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FUELS
MANAGEMENT

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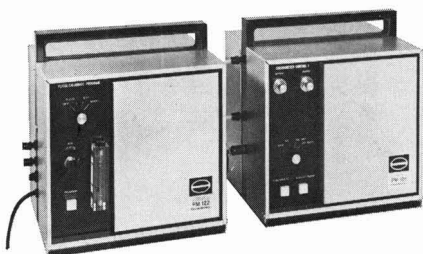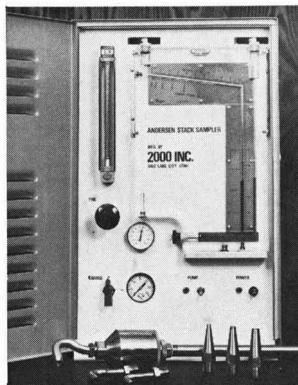
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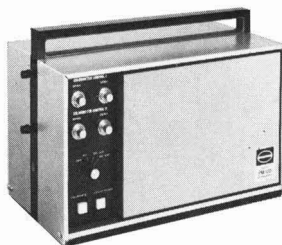
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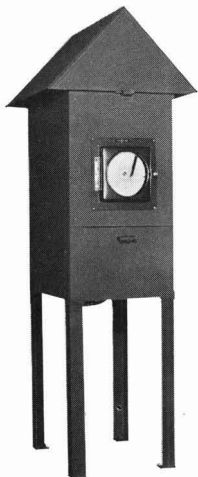
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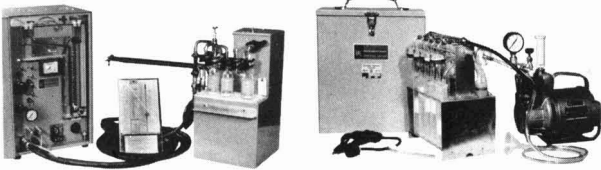- 24-hour flow recorder built into the shelter provides a permanent record

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ENVIRONMENTAL
Science & Technology

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Volume 5, Number 1,
January 1971

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Photochemical aspects of air pollution: A review 39

A. P. Altshuller and J. J. Bufalini

The literature (some 133 references) on photochemical aspects on air pollution is reviewed. Topics include photochemical mechanisms, synergistic effects in the photooxidation of organic substances, hydrocarbon reactivity scales, aerosols, natural air pollution, and actinometry. The review also notes areas for further research, including studies on olefins and arenes from combustion sources and the fate of organic and inorganic chemical species on a global scale. Effects of photochemical species on plants are not covered in this review.

Characterization of crude and residual-type oils by fluorescence spectroscopy 64

A. D. Thruston, Jr. and R. W. Knight

Oil spills on a beach, river, or harbor can now be traced to their source with a new operational technique which fingerprints the source of oil. The new technique compares the fluorescence intensities and wave number ratios of the oil sample and has been evaluated for six different oils; results compare well with earlier time-consuming analytical methods. The spilled oil should be sampled immediately; prolonged exposure to sunlight affects the fluorescence properties of the oil.

Communications

Pyrolyzed sewage sludge: Its production and possible utility 69

J. M. Beeckmans and P. C. Ng

Converting one form of solid waste into a useful resource is the goal of recycling. Now, filtered sludge material from a municipal activated sludge plant in Ontario, Canada, has been converted to a form of carbon which can be used in the tertiary treatment of waste waters. In the past, coal and fly ash have been evaluated for such treatment but each had low absorbing capacities. The pyrolyzed material was found to be intermediate in its capacity between fly ash and activated carbon.

Removal of lead from automobile exhausts by molten salts 72

S-I Cheng, H. Pitlick, and R. Siegel

Particulate emission controls have been proposed for '75 automobiles. If leaded gas has not been totally banned by then, lead particulates can be controlled by molten salts. Experimental data show that the efficiency of removal increases with the temperature of scrubbing and decreases with the screen-hole size, but optimum operating conditions for the use of such salts must await further engineering studies.

Activation analysis of airborne selenium as a possible indicator of atmospheric sulfur pollutants 74

K. K. S. Pillay, C. C. Thomas, Jr., and J. A. Sondel

In any geographic area of the country, the sulfur pollution caused by combustion products of coal can be distinguished from sulfur pollution caused by combustion products of crude oil by measuring the Se/S ratio. The latter ratio is determined by neutron activation analysis. In Buffalo, N.Y., the Se/S ratios were monitored during 1968–69 and ranged from 0.5 to 1.6×10^{-3}.

letters

Industry under attack

DEAR SIR:

I believe the idea espoused by Mr. Speer in his Viewpoint article, "Punitive legislation is not needed" (ES&T, October 1970, page 791), that government is totally responsible for "inadequately treated or untreated sewage," and that "pollution-producing disposal of solid wastes" is wrong.

It is industry which, through advertising, creates a market for all kinds of products from food to automobiles. In terms of food, so much "junk" is consumed and eliminated by the expanding population that it is no wonder that treatment cannot keep pace with increased load. Some industries also take little notice of their own waste treatment methods. When I worked for an industrial corporation, we had 16 pipes that conveyed untreated human waste from 20,000 employees directly into a local estuary. Further, it is industry that creates the product that becomes obsolete and is discarded to become a government disposal problem.

I believe Mr. Speer's article was worth reading, however, as it espoused a philosophy that must undergo change if pollution abatement and control of environmental degradation are ever to be successful. I agree with Mr. Speer that we must have government and industry working together, not in collusion, but in a responsible manner to effect these controls.

