to nitrogen or even to ammonia. The nitrogen cycle is related to dilution, oxygen, and temperature, and complicated by the effects of nitrogen fixation or denitrification by bacteria or plants.

Preliminary data on sulfate levels indicate about 25 mg. SO_4 /l. at Nyack, fairly closely related to salinity. As with nitrate, sulfate can be reduced to sulfide by bacteria in anaerobic or near anaerobic conditions.

The availability of these important anions—nitrate, phosphate and sul-

species in the Hudson River

Limnetic zone, fresh water



Common invertebrates of the lower Hudson River

	Mesohaline zone	Oligohaline zone	Limnetic zone
Protozoa	Dinoflagellates	<i>Diffugia</i> <i>Arcella</i> <i>Ochromonas</i> <i>Polytomella</i>	<i>Volvox</i> <i>Synura</i> <i>Paramecium</i> Amoebae
Coelenterates	Sea anemone (<i>Sagartia</i>) Jelly fish Ctenophores	<i>Hydra oligactis</i> Occasional jelly fish	<i>Hydra oligactis</i>
Rotifers	<i>Trichocerca</i> sp.	<i>Keratella cochlearis</i>	<i>Philodina</i>
Worms	Polychaetes	Polychaetes	<i>Tubifex</i> sp. <i>Aeolosoma</i> Nematodes
Crustacea	Harris crab (<i>Rhithropanopeus</i>) Blue crab (<i>Callinectes</i>) Prawn (<i>Palaemonetes</i>) Shrimp (<i>Crangon</i>) <i>Bosmina longirostris</i> Barnacle larvae Copepods: <i>Microarthridion</i> <i>Cyclops bicuspedatus</i> <i>Acartia tonsa</i>	<i>Gammarus fasciatus</i> Prawns Shrimps <i>Bosmina longirostris</i> Barnacle larvae Copepods: <i>Microarthridion</i> <i>Cyclops bicuspedatus</i> <i>Eurytemora hirundoides</i> <i>Ectinosoma eurticorne</i>	<i>Gammarus fasciatus</i> Crayfish (<i>Orconectes</i>) <i>Bosmina longirostris</i> <i>Daphnia pulex</i> Copepods: <i>Microarthridion</i> <i>Cyclops bicuspedatus</i> <i>Diaptomus pallidus</i>
Mollusca	Snails (<i>Physa</i>) Clam (<i>Mya</i>) Oyster (<i>Crassostrea</i>)	<i>Congeria leucophaeata</i> <i>Sphaerium</i>	<i>Elliptio complanatus</i>
Insecta	None	<i>Chaoborus albipes</i> <i>Tendipes</i>	Chironomid larvae Dragon fly larvae Stone fly larvae May fly larvae

fate—is important in a consideration of possible eutrophication of the lower Hudson. The present move to treat sewage so as to provide a liquid effluent may do little to reduce the nutrient levels of Hudson River water. In fact, it may worsen the present situation, since the treated effluent will provide nutrients in a readily available soluble form. Nitrate and phosphate levels in the Hudson are more than sufficient to develop algal blooms. Profuse blooms would result in a net oxygen depletion, with the subsequent reduction of nitrate and sulfate to noxious gases. In a flowing aquatic system, the interaction of nutrient concentrations and water temperature may be of major importance in controlling algal growth rates. If algal production exceeds the rate of removal by downstream flow and predation, nuisance blooms could result.

Heat additions

A further problem of growing importance is the use of water for industrial cooling. At the present rate of increase of water use in U.S., about 20% of the total fresh water runoff in the next 10 years will be required for cooling. Considering seasonal variations, about half of total runoff will be required for two thirds of the year. In the highly developed north-

eastern states, there are a number of rivers whose total flow is utilized, sometimes more than once in the passage downstream. Excessive water use will build up the heat load of fresh waters and estuaries; fortunately, heat is not conserved and can be dissipated to the atmosphere, provided the volume of water is adequate. Here is a situation where good management of water resources is essential to maintain water quality. The siting and design of power stations must be considered from the point of view of biological effects, so that overuse of the water resource is prevented. The difficulty lies in determining at what level of heat addition the biological effects are significant.

Long-term heat changes have been well documented for the Thames River, where heat released to the river rose from 555 mW in 1930 to about 3700 mW in 1950. The total volume of cooling water was approximately 2000 c.f.s. with a summer minimum of only 260 c.f.s. Of the total heat load in 1950, 75% was contributed by fossil fuel power stations, 6% by industrial effluents, 9% by sewage effluents, 6% by fresh water discharges, and 4% by biochemical activity. The yearly average temperature in the river over these 20 years rose from about 53° F. to

about 60° F. (an estimate corrected for changing meteorological conditions). On the basis of the proportions of contributors above, three quarters of the 7° F. rise (or about 5.3° F.) is due to about 3000 mW of power. The biological effects of such a temperature rise are not known, but the additional temperature in the Thames increased the oxygen deficit by about 4%. This effect is not large, and the estuary would have remained anaerobic even if its water had not been used for cooling. However, it was calculated that the reducing conditions, together with the temperature, increased the evolution of hydrogen sulfide by 20%. Following the introduction of strict legislation to control the quality of industrial discharges other than heat, hitherto fishless zones of the metropolitan Thames once again support fish life, albeit of species tolerant of the low oxygen.

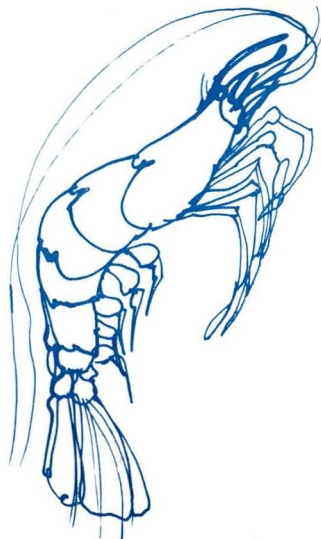
The flow of the Hudson is about 15 times greater than that of the Thames. The thermal capacity of the four power stations on the river is only 3000 mW, but projected development within the next few years includes an additional 10,000 mW. While the flow of the Hudson is not so intensively utilized as the Thames, and ambient air temperatures in the two countries are not the same, the paral-

lel is interesting, indicating the sort of temperature change, if not the magnitude, we might expect.

Biology of the Hudson

The variety of plants and animals in the Hudson is known only imperfectly. A study by the New York State Conservation Department some 30 years ago gives a good account of fish and rooted vegetation, but little information about the plankton or benthos (bottom living fauna) of the river. To evaluate the effects of such pollutants as excessive nutrients, trace metals, pesticides, and heat, we have been inventorying the kinds of animals and plants in the river, their relative abundance, and their distribution with respect to salinity. With so little baseline information, it is difficult to draw conclusions about changes in the biota that may have occurred. Even for fish studies, the methods of investigation have not been repeated. Hopefully, our present knowledge will be adequate to allow us to predict future changes in the river.

Our studies indicate there are two rather distinct environments in the Hudson River—the main channel and the shore. The main channel has abundant plankton, a rich variety of species of protozoa, diatoms, algae, rotifers, and the small crustacea which are important as food for larval fish. The shore has a rather different fauna and flora, partly because of different physical conditions, but also perhaps



because pollutants from shore-sited industry sweep along the shores before they are diluted by the main body of the river.

In the oligohaline stretch of the river, the dominant phytoplankton during the spring and summer is the *Melosira ambigua*, but, during the fall, this species gives way to others. At the same time, salinity rises with the summer seawater intrusion, allowing survival of a more marine-type biota at this site. When the estuary water is diluted by early winter or spring rains, a return of *Melosira* is

seen, together with a variety of other fresh water forms.

At a more southerly station on the river, a similar microflora to that at Indian Point was found during the summer. The limnetic zone in the summer is characterized by other species of *Melosira* and by other fresh water species. At all stations along the river, a number of species are found which might be considered as indicators of eutrophication. None of these were found as blooms, but the biological potential for nuisance algal growths (eutrophic species and more than adequate nutrient levels) undoubtedly is there.

The zooplankton characteristically is dominated by the microcrustacea, largely a flourishing copepod fauna. A number of crustaceans appear to be ubiquitous throughout many miles of the Hudson. Barnacle larvae are common in the plankton of mesohaline and oligohaline zones, derived from a benthic adult population extending to Peekskill. (Some of the copepod species show a transition with changing salinity.) An important zooplankton for fish nutrition, *Mysis oculata*, was found at Indian Point only in the fall of 1968, when salinity reached about 25% of the seawater levels.

Another group common in the zooplankton is the rotifers, sometimes frequent enough to be termed blooms, again with a succession of species inhabiting different zones. The rotifer fauna appears to be rich and varied.



Navigational aid. Esopus Meadows Lighthouse illustrates transportation, recreation, and aesthetic value of Hudson River

Fish seined on lower Hudson shores, July–August 1965-68

	Mean number/100,000 ft ²
Blueback herring	598
Freshwater killifish	512
Spot-tail shiner	333
Northern silverside	317
Johnny darter	200
White perch	180
Common sunfish	164
Alewife	102
Goldfish	93
Bay anchovy (absent 1967/68)	43
Golden shiner	42
Striped bass	30
Carp	10
Shad	9



The protozoan fauna is also rich in species in all parts of the river, but we do not have quantitative assessments of the relative dominance of species. Ciliates (25 genera) and flagellates (15 genera) are common, as are shelled amoebae (15 genera), in shore collections. Of the larger invertebrate inhabitants of the river bottom and of the shores, we know little about relative abundance, but something about distribution. Larger crustacea are represented by the Harris crab and blue crab in the more seaward stretches of the estuary, and by shrimps and prawns in less saline water. Replacing these decapods in the limnetic zone are crayfishes. The presence of the crabs upstream of Tappan Zee seems to depend on the seawater intrusion during the late summer. The apparent scarcity of crabs in very recent years may then not be due to pollution, but rather to freshening of the river after the drought years of 1964-66.

Mollusks also show a salinity related distribution. One species of oyster has been found as far north as the Tappan Zee; in the fresh water, gastropods are common. Insects are

scarcely present in the more saline reaches, only the larval *Chaoborus* and *Tendipes* extend into the oligohaline zone. Other insect larvae are found in the limnetic zone, but are restricted to the shore, except for chironomids. River mud provides habitat for worms.

The river has a large population of endemic fishes. Some 70 species recorded in 1936 include a tremendous migrant population of diadromous fish, many of which migrate into the Hudson or its tributaries to spawn. The shore environment serves as a nursery ground for the juvenile fish who feed on the snails, shrimp, and insects available there. This population has been sampled at selected stations along the river for the past five years by shore seining, and about 35 species have been recorded. The fish sampled by this technique are mostly in their first or second year, and some fish known to be present in the river—such as the hogchoker and the sturgeons—have not been seen. The shore sampling thus does not represent the true population, but only juvenile and small species which seek sheltered and shallow inshore areas. However, the consistent annual

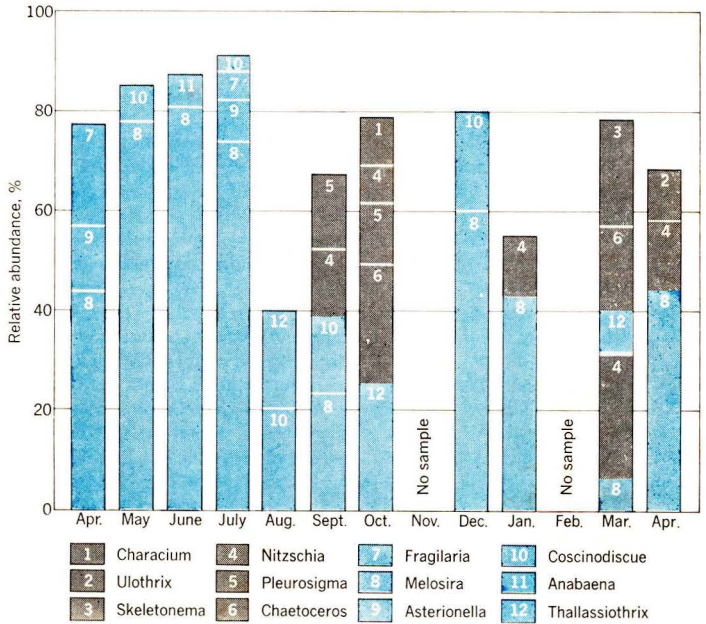
sampling can be used to indicate water quality changes. Most of the fish show little distribution related to salinity, since they are euryhaline, and able to live in waters of a wide range of salinity. The fresh water variety of killifish is dominant in the upper reaches of the river, while the euryhaline type is more common further south, and their distribution reflects the seawater intrusion. It is difficult to make valid comparison of the fish fauna of the river now and in 1936, but it is clear that the Hudson still presents an environment rich in variety and quantity of fish, even though commercial fishing in the river has severely declined.

Radionuclides

The lower Hudson River receives direct industrial waste discharges, as well as material from the watershed area, and the levels of some waste products in the river and its biota are of interest. We followed radionuclide and pesticide concentrations in the water and mud and their accumulation in the biota of the river.

The radionuclides are derived from three sources:

Phytoplankton species in Hudson River at Indian Point



• **Natural products, such as radium and potassium-40.** This group reflects the geological character of the watershed and the degree of salt water intrusion. Potassium-40 is the major contributor of radioactivity in estuarine water and its biota. South of West Point, the mean potassium-40 concentration during the past five years was 22 picocurie per liter (pCi/l.), less than 10% that of seawater, while, in the limnetic zone, it is only 1.5 pCi/l. Natural radium-226 and radium-228 derived from soils each contribute only about one tenth of a pCi/l.

• **Fission products, derived from fallout from weapons testing.** The nuclides derived from fallout are cesium-137, strontium-90, cerium-144, and ruthenium-106. Levels of these nuclides in the water or biota are low, and together contribute only about 1 pCi/l.

• **Activation products released as a result of nuclear production.** This group is the most interesting, even though levels are very low in water. Among the nuclides seen are cobalt-60 and manganese-54. Although their levels are so low that accurate estimates are difficult to make, their accumulation in plants or animals leads to the use of selected species as natural monitors. The situation is illustrated best by manganese-54, which is found in river muds, especially downstream of the nuclear power station at Indian Point, where physical and chemical conditions of seawater promote the salting out of manganese compounds.

Both stable manganese and its radioactive analog are accumulated by some water plants, especially those in the genera *Chara*, *Potamogeton*, *Valisneria*, and *Myriophyllum*, which are found along the shores of the Hudson. Those plants growing closest to a reactor effluent site naturally show the highest levels of activity. The natural soluble manganese concentration in Hudson River water ranges from less than 0.5 to 12 $\mu\text{g./l.}$, and total manganese (mostly particulate) about 1 mg./l. In *Potamogeton crispus*, it is about 2.3 mg./g. wet weight, indicating a concentration factor of about 190,000, with regard to the soluble nuclide concentration in the water, or 2300 to the total nuclide concentration. The total radioactive manganese levels in river water during 1966-68 indicate concentration factors of about 10,000 (range 3000-18,000) for this and similar species, in the same order of

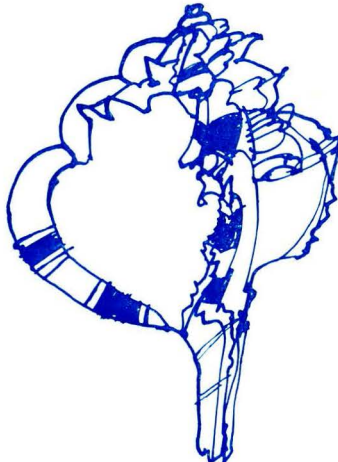
magnitude as total manganese. Plants of other genera, or phytoplankton samples, showed much lower levels of manganese or manganese-54.

Fish with a stable manganese content of only about 6 $\mu\text{g./g.}$ wet weight do not show appreciable accumulation of radioactive manganese, even though exposed to the same concentrations in the ambient water. Even if species of fish which are known consumers of plants are considered, there is no appreciable accumulation of manganese-54 observed. Hence, although these fish may ingest food high in manganese-54, low absorption by the gut probably limits its uptake in fish. Among invertebrates in the

river, blue crabs did not show any manganese-54, and only traces of two fission products, cerium-144 and cesium-137 (in 1964). Other crustaceans—crayfish, prawns, and shrimp—have similarly low concentrations. On the other hand, fresh water clams, which feed by filtering plankton and sediment from the water, showed a larger accumulation of radionuclides, including manganese-54, though not so much as plants. Other filter feeders—barnacles, oysters, etc.—were not sampled, but might be expected to have similar values. The relative accumulation from the two routes—direct uptake from the aquatic environment and uptake from ingested food—is not known.

Pesticides

While the distribution of radionuclides in the river water, mud, and biota reflects the distribution of the stable elements, as well as chemical interactions and the physiology of the biota, the distribution of pesticide residues reflects more clearly accumulation through trophic levels of the biota. Hudson River water contains numerous pesticide residues of the chlorinated hydrocarbon type, but only during the spring runoff are concentrations as high as 0.25 $\mu\text{g./l.}$ At other times of the year, the levels are too low for effective quantitation, generally less than 0.010 $\mu\text{g./l.}$, but



the residues can be more readily identified in biological samples.

Like other major northeastern rivers, the Hudson River water appears to have little DDT, although its metabolites are present. Dieldrin is present in about the same levels of concentration as the DDT metabolites. This pattern of occurrence is reflected in the biota, where accumulations of dieldrin and DDT metabolites are seen, rather than DDT itself. The muds take up pesticides from the water or retain them in settled sediments after the spring runoff. Muds contain the pesticides at 0.01-0.05 $\mu\text{g./g.}$ dry weight, generally several thousand times higher than the water. Plankton in the water, perhaps feeding on both microforms and suspended particles, build up concentrations of pesticides of about 0.02-0.06 $\mu\text{g./g.}$ wet weight (0.1-0.3 $\mu\text{g./g.}$ dry weight). This is about five to ten times higher than the sediments and about 20,000 times higher than water.

Clams feeding on the plankton would be expected to accumulate the residues to an even higher degree, but, in fact, pesticide concentrations in the fresh water clam are of the same order, 0.03-0.07 $\mu\text{g./g.}$ wet weight. Various fish species in the river have pesticide concentrations ranging from 0.05-0.8 $\mu\text{g./g.}$ wet weight. Local birds, such as heron and killdeer,

thought to be consuming fish or invertebrates from the river, have 0.3-3 $\mu\text{g./g.}$ wet weight on a whole body basis. The pesticide residues are particularly concentrated in fat. Thus, the continuing concentration through the food chain results in relatively high pesticide concentrations at the top of the food chain even though the base levels in the water are relatively undetectable. This has been observed in other environments.

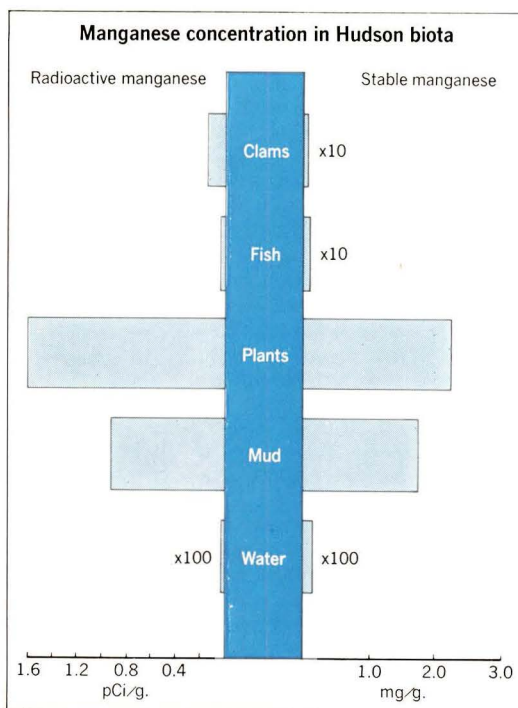
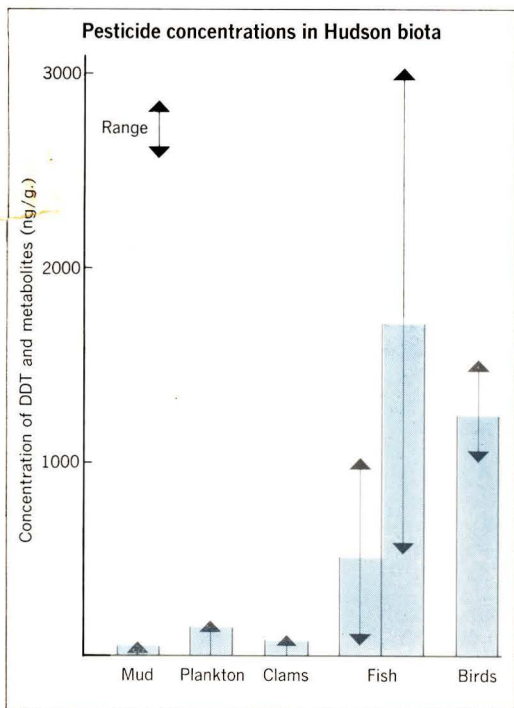
Trace element concentrations in the river water show great variability with sampling station, state of the tide, and temporal differences which, perhaps, reflect intermittent discharge of effluents from industries. Generally, in the limnetic zone, levels of trace metals are much less than those permitted by state or federal drinking water standards and do not appear to cause nuisance. In the more estuarine reaches of the river, high concentrations of iron, copper, and cadmium have been seen. Extensive studies would be required to locate the sources of such sporadic trace metal concentrations. Evaluation of potential biological effects would require application of sophisticated multivariate analysis.

Muds in the river may play an important role in the sequestration or regeneration of toxic material derived from pollutants, in addition to their

role in the oxygen cycle. Our survey of radionuclides and pesticides has indicated that muds always are much higher in concentrations of these materials than the overlying water. There are other indications from gas chromatograph tracings that they are accumulators of diverse organic residues as well.

Most mud samples from the lower river are clay silts with about 5-6% of easily oxidizable humic material, 50% silt, and 20-45% clay. The cation exchange capacity of the muds is considerable, even in the brackish reaches where cations are readily available in the water. Consequently, most of the exchange sites on the muds are occupied by hydrogen under predominantly reducing conditions.

The muds contain a substantial amount of manganese, (0.72 $\mu\text{g./g.}$ wet) compared with the ambient water, (0.01 $\mu\text{g./ml.}$). Hence, there is a sedimentary reservoir of manganese which could be available if reducing conditions prevail. Appreciable amounts of iron in the ferrous state also are present. Organic matter in the muds, oxidizable by hydrogen peroxide, accounts for more than 65% of the cation exchange capacity. Together with the unsaturated nature of the exchange sites, this indicates that, in relatively well oxygenated



conditions, the muds may have considerable capacity to absorb chemical pollutants, including radionuclides. More research is needed to evaluate the role of the muds in this capacity.

Conclusions

It is not difficult to predict an increased use of the Hudson River for the disposal of sewage wastes, industrial effluents, and cooling water, and for augmenting existing water supplies. At the same time, the burgeoning population of the area has a need and a right to use the river for recreation. How can further development be controlled, so that the water resources can be exploited, but still provide for that refreshment of the spirit so necessary for the urban inhabitant? Changes that might be expected from increased use are:

- First, an increasing nutrient load from domestic sewage and some industrial processes.
- Second, an increasing heat load.
- Third, an increased demand for industrial and domestic water.

Our studies have made clear that potential eutrophic nuisance species of algae are present in the river, and that the shores are populated by animals indicative of sewage pollution. Yet, serious fouling and deoxygenation have so far been avoided for most of the river. From this it could be deduced that the present situation need cause no concern; however, examples of other eutrophic water bodies give us warning of the potential rapidity of changes, and should encourage effective sewage treatment and the control of nutrient sources.

Heat additions to the aquatic environment are a major concern. In the Hudson, the volume of tidal flow can be utilized to disperse such heat; at the same time, it is clear that the capacity of the river as a heat sink is severely limited during the peak summer demand by a low net flow and high ambient air temperatures. If significant overall temperature rise in the river were allowed, it is highly probable that the species composition of the fauna and flora would be unbalanced. This interacting with the high nutrient levels in the river could easily tip the balance between nuisance conditions and the relatively healthy biological situation seen today. The effects of a temperature rise restricted to localized sites on the river have yet to be evaluated. There is a great need for more detailed hy-

drological and thermal studies of the river to evaluate the capacity of the Hudson to receive heat addition. There is also need for studies of species endemic to the river to determine their response, singly and together, to changes in temperatures.

The extraction of additional water for any purpose—pumped storage schemes, industrial use, or domestic use—is also of great importance, and is closely related to the other uses of the river. Almost any increased water extraction, except industrial cooling intakes, will make a volume of water unavailable at least for limited periods or limited stretches of the river. The effects of this on the present hydrological pattern in the river remain largely unknown. It seems probable, however, that the extent and duration of salt water intrusion up the river will increase. This will limit the sites for drinking water extraction and reduce the capacity for exchange of effluent discharges with the ocean which depends largely on the net fresh water flow.

How can the situation be controlled? We need more information about all aspects of the hydrology of the estuary, about the fauna and flora of the river and their response to existing and predicted conditions. We need strictly controlled use of the river for all purposes and at all levels. And, finally, we need to know how to alleviate pollution problems when they have arisen and how to channel waste materials, including heat, to other outlets.

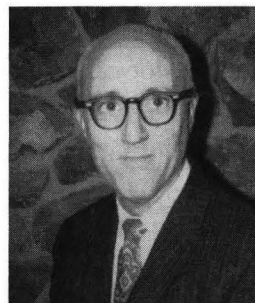
ADDITIONAL READING

- W. T. Edmondson, "Water Quality Management and Lake Eutrophication: The Lake Washington Case," in "Water Resources Management and Public Policy," edited by T.H. Campbell and R.O. Sylvester, University of Washington Press, 139-178 (1968).
- "Effects of Polluting Discharges on the Thames Estuary," Water Pollution Research Technical Paper No. 11, Department of Scientific and Industrial Research, Her Majesty's Stationery Office, London (1964).
- B.M. Ketchum, "The Flushing of Tidal Estuaries," *Sewage Ind. Wastes* 23, 198-209 (1951).
- G.G. Polikarpov, "Radioecology of Aquatic Organisms, Reinhold, New York (1966).
- D.W. Pritchard, "What is an Estuary: Physical Viewpoint," in "Estuaries," edited by G.H. Lauff, American Association for the Advancement of Science, 3-5 (1967).
- U.S. Department of Health, Education, and Welfare, "Report on Pollution of the Hudson River and its Tributaries," U.S. Government Printing Office, Washington, D.C. (Sept. 1965).

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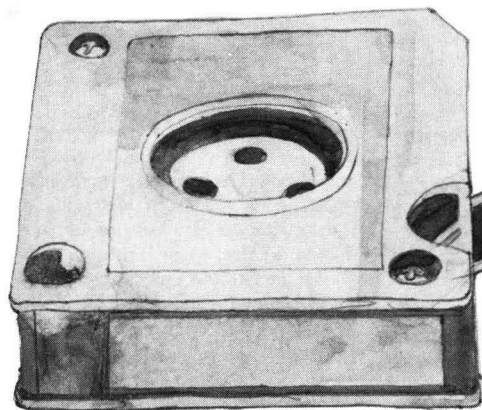
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Inhibition of Atmospheric Photooxidation of Hydrocarbons by Nitric Oxide

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■ The effects of nitric oxide concentration on the atmospheric photooxidation of propylene, ethylene, *trans*-2-butene, isobutene, and *m*-xylene have been investigated using long-path infrared spectrophotometry. Low concentrations of nitric oxide increased the photooxidation rate, while higher concentrations inhibited the rate of hydrocarbon photooxidation measured either by hydrocarbon disappearance or product formation. The nitric oxide concentration necessary for the maximum photooxidation rate for a given hydrocarbon concentration decreased as the hydrocarbon concentration decreased, but, for the olefins studied, it was relatively independent of reactivity or structure. Decreased concentrations of hydrocarbon consistently decreased the rate of hydrocarbon disappearance and product formation at all nitric oxide concentrations investigated. The results of this investigation, together with atmospheric analyses, have established that nitric oxide inhibition is important in the photochemistry of polluted atmospheres.

Nitric oxide and nitrogen dioxide promote as well as inhibit the atmospheric photooxidation of olefins. Nitric oxide has been shown to promote or inhibit the photooxidation rates of *trans*-2-butene (Tuesday, 1961), ethylene (Altshuller and Cohen, 1964), 2,3-dimethyl-2-butene (Tuesday, 1963), and propylene (Altshuller, Koczynski, *et al.*, 1967; Romanovsky, Ingels, *et al.*, 1967) depending on the concentration of nitric oxide. Nitrogen oxide inhibition and promotion of oxidant formation in hydrocarbon photooxidations have been reported by Haagen-Smit and Fox (1956) and Stephens, Hanst, *et al.* (1956), as well as the other investigators given.

Although these studies established that nitric oxide and nitrogen dioxide inhibit olefin photooxidations and smog symptoms of hydrocarbon photooxidations, the general importance of the inhibition could only be inferred, since the various studies were carried out with a variety of reactant concentrations, some substantially higher than normal atmospheric levels. A study has been carried out, therefore, with atmospheric concentrations of hydrocarbon and nitric oxide (Korth, Stahman, *et al.*, 1964; Neligan, 1962) to establish the importance of nitric oxide inhibition in the photochemistry of polluted atmospheres and to investigate the reactions responsible for the inhibition.

Experimental

Apparatus. Analyses were made with a 3-meter base path multiple reflection cell used in conjunction with a modified Perkin-Elmer Model 21 infrared spectrophotometer and attached ordinate scale expansion unit. Analyses were made with a 120 meter path length and five-fold ordinate scale expansion. Irradiation was supplied by a number of black light fluorescent bulbs (F96T8/BL) mounted in the long-path cell, which also served as the reaction vessel. Details of the cell and the irradiation system have been given elsewhere (Tuesday, 1961).

Chemicals. Airco "prepurified" nitrogen and U.S.P. oxygen were routinely used. The hydrocarbons used were Phillips Petroleum research grade. Matheson nitric oxide was used, after purification by passage through Ascarite and several bulb-to-bulb distillations. Nitrogen dioxide was prepared, as needed, by the thermal oxidation of nitric oxide, as described previously (Tuesday, 1963).

Procedure. The long-path cell was evacuated to a pressure less than 10μ of Hg before each run. Reactants at known pressures were expanded into the cell from an attached glass vacuum system. Nitrogen was then added to about 600 mm of Hg. After the addition of oxygen, (155 mm of Hg), the final pressure was brought to 760 mm of Hg with the small amount of additional nitrogen required.

The time from the addition of oxygen to the start of irradiation was 50 ± 2 min. for the ethylene photooxidation experiments, and 32 ± 3 min. for the other hydrocarbons studied. The nitrogen dioxide concentrations due to thermal oxidation can be calculated from the various experiments from the nitric oxide concentrations and the times given above, in the integrated second-order rate equation, using the rate constant of Glasson and Tuesday (1963). The thermal oxidation of nitric oxide occurring in the cell prior to irradiation was no more than 1% for initial nitric oxide concentrations of 1 p.p.m. or less.

The rate of hydrocarbon disappearance, as well as the rate of formation of several products, was followed by repeated scanning of a portion of the spectrum throughout the irradiation and the subsequent determination of concentration changes as a function of time using the appropriate absorptivities. The absorptivities of the olefins, formaldehyde, and acetone were determined by multiple calibrations based on manometric measurements. The absorptivity of *meta*-xylene was determined by multiple calibrations based on analyses made with a flame ionization detector. The absorptivity used

average rates during formation of 0.25 p.p.m. of these products, as defined by Eq. 2

$$\text{average product formation rate} = \frac{0.25}{t_p} \quad (2)$$

where t_p is the time required to form 0.25 p.p.m. of the product P .

For both ethylene and isobutene, initial increases in nitric oxide concentration increase the olefin oxidation rate, but because of nitric oxide inhibition, higher concentrations decrease this rate. The nitric oxide concentration required for the maximum rate of ethylene oxidation is 0.1–0.2 p.p.m., in substantial agreement with the results of Altshuler and Cohen (1964). Formaldehyde and acetone formation rates vary with nitric oxide concentration in the same way as the corresponding olefin oxidation rates. Since the carbonyl formation rates and olefin oxidation rates are both average rates defined somewhat differently, the agreement between these rates is quite satisfactory.

For the other olefins studied, *trans*-2-butene and propylene, the rate of olefin disappearance was the only measure of olefin photooxidation rate used. The variation of this rate with nitric oxide concentration is probably reflected in a corresponding variation in the rate of formation of the appropriate carbonyl product, in view of the agreement between these two measures of olefin photooxidation found for ethylene and isobutene.

Nitric oxide inhibition of the atmospheric photooxidation of *trans*-2-butene has been investigated at olefin concentrations of 1.0 and 2.0 p.p.m., with the results given in Figure 2. The photooxidation rate given is the average rate to the half-time, as defined in Eq. 1. For both concentrations of *trans*-2-butene, the photooxidation rate increases and then

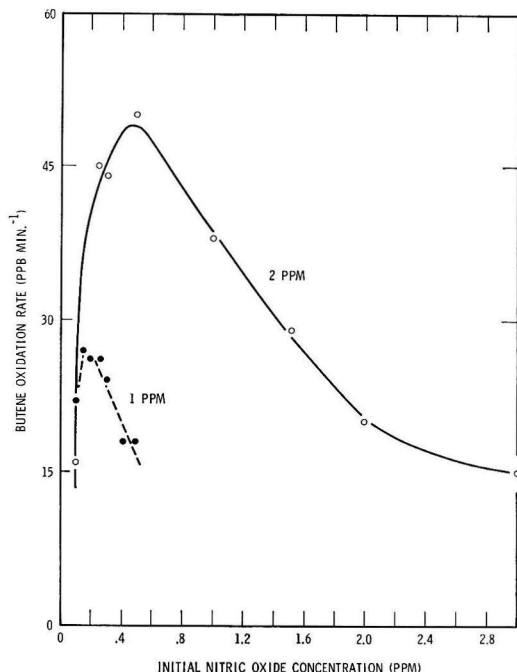


Figure 2. Nitric oxide inhibition of the atmospheric photooxidation of *trans*-2-butene

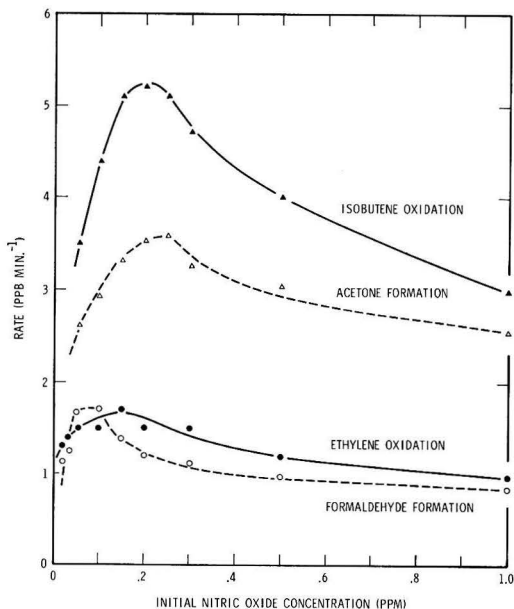


Figure 1. Nitric oxide inhibition of the atmospheric photooxidation of 1 p.p.m. ethylene and 1 p.p.m. isobutene

for ozone was that reported by Hanst, Stephens, *et al.*, (1961), while the absorptivity used for peroxyacetyl nitrate was that reported by Stephens (1964). Concentrations are reported in parts per million (p.p.m.) on a volume/volume basis. The wavelengths, in microns, used for analysis were: ethylene, 10.5; isobutene, 11.2; propylene, 11.0; *trans*-2-butene, 10.4; *meta*-xylene, 13.0; formaldehyde, 3.6; acetone, 8.2; peroxyacetyl nitrate, 8.6; and ozone, 9.5.

Light intensity was measured by photolyzing very low concentrations of nitrogen dioxide in nitrogen, and is expressed as the first-order rate constant for photolysis $K_d(\text{NO}_2)$. The details and advantages of this method of light intensity measurement in the experimental system have been described previously (Tuesday, 1961). For all of the photooxidations in the present investigation, the light intensity was equal to 0.29 min^{-1} .

Olefin Photooxidation Rate

The effect of the initial nitric oxide concentration on the rate of ethylene and isobutene photooxidation was determined at an olefin concentration of 1.0 p.p.m., and nitric oxide concentrations of 0.02–1.0 p.p.m. and 0.05–1.0 p.p.m., respectively, with the results shown in Figure 1. For these olefins, the photooxidation rate was measured both by the rate of olefin disappearance and the rate of formation of a major carbonyl product. The rates are given in parts per billion per minute (p.p.b. min^{-1}), where the p.p.b. unit is determined on a volume/volume basis. The rates of isobutene and ethylene oxidation given are the average rates to the half-time for hydrocarbon photooxidation, *i.e.*,

$$\text{average hydrocarbon oxidation rate} = \frac{(\text{HC})_0}{2t_{1/2}} \quad (1)$$

where $(\text{HC})_0$ is the initial hydrocarbon concentration and $t_{1/2}$ is the time necessary to reduce this concentration by one half. The rates of acetone and formaldehyde formation are the

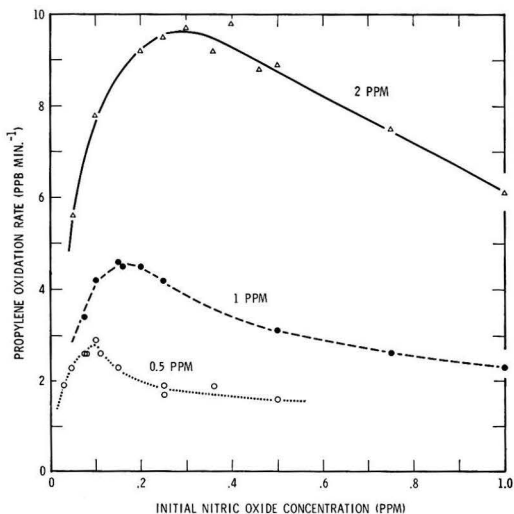


Figure 3. Nitric oxide inhibition of the atmospheric photooxidation of propylene

decreases with increased nitric oxide concentration, as was observed for ethylene and isobutene. For 2.0 p.p.m. *trans*-2-butene, however, the maximum photooxidation rate occurs at a nitric oxide concentration about twice that at which the maximum rate occurs for 1.0 p.p.m. *trans*-2-butene. The maximum photooxidation rate occurs at a *trans*-2-butene to nitric oxide ratio of about 5:1 for both hydrocarbon concentrations. This result can be compared to a ratio of about 2:1 for the photooxidation of 10 p.p.m. *trans*-2-butene (Tuesday, 1961). The explanation of this difference is not readily apparent. Altshuller (1967) found approximately the same ratio for the photooxidation of propylene at propylene concentrations from 0.5–3 p.p.m., but at a hydrocarbon concentration as high as 10 p.p.m., the ratio may change.

The effect of initial nitric oxide concentration on the rate of propylene photooxidation has been studied at olefin concentrations of 0.5, 1.0, and 2.0 p.p.m. and nitric oxide concentrations of 0.03–0.5, 0.07–1.0, and 0.05–1.0 p.p.m., respectively. The results of this investigation are given in Figure 3. The rate used is the average photooxidation rate to the half-time, as defined in Eq. 1. For all three concentrations of propylene, the photooxidation rate increases and then decreases with increased nitric oxide concentration, as was observed for ethylene, isobutene, and *trans*-2-butene. Again, the nitric oxide concentration which results in the maximum photooxidation rate for a given olefin concentration decreases as the olefin concentration decreases. For each of the propylene concentrations investigated, the maximum photooxidation rate occurs at a nitric oxide concentration such that the ratio of propylene to nitric oxide is about the same, *i.e.*, 5–7. Altshuller, Koczynski, *et al.* (1967) found the time for 50% conversion of 1.0 and 2.0 p.p.m. of propylene, in a static system, to minimize at propylene:nitrogen oxide ratios greater than or equal to 4:1, and Romanovsky, Ingels, *et al.* (1967) found the maximum rate of propylene disappearance to maximize at ratios from (1–4):1 for (0.5–2.0) p.p.m. of propylene. Our results are consistent with those of Altshuller, but are in disagreement with those of Romanovsky. This disagreement may be due, in part, to the difference in rate measures used in the two studies.

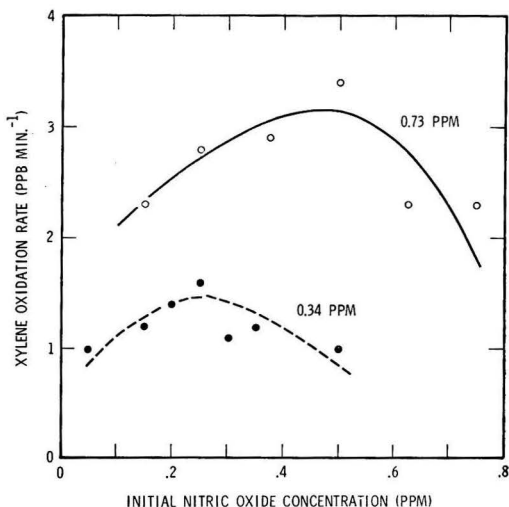


Figure 4. Nitric oxide inhibition of the atmospheric photooxidation of *meta*-xylene

The qualitative effect of nitric oxide concentration on the photooxidation rates of *trans*-2-butene, isobutene, propylene, and ethylene is insensitive to the olefin used. The nitric oxide concentration at which the maximum photooxidation rate occurs varies with olefin concentration and is relatively independent of olefin type or reactivity, at a constant olefin concentration.

Meta-Xylene Photooxidation Rate

Nitric oxide inhibition of the atmospheric photooxidation of *meta*-xylene has been studied at xylene concentrations of 0.34 and 0.73 p.p.m. The results of this study are given in Figure 4. The xylene oxidation rates used are the average rates to the half-time, as defined in Eq. 1. For both concentrations of *meta*-xylene, the photooxidation rate increases and then decreases with increased nitric oxide concentration. The variation of xylene oxidation rate with nitric oxide concentration is somewhat less than the variation found for the olefins. The nitric oxide concentration at which the maximum xylene oxidation rate occurs is roughly proportional to the xylene concentration. This is quite similar to the effect of olefin concentration observed for both *trans*-2-butene and propylene. For *meta*-xylene, however, the maximum oxidation rate apparently occurs at a higher nitric oxide concentration for the same concentration of hydrocarbon.

Ozone Formation Rate

Ozone is one of the products formed in the atmospheric photooxidation of hydrocarbons (Haagen-Smit, Bradley, *et al.*, 1953). The effect of nitric oxide inhibition on the rate of formation of this product has been determined for several hydrocarbons and several hydrocarbon concentrations. The results are given in Figures 5–7. The ozone formation rates given are the average rates to one-half the maximum ozone concentration formed, *i.e.*,

$$\text{average ozone formation rate} = \frac{(O_3)_{\max}}{2t_{1/2}} \quad (3)$$

where $(O_3)_{\max}$ is the maximum ozone concentration formed in the photooxidation and $t_{1/2}$ is the time, from the beginning of the irradiation, necessary to form one-half of this concentration.

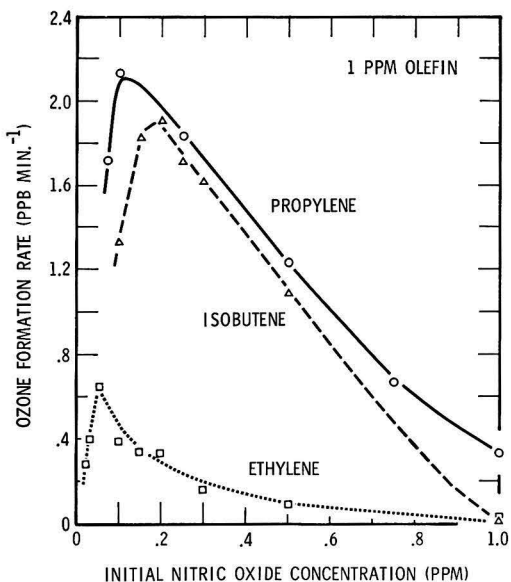


Figure 5. Nitric oxide inhibition of ozone formation

The effect of nitric oxide concentration on the rate of ozone formation in the photooxidation of ethylene, propylene, and isobutene at an olefin concentration of 1.0 p.p.m. is shown in Figure 5. For each of these olefins, the rate of ozone formation increases sharply as the nitric oxide concentration increases, but decreases rapidly again at higher nitric oxide concentrations. Nitric oxide inhibition of the ozone formation rate in the photooxidation of these olefins is similar to the inhibition of the olefin photooxidation rate given previously in Figures 1-3. The nitric oxide concentration for maximum ozone formation rate is somewhat dependent on olefin type, whereas the nitric oxide concentration for maximum olefin oxidation rate was independent of olefin type or reactivity. For isobutene, the maximum olefin oxidation rate and the maximum ozone formation rate occur at about the same nitric oxide concentration (0.15 p.p.m.). For ethylene and propylene, however, the maximum ozone formation rate occurs at a lower nitric oxide concentration than the maximum olefin oxidation rate, *i.e.*, 0.05 p.p.m. for ethylene and 0.1 p.p.m. for propylene. Since the ozone formation rate and the olefin oxidation rate are both average rates, these differences may not be significant.

The ozone results can be compared to data in the literature. Altshuller and Cohen (1964) found that the maximum oxidant yield from the photooxidation of 1.0 p.p.m. of ethylene maximized at 1.0 p.p.m. of nitric oxide. Our data indicate that the maximum ozone concentration occurs at 0.2 p.p.m. of nitric oxide. In the irradiation of 2.0 p.p.m. of propylene with nitrogen oxides, the ozone concentration formed after 2 hours irradiation (Altshuller, Kopczynski, *et al.*, 1967) maximized at a propylene:nitrogen oxide ratio of 2:1, while the peak ozone concentration (Romanovsky, Ingels, *et al.*, 1967) maximized at a ratio of 1.3:1. The results of the present study indicate a ratio for maximum ozone concentration of less than or equal to 2:1. In the photooxidation of 1.0 p.p.m. of isobutene with nitrogen dioxide (Leighton, 1961), the maximum ozone yield was obtained at a hydrocarbon:nitrogen dioxide ratio of about 1:1, whereas our results with nitric oxide gave a ratio

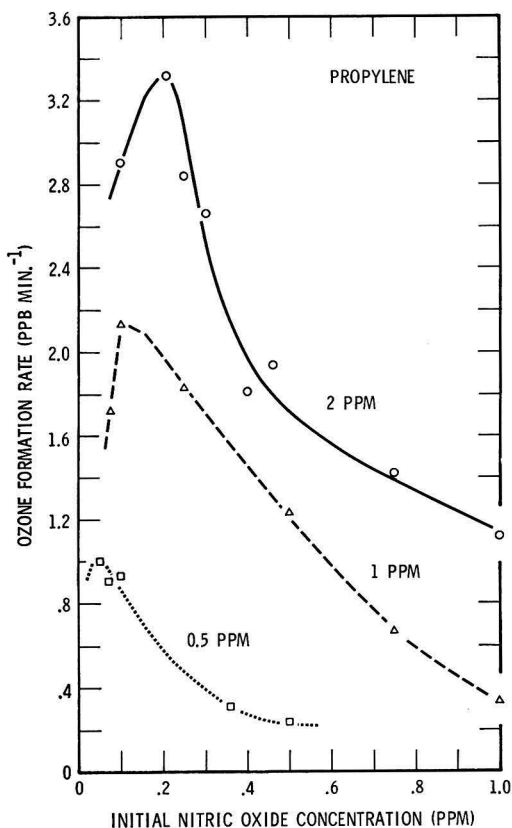


Figure 6. Nitric oxide inhibition of ozone formation

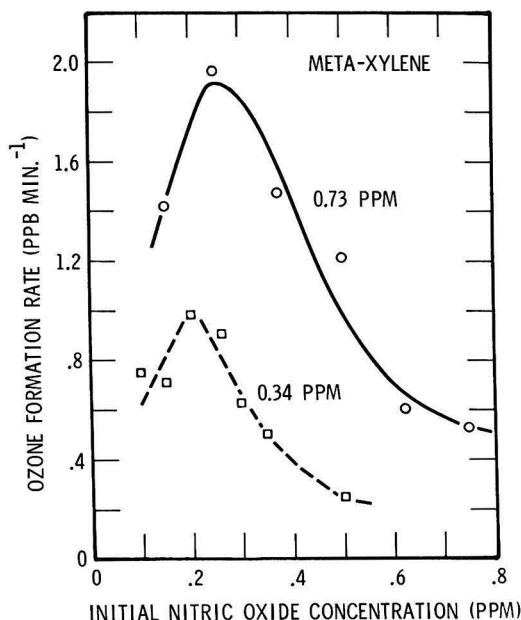


Figure 7. Nitric oxide inhibition of ozone formation

of 2.7:1. The use of nitrogen dioxide rather than nitric oxide (Tuesday, 1963) results in the maximum terminal ozone concentration from the photooxidation of tetramethylethylene occurring at a higher hydrocarbon:nitrogen oxide ratio.

Comparison of the above literature results with the data of this investigation show that maximum ozone yields occur, in general, at higher hydrocarbon:nitrogen oxide ratios in our system. The effect is not consistent, however, since the propylene results are in essential agreement with the literature, while the ethylene and isobutene results do not agree. There appears to be no explanation for these differences, although the reaction chambers used in our study and in the literature studies are rather different in composition. The methods of analysis used are also different. In any event, there is no clear-cut reason for differences of the magnitude noted, particularly in the case of the ethylene system.

The effect of olefin concentration on the nitric oxide inhibition of ozone formation is shown in Figure 6. For all three concentrations of propylene, the nitric oxide inhibition of the ozone formation rate is similar to the inhibition of the propylene oxidation rate given previously in Figure 3. The maximum olefin oxidation rate occurs at a nitric oxide concentration such that the ratio of propylene:nitric oxide is about 5-7. For each of the propylene concentrations investigated, the maximum ozone formation rate occurs at a lower nitric oxide concentration, so that in this case the ratio of propylene:nitric oxide is about 10.

The effect of nitric oxide on the rate of ozone formation in the photooxidation of *meta*-xylene was determined at *meta*-xylene concentrations of 0.34 and 0.73 p.p.m. The results shown in Figure 7 are quite similar to the results found for the olefins studied. The ozone formation rate increases as the nitric oxide concentration increases, reaches a maximum value, and then decreases with further increases in nitric oxide. The nitric oxide concentration at which this maximum value occurs increases with *meta*-xylene concentration. A similar effect was noted previously for propylene. The maximum ozone formation rates found for *meta*-xylene occur at lower nitric oxide concentrations than do the maximum xylene oxidation rates shown in Figure 4. In addition, the variation of the ozone formation rate with nitric oxide is much greater than the variation found for the xylene oxidation rate.

The nitric oxide inhibition of ozone formation shown in Figures 5-7 can be partially attributed to the use of the rate expression defined by Eq. 3. This rate definition was used, since it most nearly represents the atmospheric formation of ozone in photochemical smog. Since ozone does not accumulate until virtually all of the nitric oxide is oxidized, increased concentrations of nitric oxide can result in a delay in ozone appearance. It is interesting to note, however, that nitric oxide inhibition is still observed when the ozone-delay effect has been eliminated. The delay effect was eliminated by subtracting the time at which ozone first appeared, t_0 , from the time required for formation of one half the maximum ozone concentration, $t_{1/2}$. The modified ozone formation rate is then defined by Eq. 4 and the results are given in Table I.

$$\text{modified ozone formation rate} = \frac{(O_3)_{\max}}{2(t_{1/2} - t_0)} \quad (4)$$

Nitric oxide inhibition is clearly evident, even when the ozone-delay effect has been eliminated.

Effect of Added Nitrogen Dioxide

The effect of added nitrogen dioxide on the nitric oxide inhibition of propylene photooxidation and ozone formation was determined at a propylene concentration of 1.0 p.p.m.

Table I. Modified Ozone Formation Rate as a Function of Initial Nitric Oxide Concentration in the Photooxidation of 1.0 p.p.m. Propylene^a

(NO) ₀ (p.p.m.)	$t_{1/2}$ ^b (min.)	t_0 ^c (min.)	(O ₃) _{max} (p.p.m.)	Ozone Rate ^d (p.p.b. min. ⁻¹)
0.075	70	10	0.24	2.0
0.10	54	20	0.23	3.4
0.25	82	48	0.30	4.4
0.50	142	90	0.35	3.4
0.75	209	140	0.28	2.1
1.00	270	150	0.18	0.85

^a The reactions were carried out using the conditions given in the experimental section.

^b The total time necessary for the formation of one half of the maximum ozone concentration.

^c The time required for the onset of ozone formation.

^d Calculated according to Eq. 4.

and an initial nitrogen dioxide concentration of 0.1 p.p.m. The results are shown in Figure 8. For comparison, the results obtained without added nitrogen dioxide are also included in this figure.

Added nitrogen dioxide increases the rate of propylene oxidation at the same initial nitric oxide concentration, except at 0.5 p.p.m. A previous study (Tuesday, 1963) also indicated that nitrogen dioxide acts as both a promoter and inhibitor of olefin photooxidation. Nitrogen dioxide increases the rate of ozone formation at very low nitric oxide concentrations, but decreases this rate at higher nitric oxide concentrations.

At the same total initial nitrogen oxide concentration, *i.e.*, nitric oxide plus nitrogen dioxide, 0.1 p.p.m. of nitrogen dioxide and 0.1 p.p.m. of nitric oxide affect the propylene oxidation rate similarly at total nitrogen oxide concentrations

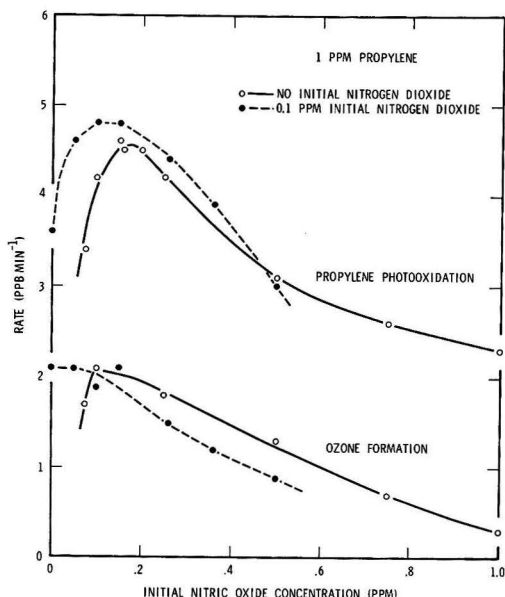


Figure 8. Effect of added nitrogen dioxide on the photooxidation of propylene

less than 0.15 p.p.m. and greater than 0.6 p.p.m. For total nitrogen oxide concentrations between 0.15 and 0.6 p.p.m., propylene oxidation is inhibited more by 0.1 p.p.m. of nitric oxide than by 0.1 p.p.m. of nitrogen dioxide. However, in terms of total initial nitrogen oxide concentration, 0.1 p.p.m. of nitric oxide and 0.1 p.p.m. of nitrogen dioxide are equally effective in inhibiting ozone formation throughout the concentration range investigated.

Peroxyacetyl Nitrate

Peroxyacetyl nitrate is another product of the atmospheric photooxidation of many hydrocarbons (Stephens, Hanst, *et al.*, 1956). The effects of initial nitric oxide concentration on the yield of this product from the photooxidation of 0.5, 1.0, and 2.0 p.p.m. of propylene are given in Figure 9. The yields given are the concentrations of peroxyacetyl nitrate formed after 2 hours of irradiation. The amount of peroxyacetyl nitrate formed varies with nitric oxide concentration in the same way as the corresponding rates of propylene oxidation and ozone formation (Figures 3 and 6).

The amount of peroxyacetyl nitrate formed increases and then decreases with increased nitric oxide concentration, and the nitric oxide concentration which gives the maximum yield of peroxyacetyl nitrate increases with propylene concentration. Altshuller, Kopczynski, *et al.*, (1967) found that the peroxyacetyl nitrate yield after a two hour irradiation of 2.0 p.p.m. of propylene with various amounts of nitric oxide maximized at approximately 0.7 p.p.m. of nitric oxide, whereas, in our system, the maximum was attained at 0.3 p.p.m. As discussed for the ozone results, there is no clear-cut reason that can be given for this difference.

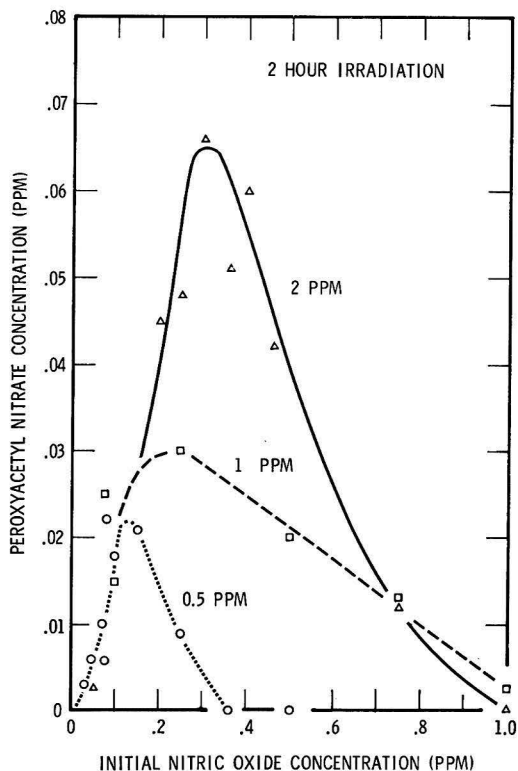


Figure 9. Peroxyacetyl nitrate from propylene photooxidation

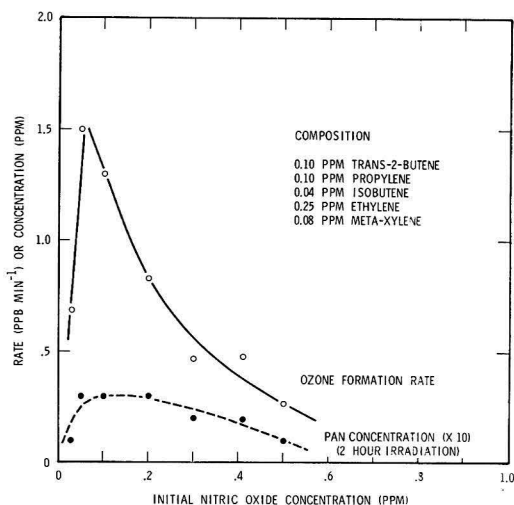


Figure 10. Nitric oxide inhibition of the atmospheric photooxidation of a hydrocarbon mixture

Photooxidation of a Hydrocarbon Mixture

Nitric oxide inhibition of the photooxidation of a hydrocarbon mixture was investigated using a mixture similar in composition and concentration to those present in polluted air. The hydrocarbon mixture was 0.1 p.p.m. of *trans*-2-butene, 0.10 p.p.m. of propylene, 0.04 p.p.m. of isobutene, 0.25 p.p.m. of ethylene, and 0.08 p.p.m. of *meta*-xylene, for a total carbon-atom concentration of 2.00 p.p.m.

The results of this investigation are given in Figure 10. Nitric oxide inhibition of the photooxidation of this hydrocarbon mixture was very similar to the inhibition found for the photooxidation of the individual components given previously in Figures 5, 6, 7, and 9. Nitric oxide concentrations higher than about 0.05 p.p.m. inhibited both the rate of ozone formation and the amount of peroxyacetyl nitrate produced after 2 hours' irradiation.

Discussion

Nitric oxide inhibition was observed in the atmospheric photooxidation of all the hydrocarbons studied. This inhibition decreased the rate of hydrocarbon photooxidation, the rate of ozone formation, the rate of carbonyl product formation in olefin photooxidation, and, at least for propylene, the yield of peroxyacetyl nitrate.

As a result of nitric oxide inhibition, the rates of hydrocarbon photooxidation and ozone formation are maximum at a certain nitric oxide concentration. At lower or higher nitric oxide concentrations, the rates of hydrocarbon photooxidation and ozone formation decrease. For the two olefins and the aromatic hydrocarbon studied, the nitric oxide concentration at which the maximum rates of hydrocarbon photooxidation and ozone formation occur decreases as hydrocarbon concentration decreases.

For the two olefins and the aromatic hydrocarbon studied, decreases in hydrocarbon concentration decreased the rate of hydrocarbon photooxidation, the rate of ozone formation, and, at least for propylene, the amount of peroxyacetyl nitrate formed.

Since nitric oxide inhibition was observed at concentrations of hydrocarbon and nitric oxide actually found in the atmosphere (Korth, Stahman, *et al.*, 1964; Neligan, 1962),

nitric oxide inhibition is apparently important in the photochemistry of polluted atmospheres. If nitric oxide inhibition is occurring, decreases in nitric oxide concentration at a constant hydrocarbon concentration will increase the rates of hydrocarbon photooxidation and ozone formation. Furthermore, decreases in hydrocarbon concentration at a constant nitric oxide concentration will increase the amount of inhibition. As a result, the rates of hydrocarbon photooxidation and ozone formation may decrease more than expected from the hydrocarbon concentration decrease.

A recent paper by Schuck, Pitts, *et al.*, (1966), of the University of California, Riverside, has verified that nitric oxide inhibition is important in the polluted atmospheres found in Los Angeles. Schuck, Pitts, *et al.*, compared the 6-9 A.M. atmospheric analysis made at the downtown station of the Los Angeles Air Pollution Control District with the daily maximum oxidant values recorded at the Pasadena Station, and with smog incidence as defined by the Control District. According to this definition, a "smoggy" day is a day when moderate to severe eye irritation is reported, or a day on which the visibility is less than 3 miles at a relative humidity less than 60%. Schuck, Pitts, *et al.*, found that both the percentage of days resulting in smog and the atmospheric oxidant concentration were a maximum when the concentration of oxides of nitrogen was about 0.15 p.p.m. Atmospheric nitrogen oxide concentrations higher than this resulted in lower atmospheric oxidant concentration and lower percentages of smoggy days, indicating that nitric oxide inhibition was occurring in the Los Angeles atmosphere.

Recent measurements made by the U.S. Public Health Service (Korth, Stahman, *et al.*, 1964) indicate that polluted atmospheres may contain 3-8 p.p.m. of hydrocarbon, expressed as p.p.m. of carbon and 0.3-0.6 p.p.m. of nitrogen oxide. If 6 p.p.m. of carbon and 0.4 p.p.m. of nitric oxide are taken as average values, and propylene is assumed typical of the hydrocarbons present in polluted atmospheres, then the hydrocarbon oxidation rate in this atmosphere is the value shown in Figure 3 for 2.0 p.p.m. of propylene and 0.4 p.p.m. of nitric oxide. The effects of various reductions in hydrocarbon and nitric oxide concentrations on the hydrocarbon oxidation rate in the "typical" polluted atmosphere are shown in Table II. All of the values used were taken from Figure 3.

This table indicates that, with no nitric oxide reduction, the hydrocarbon oxidation rate is decreased more than expected by a given hydrocarbon reduction because of increased nitric oxide inhibition. As shown in this table, reduction in both nitric oxide and hydrocarbon decrease the hydrocarbon oxidation rate less than hydrocarbon reduction alone. This illustrates the observation made previously that decreases in nitric oxide concentration decrease the amount of inhibition, and, as a result, the hydrocarbon photooxidation rate increases.

Table II. Hydrocarbon Rate Reduction^a

Nitric oxide reduction (%)	0	25	50	75
0% hydrocarbon reduction		-3	2	18
50% hydrocarbon reduction	64	58	52	56
75% hydrocarbon reduction	82	80	78	70

^a Based on assumed current atmospheric levels of hydrocarbon = 6 p.p.m., of carbon = 2 p.p.m. of C₃H₆, nitric oxide = 0.4 p.p.m.

Schuck, Pitts, *et al.*, have estimated from the Los Angeles atmospheric analyses mentioned previously the effect various reductions in atmospheric levels of nitrogen oxides and hydrocarbons would have on smog incidence, while recognizing that their estimates are based on "a limited amount of data along with many unproven assumptions." They concluded that a "50% reduction in smog active hydrocarbons would lead to a 50% reduction in the number of 'smoggy' days." The results given in Table II, on the other hand, indicate that a 50% reduction in hydrocarbon will decrease the hydrocarbon oxidation rate by about 64%.

Schuck, Pitts, *et al.*, also state that a 50% reduction in oxides of nitrogen would *not* lead to a reduction in "smoggy" days. The results given in Table I are in essential agreement with this, since they indicate only a 2% decrease in hydrocarbon oxidation rate with a 50% reduction in nitric oxide concentration. For a 75% reduction in oxides of nitrogen, Schuck, Pitts, *et al.*, estimate a 20% reduction in smog incidence, which is also in essential agreement with the 18% reduction in hydrocarbon oxidation rate given in Table II. This observation is contrary to an interpretation of atmospheric and laboratory data by Hamming and Dickenson (1966), see also Nicksic, Harkins, *et al.*, (1966).

Mechanism

Free radical mechanisms have been proposed for both the atmospheric photooxidation of olefins (Leighton, 1961; Tuesday, 1961) and aromatics (Kopczynski, 1964). Since nitric oxide and nitrogen dioxide are known inhibitors of free radical reactions (Steacie, 1954), nitrogen oxide inhibition of the atmospheric photooxidation of hydrocarbons is consistent with these mechanisms.

Although the results of this study do not define the chemical reactions responsible for nitric oxide inhibition, two pertinent conclusions can be drawn from the data. The observation that the maximum photooxidation and ozone formation rates occur at a nitric oxide concentration approximately proportional to the hydrocarbon concentration used suggests that an inhibitory reaction approximately first-order in both nitrogen oxide and hydrocarbon is important. As shown in Figures 1, 2, and 3, the nitric oxide concentration necessary for the maximum photooxidation rate is relatively insensitive to olefin structure. This result implies that the electronic and steric requirements of the inhibitory reaction(s) are similar to those of the rate-determining step for photooxidation.

Acknowledgment

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Literature Cited

- Altshuller, A. P., Cohen, I. R., *Intern. J. Air Water Pollution* **8**, 611 (1964).
 Altshuller, A. P., Kopczynski, S. L., Lonneman, W. A., Becker, T. L., Slater, R., *ENVIRON. SCI. TECHNOL.* **1**, 899 (1967).
 Glasson, W. A., Tuesday, C. S., *J. Amer. Chem. Soc.* **85**, 2901 (1963).
 Haagen-Smit, A. J., Fox, M. M., *Ind. Eng. Chem.* **48**, 1484 (1956).
 Haagen-Smit, A. J., Bradley, C. E., Fox, M. M., *Ind. Eng. Chem.* **45**, 2086 (1953).
 Hamming, W. J., Dickenson, J. E., *J. Air Pollution Control Assoc.* **16**, 317 (1966).
 Hanst, P. L.; Stephens, E. R., Scott, W. E., Doerr, R. C., *Anal. Chem.* **33**, 1113 (1961).

Kopczynski, S. L., *Intern. J. Air Water Pollution* **8**, 107 (1964).
Korth, M. W., Stahman, R. C., Rose, A. H., Jr., *J. Air Pollution Control Assoc.* **14**, 168 (1964).
Leighton, P. A., "Photochemistry of Air Pollution," p. 269, Academic Press, New York, 1961.
Neligan, R. E., *Arch. Environ. Health* **5**, 581 (1962).
Nicksic, S. W., Harkins, J., Painter, L. J., *Intern. J. Air Water Pollution* **10**, 15 (1966).
Romanovsky, J. C., Ingels, R. M., Gordon, R. J., *J. Air Pollution Control Assoc.* **17**, 454 (1967).
Schuck, E. A., Pitts, J. N., Jr., Wan, J. K. S., *Intern. J. Air Water Pollution* **10**, 689 (1966).

Steacie, E. W. R., "Atomic and Free Radical Reactions," Vol. 1, p. 56, Reinhold, New York, 1954.
Stephens, E. R., *Anal. Chem.* **36**, 928 (1964).
Stephens, E. R., Hanst, P. L., Doerr, R. C., Scott, W. E., *Ind. Eng. Chem.* **48**, 1498 (1956).
Tuesday, C. S., *Arch. Environ. Health* **7**, 72 (1963).
Tuesday, C. S., "Chemical Reactions in the Lower and Upper Atmosphere," p. 15, R. D. Cadle, Ed., Interscience, New York, 1961.

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Photochemical Reactivities of Aromatic Hydrocarbon-Nitrogen Oxide and Related Systems

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■ The photochemical reactivities of the two most atmospherically abundant alkylbenzenes, toluene and *m*-xylene, were determined. Data were obtained on hydrocarbon consumption; nitrogen dioxide formation; yields of formaldehyde, oxidant, and peroxyacetyl nitrate; and eye irritation response. Some additional measurements were made on other alkylbenzenes and alkylbenzene-*n*-butane-nitrogen oxide systems. The carbon and nitrogen balances were computed and, as in previous work, were less than satisfactory. Dosages in p.p.m. per hr. for nitrogen dioxide, oxidant, and peroxyacetyl nitrate were computed. These dosages, along with intensity of eye irritation response, are discussed in terms of the effects of reducing hydrocarbon and nitrogen oxide levels and changing hydrocarbon composition.

A number of investigators have measured the photooxidation of olefin-nitrogen oxide system in considerable detail (Altshuller and Bufalini, 1965; Altshuller, Kopczynski, *et al.*, 1967; Romanovsky, Ingels, *et al.*, 1967). Similar studies are not available on aromatic hydrocarbon-nitrogen oxide systems (Altshuller and Bufalini, 1965). Measurements of rates of consumption, formation of oxidant or other products, and eye irritation responses have been reported for several aromatic hydrocarbon-nitrogen oxide systems. These measurements, however, have involved the use of only a single concentration of the aromatic hydrocarbon and of the nitrogen oxide (Altshuller and Bufalini, 1965; Heuss and Glasson, 1968).

In the work reported here, toluene and *m*-xylene were selected because of their abundance in the atmosphere (Altshuller, Kopczynski, *et al.*, 1968) and because these two aromatic hydrocarbons should be representative of the photochemical reactivities of the aromatic hydrocarbons. Hydrocarbon consumption, formaldehyde yields, dosages of nitrogen dioxide, oxidant, and peroxyacetyl nitrate, and eye irritation responses were measured during ultraviolet irradiations

of toluene or *m*-xylene with nitric oxide in air over a range of initial concentrations. Photooxidation experiments were conducted with the addition of *n*-butane to toluene-nitrogen oxide mixtures. In addition, data from a few photooxidations of *o*-xylene or 1,3,5-trimethylbenzene with nitrogen oxide are available for comparison.

The results from these experiments are compared with those obtained from photooxidation of olefins or *n*-paraffins with nitrogen oxides. The results also are discussed as they relate to control of hydrocarbon concentration and composition and of nitrogen oxides.

Experimental

The ultraviolet irradiations were carried out in a 335-cu.-ft. chamber, described earlier (Korth, Rose, *et al.*, 1964). All of the experiments were done at full chamber ultraviolet intensity, with static irradiations over a 6-hr. period. The temperature was maintained at $31 \pm 1^\circ \text{C}$. with the relative humidity held near 50%.

At the start of the irradiation, most of the nitrogen oxide was in the form of nitric oxide. At initial nitrogen oxide concentrations at or above 0.15 p.p.m., the nitrogen dioxide made up from 5 to 20% of the total nitrogen oxides. At initial nitrogen oxide levels above 0.5 p.p.m., the nitrogen oxide made up only 5 to 10% of the nitrogen oxides, while at initial levels below 0.25 p.p.m., the nitrogen dioxide made up 20% of the nitrogen oxides.

The products were analyzed by methods described previously (Altshuller, Kopczynski, *et al.*, 1967). The aromatic hydrocarbons were separated on an open tubular column, 300 feet long and 0.061-in.-ID, of copper tubing coated with *m*-bis(*m*-phenoxyphenoxy)benzene combined with apiezon grease; they were analyzed with a flame ionization detector. Procedures for measuring eye irritation response were described previously (Altshuller, Kopczynski, *et al.*, 1969a).

Results

Consumption of Alkylbenzenes. During the 6-hr. irradiation period the average percentage consumption of toluene varied

with concentration level as follows: 4.5 p.p.m. with 1.3 or 0.3 p.p.m. nitrogen oxides, 40%; 3.0 p.p.m. with 1.3, 0.6, 0.33, or 0.2 p.p.m. nitrogen oxides, 48%; 1.5 p.p.m. with 1.3, 0.6, or 0.33, p.p.m. nitrogen oxides, 50%. In mixtures containing 1.5 p.p.m. of toluene with 3 p.p.m. of *n*-butane and 1.2, 0.6, or 0.35 p.p.m. nitrogen oxide, the average consumption of toluene was only 32%.

The percentage consumption of *m*-xylene averaged 72% at 3 p.p.m. *m*-xylene with 1.25, 0.7, 0.55, and 0.3 p.p.m. nitrogen oxides and 76% at 1.7 p.p.m. *m*-xylene with 0.25 p.p.m. nitrogen oxides. In mixtures containing 1.7 p.p.m. of *m*-xylene with 3 p.p.m. of *n*-butane and 0.3 p.p.m. of nitrogen oxide, the *m*-xylene consumption was only 59%.

Several irradiation experiments were performed with *o*-xylene and 1,3,5-trimethylbenzene at the 3 p.p.m. level with about 1.5 p.p.m. of nitrogen oxide. In the 6-hr. irradiation period, the consumption of *o*-xylene was 83% and 1,3,5-trimethylbenzene, 92%.

Formation of Organic Products. The formaldehyde yield from the reactions of toluene was small, ranging from 0.15 to 0.3 p.p.m.; these values are equivalent to a range of 0.1 to 0.2 in molar yield of formaldehyde formed per mole of toluene consumed. Only traces of acetaldehyde or other lower-mol.-wt. carbonyls could be detected.

The formaldehyde yield from the reactions of *m*-xylene ranged from 0.4 to 0.7 p.p.m.; these values are equivalent to a range of 0.25 to 0.3 in molar yield of formaldehyde formed per mole of *m*-xylene consumed. Only 0.05 to 0.15 p.p.m. of acetaldehyde was formed. The molar yield of acetaldehyde formed per mole of *m*-xylene consumed was only 0.05 to 0.1.

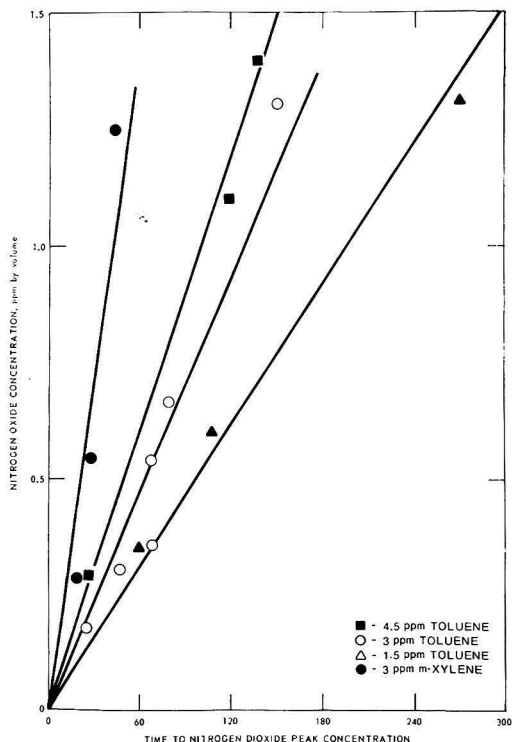


Figure 1. Times of nitrogen dioxide peak concentration as a function of nitrogen oxide concentration at various toluene and *m*-xylene concentration levels

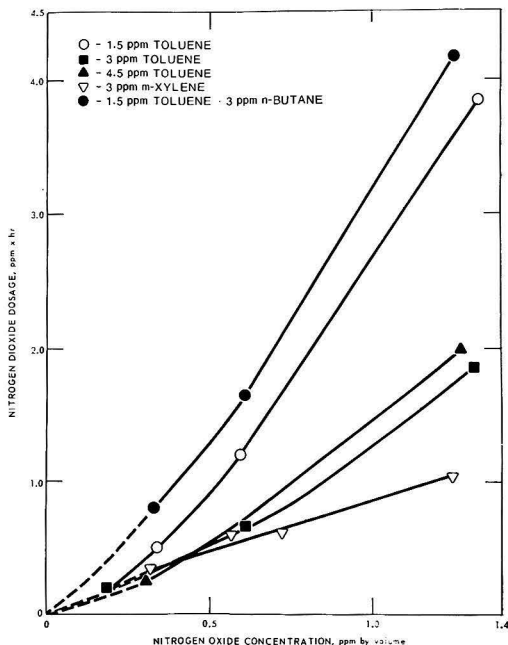


Figure 2. Nitrogen dioxide dosages (p.p.m. per hr.) as a function of initial nitrogen oxide concentration at various levels of toluene, *m*-xylene, and toluene-*n*-butane

Other carbonyl compounds could not be detected as products.

Nitrogen Dioxide Formation and Consumption. The time to nitrogen dioxide peak concentration in irradiation of toluene or *m*-xylene with nitric oxide increased linearly with increasing nitrogen oxide level. A different linear relationship between time to nitrogen dioxide peak concentration and initial nitrogen concentration was obtained at each toluene level (Figure 1). For a given nitrogen oxide level, the time to nitrogen dioxide peak concentration increased by a factor of 2 when the toluene concentration decreased by a factor of 3. This relationship can be associated with the suppressive effect of increasing the ratio of nitrogen oxide to toluene on the rate of conversion of nitric oxide to nitrogen dioxide. A similar relationship was observed in photooxidation of propylene-nitrogen oxide systems (Altshuller, Koczynski, *et al.*, 1967). The time to nitrogen dioxide peak concentration in photooxidation of the *m*-xylene-nitrogen oxide mixtures was about one-third that in photooxidation of the corresponding toluene-nitrogen oxide mixtures (Figure 1). Irradiation of the toluene-nitrogen oxide and *m*-xylene-nitrogen oxide mixtures usually caused consumption of over 90% of the nitrogen dioxide formed by the end of the 6-hr. reaction period.

Nitrogen dioxide dosages in p.p.m. per hr. consistently decrease with decreasing nitrogen oxide concentration (Figure 2). The absolute levels of nitrogen dioxide dosages decrease with increasing reactivity of the system photooxidized. However, the slopes of the curves for the less reactive mixtures decrease with decreasing nitrogen oxide concentration. At the 1.2-p.p.m. nitrogen oxide level, the nitrogen dioxide dosage was about 1 p.p.m. per hr. for the *m*-xylene-nitrogen oxide mixtures; dosage was 2 to 4 p.p.m. per hr. for the lower-reactivity toluene-nitrogen oxide and toluene-*n*-butane-nitrogen oxide mixtures. At the 0.3 p.p.m. nitrogen oxide level, however, the nitrogen dioxide dosage for the *m*-xylene-

nitrogen oxide mixture was about the same as that for the toluene-nitrogen oxide mixtures, although still much less than that for the toluene-*n*-butane-nitrogen oxide mixture.

Nitrogen dioxide dosage usually increases and then levels off, or reaches a peak and then decreases, as a function of decreasing hydrocarbon concentration. Results obtained for the toluene-nitrogen oxide system are typical (Figure 3). The nitrogen dioxide dosages tend to level off or decrease at toluene to nitrogen oxide ratios below 1:1. However, as is shown in Figure 3, there is an appreciable nitrogen dioxide dosage even with no added toluene, because of trace organic contaminants in the dilution air or desorbed from the walls. When almost completely uncontaminated small reactors are used (Bufalini and Altshuller, 1969), the reduction in hydrocarbons was shown to have a much greater effect in reducing nitrogen dioxide dosage than observed in the present study in a large irradiation chamber.

Oxidant. The oxidant produced from irradiation of toluene-nitrogen oxide mixtures leveled out after 1 to 3 hr. The maximum oxidant concentrations ranged from 0.2 to 0.4 p.p.m. These levels are lower than those formed from many other reactive hydrocarbon-nitrogen oxide mixtures when irradiated under comparable conditions. Irradiation of *m*-xylene-nitrogen oxide mixtures produced appreciably higher concentrations of oxidant, ranging from 0.35 to 0.7 p.p.m.

Oxidant dosages in p.p.m. per hr. at the 1.5, 3, and 4.5 p.p.m. levels of toluene are plotted vs. nitrogen oxide concentration in Figure 4. Except at a 1:1 ratio of toluene to nitrogen oxide and at lower ratios, at which oxidant is totally suppressed, the oxidant dosages are relatively insensitive to ratio over a wide range.

In Figure 5, the oxidant dosages obtained in 6-hr. irradiations are plotted for mixtures containing toluene, toluene-*n*-butane, and *m*-xylene; results obtained earlier with propylene and *n*-butane are also shown (Altshuller, Kopczynski, *et al.*, 1967; Altshuller, Kopczynski, *et al.*, 1969a). The curves for oxidant dosages obtained by irradiating nitrogen oxides with *n*-butane, toluene, toluene-*n*-butane, and *n*-butane-propylene contrast markedly with those obtained by irradiating nitrogen oxide with hydrocarbons such as propylene and *m*-xylene. Oxidant dosages from the irradiated mix-

tures of nitrogen oxides with hydrocarbons such as propylene or *m*-xylene start decreasing at hydrocarbon to nitrogen oxide ratios above 2:1. However, the oxidant dosages from irradiation of mixtures of nitrogen oxides with toluene, toluene-*n*-butane, or *n*-butane-propylene continue to increase not only at ratios above 2:1, but in some systems, at ratios above 5 and even 10:1 of hydrocarbon to nitrogen oxide.

Oxidant dosages at constant reactant ratios in irradiations of *m*-xylene, toluene, or *n*-butane with nitrogen oxide are presented in Figure 6. For *n*-butane-nitrogen oxide mixtures,

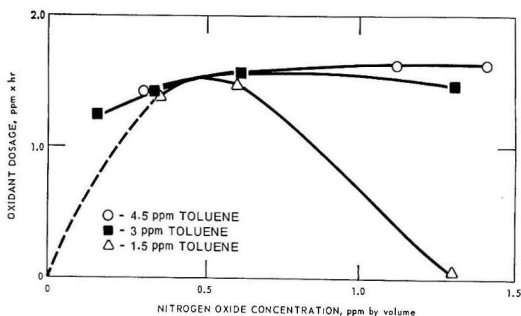


Figure 4. Variation in oxidant dosages (p.p.m. per hr.) with nitrogen oxide concentration at three toluene levels

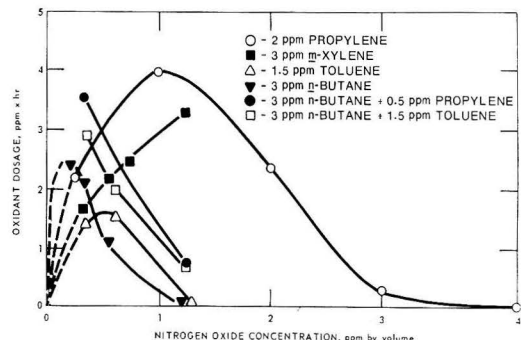


Figure 5. Variation in oxidant dosages (p.p.m. per hr.) with nitrogen oxide concentrations at various hydrocarbon levels

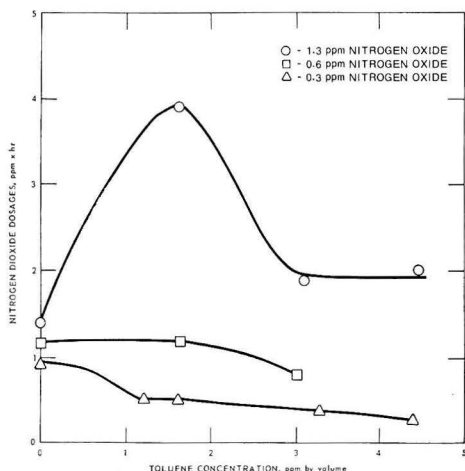


Figure 3. Nitrogen dioxide dosages (p.p.m. per hr.) as a function of toluene concentration at three nitrogen oxide levels

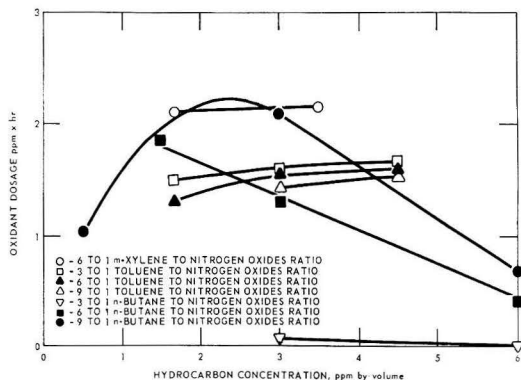


Figure 6. Variation in oxidant dosages (p.p.m. per hr.) with hydrocarbon concentration for various ratios of toluene, *m*-xylene, or *n*-butane to nitrogen oxide

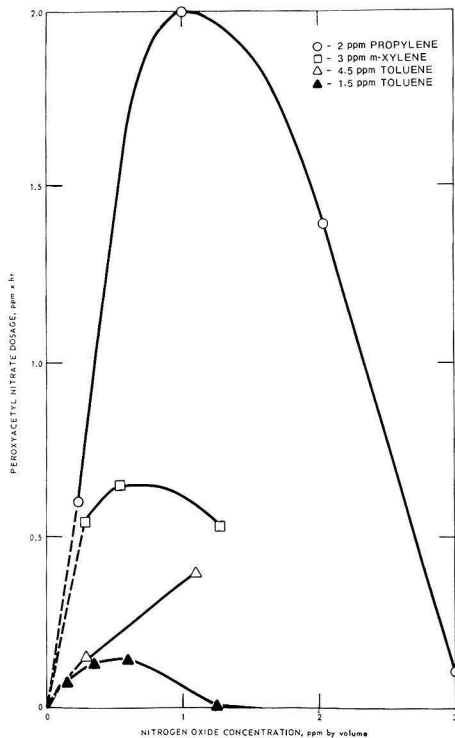


Figure 7. Peroxyacetyl nitrate dosages (p.p.m. per hr.) as a function of nitrogen oxide concentration at various toluene, *m*-xylene, and propylene levels

oxidant dosages actually increase as concentrations of the reactants are decreased several-fold. Even at 0.5 p.p.m. of *n*-butane and 0.05 p.p.m. of nitrogen oxide, the oxidant dosage is almost 50% of the maximum dosage and is as high as that for a mixture of 5.3 p.p.m. *n*-butane and 0.6 p.p.m. nitrogen oxide. For mixtures of toluene or *m*-xylene with nitrogen oxide, the oxidant dosages decreased very slightly with a 2- to 3-fold decrease in concentration of reactants.

Peroxyacetyl Nitrate. Peroxyacetyl nitrate was analyzed as an irradiation product in some of the experiments. Results computed as peroxyacetyl nitrate dosages, p.p.m. per hr., are plotted vs. nitrogen oxide concentrations for irradiated toluene-nitrogen oxide and *m*-xylene-nitrogen oxide mixtures (Figure 7). Peroxyacetyl nitrate dosages reported previously for the propylene-nitrogen oxide system (Altshuller, Kopczynski, *et al.*, 1967) also are plotted for comparison. Even at low nitrogen oxide concentrations, the peroxyacetyl nitrate dosages from the irradiated propylene-nitrogen oxide system are much greater than those from the irradiated *m*-xylene-nitrogen oxide system. Irradiation of toluene-nitrogen oxide mixtures results in only small dosages of peroxyacetyl nitrate. The peroxyacetyl nitrate dosages decrease rapidly in the more reactive systems at the lower nitrogen oxide concentrations. Peroxyacetyl nitrate yields, like oxidant or ozone yields, are readily suppressed by nitrogen oxides, so peroxyacetyl nitrate dosages also decrease rapidly when the initial nitrogen oxide concentration is higher than that causing the maximum peroxyacetyl nitrate dosage.

The oxidant dosages are only two or three times greater than the peroxyacetyl nitrate dosages from irradiation of pro-

pylene-nitrogen oxide mixtures. The ratios of oxidant dosages to peroxyacetyl nitrate dosages are usually higher for the irradiated alkylbenzene-nitrogen oxide systems than for the propylene-nitrogen oxide system. The ratios vary from 3 to 1 at lower nitrogen oxide concentrations for irradiated *m*-xylene-nitrogen oxide mixtures to 10:1 and higher for many of the irradiated toluene-nitrogen oxide mixtures.

Carbon and Nitrogen Balances. Only 3% of the toluene consumed on a carbon p.p.m. basis could be accounted for as formaldehyde and peroxyacetyl nitrate or other lower-mol.-wt. products. From 10 to 20% of the nitrogen originally present as nitric oxide and nitrogen dioxide could be accounted for as peroxyacetyl nitrate. The percentage of nitrogen accounted for increased from 10 to 20% as the initial nitrogen oxide concentration decreased from the 1-p.p.m. level to 0.15 p.p.m.

From 5 to 10% of the *m*-xylene consumed on a carbon p.p.m. basis could be accounted for as formaldehyde, acet-aldehyde, peroxyacetyl nitrate, or other lower-mol.-wt. products. From 10 to 75% of the nitrogen originally present as nitric oxide and nitrogen dioxide could be accounted for as peroxyacetyl nitrate. The percentage of nitrogen accounted for increased rapidly as the initial nitrogen oxide concentration decreased from 1.2 p.p.m. to 0.3 p.p.m. A similar result was obtained previously in irradiations of propylene-nitrogen oxide mixtures (Altshuller, Kopczynski, *et al.*, 1967).

Eye Irritation Panel Responses. The eye irritation intensity responses of the panel were averaged and reported on a scale of 0 to 5. Exposure of the panel to various levels of nitrogen oxide without added hydrocarbon gave the following results: 0.2 p.p.m., 0.75; 0.3 p.p.m., 0.6; 1.2 p.p.m., 0.5 unit. These eye irritation levels represent the total background responses of the panel in the absence of the products from hydrocarbon photooxidation.

The average eye irritation responses for toluene and *m*-xylene are compared with the responses obtained in an earlier study, but not published previously, for propylene as a function of nitrogen oxide concentration (Figure 8). With one exception, the eye irritation responses decrease with decreasing nitrogen oxide concentration. With subtraction of background response, a 4-fold decrease in nitrogen oxide concentration results in only a 2-fold decrease or less in eye irritation intensity response.

At the 1.5 p.p.m. toluene concentration, eye irritation intensity response increases with decreasing nitrogen oxide

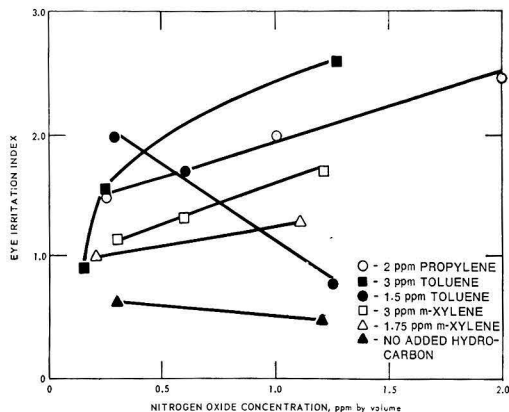


Figure 8. Intensity of eye irritation response as a function of nitrogen oxide concentration at various hydrocarbon levels

concentration. This type of eye irritation response curve corresponds to those obtained for oxidant and peroxyacetyl nitrate (Figures 4, 5, and 7). Heuss and Glasson (1968) reported that the eye irritant produced by photooxidation of toluene is peroxybenzoyl nitrate. These investigators also showed that this substance does not form until nitric oxide is consumed, just as is observed for ozone and peroxyacetyl nitrate. Therefore, it is likely that the eye irritation response curve obtained corresponds to the curve for peroxybenzoyl nitrate yield.

Eye irritation responses also have been obtained for a number of other hydrocarbons, including two additional alkylbenzenes at 3 p.p.m. of hydrocarbon and approximately 1.5 p.p.m. of nitrogen oxide. At these concentrations, the eye irritation responses are as follows: toluene, 2.3; *m*-xylene, 1.9; *o*-xylene, 0.9; 1,3,5-trimethylbenzene, 2.2; ethylene, 1.1; 2-methyl-2-butene, 1.6. Thus, toluene and *m*-xylene are among the hydrocarbons causing high eye irritation responses.

Discussion of Results

Neither the carbon nor the nitrogen balance is satisfactory in the photooxidation reactions of alkylbenzenes. The nitrogen balance was less than adequate in previous studies of the photooxidation of olefin (Altshuller and Bufalini, 1965) or paraffinic hydrocarbons (Altshuller, Kopczynski, *et al.*, 1969a). Formation of peroxyacetyl nitrates is only a minor pathway for conversion of nitrogen oxides to end-products in many hydrocarbon-nitrogen oxide systems. The nitrogen balance can be accounted for as nitric acid and nitrate (Bufalini and Gay, 1970; Price and Stephens, 1969). The nitrogen balance in photooxidations of alkylbenzenes can be accounted for similarly. The carbon balance in the photooxidation of a number of lower-mol.-wt. olefins and paraffins is not perfect, but most of the carbon atoms can usually be accounted for as identified products (Altshuller and Cohen, 1964; Tuesday, 1961; Altshuller, Kopczynski, *et al.*, 1967). The carbon balance in the photooxidation of alkylbenzenes is poor in this study. A similar inability to account for carbon atoms in the photooxidation of alkylbenzenes has been reported in previous investigations (Kopczynski, 1964; Heuss and Glasson, 1968). Recently, peroxybenzoyl nitrate, a previously unidentified minor product of the photooxidation of toluene and certain other monoalkylbenzenes, was shown to be a potent eye irritant. Other alkylbenzenes, such as *m*-xylene and 1,3,5-trimethylbenzene, that cause appreciable eye irritation upon nitrogen oxide induced photooxidation, may also produce structurally related eye irritants. Other biologically potent products could be formed also. Alkylbenzenes certainly are as important as olefins in forming biologically important products, particularly in the presence of lower concentrations of nitrogen oxides.

Recent studies (Altshuller, Kopczynski, *et al.*, 1969, a and b) on the nitrogen oxide induced photooxidation of *n*-butane alone and mixtures of *n*-butane with propylene or toluene have shown that earlier results obtained with olefins could be misleading in interpretations of results obtained under real atmospheric conditions. For example, oxidant yields or dosages can still be increasing rapidly in mixtures simulating the composition and reactivity of atmospheric hydrocarbons at low nitrogen oxide concentrations. Recent measurements of irradiated automobile exhaust mixtures (Dimitriades, 1969) at hydrocarbon (carbon p.p.m.) levels of 0.65 to 3.3 p.p.m. and nitrogen oxide levels between 0.08 and 0.6 p.p.m. also show oxidant dosages that are still increasing or are near peak values at nitrogen oxide concentrations of 0.1 p.p.m. or slightly lower. In contrast, oxidant yields or dosages are

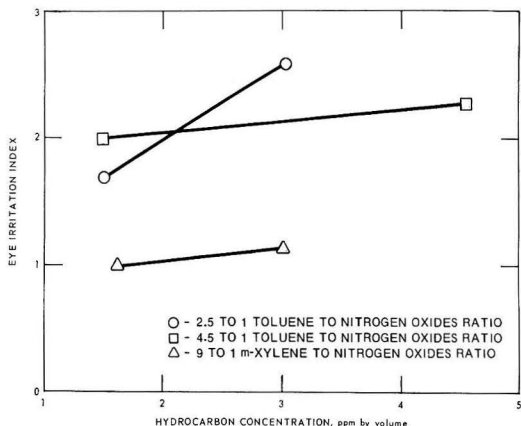


Figure 9. Intensity of eye irritation response as a function of hydrocarbon concentration at various ratios of toluene or *m*-xylene to nitrogen oxide

decreasing rapidly with similar concentrations of olefins and nitrogen oxides (see propylene curve in Figure 5).

The values for toluene and *m*-xylene in this study illustrate the markedly different results that can be obtained with hydrocarbons of significantly different reactivities. Nitric oxide is converted to nitrogen dioxide much more rapidly by *m*-xylene than by toluene. Yields of both oxidant and peroxyacetyl nitrate are higher from *m*-xylene-nitrogen oxide photooxidations than from toluene-nitrogen oxide photooxidations. Oxidant dosages, however, decrease rapidly in the *m*-xylene-nitrogen oxide system in a range of nitrogen oxide concentrations that cause oxidant dosages from the toluene-nitrogen oxide system to increase or remain constant. As a result, oxidant dosages from the two systems are about equal when the nitrogen oxide concentration is reduced to 0.25 p.p.m. The eye irritation results show a different relationship to nitrogen oxides. The nitrogen oxide induced photooxidation of toluene produces more eye irritation than does photooxidation of *m*-xylene, even at high nitrogen oxide concentrations.

Some comparisons can be made with the eye irritation results tabulated as eye irritation reactivities by Heuss and Glasson (1968). Both studies agree on toluene, propylene, *m*-xylene, and 1,3,5-trimethylbenzene as being important hydrocarbon pollutants with substantial eye irritation potential. Both studies also indicate that hydrocarbons such as *o*-xylene and 2-methyl-2-butene are somewhat less potent eye irritants. There are some differences in order and magnitude. In particular, ethylene is rated lower in eye irritation potential by Heuss and Glasson than in the present investigation.

The results for toluene, like those previously reported for *n*-butane and its mixtures, indicate that large decreases of nitrogen oxide can be ineffective in reducing oxidant yields. Although eye irritation is reduced with decrease in nitrogen oxide, an appreciable reduction requires a very large decrease.

The results plotted in Figures 6 and 9 suggest that large reductions in oxidant concentrations and eye irritation may require a high degree of control of hydrocarbon and nitrogen oxides if they are reduced concurrently. This type of result is consistent with two sets of results of atmospheric investigations. Although reactant levels of hydrocarbon and nitrogen oxides are a factor of 2 to 3 lower on Sundays than on weekdays at CAMP sites in various cities, oxidant levels are the

same on Sundays as on weekdays (U.S. Dept. of Commerce, 1967). Oxidant levels at Azusa in the Los Angeles Basin can be substantially higher than in downtown Los Angeles despite much higher reactant concentrations in downtown Los Angeles (State of California, Clear Air Quarterly, 1966, 1967, 1968). Such comparisons are by no means conclusive. Other factors can be important in atmospheric measurements. For example, differences in air trajectories can result in significant differences in the length of irradiation of a given volume of air. Nevertheless, both atmospheric and laboratory measurements suggest that anything short of large concurrent reductions in hydrocarbon and nitrogen oxides may not afford reduced reductions in oxidant levels. The results of this study agree with our previous findings that only a very high degree of nitrogen oxide control may prove successful in providing marked improvements in oxidant levels. However, as suggested earlier (Altshuller, Kopczynski, *et al.*, 1969b), control of the more reactive hydrocarbons can greatly reduce oxidant levels if the ratio of nitrogen oxides to hydrocarbons also is maintained just above that needed to suppress oxidant.

Most of the foregoing discussion is concerned with the relationships between hydrocarbon and nitrogen oxide control and oxidant reduction. The results of this study does indicate that reduction in nitrogen dioxide dosage can best be obtained by control of nitrogen oxides.

Peroxyacetyl nitrates are formed in the nitrogen oxide induced photooxidation of propylene and higher-mol.-wt. olefins, of dialkylbenzenes and trialkylbenzenes, and of acetaldehyde and higher aldehydes. Although paraffinic hydrocarbons, acetylene, ethylene, toluene, and higher monoalkylbenzenes make up the bulk of atmospheric hydrocarbons, the peroxyacetyl nitrate yields from these hydrocarbons range from small to undetectable. Thus, control of specific types of reactive hydrocarbons should control peroxyacetyl nitrates very effectively. In addition, an appropriate ratio of nitrogen oxide to hydrocarbon suppresses peroxyacetyl nitrates, as it does ozone. The nitrogen oxide level at which yields of dosages of peroxyacetyl nitrate are highest may shift to lower levels as overall reactivity decreases, as occurs with ozone yields and dosages. In recent measurements of irradiated automobile exhaust mixtures (Dimitriades, 1969) at hydrocarbon (carbon p.p.m.) levels of 0.65 to 1.5 p.p.m. and nitrogen oxide levels of 0.08 to 0.4 p.p.m., peroxyacetyl nitrate dosages, just as the oxidant dosages, were still increasing or were near peak values at 0.1 p.p.m. of nitrogen oxide.

Inorganic particulate nitrate is an important end-product of nitrogen oxide photooxidation. The yield of such nitrates should be related to nitrogen oxide levels. Experimental work is lacking on the relationship of nitrate yields to ratios of nitrogen oxide to hydrocarbon.

The results of this investigation, like those of other recent studies (Altshuller, Kopczynski *et al.*, 1969, a and b), show

clearly that reducing nitrogen oxide concentration reduced nitrogen dioxide dosage and usually also yielded modest reductions in eye irritation response. Conversely, reducing nitrogen oxide concentrations over a wide range increased the oxidant dosages or changed them only slightly.

Control of olefins and alkylbenzenes effectively reduces ozone and peroxyacetyl nitrate levels and decreases eye irritation response. As suggested in other recent work (Altshuller, Kopczynski, *et al.*, 1969b), investigators concerned with reducing the adverse effects of photochemical air pollution should give additional attention to preferential control of olefins and alkylbenzenes.

Literature Cited

- Altshuller, A. P., Bufalini, J. J., *Photochem. Photobiol.* **4**, 97 (1965).
- Altshuller, A. P., Kopczynski, S. L., Lonneman, W. A., Becker, T. L., Slater, R., *ENVIRON. SCI. TECHNOL.* **1**, 899 (1967).
- Altshuller, A. P., Kopczynski, S. L., Lonneman, W. A., Sutterfield, F. D., "Hydrocarbon Composition of the Atmosphere in the Los Angeles Basin," presented before Division of Water, Air, and Waste Chemistry, 156th National Meeting, American Chemical Society, Atlantic City, N.J., Sept. 8-13, 1968.
- Altshuller, A. P., Kopczynski, S. L., Wilson, D., Lonneman, W. A., Sutterfield, F. D., *J. Air Pollution Control Assoc.* **19**, (1969a).
- Altshuller, A. P., Kopczynski, S. L., Wilson, D., Lonneman, W. A., Sutterfield, F. D., *ibid.*, 1969b.
- Altshuller, A. P., Cohen, I. R., *Intern. J. Air Water Pollution* **8**, 611 (1964).
- Bufalini, J. J., Altshuller, A. P., *ENVIRON. SCI. TECHNOL.* **3**, 469 (1969).
- Bufalini, J. J., Gay, B., *Science*, to be published.
- Dimitriades, B., unpublished results, Bureau of Mines Petroleum Research Laboratory, Bartlesville, Okla.
- Heuss, J. M., Glasson, W. A., *ENVIRON. SCI. TECHNOL.* **2**, 1109 (1968).
- Korth, M. W., Rose, A. H., Jr., Stahman, R. C., *J. Air Pollution Control Assoc.* **14**, 168 (1964).
- Kopczynski, S. L., *Intern. J. Air Water Pollution* **8**, 107 (1964).
- Price, M. A., Stephens, E. R., "Analysis of Gas Phase Inorganic Nitrate," 10th Conference on Methods in Air Pollution and Industrial Hygiene Studies, San Francisco, Calif., Feb. 19-21, 1969.
- Romanovsky, J. C., Ingels, R. M., Gordon, R. J., *J. Air Pollution Control Assoc.* **17**, 454 (1967).
- State of California, Clear Air Quarterly, Vol. 10, No. 4, 1966; Vol. 11, No. 1, 1967; Vol. 11, No. 4, 1967; Vol. 12, No. 1, 1968.
- Tuesday, C. S., "Chemical Reactions in the Lower and Upper Atmosphere," p. 1, R. D. Cadle, Ed., Interscience, New York, 1961.
- U.S. Dept. of Commerce, The Automobile and Air Pollution, Part II, p. 14-15, U.S. Printing Office, Dec. 1967.

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Thermal Neutron Activation Analysis of Particulate Matter in Surface Air of the Chicago Metropolitan Area

One-Minute Irradiations

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■ A procedure is described for the simultaneous determination of aluminum, vanadium, manganese, sodium, chlorine, and bromine in surface air of the Chicago Metropolitan Area. The particulates (dust) in approximately 5 standard cubic meters of air were irradiated for one minute in a thermal neutron flux of approximately 2×10^{13} n. per sq. cm. per second, and the activated nuclides obtained were analyzed by means of their γ -ray spectra. Samples were collected April 4, 1968, at 22 air-sampling stations: 20 at selected sites throughout the city of Chicago, one at Morton Grove, and one at Argonne, Ill. The following values, in micrograms per standard cubic meter of air, were obtained: Al (0.48 to 3.2), V (0.0022 to 0.12), Mn (0.10 to 0.90), Na (0.10 to 0.67), Cl (0.61 to 5.9), and Br (0.024 to 0.32). Evidence is included of the presence of calcium and/or sulfur in these samples.

In recent years, increasing attention has become focused on the rate of pollution of our natural environment. Technological and industrial development, coupled with the vast urbanization of the population, have been the prime contributors to this pollution. Adding to the combustion products from fuel and refuse, many industrial processes continuously introduce a large variety of trace elements into the atmosphere. No valid judgment as to the relative potential threat to health or property from these industrial byproducts is possible without precise knowledge of their composition. Great strides have been made during the past decade in recognizing, and coping with, this ever-mounting problem (Smith, 1968; Stewart, 1966; Tetzlaff, 1962). Important pioneer work both at leading universities and by the United States Public Health Service has contributed to this knowledge. Vigorous efforts are now directed toward identifying and developing suitable methods for the specific detection of atmospheric contaminants.

Emission spectroscopy, atomic absorption, and neutron activation are three sensitive techniques applicable to the study of elemental constituents in air particulates. Emission spectroscopy, for example, was applied successfully to the measurement of 17 metals in the atmosphere (Tabor and Warren, 1958). Atomic absorption was used to detect and measure some elements in the atmosphere (Lewis, 1968; Robinson and Ramakrishna, 1965), and still remains to be used on others. With the current availability of high neutron fluxes, on the

other hand, the neutron activation technique (Duce, Winchester, *et al.*, 1965; Gordon and Larson, 1964; Lininger, Duce, *et al.*, 1966; Parkinson and Grant, 1963) possesses greater sensitivity for most elements than either of the other two methods. This method was used in the present study.

Experimental Methods and Materials

Air Sampling. Samples were collected by using the city of Chicago high-volume air-sampling pumps (Model GMWL 2000, with an 18×23 cm. stainless steel filter holder, equipped with an outdoor shelter, General Metal Works, Cleves, Ohio). Each pump was equipped with an automatic timer to ensure 24-hour collection and an appropriate meter to record the initial and final flow rates of air. Twenty-two collecting stations, 20 scattered through the city of Chicago, one located at Morton Grove, and another at Argonne, Ill., participated in the collection.

Filters. The filter material employed must have a low concentration of thermal neutron-activable elements in its matrix, in addition to fulfilling the usual requirements of high efficiency and uniform flow rate. The commonly used asbestos and glass fiber-base filters were ruled out as primary filters because, in spite of their screening efficiency, they have too many interfering elements—particularly sodium. The filter finally selected was chosen because of its low background after irradiation (Table I). It was of previously untested cellulose fiber construction (Grade X-1215-2, 33 pounds., C. H. Dexter and Sons, Windsor Locks, Conn.), and no claim is made, therefore, for ideal efficiency of collection.

Two filters, a primary or face filter and one backup filter, were used in each air-sampling pump. At all stations the primary or face filter was cellulose fiber. At six stations, the backup filter was also of cellulose fiber, while at 16 stations it was glass fiber.

Handling and Processing of Filters and Samples. Precautions in handling these filters were basically those ordinarily exercised during any quantitative analysis. Emphasis was placed, to a great degree, upon the individual himself (clean dry hands, free from soap), the environment in the operating area (air-filtered room, free from smoke, dust, and air currents), and clean tools.

Each 18×23 cm. filter was marked with a code, dried, and weighed to a constant weight both before and after exposure. The difference between the initial and the final weights was the

Table I. Concentrations ($\mu\text{g. per Sample}$) of Several Elements in the Blank, an Average Sample, and the Weakest Sample

Blank ^a	Mn	Na	Al	Cl	Br	V
1	1.40	1.31	0.93	0.37	0.02	0.005
2	1.35	1.22	0.94	0.27	0.01	0.006
3	1.46	1.20	1.10	0.54	0.01	0.005
Av.	1.40	1.24	0.99	0.39	0.01	0.005
Blank + weakest sample	1.98	1.69	3.94	4.36	0.27	0.018
Blank + average sample	4.83	3.66	12.23	15.25	0.88	0.160

^a 1-cm. cellulose filter sealed in polyethylene sheet.

total amount of solids collected over a 24-hour period at each station.

A 1-sq. cm. piece was cut from near the center of each exposed filter and heat-sealed between two sheets of 0.08-mm. thick clean polyethylene by means of a Teflon-coated, rotary heat sealer (Catalog No. 0548/72, Chemical Rubber Co., Cleveland, Ohio). After trimming away the excess polyethylene, the sealed sample was rinsed in 5% nitric acid and three rinses of specially prepared distilled water.

Standards. Aqueous solutions were prepared from analytical grade salts of the elements measured $\text{AlK}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$; NH_4VO_3 ; NH_4Br ; NH_4Cl ; $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and Na_2CO_3 . The distilled water was prepared by passing it through anion-cation resin (Amberlite, MB-1, Rohm and Haas Co., Philadelphia, Pa.). The conductivity was measured frequently, the observed resistance varying between 2,000,000 and 2,400,000 ohm-cm. One hundred-microliter quantities of each standard solution were placed on 3-sq. cm. pieces of clean polyethylene, frozen, and lyophilized. Each dried standard was then heat-sealed in the same way as the air particulate samples. Blanks consisting of 1-sq. cm. pieces of unexposed filter were similarly sealed in polyethylene.

Neutron Irradiation and Scintillation Counting. Blanks, standards, and the air particulate samples were neutron-activated in the Rabbit Facility (a pneumatic tube for the insertion of samples for irradiation) of the CP-5 Research Reactor at Argonne National Laboratory. The irradiation time for all samples was 1 minute and the neutron flux was approximately 2×10^{13} n. per sq. cm. per second. The mean exposure time was marked at $1/2$ minute after insertion of the Rabbit (a cylindrical polyethylene capsule, 9×3.6 cm., with a snap cap) into the core of the reactor. For scintillation counting, the irradiated specimen was immediately placed 10 cm. above a $\text{NaI}(\text{Tl})$ crystal. The crystal (a 4×4 inch cylinder with 8% resolution) was shielded by 1 inch of stainless steel-clad mercury. This scintillation detector was used in conjunction with a 400-channel pulse-height analyzer. This data-collecting system is equipped with automatic type-out.

The mean counting time was assumed to be the midpoint of the counting interval. Because of the short half lives of the activated nuclides (^{28}Al and ^{52}V), as a rule only two samples were irradiated at a time and each was counted twice. The weaker sample was counted first at about 2 minutes after mean irradiation for 1 minute (live time). Then, at about 9 minutes after irradiation, the second sample was counted, with the intervening time used for data print-out. Twenty minutes later each sample was counted again for 5 minutes (live time). The neutron flux was monitored by the simultaneous irradiation of a manganese standard with each set of samples tested.

Data Processing. The typed data were transferred onto IBM cards and processed through a GE-225 computer. Analyses

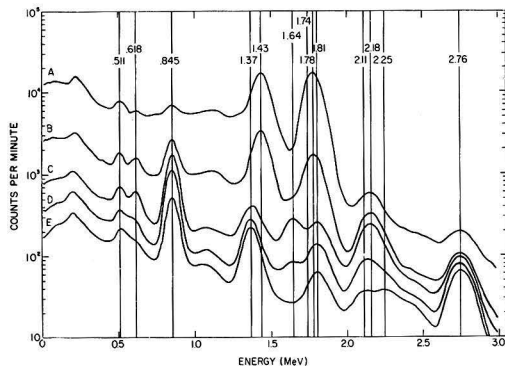


Figure 1. Sequentially observed gamma-ray spectra of air particulates after 1-minute irradiation with a thermal neutron flux of 2×10^{13} n. per second per sq. cm.

A = 3.9, B = 11.7, C = 33, D = 120, and E = 320 minutes after irradiation

Table II. Physical Properties of Radionuclides Observed after a 1-Minute Irradiation of Air Particulates by Thermal Neutrons

Isotope	Half Life, Min.	Principal γ -Ray Energies, M.E.V.				
^{26}Al	2.3	1.78				
^{52}V	3.77	1.43				
^{37}S	5.04	3.10				
^{46}Ca	8.7	3.10				
^{80}Br	17.6	0.618	0.511			
^{38}Cl	37	1.64	2.18			
^{56}Mn	156	0.845	1.81	2.11		
^{24}Na	900	1.37	1.74 ^a	2.25 ^a	2.76	

^a Escape peaks.

in this program were based on the method of simultaneous equations (Nelson, Dipert, *et al.*, 1965; U.S. Department of Health, Education, and Welfare, 1967) with appropriate corrections for decay, size of sample, blank, and strength of standards.

Results

Table II summarizes some of the important physical characteristics of the nuclides. A time sequence of γ -ray spectra for a typical sample is presented in Figure 1. The various nuclides can be identified by the energies and half lives of their gamma lines. The data from spectra A and B give the most accurate

Table III. Weight of Air Particulates Collected on 18 × 23 Cm. Face Cellulose and Backup Fiber Glass Filters after Collection Period of 24 Hours at 16 Sampling Stations

Station	Cellulose-Top		Filter Fiber Glass-Bottom		Total Weight, Grams
	Grams	%	Grams	%	
Morton Grove Chicago	0.078	71	0.032	29	0.110
Taft	0.089	75	0.029	25	0.118
Lakeview	0.180	80	0.045	20	0.225
Steinmetz	0.099	80	0.024	20	0.123
GSA	0.206	74	0.071	26	0.277
Austin	0.140	80	0.036	20	0.176
Kelly	0.141	75	0.048	25	0.189
Lindbloom	0.072	71	0.030	29	0.102
Hyde Park	0.230	89	0.029	11	0.259
CVS	0.119	82	0.027	18	0.146
Fenger	0.107	78	0.031	22	0.138
Carver	0.128	80	0.033	20	0.161
Clay	0.109	77	0.032	23	0.141
Sullivan	0.160	82	0.036	18	0.196
Von Stuben	0.130	77	0.039	23	0.169
Av.		78		22	
Std. dev.		5		5	
Cooley, Chicago (48-hour collection period)	0.524	88	0.072	12	0.596

Table IV. Weight of Air Particulates Collected on 18 × 23 Cm. Face and Backup Cellulose Filters after a Collection Period of 24 Hours at Six Sampling Stations

Station	Cellulose-Top		Filter Cellulose-Bottom		Total Weight, Grams
	Grams	%	Grams	%	
ANL (4 × 13 cm.)	0.038	73	0.014	27	0.052
Chicago Calumet	0.142	81	0.033	19	0.175
Logan Sq.	0.270	82	0.059	18	0.329
Hale	0.159	81	0.038	19	0.197
Stevenson	0.127	77	0.037	23	0.164
Av.		79		21	
Std. dev.		4		4	
Crane, Chicago (48-hour collection period)	0.458	90	0.052	10	0.510

assay of ²⁸Al (1.78 m.e.v.) and ⁵²V (1.43 m.e.v.). The data from spectrum C show ⁸²Br (0.618 and 0.511 m.e.v.) and ³⁸Cl (1.64 and 2.18 m.e.v.) most clearly, while spectra D and F give best results for ⁵⁶Mn (0.845, 1.81, and 2.11 m.e.v.) and ²⁴Na (1.37, 1.74, 2.25, 2.76 m.e.v.). The energy scale for Figure 1 is from 0 to 3.0 m.e.v.; consequently, the 3.1-m.e.v. line from ⁴⁸Ca and/or ³⁷S, present in most samples, is not apparent.

As indicated earlier, 24-hour air particulate samples were simultaneously collected at the 22 sampling stations on April 4, 1968. Tables III and IV give the weight of particulates collected on both the face and backup filters. For elemental

Table V. Summary of Concentrations of Elements Observed in Air Particulates Collected on April 4, 1968, over Chicago Metropolitan Area as Derived from Exposed Face Cellulose Filters at 22 Sampling Stations

($\mu\text{g. per cu. meter of air}$)

Station	Dust	Br	Mn	V	Al	Cl	Na
M.G.	53	0.086	0.22	0.0022	0.85	0.76	0.24
ANL	28	0.024	0.34	0.0037	0.72	0.72	0.20
Taft	49	0.15	0.28	0.0028	0.89	0.95	0.20
Lakeview	90	0.15	0.46	0.015	2.7	3.7	0.41
Steinmetz	50	0.078	0.21	0.0036	0.87	0.62	0.23
GSA	99	0.17	0.38	0.12	1.5	3.6	0.46
Austin	70	0.31	0.63	0.016	1.4	3.0	0.34
Kelly	75	0.084	0.90	0.014	1.4	2.1	0.24
Lindbloom	32	0.060	0.10	0.0059	0.48	0.71	0.10
Hyde Park	144	0.27	0.70	0.024	1.9	5.9	0.56
CVS	59	0.098	0.73	0.0060	0.96	1.4	0.10
Fenger	54	0.053	0.18	0.0047	0.96	0.95	0.20
Carver	69	0.046	0.33	0.0051	0.92	1.8	0.40
Clay	56	0.069	0.47	0.0046	1.1	1.3	0.19
Sullivan	72	0.11	0.31	0.0085	1.5	3.4	0.30
Von Stuben	71	0.13	0.34	0.013	1.6	2.9	0.32
Calumet	54	0.095	0.26	0.027	1.1	1.7	0.18
Crane ^a	102	0.32	0.81	0.027	3.1	4.3	0.67
Cooley ^a	128	0.18	0.79	0.025	3.2	2.1	0.54
Logan Square	98	0.14	0.52	0.11	2.0	3.4	...
Hale	55	0.048	0.38	0.027	1.4	0.61	0.42
Stevenson	46	0.041	0.19	0.0086	0.98	0.67	0.16

^a 48-hour collection period.

Table VI. Per Cent of Dust, Br, Mn, V, Al, Cl, and Na Present on Some Exposed-Face Cellulose Filters

Station	Dust	Br	Mn	V	Al	Cl	Na
Calumet	81	85	98	96	97	86	88
Crane ^a	90	87	98	97	99	79	93
Logan	80	87	100	97	100	70	
Square							
Hale	81						
Steven- son	78						

^a 48-hour collection period.

analyses, 1 sq. cm. was cut from the central portion of each of the exposed cellulose filters. Twenty-two samples from the face filters and three from the backup filters were irradiated, and their subsequent gamma spectra were analyzed for Na, Cl, Br, V, Mn, and Al (Tables V and VI). Figure 2 presents the distribution of concentrations (also see Table V) separately for each isotope detected and quantitated in this study.

The U.S. Weather Bureau station at Midway Airport reported averages for April 4 as: temperature 47° F.; humidity 90%; wind velocity 20.4 m.p.h.; and wind direction 220°. The total precipitation at Midway Airport for that date was 0.03 inch, but it had rained on April 3.

Discussion

Each collecting station sampled approximately 2000 cu. meters of surface air in the 24-hour period. The distribution of dust across the face of the filters was observed to be uniform. A portion from the center of each filter was removed and neu-

tron-irradiated. Each sample was calculated to hold particulates from approximately 5 cu. meters of air. The absolute error in the concentrations reported in Table V and Figure 2 is estimated to be between 10 and 20%. Errors due to irradiation time, flux, and flux monitoring standards did not exceed 2%, as indicated by counting the monitors. Each sample was counted long enough to reduce counting errors below 2%. Consecutive counts on several samples at different decay times showed an agreement to within 5% between the computed concentrations, indicating that contributions from unidentified gamma-emitters were not important. No duplicate samples (except blanks) were run and therefore no error figure can be placed on the intrinsic variability of the sample across the face of each filter, other than to state that a 24-hour collection time is more likely to produce a uniform and a representative sample than a much shorter time. The final flow rate of air varied from station to station—from 0.70 to 1.04 of the initial rate. However, the majority of the stations showed a final flow rate in the vicinity of 0.90 of initial rate. The average of initial and final flow rates was used in determining the total air flow.

Collection efficiency of the cellulose fiber filter used in this study is required before it can be compared effectively with that of the glass fiber filter. Data presented in Tables III and IV indicate that two cellulose filters in cascade possess particulate retention (by weight) capability similar to that of the glass fiber filter, which is designed to retain particles greater than 0.3 micron with over 99% efficiency. By weight, the primary (face) or cellulose filter retained about 80% of the particles. On the other hand, according to the partial study presented in Table VI, the face filter retained over 96% of aluminum, vanadium, and manganese, and lesser amounts of sodium, bromine, and chlorine.

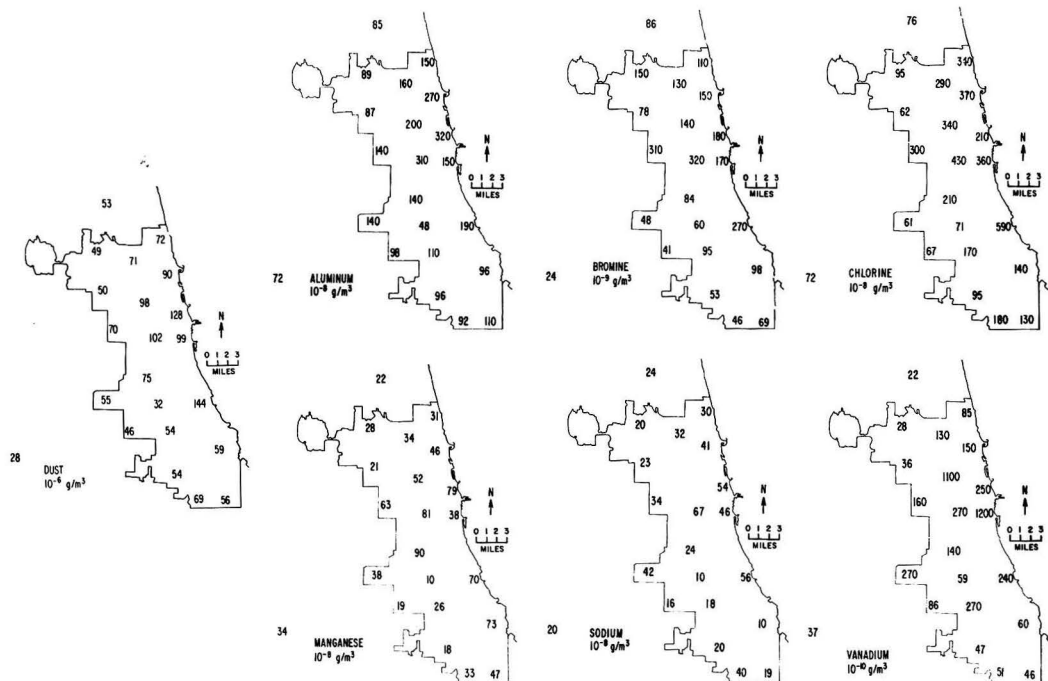


Figure 2. Distribution of dust, Br, Mn, V, Al, Cl, and Na in Chicago metropolitan area

As derived from analysis of face-cellulose filter of air particulates collected April 4, 1968

On April 4, the amounts of air particulates collected at Chicago sampling stations were larger, in general, than those collected at Morton Grove and Argonne (Tables III and IV and Figure 2). The highest concentration was obtained at Hyde Park (station L) and the lowest at Argonne. The average concentration of the city of Chicago was 92 μg . per cu. meter, assuming face filter particulate collection efficiency of 80%. This value is somewhat lower than the April average of 135 μg . per cu. meter for the years 1964–1967 recorded by the city of Chicago (Department of Air Pollution Control, 1967). The threshold limit value (TLV)—*i.e.*, the level of inert dust safely tolerated by a workman throughout a week—is 15 mg. per cu. meter (American Conference of Governmental Industrial Hygienists, 1966; Smith, 1968). Only $1/150$ of that level, or 100 μg . per cu. meter (Smith, 1968), may be regarded as safe for the general population. Again assuming an 80% filter collection efficiency, the data obtained in the present study reveal that several stations exceeded that limit on April 4 (Table IV). The concentration of the dust in the air varies, however, both from day to day and from season to season.

Although a knowledge of the total concentration of air particulates may serve as a crude index of air pollution, more serious consideration should be given to the composition of these particulates. Since significantly different physiological effects on man may be exerted by various individual components, much more information is needed to assess hazards. The concentrations of six elements (Na, Cl, V, Mn, Br, and Al) determined in Chicago metropolitan surface air have been found to be below the TLV levels proposed for inhalation by the population at large. Normal concentrations of sodium and chlorine in the body are large (105 grams each for a standard 70-kg. man); therefore, the small additions to the body burden possible from the atmosphere are not likely to be harmful to man. Aluminum is surprisingly inert, as evidenced by the high TLV levels (15 mg. per cu. meter). The physiological role of less abundant elements in the human body could conceivably be altered, should small additional amounts find their way into the body from the atmosphere. The amount of manganese typically reported in the human body is about 20 mg., while that of vanadium is less than 1 mg.

The effect on man and property resulting from air contaminants which are also chemical catalysts is also important. Under certain conditions (the presence of oxygen, moisture, an elevated temperature, and finely dispersed salts of some metals acting as catalysts—the condition which may prevail either in polluted atmosphere or within a human lung) sulfur dioxide may be converted to toxic sulfurous and/or sulfuric acid (Johnstone and Moll, 1960).

A discussion of the physiological effects of trace elements found in the atmosphere is not the concern of this paper. The presence in the atmosphere of certain elements has been established through this and similar studies, and serious consideration should be given to their possible long-term effect on man and property, particularly with respect to their involvement in chronic diseases and/or in cumulative poisoning.

A contribution of this study may well be the specific geographical distribution over the Chicago metropolitan area of the trace elements. As can be seen in Figure 2, the heaviest concentrations of all elements were observed near the center of the city. The lowest amounts were found in the north and west portions of the city, and in the suburban areas of Morton Grove (north) and Argonne (southwest). This information may prove valuable in locating the pollution sources. However, the average wind velocity and direction on April 4 were 20.4 m.p.h. from the southwest. This may have influenced the trace element concentrations obtained northwest of Chicago.

Reference to the literature permits some cross-comparison of the results obtained with those reported by others. Tabor and Warren (1958), using emission spectroscopy, analyzed air particulates for 17 different metals in several American cities. Manganese and vanadium are the only two elements in the present study common to the results reported by them. The comparison of range concentrations indicate essentially good agreement. Duce, Winchester, *et al.* (1965) measured iodine, chlorine, and bromine in the Hawaii marine atmosphere (“unpolluted” air); and Lininger, Duce, *et al.* (1966) did the same for “polluted” air of Cambridge, Mass. The results of our study are comparable with those obtained at Cambridge. Both Duce and Lininger employed thermal neutron irradiation, followed by radiochemistry and beta counting. A major portion of the chlorine and bromine in a “polluted” atmosphere is thought to originate (Winchester and Duce, 1967) from vehicles that burn leaded gasoline.

A noteworthy feature of the neutron activation analysis technique is its relatively nondestructive property, which permits the assay of the same material for elements other than those obtained under the conditions of this study. Longer irradiation of the same samples will permit analysis of nuclides having longer half lives than those obtained by 1-minute irradiations. Studies of other elements present in air particulate samples after a 24-hour irradiation are currently in progress. Preliminary observations indicate that in addition to the elements reported in this study, cobalt, iron, mercury, scandium, chromium, zinc, and antimony also were present in April 4 particulates.

Literature Cited

- American Conference of Governmental Industrial Hygienists, “Documentation of Threshold Limit Values,” 1966.
 Department of Air Pollution Control, City of Chicago, Annual Report, 1967.
 Duce, R. A., Winchester, J. W., Van Nahl, T. W., *J. Geophys. Res.* **70**, 1775–99 (1965).
 Gordon, C. M., Larson, R. E., *J. Geophys. Res.* **69**, 2881–5 (1964).
 Johnstone, H. F., Moll, A. J., *Ind. Eng. Chem.* **52**, 861–3 (1960).
 Lewis, L. L., *Anal. Chem.* **40**, No.12, 28A–47A (1968).
 Lininger, R. L., Duce, R. A., Winchester, J. W., Matson, W. R., *J. Geophys. Res.* **71**, 2457–63 (1966).
 Nelson, D. M., Dipert, M. H., Gustafson, P. F., Biological and Medical Research Division, Argonne, Ill., Annual Rept. ANL-7136, 1965.
 Parkinson, T. F., Grant, L. G., *Nature* **197**, 479–80 (1963).
 Robinson, J. W., Ramakrishna, T. V., “Trace Analysis Methods for Air Pollution Studies,” Science Information Exchange, SIE No. 7, GX-851-05 (1965).
 Smith, R. G., *Anal. Chem.* **40**, No 7, 24A–34A (1968).
 Stewart, W. H., “Air Pollution—Time for Action,” Air Pollution Control Association, 59th Annual Meeting, San Francisco, Calif., June 1966.
 Tabor, E. C., Warren, W. V., *A.M.A. Arch. Ind. Health* **17**, 141–5 (1958).
 Tetzlaff, F., “Guiding Principles,” State Air Pollution, U.S. Dept. Health, Education and Welfare, Division of Air Pollution, Public Health Service, Washington, D. C., May 1962.
 U. S. Department of Health, Education and Welfare, Public Health Service, National Center for Radiological Health, Rockville, Md., “Radioassay Procedures for Environmental Samples,” pp. 1–51 to 1–55, 1967.
 Winchester, J. W., Duce, R. A., *Naturwissenschaften* **5**, 110–13 (1967).

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Lead and Other Metal Ions in United States Precipitation

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■ Atmospheric precipitation samples collected by a nationwide network of 32 stations throughout the United States were analyzed for lead, zinc, copper, iron, manganese, and nickel by atomic absorption. Values for each station averaged over approximately six months during 1966 and 1967 indicate human activity as the primary source of these materials in atmospheric precipitation. The concentration of lead in precipitation was found to be correlated with the amount of gasoline consumed in the area in which the sample was collected. The overall mean concentrations of the metals in precipitation are compared with analogous values in surface water supplies.

The geographical patterns of contaminant concentrations in atmospheric precipitation indicate the nature of the sources of the contaminants. A nationwide precipitation sampling network has made it possible to determine these patterns for a number of constituents, including several trace metals: lead, zinc, copper, iron, manganese, and nickel.

Because of the biological activity of several of these metals, there has been increasing concern over their allowable concentration limits in drinking water. One source is the atmosphere, from which aerosols may be deposited in surface water supplies by dry fallout or by entrapment in atmospheric precipitation. A survey of the concentrations of these contaminants should indicate the possible importance of this second mechanism.

Experimental

The sampling network consisted of 32 stations distributed throughout the United States.

- | | |
|--|--|
| (1) Caribou, Me., WBAS | (12) Charleston, S.C., WBAS |
| (2) Nantucket, Mass., WBAS | (13) Nashville, Tenn., WBAS |
| (3) Albany, N.Y., WBAS | (14) Chicago, Ill., Midway Airport, WBAS |
| (4) Philadelphia, Pa., WBAS | (15) Chicago, Ill., O'Hare International Airport, WBAS |
| (5) Cincinnati, Ohio, Greater Cincinnati Airport, WBAS | (16) Sault St. Marie, Mich., WBAS |
| (6) Cincinnati, Ohio, WBRS | (17) St. Cloud, Minn., WBAS |
| (7) Buxton, N.C., WBO | (18) Springfield, Mo., Drury College |
| (8) Sterling, Va., WBOTDC | (19) Grand Island, Neb., WBAS |
| (9) Montgomery, Ala., WBAS | (20) Lake Charles, La., WBAS |
| (10) Tampa, Fla., International Airport, WBAS | (21) Amarillo, Tex., WBAS |
| (11) Greenville, S.C., WBAS | (22) Brownsville, Tex., WBAS |

- | | |
|----------------------------------|--|
| (23) San Angelo, Tex., WBAS | WBAS |
| (24) Grand Junction, Colo., WBAS | (28) Avalon, Calif., WBAS |
| (25) Kimberly, Idaho, WBASO | (29) Medford, Ore., WBAS |
| (26) Ely, Nev., WBAS | (30) Rapid City, S.D., WBAS |
| (27) Glasgow, Mont., WBAS | (31) Mauna Loa Observatory, H.I., WBRS |
| | (32) Winslow, Ariz., WBAS |

WBAS—Weather Bureau Airport Station
WBRS—Weather Bureau Research Station
WBASO—Weather Bureau Agricultural Service Office
WBO—Weather Bureau Office
WBOTDC—Weather Bureau Observational Test and Development Center

At each station, an automated precipitation collector remains open during periods of precipitation only, excluding dry fallout from the sample. The moisture-sensing grid that activates the lid is thermostated so that snow and sleet as well as rain are collected. The sensing grid is maintained at a temperature sufficient to evaporate moisture from the grid shortly after precipitation ceases, causing the lid to close. The collected precipitation, contained in a polyethylene bucket, is removed after each precipitation period and transferred to a polyethylene bottle, which is returned to the National Center for Atmospheric Research where pooled monthly samples are analyzed. The polyethylene bottles contain a small amount of toluene to minimize biological activity in the sample.

Iron, manganese, copper, lead, nickel, and zinc were measured by atomic absorption photometry of the diethylamino-dithiocarbamate complexes of these metals dissolved in 2-heptanone. The precipitation samples were first filtered through a prewashed 5- μ , 1-in. diameter polyvinylchloride membrane filter. Two ml. of 1N HCl is then added to 100 ml. of the sample contained in a 250-ml. separatory funnel. Ten ml. of 2-heptanone containing 3.0% (w/v) of the diethylammonium salt of diethylaminodithiocarbamic acid is added. The mixture is agitated for 45 min. on an automatic shaker, and the organic layer removed for atomic absorption photometry. This method was found to be superior to current concentration techniques since the complexing agent was easily soluble in the organic solvent, was commercially available in pure form, does not hydrolyze readily in contact with water, forms complexes that are stable for at least several days (except manganese and iron, which are stable for several hours), yields a high enhancement factor in sensitivity, and the salt of the weak acid of the complexing agent forms an appropriate buffer with the added acid, eliminating the need for a separate buffering agent (Lazrus, 1969).

For each metal the method was sensitive to at least 1 p.p.b. in the original precipitation sample using a Perkin-Elmer 290 atomic absorption spectrophotometer. Concentrations below this were recorded as zero.

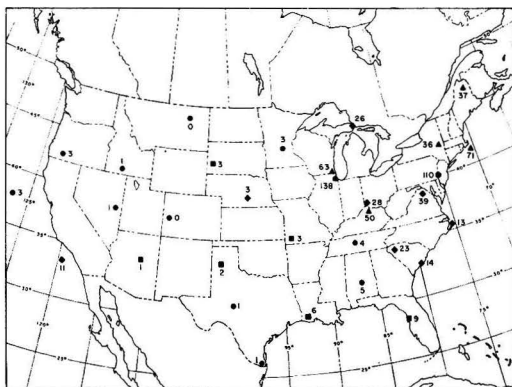


Figure 1. Lead values averaged from September 1966 to March 1967. Plotted numerals are g./ha./mo. Symbols are g./ha./cm. of precipitation

● 0-0.4 ■ 0.5-0.9 ◆ 1-4 ▲ 5-9 ○ 10-14
▲ 15-

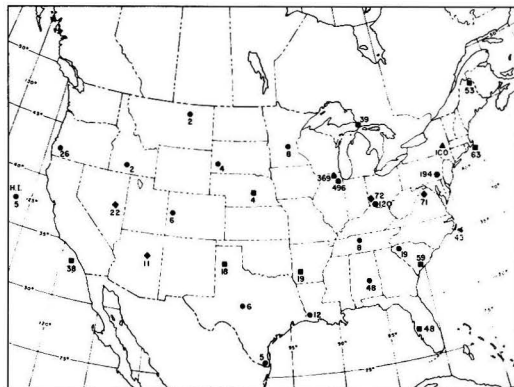


Figure 2. Zinc values averaged from September 1966 to January 1967. Plotted numerals are g./ha./mo. Symbols are g./ha./cm. of precipitation

● 0-3.0 ■ 4.0-7.0 ◆ 8.0-11.0 ▲ 12.0-15.0 ○ 16.0-19.0
▲ 20.0-

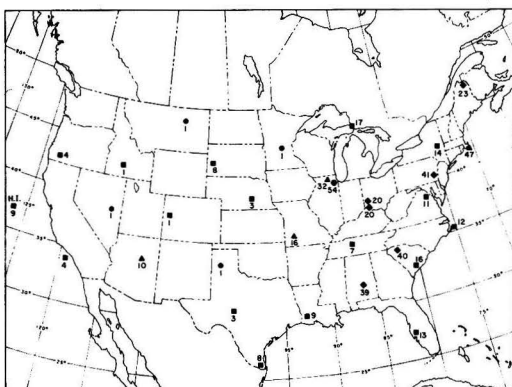


Figure 3. Copper values averaged from September 1966 to January 1967. Plotted numerals are g./ha./mo. Symbols are g./ha./cm. of precipitation

● 0-0.4 ■ 0.5-1.5 ◆ 1.6-3.5 ▲ 3.6-5.5 ○ 5.6-8.0

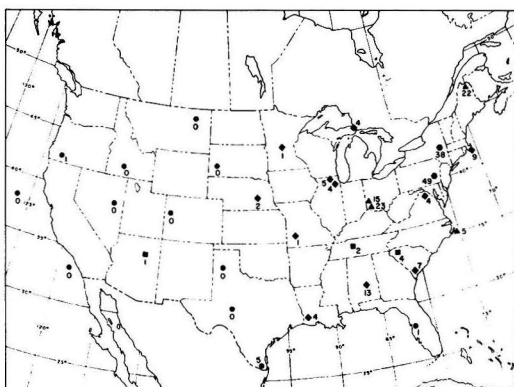


Figure 4. Iron values averaged from September 1966 to January 1967. Plotted numerals are g./ha./mo. Symbols are g./ha./cm. of precipitation

● 0-0.19 ■ 0.20-0.39 ◆ 0.40-1.9 ▲ 2.0-3.9 ○ 4.0-5.9

Results and Discussion

Figures 1 through 6 are maps of average concentrations of elements for the specified periods. The symbol representing a station indicates the average grams of the metal ion, deposited on 1 hectare by 1 cm. of precipitation. This figure suggests the contaminant concentration in the atmosphere and is relatively independent of the total amount of precipitation. It is, however, not completely independent of amount of rainfall, since frequent showers keep the air cleaner and contaminant concentration tends to decrease with duration of a rainfall. The numeral under the symbol represents grams of contaminant deposited per hectare per month, averaged over the appropriate sampling period. This figure is directly proportional to both contaminant concentration and quantity of rainfall.

Certain generalizations are applicable to all the metals. The northwest portion of the United States is conspicuously low in contamination. The northeast is relatively high. The southeast and southwest vary from low to moderate in contamination, depending upon the metal. The maps suggest that the concentration patterns of these minor trace contaminants could be

engendered primarily by human activity. Concentrations tend to increase in areas of mining and manufacturing.

The possible significance of adsorption on the polyethylene surfaces introduces some uncertainty. In the case of lead (Ter Haar, Holtzman, *et al.*, 1967) and zinc (Robertson, 1968), this source of error is probably not serious. In the case of the other elements it is difficult to assess this problem. Investigations of adsorption have generally utilized new polyethylene containers, whereas these samples were in containers which had been used for several years in the operation of the network. Secondly, the concentration of suspended micron-range particles varies from sample to sample. It appears, however, that the concentration patterns of all the metals are reasonable and resemble each other fairly clearly. It was unfortunately not possible to include additives in the samples to eliminate adsorption, since this would have interfered with the analyses of other materials of primary concern.

Table I compares average concentrations found in precipitation with those in surface water supplies before treatment (Durfor and Becker, 1964b). This data was obtained in 1962,

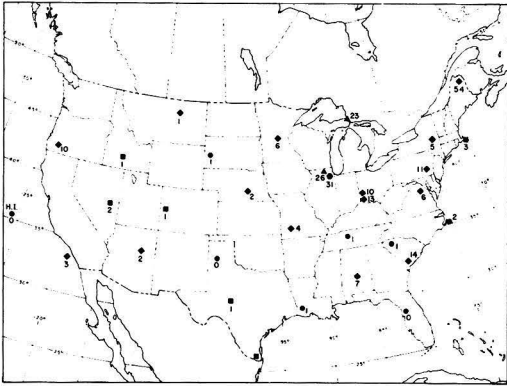


Figure 5. Manganese values averaged from September 1966 to January 1967. Plotted numerals are g./ha./mo. Symbols are g./ha./cm. of precipitation

● 0-0.19 ■ 0.20-0.39 ◆ 0.40-1.9 ▲ 2.0-3.9 ○ 4.0-5.9

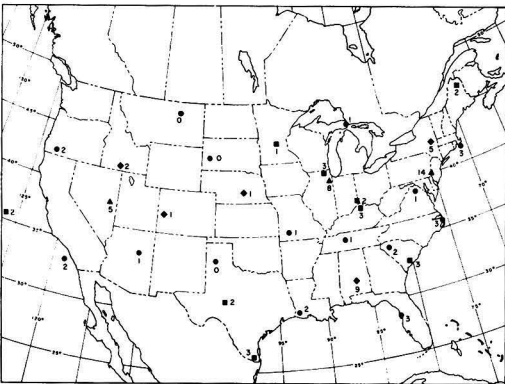


Figure 6. Nickel values averaged from September 1966 to March 1967. Plotted numerals are g./ha./mo. Symbols are g./ha./cm. of precipitation

● 0-0.2 ■ 0.3-0.5 ◆ 0.6-0.8 ▲ 1.2-

and comparing it with 1966 precipitation data assumes that values for national averages will not have changed radically in four years. There is, on the average, twice as much lead in atmospheric precipitation as in water supplies. This ratio implies the existence of a process whereby lead is depleted after precipitation reaches the surface. Recent evidence confirms the tendency of lead to occur in suspended matter rather than in solution in Russian rivers (Korovalov, *et al.*, 1966). In the case of copper, the quantity found in precipitation could account for the average value found in surface water. Nickel and manganese, however, must have other sources in addition to atmospheric precipitation.

Only the lead average in precipitation comprises a significant percentage of the limits established by the U.S. Public Health Service Drinking Water Standards (1962). A plot of average lead values for September 1966 to March 1967 vs. gasoline sales in the locale of the sampling station (Editor and Publisher Marketing Guide, 1966), though showing considerable scatter, indicate a definite relationship. The rank correlation coefficient (Kendall, 1955) relating lead in rain-

Table I. Trace Contaminants in Precipitation and in Untreated Water Supplies

Element	A Av. conc. in ppt. ^a p.p.m.	B Av. conc. in untreated surface water supplies, ^b p.p.m.	C U.S.P.H. conc. limits (1962), p.p.m.	$\frac{A}{C} \times 100$ (%)
Pb	0.034	0.017	0.05	68
Mn	0.012	0.070	0.05	24
Cu	0.021	0.021	1.0	2
Zn	0.107	...	5.0	2
Ni	0.0043	0.0065		

^a Average of samples collected from Sept. 1966 through Jan. 1967.
^b Average computed from Durfor and Becker (1964b).

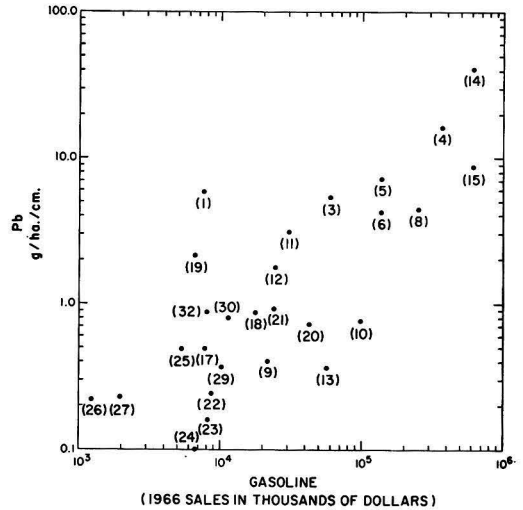


Figure 7. The dependence of lead on gasoline consumption plotted, or average gram of lead deposited on one hectare by one centimeter of precipitation vs. sales of gasoline in the locale of the collecting station in thousands of dollars

water to sale of gasoline is 0.55 with a significance level under 0.5%. Two stations, Sault St. Marie and Nantucket, had anomalously high lead concentrations and were not included in the plot or computation. There are ore docks and heavy metal industry in Sault St. Marie, Ontario, located across the Sault St. Marie Canal. In the case of Nantucket Island, it is likely that lead is advected from the large industrial complexes on the coast. Several points for which gasoline consumption data were available are missing. As might be expected, samples from areas where much gasoline is consumed tend to exert a large influence on the total lead average in precipitation. If median, rather than average, values are considered, the result is somewhat less startling: Both precipitation and untreated surface water supplies have median lead concentrations of approximately 0.01 p.p.m. (Durfor and Becker, 1964a).

A recent study indicates that rainwater in the Chicago area during summer months contains less lead than our values for autumn and early winter (Ter Haar, *et al.*, 1967). This is possibly due to fewer inversion periods in summer and also

possibly to differences in sampling location.

The appreciable lead contamination in precipitation is plausible in view of earlier investigations. Environmental lead contamination is widespread. Tatsumoto and Patterson (1963b) found lead concentrations in snow four orders of magnitude greater than the amount attributable to naturally formed dust in a remote area 500 miles east of the Los Angeles complex at an altitude of 7000 feet. They estimate that the concentration of lead in the surface layer of the Pacific Ocean off the coast of southern California has increased tenfold during the past three or four decades; the input of lead into the atmosphere by combustion of leaded gasoline could account for this (Tatsumoto and Patterson, 1963a). In the Tatra Mountains, contemporary ice samples (1960-65) contain about 16 times more lead than century-old samples (1861-66) (Jaworowski, 1968). Similarly, lead in Greenland snow of 1964 was 16 times more concentrated than in snow dating from 1905 (Murozumi, *et al.*, 1965).

Ettinger (1966) has discussed likely sources of lead contamination in water supplies. Large industrial complexes with associated high consumptions of coal and leaded gasoline do not necessarily cause appreciable dissolved lead enrichment of nearby water supplies. Samples showing high lead concentration were exposed to contamination by metalworking and chemical industries. Apparently natural processes, such as precipitation and coprecipitation, control the concentration of dissolved lead in surface water. Ettinger concluded that only a fraction of lead in surface water remains dissolved and that low turbidity of drinking water reduces the likelihood of the consumer's exposure to lead.

It is probable that lead aerosol in the atmosphere remains in a soluble form, either as the halide salts emitted from leaded gasoline engines or as the sulfate. The very insoluble dioxide of lead, PbO_2 , reacts with atmospheric sulfur dioxide to produce the sulfate, which is soluble at the concentration levels involved. This reaction is currently used as an analytical determination of atmospheric sulfur dioxide. Atmospheric sulfur dioxide may maintain the lead as the relatively soluble sulfate, while in surface waters oxides and other insoluble salts form and precipitate. This may account for the apparent discrepancy of considerable lead found in atmospheric precipitation over those areas where much leaded gasoline is con-

sumed, but comparatively little dissolved lead is found in the surface waters.

Conclusions

On the basis of geographical distributions, lead, zinc, copper, iron, and manganese in atmospheric precipitation are derived primarily from human activity. The concentration of only lead is significantly high with respect to the allowable concentration in drinking water. However, the evidence indicates that lead forms insoluble materials in surface waters and is removable by sedimentation or by filtration. A rank correlation coefficient with high significance exists between lead in precipitation and the consumption of gasoline.

Literature Cited

- Durfor, C., Becker, E., *J. Amer. Water Works Assoc.* **56**, 237-46 (1964a).
- Durfor, C., Becker, E., U.S. Geological Survey Water-Supply Paper No. 1812 (1964b).
- Editor and Publisher Marketing Guide*, 1966, Editor and Publisher Co., N.Y.
- Ettinger, M., "Symposium on Environmental Lead Contamination," U.S. Department of Public Health Service Publication No. 1440 (1966).
- Jaworowski, Z., *Nature* **217**, 152-3 (1968).
- Kendall, M., *Rank Correlation Methods*, 2nd ed., Charles Griffin & Co., Ltd., London (1955).
- Korovalov, G., Ivanova, A., Kolesnikova, T., *Gidrokhim. Mater.* **42**, 94-111 (1966).
- Lazrus, A. L., National Center for Atmospheric Research, Boulder, Colo., unpublished data (1969).
- Murozumi, M., Chow, T. J., and Patterson, Clair C., *Mar. Geochem., Proc. Symp.*, Kingston, R.I., 1964, 213-15 (Pub. 1965).
- Robertson, D. E., *Anal. Chim. Acta* **42**, 533-6 (1968).
- Tatsumoto, M., Patterson, C., National Academy of Sciences-National Research Council Publication No. 1075, Report No. 38, 167-75 (1963a).
- Tatsumoto, M., Patterson, C., *Nature* **199**, 350-2 (1963b).
- Ter Haar, G., Holtzman, A., Lucas, H., Jr., *Nature* **216**, 353-4 (1967).
- U.S. Public Health Service, "Public Health Service Drinking Water Standards," Publication No. 956 (1962).

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Kinetics of the Reaction of SO₂ with Calcined Limestone

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■ Differential reactor techniques were used to measure the rate of reaction of sulfur dioxide with four natural specimens of limestone, after calcination at standardized conditions. The rates were measured as a function of SO₂ concentration, particle size, and CaO conversion between 540° and 1100° C. A first-order chemical reaction was the predominant resistance limiting the rate of sorption of SO₂ by small particles. The activation energy was dependent upon the type of stone, and ranged between 8.1 and 18.1 kcal./g. mole. The rate was essentially independent of particle size for $D_p < 0.05$ cm. Reaction occurs initially throughout the particle volume under the isothermal reaction conditions studied and the internal diffusion resistances become limiting only after conversion of at least 20% CaO. The reaction rate decreased rapidly with increasing conversion, explained by an exponential relationship between the frequency factor and the sulfate loading.

Processes in which limestone and dolomite are used to desulfurize flue gas are being intensively investigated under the sponsorship of the National Air Pollution Control Administration. Such processes include dry injection of pulverized stone into boiler furnaces and the use of fluidized bed contactors, fluid bed combustion, and thin fixed beds.

It is generally assumed that limestone absorbs SO₂ by a mechanism involving two consecutive steps—dissociation of the calcium carbonate, followed by reaction of CaO with sulfur dioxide. It is expected that the rate of the second step will be important in any of the proposed pollution control processes, and especially in the dry injection process (Potter, Harrington, *et al.*, 1968). Several investigators (Harrington, Borgwardt, *et al.*, 1968; Potter, 1969) have determined the saturation capacities of a large number of naturally occurring limestones and dolomites under various conditions of reaction with SO₂. Other studies under way will define the rate of reaction of uncalcined limestones in the disperse phase (Coutant, 1968). The purpose of the investigation reported in this paper is to determine the rate of reaction of limestones after calcination under standardized conditions.

Experimental

Complete geological descriptions of the stones used in this work are given in a separate report (Harvey, 1968). Table I shows the chemical composition and primary physical characteristics of the calcined stones. Calcination was carried out in 180-g. batches in an Inconel kiln 12.5 cm. long and 8 cm. in diameter, rotated at 1 r.p.m. It was heated to 980° C. in an electric furnace and then charged with 10/28-mesh stone. The

Table I. Properties of Calcines

Stone	LOI ^a	% CaO	% MgO	% Fe ₂ O ₃	% SiO ₂	Bulk density, ^b g./cc.	Porosity, ^b cc./cc.
1337	47.4	55	43	0.33	0.92	1.41	0.58
1351	42.4	54	28.5	7.0	8.2	1.59	0.56
1343	42.8	94	0.8	0.66	2.98	1.88	0.45
1360	43.8	81	13.0	1.25	3.65	1.51	0.56

^a Weight loss on calcination at 980° C.

^b 150/170 mesh particle size.

kiln was maintained at 980° C. and purged with air for 2 hours to remove CO₂ during calcination. Conversion to the oxide was complete under these conditions (CO₂ < 0.5%). The calcined stone was cooled, crushed, and screened into size ranges of 12/16, 42/65, and 150/170 mesh (Tyler). The calcined samples were stored in airtight containers until used.

The rate of reaction with SO₂ was determined in a differential reactor (Figure 1) constructed of Inconel alloy. In this type of reactor the thin layer of solid and high gas flow prevent gas-phase concentration gradients in the reacting solid. The gases enter the bottom of the reactor housing, are passed upward through an annular preheat section 73 cm. long and 5.25 cm. in diameter, and then back downward through the inner, concentric reactor tube containing the limestone sample. The outer diameter of the reactor tube is 4.13 cm., and the inner diameter 3.42 cm. The sample is supported on a 30-mesh Inconel screen in a removable carrier. The carrier is sealed against a flange in the center of the reactor tube so that the entire gas flow passes through the solid during exposure.

In this investigation a sample consisted of 30 mg. of calcined stone, distributed uniformly over the 2.65-cm. diameter screen. For small particle sizes a disk of woven refractory fabric was placed on the screen and a 1-cm. thickness of refractory (fused quartz) gauze was placed on the fabric. The lime particles were dispersed into the gauze.

The mass flow rate of gas through the screen was maintained constant at 0.075 g./(sq. cm.) (sec.), which at 870° C. corresponds to a superficial velocity of 240 cm. per sec. A high gas velocity reduced gas film resistance to a negligible value, so that mass transfer to the particle surface did not affect rate measurements. The gas fed to the reactor was a flue gas generated by combustion of fuel oil containing carbon disulfide. The composition of the flue gas was 10.5% CO₂, 3.4% O₂, 9.9% H₂O, 0.27% SO₂, 0.003% SO₃, and 75.9% N₂ by volume. The sulfur dioxide concentration was monitored continuously with an infrared analyzer after removal of the water vapor from the sample stream.

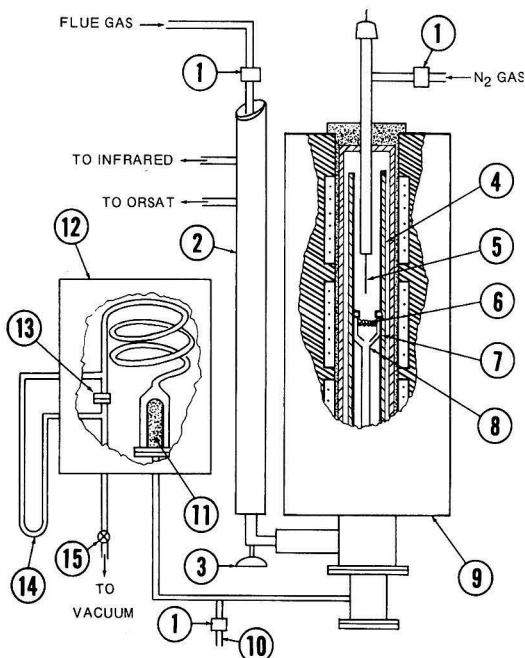


Figure 1. Apparatus

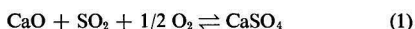
1. Teflon solenoid valve 2. Heating tapes 3. Thermometer 4. Preheat section 5. Thermocouple 6. Sample 7. Reactor tube 8. Sample carrier 9. Heating furnace 10. N₂ Purge exhaust 11. Alundum filter 12. Constant-temperature oven 13. Orifice 14. Manometer 15. Flow control valve

The reactor was mounted in an electric furnace containing three heating sections. The center section was energized by a proportional controller acting on a thermocouple located 3.4 cm. above the screen supporting the lime sample. The other two sections were equipped with variable transformers set by thermocouples in the top and bottom of the reactor tube to maintain a uniform temperature over the full length of the reactor and preheater assembly. The thermocouples were calibrated *in situ* against a multiply shielded, high-velocity thermocouple. A multipoint recorder continuously monitored reactor temperatures.

Before a run was started, the carrier and sample were allowed to heat up for 5 min. to the reactor temperature. The time of exposure of the solid to the gas stream was controlled by solenoid valves that started the gas flow at the beginning of the run and purged the reactor with nitrogen at the end of the run. The sample was removed from the carrier after exposure (along with the refractory gauze, if used) and analyzed for sulfate. The exposed sample was dissolved in water by soaking with ion exchange resin, filtered, and the filtrate titrated in 80% isopropyl alcohol with barium perchlorate using thorin indicator.

Results and Discussion

The chemical reaction between limestone and sulfur dioxide at high temperature in the presence of excess oxygen is:



Equilibrium data for the reaction have been summarized by researchers at Battelle Memorial Institute (Ward, *et al.*, 1966). The reaction proceeds to the right at temperatures up

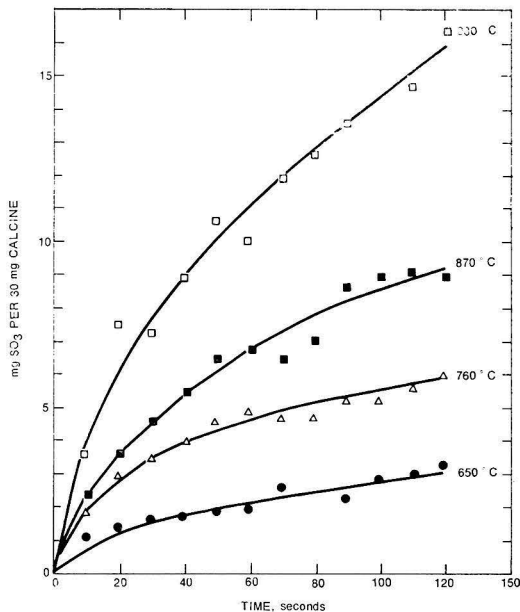


Figure 2. Sorption of sulfur dioxide by dolomite-1351 at various reactor temperatures

SO₂ concentration = 3000 p.p.m. (dry basis), particle size = 150/170 mesh

to 1230° C. at partial pressures of SO₂ corresponding to flue gas concentrations of about 3000 p.p.m. Equilibrium would also permit the MgO component of dolomite to react at temperatures below 840° C., and it has been reported to participate in the reaction with SO₂ in the presence of iron oxide impurities (Wickert, 1963). More recent investigations (Bertrand, Frost, *et al.*, 1968) have shown that SO₂ reacts only slightly with MgO at 430° to 700° C. in a fluidized bed, reaction occurring preferentially with calcium even when Fe₂O₃ content is as high as 7%. Calcined magnesite (MgCO₃) and calcined brucite [Mg(OH)₂] were shown to have low capacities for sorption of sulfur dioxide. Dolomites injected into a pilot furnace (Attig, 1968) have been examined by x-ray diffraction analyses, but showed no MgSO₄ as a reaction product, although small amounts were detectable by DTA methods. No distinction is made in this study between CaO and MgO, although the data support the conclusion that only CaO has a significant reaction rate under the conditions investigated.

When reaction 1 takes place in flue gas containing high concentrations of carbon dioxide, equilibrium also favors a competing reaction (Ward, *et al.*, 1966) below 770° C.:



Typical experimental results for the sorption of SO₂ are shown in Figure 2; the mg. of SO₂ found in 150/170-mesh particles ($\bar{D}_p = 0.0096$ cm.) after reaction is plotted against exposure time at various reaction temperatures. Figure 3 shows a similar plot for different particle sizes at a reaction temperature of 870° C. Total conversion of the CaO in this dolomite would correspond to an ordinate value of 23.2 mg. These figures illustrate the strong sensitivity of the reaction to temperature and the surprisingly low sensitivity to particle size, which were characteristic of all the stones examined.

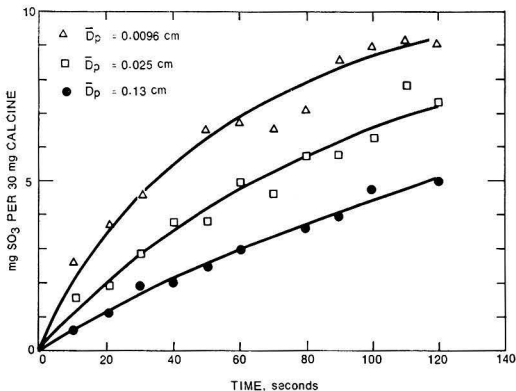


Figure 3. Sorption of sulfur dioxide by different particle sizes of dolomite 1351

SO₂ concentration = 3000 p.p.m. (dry basis), temperature = 870° C.

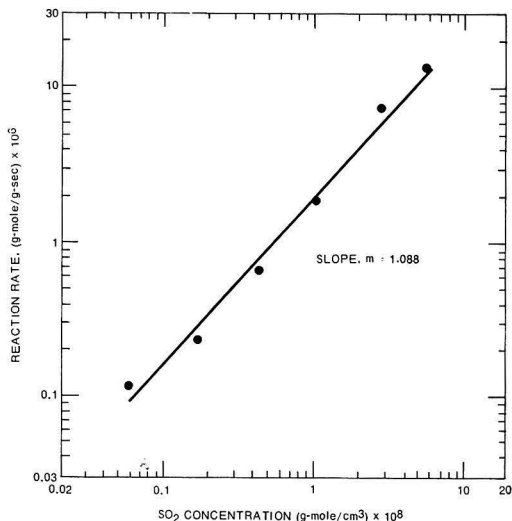


Figure 4. Log r vs. log C to estimate m
Dolomite 1337, 12/16 mesh particle size, 870° C.

The rate of sorption was measured as the tangent to the smooth curve drawn through the data and is defined as:

$$r = \frac{1}{W} \frac{dn'}{dt} \quad (3)$$

where W is the grams of calcined stone exposed in the reactor, and n' is the gram moles of SO₃ in the stone at time t .

The data were correlated according to the rate expression for chemical reaction in a porous solid (Satterfield and Sherwood, 1963):

$$-\frac{dn}{dt} = k_p V C^m \eta \quad (4)$$

since $dn'/dt = -dn/dt$

$$\frac{1}{W} \frac{dn'}{dt} = \frac{\eta}{\rho} k_p C^m \quad (5)$$

The effect of SO₂ concentration, C , on the rate of sorption is shown in Figure 4. The SO₂ concentration was varied between 58 and 6000 p.p.m. by changing the carbon disulfide content of the fuel oil burned in the furnace. The rate was measured at a conversion of 10.5% of the CaO in 12/16-mesh stone reacted at 870° C. The line fitted to these data by the method of least mean squares has a slope of 1.008 or $m \approx 1$, indicating that the reaction is first order with respect to the concentration of SO₂ in the gas phase. For the remainder of the experimental work, which is reported below, the SO₂ concentration was fixed at 3000 p.p.m. (dry basis) or 2.9×10^{-8} g. moles/cc. (wet basis, 870° C., 1 atm.).

The rate constant k_p is a function of temperature and also some function of n'/W , the sulfate loading; it decreases as the reaction progresses and the solid reactant is consumed. The temperature dependency was correlated by the Arrhenius equation:

$$k_p = A e^{-E/RT} \quad (6)$$

An Arrhenius plot for each of the four calcined stones is shown in Figure 5 for reactions with SO₂ at temperatures between 650° and 980° C. The rates were measured at a sulfate loading of 1×10^{-3} g. mole/g. of 150/170-mesh particle size sample. This loading corresponds to approximately 10% conversion of the CaO. The data show a linear correlation between log r and $1/T$, as specified by Equations 5 and 6. The apparent activation energy determined from the slope of these plots was distinctly different for each stone, ranging from 8.1 to 18.1 kcal/g. mole. When rates were measured at higher CaO conversions—up to 20%—the plots shifted toward the abscissa, but remained parallel to the lines shown in Figure 5, thus indicating no significant change in the activation energy.

The high sensitivity of the rate to temperature suggests

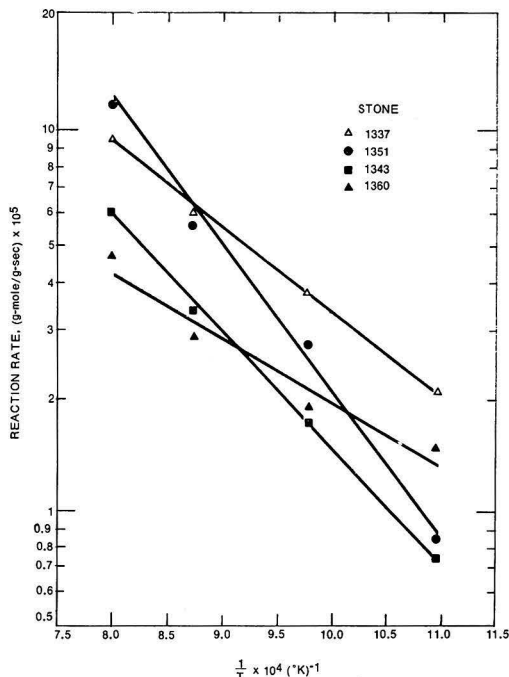


Figure 5. Arrhenius plots for the reaction of sulfur dioxide with four limestones

Table II. Kinetic Parameters^a for Sorption of SO₂ by Calcined Limestones

Stone	Activation energy, <i>E</i> , cal./g. mole	Reaction rate constant, <i>k_s</i> , sec. ⁻¹	Frequency factor, <i>A</i> , sec. ⁻¹
1337	10,000	4.8 × 10 ³	2.4 × 10 ⁵
1351	18,100	7.2 × 10 ³	9.0 × 10 ⁶
1343	14,200	4.0 × 10 ³	1.1 × 10 ⁶
1360	8,100	2.3 × 10 ³	5.5 × 10 ⁴

^a Evaluated at sulfate loading of 1 × 10⁻³ g. moles/g., 150/170 mesh particle size; 980° C.

chemical reaction to be the predominant rate-controlling resistance during the initial period of SO₂ sorption by small particles. The apparent activation energy for sorption, controlled solely by bulk diffusion, would be only 3.4 kcal./g. mole. A summary of the empirical kinetic parameters estimated for the four stones is given in Table II.

The data in Figure 5 further indicate that reduction in rate of reaction with SO₂ as a result of competition with CO₂ was not important at 650° C. At 540° C., however, there was evidence that reaction 2 was significant and the Arrhenius plots could not be extrapolated to that temperature. The plots also failed when the reaction temperature was raised from 980° to 1100° C., sorption rates decreasing at the higher temperature. Subsequent experiments in which the calcine was heated for 10 min. at 1100° C. and then reacted at 870° C. showed the same difference in rate when compared to a sample which was not exposed to the high temperature. It was concluded that the loss of reactivity was due to the changes in porosity and bulk density which occur when lime is "hard-burned" (Boynton, 1966).

To ensure that gas film diffusion was not influencing the rate measurements, a supplementary experiment was made with a 0.95-cm. diameter sample carrier which permitted exposure of the solid at high gas velocity. Samples of dolomite 1337 ($\bar{D}_p = 0.13$ cm.) were exposed for 2 min. at 980° C. The amount of sulfate found in the stone was only 5.3% greater at 2400 cm./sec. gas velocity than found at 225 cm./sec. The negligible effect of gas velocity verified that the rate of sorption was not limited by mass transfer to the solid surface.

The effect of particle size on reaction rate is shown in Figure 6, in which the value of *r* at a sulfate loading of 2 × 10⁻³ g. mole/g. is plotted against the inverse of particle diameter. If the particles are assumed to be spherical, the total exterior surface of a given mass of stone (specific surface) would increase with 1/ \bar{D}_p when the particle size is reduced. If the reaction were occurring only at the outer surface, the plot shown in Figure 6 would be expected to be a straight line through the origin. It is clear that the rate was not proportional to specific surface and for fine particles was essentially independent of it. The results suggest that some reaction takes place within the interior structure of the solid and that the relative importance of the internal reaction becomes greater as the particle size decreases. These observations are similar to the effects associated with highly porous catalysts and are consistent with the fact that the pore space in calcined limestones usually accounts for 50% or more of the total volume of the particles. The porosities (or fraction of particle volume that is pore space) for the four calcined stones are given in Table I.

Figure 7 shows the conversion vs. time response for different particle sizes of stones 1351 and 1343 over long periods of exposure at 870° C. An analysis of the response according to

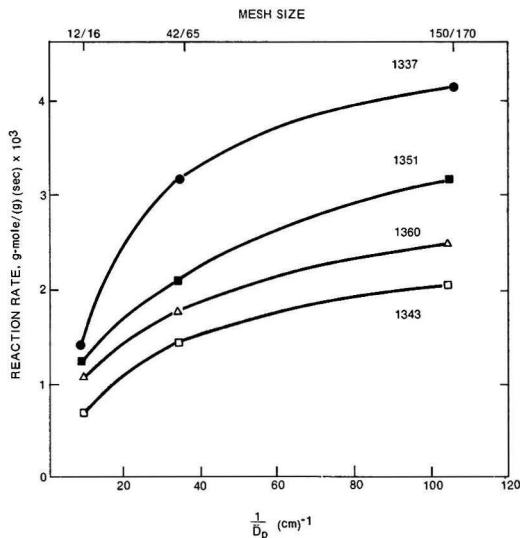


Figure 6. Reaction rate vs. 1/ \bar{D}_p
Sulfate loading = 2 × 10⁻³ g. moles/g.

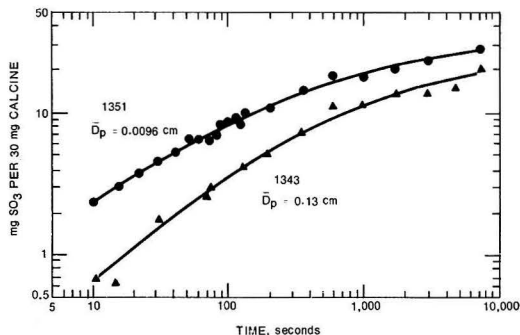


Figure 7. Sorption of sulfur dioxide by calcined limestones

the method of Shen and Smith (1965) was made to test for intraparticle diffusion. This model is based on diffusion through the product crust as the rate limiting mechanism and a nonporous solid reactant in which reaction occurs only at the interface of the unreacted core. The data from this investigation could not be correlated by the shell diffusion model given by Shen and Smith's Equation 31. Figure 6 shows that the model for shell diffusion, which predicts that the rate of sorption at a given sulfate loading will increase with 1/ \bar{D}_p^2 , is clearly inconsistent with data on particle size vs. reaction rate.

The data could be correlated empirically by a plot of $\log r$ against sulfate loading, n'/W , as shown in Figure 8. The data were linear for all particle sizes of each of the four stones examined at the reaction temperature of 870° C. The observed response can be interpreted in terms of a change in the frequency factor, *A*, of Equation 5. The frequency factor, which relates the reaction rate to the number of molecular collisions occurring per unit volume per unit time, is dependent upon the amount of SO₂ and the amount of unreacted CaO present

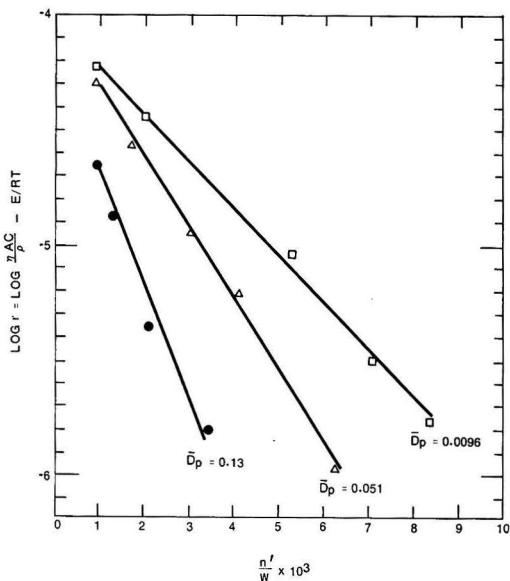


Figure 8. Relation of reaction rate and sulfate loading for dolomite 1337

(as well as other factors such as surface effects and probability of reaction of the molecules). As the reaction progresses and CaO is consumed, the frequency factor will be expected to decrease in some manner related to the amount of sulfate formed. If r_0 and A_0 are the rate and frequency factor at zero sulfate loading, then, from Equations 3, 5, and 6,

$$r_0 = \frac{\eta A_0 C}{\rho} e^{-E/RT} \quad (7)$$

designating the slope of the straight line fitted to the data in Figure 8 as β , the equation for the rate of reaction can be written as a function of sulfate loading:

$$\log \frac{\eta AC}{\rho} - \frac{E}{RT} = -\beta \frac{n'}{W} + \log r_0 \quad (8)$$

Equations 9 and 10 reduce to

$$A = A_0 e^{-\beta n'/W} \quad (9)$$

The observed relationship between rate and sulfate loading thus indicates an exponential decrease in the frequency factor. The data of Figure 8 show that coefficient β is a function of particle size, the rate of reaction of large particles being more sensitive to sulfate loading than small particles. Estimates of the effectiveness factor, obtained by extrapolation of the straight lines of Figure 8 to zero sulfation, indicate $\eta \approx 1$ for particles smaller than 0.05 cm. as shown by the approximately equal intercept of the two lines on the ordinate. The lower intercept for $\bar{D}_p = 0.13$ cm. indicates $\eta < 1$, implying the presence of pore diffusion resistance of significant magnitude for the larger size particles.

The results of this study show that the rate of sorption of SO_2 by calcined limestones is dependent to a very large extent upon the kinetics of the chemical reaction, particularly at small particle sizes, and that the rate of reaction predominates as the over all rate-controlling resistance for conversion of at least the first 20% of the CaO.

Acknowledgment

The author thanks Robert Larkin for development of the procedure for analysis of sulfate in limestone.

Nomenclature

- A = frequency factor, sec.^{-1} (g. moles/cc.) $^{m-1}$
- A_0 = frequency factor at zero solid conversion, sec.^{-1} (g. moles/cc.) $^{m-1}$
- C = gas phase concentration of sulfur dioxide, g. moles/cc.
- \bar{D}_p = mean particle diameter, cm.
- E = activation energy, cal./g. mole
- k_v = reaction rate constant per unit volume of solid, sec.^{-1} (g. moles/cc.) $^{m-1}$
- m = order of reaction with respect to sulfur dioxide
- dn/dt = rate of change of SO_2 in the gas phase, g. moles/sec.
- n' = sulfate in solid as SO_3 , g. moles
- R = gas constant, 1.987 (cal./g. mole $^\circ\text{K.}$)
- r = rate of formation of SO_3 in solid, g. moles/(g. sec.)
- r_0 = rate at zero solid conversion, g. moles/(g. sec.)
- V = volume of solid, including intraparticle pores, cc.
- W = weight of solid sample, g.
- T = temperature, $^\circ\text{K.}$
- t = time, sec.
- β = empirical correlation coefficient defined by Equation 9
- η = effectiveness factor, ratio of reaction rate to the rate that would be obtained if entire volume of particle participated equally in reaction
- ρ = bulk (particle) density of solid, g./cc.

Literature Cited

- Attig, R. C., "Dispersed-phase Additive Tests for SO_2 Control," Interim report LR:68:4078-01:9 by Babcock & Wilcox Co. for contract PH 86-67-127, pp. 4-5 (Dec. 10, 1968).
- Bertrand, R. R., Frost, A. C., and Skopp, A., "Fluid Bed Studies of the Limestone Based Flue Gas Desulfurization Process," Progress reports 9 and 10 by Esso Research and Engineering Co. for contract PH 86-67-130 (1968).
- Boynton, R. S., "Chemistry and Technology of Lime and Limestones," Wiley, New York, 1966.
- Coutant, R. W., Lougher, E. H., Barrett, R. E., and Campbell, B., "Investigation of the Reactivity of Limestone and Dolomite for Capturing SO_2 from Flue Gas," Interim report by Battelle Memorial Institute for contract PH 86-67-115 (Aug. 30, 1968).
- Harrington, R. E., Borgwardt, R. H., and Potter, A. E., *Am. Ind. Hyg. Assoc. J.*, **29**, 52-8 (1968).
- Harvey, R. D., *Environmental Geology Notes*, **21**, Illinois State Geological Survey (1968).
- Potter, A. E., Harrington, R. E., and Spaite, P. W., *Air Engineering*, 22-6 (Apr., 1968).
- Potter, A. E., "Sulfur Oxide Capacity of Limestones," *Ceramic Bulletin*, Am. Ceram. Soc., in press (1969).
- Satterfield, C. N., and Sherwood, T. K., "The Role of Diffusion in Catalysis," Addison-Wesley, Reading, Mass., 1963.
- Shen, J., and Smith, J. M., *Ind. Eng. Chem. Fundam.*, **4**, 293-301 (1965).
- Ward, J. J., and Pettit, D. A., "Fundamental Study of the Fixation of Lime and Magnesia," Report by Battelle Memorial Institute for contract PH 86-66-108, pp. 6 (June 30, 1966).
- Wickert, K., *Mitt. Ver. Grosskesselbes.*, **83**, 74-82 (1963).

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Influence of pH on the Adsorption of Aromatic Acids on Activated Carbon

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■ Studies are reported of the adsorption on activated carbon over a wide pH range of three herbicides: 2,4-dichlorophenoxyacetic acid (2,4-D); 2-methoxy-3,6-dichlorobenzoic acid (Dicamba); and 3-amino-2,5-dichlorobenzoic acid (Amiben). Equilibrium adsorption data on these and seven other structurally related compounds fit Langmuir isotherms in the range of concentrations studied at all pH levels. There is a marked increase in the removal of all solutes from aqueous solutions on lowering the pH below 7.0. Adsorption in the acid region is greater than that expected from the molecular-ionic ratio of the bulk solution. This effect is explained in terms of an enhanced specific ion adsorption resulting from increasing proton concentration as the pH is lowered and a subsequent alteration in the surface properties of the carbon. Maximum adsorption is attained near the point where $\text{pH} = \text{pKa}$.

The adsorption of acidic organic compounds from aqueous solutions by various carbons has received considerable attention in the past (Kipling, 1965). Most of the theoretical work has been confined to aliphatic carboxylic acids and phenols, with relatively little attention being directed to the adsorption of aromatic acids. However, recent concern with the accumulation of aromatic, organic pesticides in natural waters and the soil has focused attention on a better understanding of the effect of chemical and physical properties of the aromatic pesticides and adsorbents on adsorptive mechanisms. Chlorinated aromatic acids have widespread use and, as they are becoming an increasing residue problem, their adsorptive behavior on activated carbon seems pertinent. Among the more recent related investigations are those of Leopold, van Schaik, *et al.* (1960), adsorption of 2,4-D on charcoal; Weber and Morris (1964), effect of pH on adsorption of alkylbenzenesulfonates on carbon; Schwartz (1967), the herbicide CIPC on activated carbon; and the adsorption equilibrium studies of Haque and Sexton (1968) of 2,4-D on humic acid.

The present investigation was instituted to determine the influence of pH on the extent of adsorption on activated carbon of three aromatic acidic herbicides: 2,4-D (2,4-dichlorophenoxyacetic acid), Amiben (3-amino-2,5-dichlorobenzoic acid), and Dicamba (2-methoxy-3,6-dichlorobenzoic acid). Also included were structurally related compounds to determine if significant adsorption differences can be related to electronic differences or to certain steric factors, as was noted previously by Wheeler and Levy (1959) in their investigation of the adsorption of sterically hindered phenols on carbon. Also of interest to this study is the possibility of changing the pH of aqueous discharges, so as to enhance the removal of acidic pesticides by activated carbon.

Experimental

The carboxylic acids used in this investigation were supplied by Amchem Products, Inc., and were recrystallized from suitable solvents until their constant melting points agreed with literature values. A single batch of Pittsburgh Chemical Company activated carbon (Type BL) was used for all determinations after it has been repeatedly washed with acid and water. The carbon had a surface area of 1000–1100 meters^2/g . as determined by N_2 adsorption using the BET method. Distilled, de-ionized water was used throughout and the temperature was maintained at $25 \pm 0.5^\circ \text{C}$.

Aqueous solutions of each acid were prepared having varying concentrations ($0.25 \times 10^{-4} \text{ M}$ to $1.00 \times 10^{-4} \text{ M}$) at pH 3.0, 7.0, and 11.0. The pH of each solution was adjusted with minimum amounts of HCl and NaOH solutions. A 100 ml. aliquot of each acid solution was added to 10 mg. of carbon and shaken in glass-stoppered bottles until equilibrium conditions were attained. After 4 hours of shaking, no appreciable increase in the amount of adsorption could be detected. The mixture was separated by filtration through a small cellulose filter in a Gooch crucible. The concentrations of the original solution and the filtrate were determined from their ultraviolet absorbance at a characteristic wavelength and reference to Beers law plots of absorbance *vs.* concentration. A Beckman DU spectrophotometer was used. The amount of acid adsorbed by the carbon was determined by difference. Blank and reference solutions were also included. In addition to adsorption determinations at pH 3.0, 7.0, and 11.0 for all the chemicals, the adsorption of phenoxy acetic acid was studied at additional pH values between 1.0 and 11.0. Determinations were in duplicate from three different solutions of each acid. Calculations of curve fittings and isotherm constants were performed on a computer.

Results and Discussion

Varying but significant quantities of the carboxylic acids under investigation were removed from aqueous solution by the carbon adsorbent at all pH levels (Table I). At pH 3.0, approximately half of the acid in a 10^{-4} molar solution was adsorbed by 0.01 g. of activated carbon in 4 hours. At pH 7.0, the removal generally ranged from 8–22%, and at pH 11.0 from 2.5–15%, depending on the solute present.

Isotherms. Adsorption data at equilibrium conditions for all compounds fitted Langmuir equations. Representative Langmuir plots ($x/m = abC/(1 + aC)$) at three pH levels are shown in Figure 1 and the values of a , b , and x/m at a concentration of $1 \times 10^{-4} \text{ M}$ for all solutes are given in Table II. The values of x/m at 10^{-4} M concentration can be used to compare the relative magnitude of adsorption of the various acids by like samples of carbon. Data in Table II reveal that in every case there was a marked decrease in the amount

Table I. Percentage of Aromatic Acids Adsorbed by Carbon and Percentage of Molecular Species in a pH 3.0 Solution

No.	Adsorbate	% Adsorbed ^a		Molecular % at pH 3.0	
		pH: 3.0	7.0	11.0	
1	Benzoic acid	49.7	11.2	2.5	93.6
2	—2,4-dichloro	62.2	14.8	6.5	38.0
3	—3-amino-2,5-dichloro	50.5	12.4	5.2	71.5
4	—3-nitro-2,5-dichloro	49.0	12.0	7.0	62.0
5	—2-methoxy-3,6-dichloro	37.5	11.2	6.0	9.5
11	Phenoxyacetic acid	44.0	8.0	4.0	51.0
12	—4-chloro	55.0	17.7	9.8	20.2
13	—2,4-dichloro	60.1	18.8	14.3	66.2
14	—2,4,6-trichloro	65.3	21.8	12.5	68.8
21	Phenylacetic acid	40.1	12.6	8.5	95.0
23	—2,4-dichloro	61.3	21.8	11.5	89.0

^a By 10 mg. activated carbon from 10^{-4} M aqueous solutions.

of acid removed from solution on going from pH 3.0 to pH 7.0, and a smaller decrease from pH 7.0 to pH 11.0. Such uniform behavior indicates a general increase in adsorption as the concentration of molecular species increases and that of ionic species decreases. Similar correlations have been observed by Rovinskaya and Koganovskii (1961) for salicylic acids on charcoal and by Schwartz (1962) for 2,4-D on charcoal. On the other hand, Leopold, van Schaik, *et al.* (1960) state that they observed a uniform adsorption of 2,4-D on activated carbon over a buffered range of pH 2.2 to 8.0. Further consideration of this is given below in a more extensive investigation of one acid, phenoxyacetic acid. The magnitude of b indicates that the amount of acid required to give a saturation value on 1 g. of carbon decreases markedly with an increase in pH. Noteworthy also is the fact that at each pH the magnitude of b is fairly constant among the compounds, averaging about 543 μ moles per gram of carbon at pH 3.0 and 165 μ moles per gram at pH 7.0. An interesting comparison can be made between the present results at pH

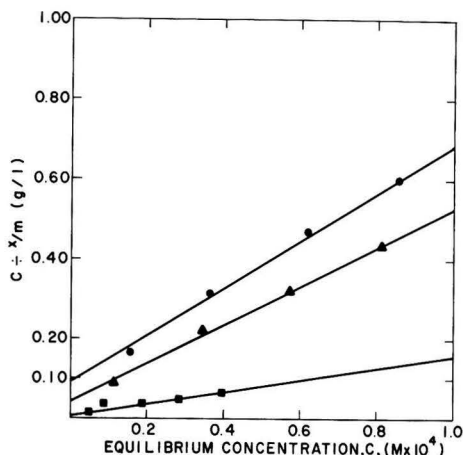


Figure 1. Langmuir isotherms for adsorption of 2,4-dichlorophenoxyacetic acid on activated carbon at pH 3.0 (■), 7.0 (▲), and 11.0 (●)

7.0 and the theoretical capacity of 0.334 mg. of isopropyl-*N*-(3-chlorophenyl) carbamate (the herbicide CIPC) per mg. of activated carbon at pH 6.9, as reported by Schwartz (1967). The molar adsorptive capacity of one gram of carbon is approximately 10 times greater for CIPC than for the three herbicidal acids included here: CIPC, 1.56×10^{-3} moles; 2,4-D (No. 13), 0.22×10^{-3} moles; Amiben (No. 3), 0.13×10^{-3} moles; Banvel-D (No. 5), 0.15×10^{-3} moles. Two factors must be considered, however. The use of different carbon samples may somewhat bias the comparison, and, secondly, at pH 7.0, the acid species in solution are mostly ionic, while the carbamate is molecular. Nevertheless, a comparison of orders of magnitude is appropriate and informative. There is an increase in the magnitude of x/m at $C = 10^{-4}$ molar among the compounds of each group with increasing chlorination of the ring, indicating that molecular size is not a unique factor in capacity parameters. The fit of the adsorption data to the Langmuir model (Fig. 1) suggests a monolayer coverage of the accessible sites on the surface of the carbon. Since only part of the surface is occupied by the adsorbed species (certain sites are possibly inaccessible because of pore size), it appears that specific sites on the surface are involved in the adsorptive process at each pH.

Ionization Effects on Adsorption. At pH 11.0, all the aromatic carboxylic acids considered here exist almost entirely in ionic form in aqueous solution (Fig. 2). At pH 7.0, less than 1% of the total species are molecular in nature, an amount, however, much larger than at pH 11.0. At pH 3.0, the ionic and molecular concentrations vary among the compounds and can be determined from the respective pK_a values (Table II and Fig. 2). The percentage of molecular species present in a pH 3.0 solution of each acid (Table I) ranges from 10 to 95%. In order to elaborate on adsorptive behavior as a function of pH, a more extensive study was made of one solute, phenoxyacetic acid. Figure 3 illustrates the μ moles adsorbed from a 1×10^{-4} M solution by 1.0 g. of carbon over a wide pH range (curve A). It is apparent that from pH 12.0 to 8.5, there is low, constant adsorption of the acid, followed by slowly increasing increments down to about pH 6.0. Between approximately pH 6.0 and 4.0, a sharp increase is observed, then a leveling off, and finally a decrease in adsorption at pH levels below 2.5. Also shown in Fig. 3 is the per cent of molecular species relative to the total acid population in the bulk solution as a function of pH (curve C). The difference between this line and 100% gives the per cent ions relative to the total acid. Curve B is an estimate of the adsorption (μ moles/gram of carbon) *vs.* pH which could be expected for the case where the molecule and ion adsorption is simply additive, depending on the relative concentration of each in the bulk solution.

An informative comparison can be made among the three curves. At high pH, curves A and B coincide. Here the solute in solution is largely in ionic form and adsorption is low, but constant over a spread of about three pH units. At pH 6.0, even though the solute is still practically all ionic (Fig. 2), the adsorption of solute has increased substantially and at pH 5.0 (>99% ions) there is a still larger difference between curves A and B. This enhanced adsorption can be attributed to the increase in hydrogen ion concentration of the bulk solution as the pH is lowered. The protons increasingly bind to the available sites on the carbon and in turn enhance the removal of the acid anions from solution. However, this augmentation of the total adsorption must decrease at some point as the pH is lowered because the per cent of ions decreases rapidly (Fig. 2). The corresponding increase in molecular species and the high specific adsorptive capacity of the

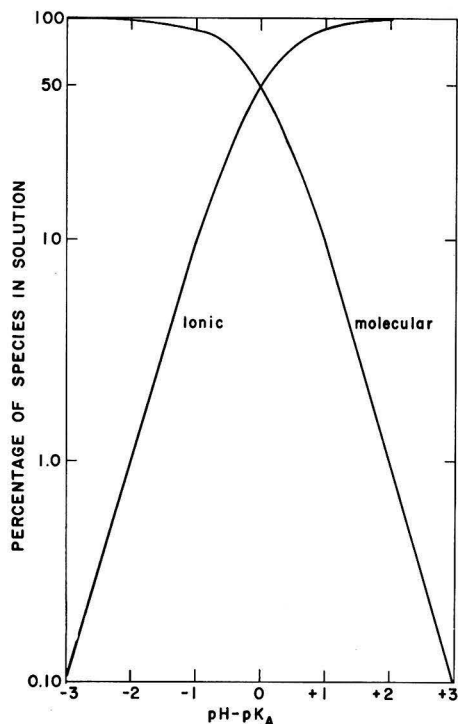


Figure 2. Ionization of aromatic carboxylic acids as a function of solution pH

molecule causes the experimental curve (A) to rise. At the pKa point, where the solution contains 50% molecules and 50% ions, the adsorption curve (A) nears a maximum, still markedly higher than the amount of adsorption shown by curve B. Below pH 3.0, (near pH = pKa) there is a downward deflection of the curve, indicating a decrease in the number of μ moles of total acid adsorbed by the carbon. Thus, even though the surface has sites available for ion adsorption and even though the specific adsorption capacity of the ion is high in this region, the number of anions of solute is decreased so much at low pH levels that adsorption is practically all molecular in nature. Phelps and Peters (1929) noted a similar decrease in the adsorption of aliphatic acids on carbon at low pH levels, as well as a displacement of the adsorption curves from the ionization curves toward the alkaline side.

A similar enhancement behavior could be expected for the other acids investigated here, as can be seen from a comparison of the magnitude of their adsorption at pH 11.0 and at pH 7.0, the latter pH level being well above the pKa value of each compound. In all cases there is enhanced adsorption at the lower pH (Table I).

Previous investigations on the adsorption of pesticides by synthetic models of the organic fraction of soils led to correlations of the extent of adsorption with parameters such as solubility, molecular structure, electronic forces, polarization by substituents, and steric factors (Ward and Upchurch, 1965; Ward and Holly, 1966). It was anticipated that results from the present adsorption data could give a similar insight into adsorption mechanisms. Of particular interest were steric influences of substituents in the 2 and 6 positions, since it has been reported that 2-alkyl substitution of benzoic acid (Hartmen, Kern, *et al.*, 1946) and phenol (Wheeler, Levy,

Table II. Properties of Aromatic Acids and Equilibrium Data for Their Adsorption on Activated Carbon

No.	Acid	pK _A	pH of Solution	$\frac{x/m}{abC/(1+aC)^2}$		
				a	b	x/m
1	Benzoic	4.20	3	0.238	510	489
			7	0.108	124	113
			11	0.081	75	67
2	—2,4-dichloro	2.76	3	0.259	676	651
			7	0.123	159	147
			11	0.108	73	69
3	—3-amino-2,5-dichloro	3.40	3	0.928	515	510
			7	0.283	131	127
			11	0.025	72	51
4	—3-nitro-2,5-dichloro	3.23	3	0.360	505	491
			7	0.118	130	120
			11	0.035	93	72
5	—2-methoxy-3,6-dichloro	1.94	3	0.181	394	313
			7	0.317	154	149
			11	0.068	68	59
11	Phenoxyacetic	3.03	3	0.423	446	436
			7	0.229	105	86
			11	0.209	64	43
12	—4-chloro	2.36	3	0.362	575	560
			7	0.101	198	180
			11	0.115	145	133
13	—2,4-dichloro	3.31	3	0.279	629	607
			7	0.112	223	205
			11	0.070	154	135
14	—2,4,6-trichloro	3.35	3	0.672	676	666
			7	0.095	239	216
			11	0.073	144	127
23	2,4-dichloro-phenylacetic	3.92	3	0.431	645	630
			7	0.125	235	218
			11	0.100	59	54

^a Units: a = liters/ μ mole, b = μ moles/g, C = μ moles/liter. x/m = μ moles/g.

1959) led to decreased adsorption on carbon. While the adsorption of 2-methoxy-3,6-dichlorobenzoic acid is less than that of the other benzoic acids, this single case is too limited to confirm general steric influences on adsorption of acids on charcoal. Further, a comparison of the three 2,4-dichloro substituted acids (No. 2, 13, 23) reveals a marked similarity in the extent of their adsorption—evidence that differences in the molecular structure of the parent acid has little to do with the adsorption mechanism on carbon. Since nitro and amino substituents have opposite inductive effects on electron densities and polarization, compound No. 4 (3-nitro-2,5-dichlorobenzoic acid) was included in the study for comparison with 3-amino-2,5-dichlorobenzoic acid (the herbicide Amiben). The data in Table II reveals no significant difference in the amount of each adsorbed by the carbon. It would seem,

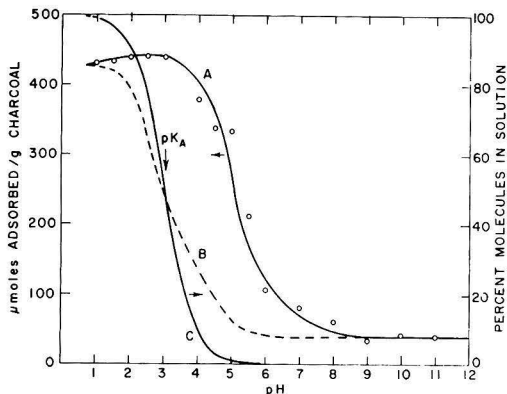


Figure 3. Effect of pH on the adsorption of phenoxyacetic acid on activated carbon

A. Experimental curve. B. Estimated curve for sum of molecules and ions only. C. Percent of molecules in bulk solution

therefore, that an extensive generalization of the effect of molecular structure on adsorption can not be made from the present data.

In view of the similarity in adsorption, it is suggested that the acids are adsorbed with the phenyl ring parallel to the surface of the adsorbent and interaction is between the π -electron system of the acid ring and the aromatic surface structure (Coughlin and Ezra, 1968) of the carbon. In addition, functional groups containing oxygen, such as phenolic, carbonyl, lactone, and quinone (Boehm, 1964) offer adsorptive sites for hydrogen bonding of the acid adsorbates, particularly at low pH levels where the acids are predominantly in molecular form.

The similar magnitude of adsorption among the acids at each pH by the charcoal points out the indiscriminate nature

of the adsorbent. However, the extreme enhancement of the magnitude of adsorption upon decreasing the pH of the solutions slightly emphasizes the possibility of removal of greater quantities of undesirable solutes from waters by addition of charcoal at a pH level somewhere between optimum and that physically obtainable under natural conditions. In addition, such behavior can be offered as an explanation for the residue accumulations of such pesticides in the acidic, high organic soils in certain sections of the country.

References

- Boehm, H. P., *Advan. Catalysis* **16**, 179-274 (1964).
 Coughlin, R. W., Ezra, F. S., *ENVIRON. SCI. TECHNOL.* **2** (4), 291-7 (1968).
 Haque, F., Sexton, R., *J. Colloid Interface Sci.* **27** (4), 818-27 (1968).
 Hartman, R. J., Kern, R. A., Bobalek, E. G., *J. Colloid Sci.* **1**, 271-6 (1946).
 Kipling, J. J., "Adsorption from Solutions of Non-Electrolytes," Academic Press, New York, 1965.
 Leopold, A. C., van Schaik, P., Neal, M., *Weeds* **8**, 48-54 (1960).
 Phelps, H. J., Peters, R. A., *Proc. Roy. Soc.* **124**, 554-68 (1929).
 Rovinskaya, T. M., Koganovskii, A. M., *Kolloidn. Zh.* **23** (6), 739-48 (1961).
 Schwartz, H. G., *ENVIRON. SCI. TECHNOL.* **1** (4), 332-7 (1967).
 Schwartz, H. G., "Removal of a Selected Organic Pesticide by Specific Water Treatment Unit Processes," Washington University, St. Louis, Mo., 1962.
 Ward, T. M., Holly, K., *J. Colloid Interface Sci.* **22** (3), 221-30 (1966).
 Ward, T. M., Upchurch, R. P., *J. Agr. Food Chem.* **13** (4), 334-40 (1965).
 Weber, W. J., Morris, J. C., *J. Sanit. Eng. Div., Proc. Am. Soc. Civil Engrs.* **90**, 79 (1964).
 Wheeler, O. H., Levy, E. M., *Can. J. Chem.*, **37**, 1235-40 (1959).

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Automated Variable Flow for Pilot Plants

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University of Minnesota, Minneapolis, Minn. 55455

■ A device was developed for use with continuous flow pilot plants whereby the input rate of flow was varied continuously and automatically. The equipment was used on a pilot scale to simulate the sinusoidal flow patterns normally encountered in municipal waste water treatment plants. With the particular equipment used and commercially available, average flow rates ranging from 13 to 3800 ml./min. were used. The motion and pumping rates of the equipment are described mathematically and compared with the discharge rates from the actual installation.

The operation of continuous flow pilot plants for waste water treatment offers many unique problems. When the objective is to simulate operation of a prototype plant, both the flow rate and input waste water solids concentration must vary continuously.

One phase of a research project on nitrogen removal by denitrification conducted at the University of Minnesota Sanitary Engineering Laboratories has been to investigate the effect of variable flow on the process. A device for continuously varying the flow rate was developed and used both in the laboratory and as part of a pilot plant located at a municipal treatment plant. Because a synthetic waste water was used in the laboratory application, the composition of the waste was constant. However, in the field application using a municipal waste water, the composition varied continuously.

Pumping Equipment

Feed pumps selected for use were Sigmamotor pumps driven by electric motors through Zero-Max speed reducers. These reducers operate with a lever such that small angular changes in lever settings produce approximately linear responses in speed change. Since a Sigmamotor pump output varies linearly with input speed, the pumping rate in this application varied approximately as a linear function of the angular movement of the lever on the speed changer.

Adaptation to Variable Flow

Using the above equipment, a sinusoidal flow pattern was achieved by using a disk rotating once every 24 hours. A simple 24-hour timer was used for this purpose. By pin-connecting one end of an operating arm at an experimentally determined distance from the center of the rotating disk and the other end to the operating lever of the speed reducer, the pumping rate was controlled as desired. The arrangement of the equipment is shown graphically in Figure 1.

Using the notation in Figure 1:

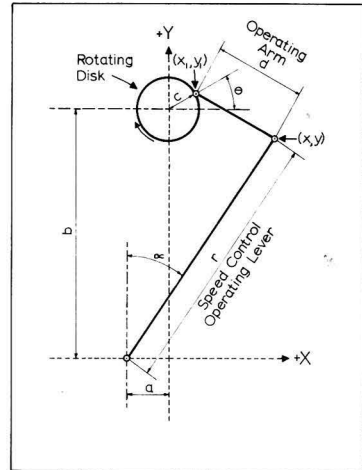


Figure 1. Schematic diagram of speed control linkage

$$(x - x_1)^2 + (y - y_1)^2 = d^2 \quad (1)$$

$$(x + a)^2 + y^2 = r^2 \quad (2)$$

$$x_1 = c \cos \theta \quad (3)$$

$$y_1 = c \sin \theta + b \quad (4)$$

By substituting Equations 3 and 4 in Equation 1 and solving Equations 1 and 2 simultaneously, Equation 5 is obtained as:

$$x(2a + 2c \cos \theta) + (2c \sin \theta + 2b)\sqrt{r^2 - (x + a)^2} = 2bc \sin \theta - m \quad (5)$$

where: $m = b^2 + c^2 + r^2 - a^2 - d^2$

The lengths $a, b, c, d,$ and r are all characteristic lengths of the particular control system utilized. A further inspection of Equation 5 will indicate that with reasonable values for the constants, a simplification of the equation shows the distance x to be essentially a function of $\sin \theta$. Because the distance x establishes the position of the control lever it also establishes the pumping rate. Since x is a function of $\sin \theta$, the pumping rate also is a function of $\sin \theta$ in view of the linear relationship between the angular position of the speed control lever and the pumping rate. Equation 5 may be solved by graphical methods or, as in this case, by an iterative process using a digital computer. An example of the use of this concept is given below.

Table I. Pump Discharge Rates as Functions of Disk Rotation*

θ Degrees	x Inches	$\frac{x+a}{r} = \sin \alpha$	$\sin^{-1}\left(\frac{x+a}{r}\right)$ Degrees	$39.4-\alpha$ Degrees	Pump RPM	Pump Discharge ml./min.
1	2	3	4	5	6	7
0	5.9	.604	37.2	2.2	10.5	6.3
30	5.8	.596	36.6	2.8	13.5	8.1
60	5.6	.579	35.4	4.0	19.2	11.5
90	5.4	.563	34.3	5.1	24.5	14.7
120	5.2	.547	33.2	6.2	29.8	17.9
150	5.0	.530	32.0	7.4	35.5	21.3
180	5.0	.530	32.0	7.4	35.5	21.3
210	5.1	.538	32.6	6.8	32.6	19.6
240	5.3	.555	33.7	5.7	27.3	16.4
270	5.5	.571	34.8	4.6	22.0	13.2
300	5.8	.596	36.6	2.8	13.5	8.1
330	5.9	.604	37.2	2.2	10.5	6.3

* For identification of θ , x , a , r , and α , see Figure 1.

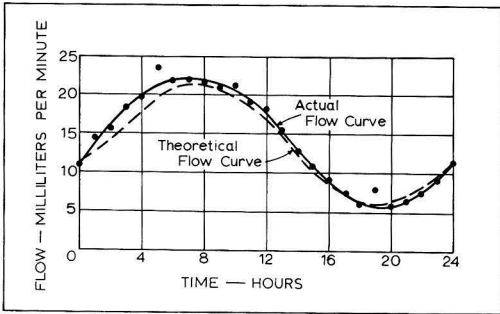


Figure 2. Comparison of actual and theoretical flow variations

Geometry measured and related to Figure 1:

$$\begin{aligned}
 a &= -1.5'' & d &= 5.5'' \\
 b &= 12.5'' & r &= 12.25'' \\
 c &= 0.5'' & m &= -274
 \end{aligned}$$

Then Equation 5 becomes:

$$x(\cos \theta - 3.0) + (\sin \theta + 25)\sqrt{150 - (x - 1.5)^2} = 12.5 \sin \theta + 274$$

Values for x corresponding to selected values of θ are presented in Table 1.

Columns 3, 4, and 5 in Table I are a conversion of the data into angular positions (α) of the speed reducer control arm.

The use of 39.4 degrees in obtaining the data for column 5 is simply to convert the angular positions to a convenient scale characteristic of the speed reducer. The data in column 5, together with a manufacturer's curve showing the Zero-Max output speed as a function of the degrees of movement of the control lever, were used to obtain the RPM data of column 6. In this example, a 1/4 in. I.D. tubing was used in a Model T-8 Sigmamotor pump to give a discharge of 0.6 ml./min. RPM. The discharge data for these conditions are shown in column 7 of Table I and plotted on Figure 2 together with actual discharge data.

The pattern of flow in Figure 2 shows a continuously varying flow pattern as one might normally encounter at municipal waste treatment plants. The maximum and minimum rates are approximately 50% above and below the average rate, respectively.

Equipment was used to obtain average flow rates of as low as 13 ml./min. and as high as 3800 ml./min. For the latter rate, the largest Sigmamotor pump (Model T-4) with a 1-inch I.D. tubing was used and powered by a Model QXI Zero-Max power block assembly. Because this pump was the largest available, this pumping rate was a controlling factor in sizing the pilot plant which it was to serve.

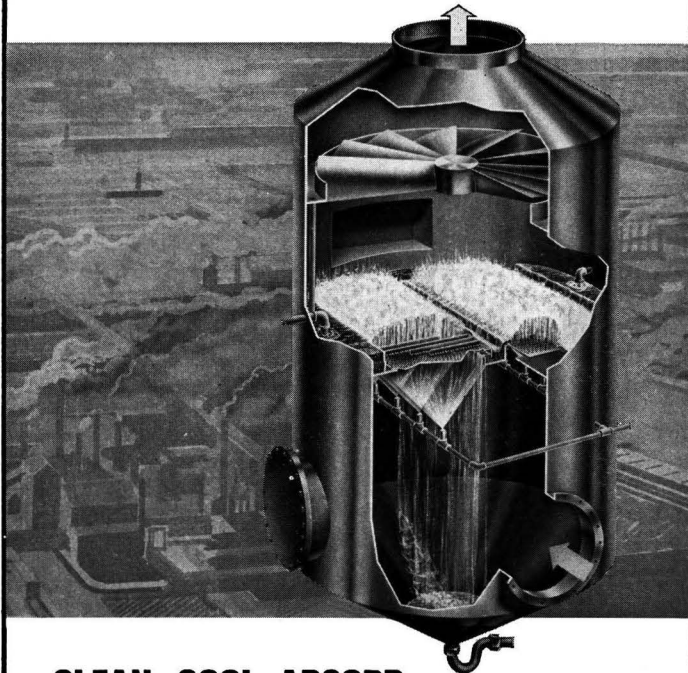
Acknowledgment

This work was part of an FWPCA sponsored research project (WP-01028). Loren Leach, Student Engineering Assistant, was employed part time on the project and assisted in the development of the equipment.

Received for review April 2, 1969. Accepted October 16, 1969.

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bookshelf

Air Pollution Experiments for Junior and Senior High School Science Classes. Edited by Donald C. Hunter and Henry C. Wohlers. 64 pages. Air Pollution Control Association, 4400 Fifth Ave., Pittsburgh, Pa. 15213. 1969. \$1.00 (in quantities of 10 or more, 50 cents), paper.

Aiming to arouse in secondary school students an acute awareness of air pollution and its effect on their lives, as well as an interest in the field of air pollution control as a possible career, the editors include 19 experiments in the publication. Object, suitability and usefulness, theory and background, equipment, and procedures are given for each experiment. Experiment titles include: Effect of air pollution on dyed fabrics; detection and measurement of atmospheric carbon monoxide, and effect of SO₂ on vegetation. ■

Sludge Dewatering. Manual of Practice 20. 120 pages. Water Pollution Control Federation, 3900 Wisconsin Ave. NW, Washington, D.C. 20016. \$3.00, members, \$4.00 nonmembers; paper. ■

Land, People, and Policy. Gordon Edwards. 159 pages. Chandler-Davis Publishing Co., P.O. Box 36, West Trenton, N.J. 08628. 1969. \$5.00, hard cover; \$3.00, paper. ■

Community Water Supply: Report of a WHO Expert Committee. World Health Organization Technical Report Series No. 420. 21 pages. World Health Organization, American Public Health Association, Inc., 1740 Bdwy., New York, N.Y. 10019. 60 cents, paper. ■

A Sulfur-Free Fuel for Power Generation. 559 pages. Clearinghouse for Federal Scientific and Technical Information, U.S. Department of Commerce, Springfield, Va. 22151. 1969. \$6.00, paper. ■

Effects of Watershed Changes on Streamflow. Water Resources Symposium No. 2. Edited by Walter L. Moore and Carl W. Morgan. xiv + 289 pages. University of Texas Press, Austin, Tex. 78712. 1969. \$12.50, hard cover. ■

Indian Creek Reservoir: America's Newest Water Resource. Advanced Waste Treatment Seminar II. 66 pages. BSP Corp., P.O. Box 8158, San Francisco, Calif. 94128. 1969. \$10.00, binder. ■

Glossary—Water and Wastewater Engineering. Revised edition. 387 pages. American Water Works Association. Publication Sales, Two Park Ave., New York, N.Y. 10016. 1969. Members, \$7.00, nonmembers, \$10.00; hard cover. ■

Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants. 123 pages. Publications Section, American Petroleum Institute, 1271 Avenue of the Americas, New York, N.Y. 10020. 1969. \$2.50, paper. ■

Flood Plain Management: Iowa's Experience. Edited by Merwin D. Dougal. 270 pages. Iowa State University, Ames, Iowa 50010. 1969. \$6.95, hard cover. ■

Sewers for Growing America. Norris M. Cohn. 202 pages. Certain-teed Production Corp., 540 Pennsylvania Ave., Fort Washington, Pa. 19034. 1966. \$10.00, hard cover. ■

Our Environment Battles Water Pollution. Charles E. Renn. 32 pages. LaMotte Chemical Products Co., Chestertown, Md. 21620. 1969. 50 cents, paper. ■

Proceedings of the 23rd Annual Power Sources Conference. 181 pages. psc Publications Committee, P.O. Box 891, Red Bank, N.J. 07701. 1969. \$15.00, paper. ■

Analysis of Ground Water Use, Replenishment, and Aquifer Characteristics in Bartholomew County, Ind. L. G. Davis, A. K. Turner, and W. N. Melhorn. v + 83 pages. Purdue University Water Resources Research Center, Lilly Hall of Life Sciences, Lafayette, Ind. 47907. 1969. Paper. ■

Absorption of Gases. V. M. Ramm. vii + 648 pages. Daniel Davey & Co., 964 Asylum Ave., Hartford, Conn. 06105. 1968. \$20.00, hard cover. ■

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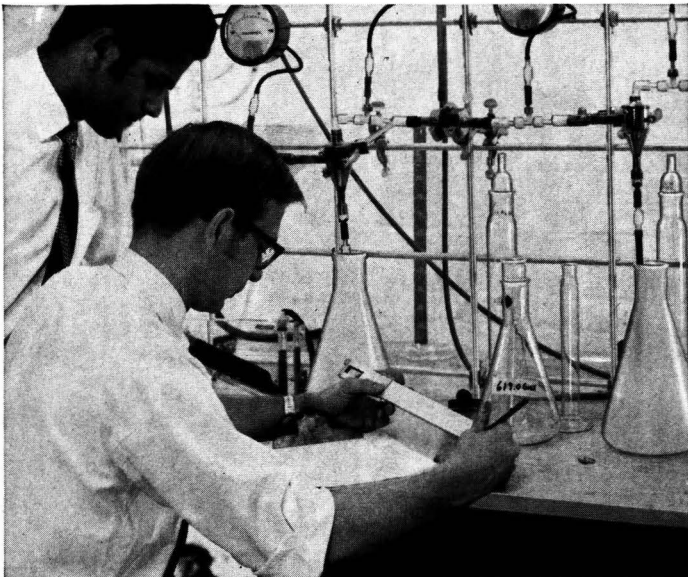
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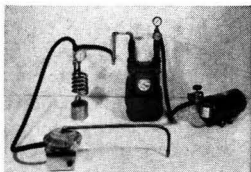
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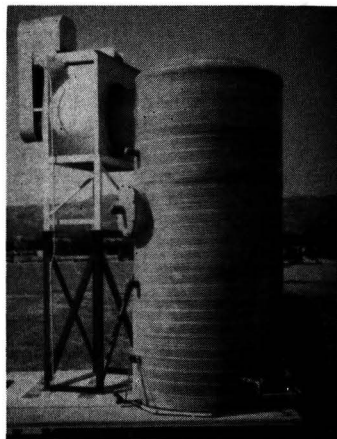
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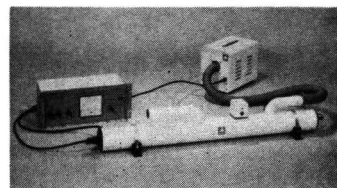
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new products digest



Fume scrubber

Using a modified impingement principle (the gas stream lifts the water and mixes it with fumes or dust), a glass fibre wet system serves as fume scrubber and particle separator in gas streams for cleanup of air pollution. The body of the unit is round, standing vertical with a one foot deep water sump at the bottom, and exhausted through the top where the fan is located on the clean side of the air stream, according to the manufacturer. Fiber-Dyne 61



Monitoring air quality

An instrument for the continuous monitoring of air quality by measurement of the light scatter by aerosols over almost 180° of scattering angle is available. The Model 1550 Integrating Nephelometer features a wide sensitivity range—from 450 yards to more than 100 miles—is suitable for fixed installations as well as mobile surveys, is versatile and designed for unattended operation, according to the company. Meteorology Research, Inc.

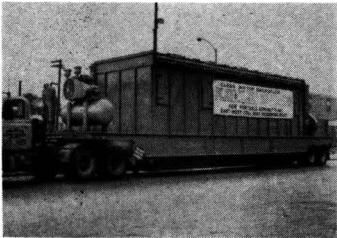


Automatic analyzer controllers

The Series 8000 is a line of automatic analyzer controllers for continuous monitoring and control of 25 water, wastes, and process liquids tests. The company claims that proportional output signals and high/low limit contractors permit the monitors to automatically control the operation of process valves, chemical feed pumps, alarms. Delta Scientific Corp. 63

Water quality monitor

A new series of water quality monitors to measure automatically the physical and chemical properties of water is available. Units provide continuous, unattended surveillance of rivers, lakes, waterways, and outfalls from municipal and industrial waste treatment plants, the manufacturer says. Monitors feature modular construction, solid-state electronic circuits, and choice of data output displays and data transmitting and/or recording capabilities. Union Carbide Corp. 64



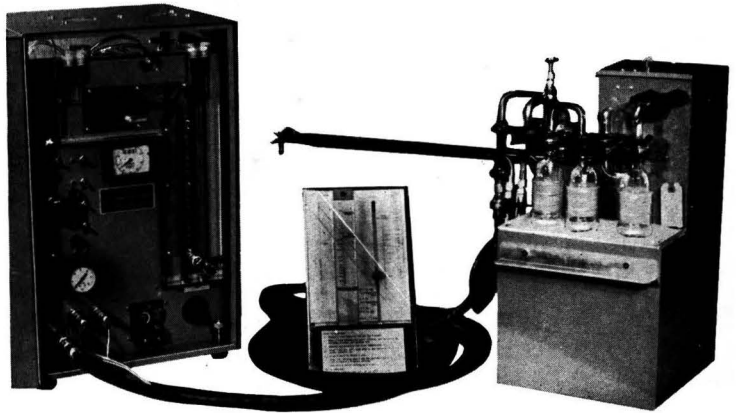
Dust collector

A portable dust collector for asphalt plants is available. The Porta-Kleen can handle up to 54,000 c.f.m. of gases at operating temperatures to 425° F, removing up to 10,000 pounds per hour of rock dust from exhaust gases, the manufacturer claims. Flex-Kleen Corp. 65

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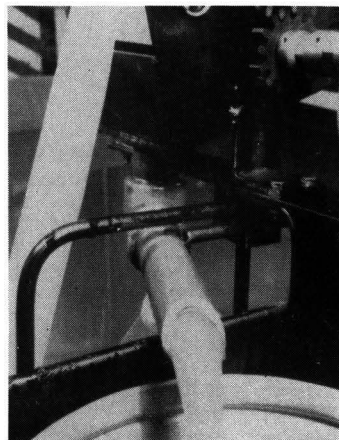
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Combustible gas detector

The Model 510 combustible gas detector for sensing hydrogen, hydrocarbon gases, and natural gas is available. Called the Two-Headed Monster, the unit features two sensing probes with each control unit. Based on a low temperature catalytic principle, the low cost detector is virtually drift free, requires only an annual calibration check, and has no moving parts, the company says. General Monitors, Inc.

67



Oil skimmer

The Model 843 Belt Type Oil Skimmer will recover up to 50 gallons per hour of oil in continuous operation with less than 2% entrained water, the company claims. Featuring adjustable belt track, adjustable oil discharge system, and variable roller pressure, the Model 843 comes with a universal mounting bracket, and can be mounted on any type tank. Industrial Filter & Pump Mfg. Co.

68

CO Analyzer

The CO Tester for measurement of carbon monoxide levels in automobile exhaust gases is available. The compact instrument works on a principle of nondispersive infrared light, features simple operation, accuracy, and rapid response. Applications include automobile inspection lanes, automobile engine production control, and to minimize fuel consumption and optimize performance. Intertech Corp.

69

Industrial processing equipment. A 12 page publication features an updated listing of the company's line of equipment and systems for industrial processing and water and waste treatment. "Continuing Processing Capabilities" (Bulletin 7005) incorporates recent developments and mechanical design improvements, and discusses such operation applications as industrial waste treatment, pilot plant equipment, pumping, and sedimentation. Dorr-Oliver, Inc. **91**

Adsorption dryers. A 4 page brochure describes the DP Dryer Series of closed-circuit, dry-desiccant adsorption dryers for compressed air, process gas, and liquid streams. Standard design features, standard models, and operating principles are included, as well as a flow diagram and listing of system specifications. Desomatic Products. **92**

Portable oxygen analyzer. The OA. 150 Oxygen Analyzer is described and illustrated in Bulletin TD 99-261. The 2 page publication gives applications of the device, and outlines design and construction features, as well as operating specifications, power supply information, and physical dimensions. Westinghouse Electric Corp. **93**

Gas chromatographs. "Unimodular Series 4000" is a 12 page bulletin (GC 4000) describing a line of gas chromatographs with specific application in chemical, biomedical, and pesticide research. Units combine building block design with four column and four detector oven systems for maximum flexibility, the manufacturer says. Fisher Scientific Co. **94**

Air test instruments. The company's line of instruments for measuring air pressure, velocity, moisture content, and motion are described in an 8 page catalog. Photos, description, and price are included for such devices as pitot tubes, anemometers, hygrometers and moisture meters, and relative humidity and temperature recorders. E. Vernon Hills, Inc. **95**

Spectrophotometry. The Models 330 and 350 spectrophotometers are the subject of an 8 page bulletin (Form 330-869). In addition to description of the instruments (including drawings and specifications), the publication includes discussion of spectrophotometry, as well as a listing of various accessories. G. K. Turner Assoc. **96**

Low cost industrial waste treatment. The Broadway "All In One" Package Plant, for complete treatment of industrial waste waters, is described in a 4 page bulletin (8-68-ESI-200). The company claims that the plant meets a wide range of waste water treatment problems—biological oxygen demand, chemical oxygen demand, pH,

suspended solids, and color—to ensure compliance with federal, state, and local requirements, and will treat effluent at a rate to 50 g.p.m. The publication also includes description of the treating sequence, schematic drawing of the unit, and a flow diagram. Environmental Services, Inc. **97**

Publications list. The revised edition of the "ASTM List of Publications" is available. The 34 page book contains more than 550 publications dealing with materials, materials evaluation, and standardization of methods of test and specification for materials. American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103. (Write direct)

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ES&T's Morgan appoints three new advisors

Dr. James J. Morgan, editor, has named Dr. J. Carrell Morris, Dr. Peter K. Mueller, and Dr. James N. Pitts, Jr., as ES&T editorial advisors to serve a three year term beginning January 1970 and extending through 1972. Dr. Pitts has been reappointed, having served for the period 1967-69. He was one of the original advisors when ES&T was launched in January 1967.

Members whose tenure on the board expired at the end of 1969 were: Dr. S. K. Friedlander, Dr. E. D. Goldberg and Dr. H. P. Gregor.

Advisory Board members assist the editor by advising on the content of ES&T, most especially the current research papers.

Other members of the ES&T editorial advisory board are:

Terms expire 1970

Dr. Richard D. Cadle

Dr. D. J. O'Connor

Dr. W. J. Weber, Jr.

Terms expire 1971

Dr. C. E. Moser

Dr. Ulrich Merten

Dr. E. D. Palmes



Dr. James J. Morgan, editor, is associate professor of environmental health engineering at California Institute of Technology, which he joined in 1965.

Dr. Morgan received his B.C.E. (1954) from Manhattan College, M.S.E. (1956) from the University of Michigan, and A.M. (1962) and Ph.D. (1964) from Harvard University. From 1956-60, he was an instructor in civil engineering at the University of Illinois. In 1960-61, he held a Danforth Foundation Teacher Study Grant at Harvard, and in 1961-63, continued his studies under a U.S. Public Health Service predoctoral fellowship.

Dr. Morgan was associate professor of water chemistry at the University of Florida (1963-66). In 1964, he served as a member of the National Institutes of Health's Environmental Sciences and Engineering Study Section. The recipient of a variety of professional awards, he is a member of ACS, AWWA, ASCE, American Society for Limnology and Oceanography, AAAS, Sigma Xi, and Chi Epsilon.



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Dr. Peter K. Mueller is chief, Air and Industrial Hygiene Laboratory, California Department of Public Health (Berkeley), a position he has held since 1963.

Dr. Mueller received his B.S. from George Washington University (1950), and his M.S. (1953) and Ph.D. (1955) from Rutgers University. In 1955, he joined Komline-Sanderson Engineering Corp., working for two years on colloid chemistry problems related to dewatering of sewage sludge. In 1957, he went to the California Department of Public Health at Berkeley to initiate a research program in the Air and Industrial Hygiene Laboratory.

Dr. Mueller's work at Berkeley has involved performance characteristics of aerosol sampling equipment, the occurrence of aerosols in air and the relationship between concentration and visibility reduction, the biological effects of pollutants on microorganisms and animals, and specificity problems which arise in the analysis of air pollutants.

From 1966-68, Dr. Mueller served as a member of the Research Grants Advisory Committee for the National Air Pollution Control Administration. He and his staff presently are writing recommended procedures for air analysis to be considered by several national committees. They also are contributing to documents delineating air quality criteria.

Dr. Mueller is a member of ACS, Sigma Xi, and the American Institute of Chemists.



Dr. James N. Pitts, Jr., is professor of chemistry, University of California, Riverside (UCR), a position he has held since 1959. Previously (1954-59), he was associate professor of chemistry and served as chairman of the chemistry department (1961-63). He is also a member of the UCR branch of the Institute of Geophysics and Planetary Physics.

In 1961, Dr. Pitts was a Guggenheim Fellow at Oxford University (England), and he returned to Oxford in 1965 as a visiting research fellow of Merton College. Dr. Pitts received his B.S. (1945) and his Ph.D. (1949) from UCLA. He worked as a research assistant (1942-45) for Division 10, National Defense Research Committee, Office of Scientific Research and Development, and as research associate, Special Projects Division, U.S. Army (1945-46). He was instructor and then assistant professor of chemistry at Northwestern University (1949-54).

Dr. Pitts' research interests involve photochemistry and photochemical air pollution, and he has served on a number of state and federal committees in these areas. He is a member of the technical advisory committee of the State of California Air Resources Board, and the advisory committee on chemistry and physics of the National Air Pollution Control Administration. He is a member of ACS, APCA, the Faraday Society, the American Physical Society, Sigma Xi, Alpha Chi Sigma, Phi Lambda Upsilon, and Phi Beta Kappa.



Dr. J. Carrell Morris has been Gordon McKay professor of sanitary chemistry, Harvard University, since 1958.

Dr. Morris received his B.S. from Rutgers University (1934), then went on to Princeton University where he obtained his A.M. (1935) and Ph.D. (1938). He was instructor in chemistry at Harvard University (1938-41), assistant professor at Bucknell University Junior College (1941-42), assistant professor at Worcester Polytechnic Institute (1942-43), and editorial assistant on the *Journal of the American Chemical Society* (1943-44). In 1944, Dr. Morris began his long association with Harvard University when he became instructor in sanitary chemistry at the graduate school of engineering. From 1946-49, he was assistant professor of sanitary chemistry; he was appointed associate professor in 1949. In 1964-65, Dr. Morris was visiting professor, international courses in sanitary engineering, Delft Technological University, The Netherlands.

Dr. Morris is a member of numerous professional and scientific societies—including ACS (in which he was chairman of the Water, Sewage, and Sanitation Division in 1955-56), AWWA, American Public Health Association, Phi Beta Kappa and Sigma Xi—and is a fellow of AAAS. He has served as consultant for the World Health Organization (WHO) in Egypt and India, and is a member of the WHO expert advisory panel on environmental health for 1965-70.

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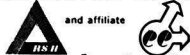
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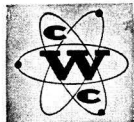
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January 15-16 Tappi, Michigan Division of the Paper Industry, and Western Michigan University

14th Annual Pulp and Paper Conference
Western Michigan University Student
Center, Kalamazoo

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

January 19-21 Cornell University

Agricultural Waste Management Conference

Sheraton Hotel and Motor Inn,
Rochester, N.Y.

Major focus of this year's conference is on possible contamination involved in the application of agricultural wastes and chemicals to the soil, and solutions to such problems. Topics covered include water movement in soils; land disposal of dairy farm waste; and effect of agricultural activities on water pollution.

January 25-30 Engineering Foundation

Research Conference on Waste Water
Engineering in the Food Industry

Asilomar Conference Grounds, Pacific
Grove, Calif.

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

January 26-28 Cooling Tower Institute

Semi Annual Meeting

Fontainebleau Motor Hotel, New
Orleans

In addition to discussion of materials of construction, and performance testing techniques and methods, the session will feature consideration of the use of cooling towers at power generating stations as a means of controlling thermal effects resulting from condenser discharge water.

meeting guide

January 26-30 American Society of Civil Engineers National Meeting on Water Resources Engineering

Memphis, Tenn.

Water Resources in the Seventies is the theme of this meeting, which will feature discussion and presentation of the latest knowledge that civil engineers have developed to solve some aspects of the U.S. water resource problem. More than 50 technical sessions will cover such topics as air and water pollution, irrigation systems, possibilities of refuse incineration and power generation, and estuary pollution.

February 2-5 Weed Science Society of America

Annual Meeting

Queen Elizabeth Hotel, Montreal,
Canada

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

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

12th Sanitary Engineering Conference
Urbana, Ill.

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

March 12 and 13 American Society of Civil Engineers Specialty Conference on Water Quality Enhancement

Sheraton-Park Hotel, Washington,
D.C.

Participants at the 2 day conference will attempt to find some answers to the question, "Is water quality enhancement feasible?" Divergent views of federal, state, and local policy makers, regulatory agencies, conservationists, and the public will be debated. The sponsors hope new policy ideas and recommendations for the national pollution control effort will result.

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

2nd Mineral Waste Utilization Symposium

Chicago, Ill.

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

(Meeting guide continued on page 80)

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March 24-26

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National Industrial Solid Wastes Management Conference

University of Houston, Tex.

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

April 14

Midwest Chapter Filtration Society and the Chicago Industrial Water, Waste, and Sewage Group

Seminar on Air and Water Pollution Control

Swithiod Singing Club, Chicago

The one day session will seek to cover all aspects of both air and water pollution, as well as possible control techniques. The morning session will be devoted to codes, monies, and approaches to problems, while the afternoon session will consider methods and controls.

Call for papers

January 31 deadline

International Union of Air Pollution Prevention Associations

2nd International Air Pollution Conference

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

Special notice

University of Illinois, Urbana

U.S. Public Health Service Traineeships in Solid Wastes Management

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