John W. Foerster
Department of Biological Sciences
Goucher College
Towson, Md. 21204

DEAR SIR:

Mr. Speer suggests that industry be allowed accelerated write-off of all air and water quality control expenditures; he states that this is not a tax giveaway and does not involve the principle of subsidy. The accelerated write-off will reduce the amount of taxes paid by industry and increase its profits. What name shall we call this? Furthermore, accelerated write-off would favor capital-intensive pollution control measures while the efficient solution to society may not be capital-intensive.

If one wants to advocate the profit incentive as a means for solving the pollution problem, then all costs of production should be incurred by the industry, as free-market economics assumes.

Pio Lombardo
Department of Civil Engineering
University of Washington
Seattle, Wash. 98105

Incinerator emissions . . .

DEAR SIR:

In the Environmental Currents portion of your September 1970 issue (page 718), you presented a brief review of our recent report to NAPCA on municipal incinerator air pollution.

I am concerned in that the textual material presented our conclusions regarding the increases in *stack* emissions (after the air pollution control device), whereas the tabular material concerns *furnace* emissions (before the control device). Confusion of these two measures of air pollution problems

is common and, particularly in publications such as yours, should not be perpetuated.

Walter R. Niessen
Arthur D. Little, Inc.
Cambridge, Mass. 02140

. . . not as black as painted

DEAR SIR:

The Environmental Currents section of your September 1970 issue, page 718, included a short commentary on air pollution from municipal incinerators. The summary of the Arthur D. Little study on municipal incineration in this country suggested that air pollution emissions from municipal incinerators could, by the end of this century, constitute a major source of air pollution.

The initial reaction of a reader, as a result of this summary, may be prejudicial against the use of municipal incineration in dealing with our solid waste problem. It is evident, however, that the application of incinerator technology for controlling diverse forms of pollution will become increasingly great in the future.

In addition, the reader may infer that the relative figures for emission are based on application of present technology. While it is true that control technology for incineration can be, should be, and will be improved, it is also true that the application of existing control technologies would bring about a significant reduction of present emissions. Utilization of such technologies would also stimulate more accelerated growth in the application of incineration to replace less desirable methods of solid waste disposal.

The problem, particularly with regard to municipal incinerator systems, lies not with available technology, but with its application. All too often, selections are made by bidding methods which emphasize low initial cost rather than value per unit cost.

The technology exists, and is being further developed, to increase efficiencies markedly, even beyond the 90% mentioned in the Currents item, to the 95 to 99% efficiencies demonstrable in present industrial units. Government-funded research will stimulate studies to gain even greater efficiencies with optimum, economical cost for incinerator systems.

Richard C. Reed
Incinerator Institute of America
New York, N.Y. 10017

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Why, Daddy, why?

Many of society's common practices are environmentally ridiculous, but it is seldom that they are challenged

Anyone who has children can testify to the accuracy of their pesky reputation for asking awkward questions. If it isn't "Why the birds and the bees?" it's "How do they get all that toothpaste into that itsy-bitsy little tube?" One sad thing in life is that education in school and in the home all too often manages to teach children that asking questions is a waste of time and breath. After a sufficient number of rebuffs, the average child learns never to question anything. And for an adult to charge about enthusiastically firing off question at others is regarded as at least unusual, and quite possibly impolite. For a supposedly innovative society, we are in many ways remarkably uninquisitive.

Fortunately, of course, it does not take too many inquisitive souls to set the pace for society. The conveniences of modern life—television, automobiles, etc.—were conceived by a handful of thoughtful men, and are used by millions who never even wonder how appliances work. If this lack of inquisitiveness were confined to the mass of society—if, in other words, it did not characterize its leaders—then it would be harmless indeed. But there are signs that even those whose efforts are depended upon to carry society forward—the scientists, technologists, politicians, and professional civil servants, many of them readers of this publication—are getting so bogged down in the day-to-day morass of research or paperwork or whatever, that they are becoming less and less able to question the purpose of what they are doing. Which is a pity, because there are lots of purposes that need questioning and lots of assumptions that should be challenged.

In the environmental area, there are certainly some questions that should be asked. This month's Viewpoint contributor, Harold Leich (see page 11), brings up a good one. Why do we continue to use such an obviously inefficient way to dispose of human wastes? By diluting the wastes with huge amounts of water, as we casually flush them away, we force ourselves to buy large pipes, large pumps, and large (and costly) sewage treatment plants. Why don't we contrive a method to return the nutrients in the waste to the land, rather than synthesize fertilizers to replenish the soil? Then again, why do we spend a heap of money to provide water pure enough to drink, then use much of it for washing dishes, doing the laundry, cleaning our teeth, and watering our roses (and flushing wastes down the toilet)? What childish questions! One can add to the list: Why does society arrange itself so that commuter automobiles are all in the same place at the same time, so contributing mightily to air pollution while standing motionless on what is ironically referred to as a high-speed freeway? One could go on.

Of course, we are not so naive as to be unaware that there are conventional answers to most of these questions. Generally, the answer is either: (1) We've always done it that way; or (2) It's the cheapest way there is. As Alex Mills and his colleagues point out in this month's feature article on fuels management (page 30), such answers are really not good enough. We had better start asking some questions. If you find it hard to ask them, maybe your children should ask for you. Perhaps, as Tom Lehrer's song says about the new mathematics, "It's so simple, only a child can do it."

D. H. Michael Bowen

viewpoint

Harold H. Leich

Self-styled layman

A challenge to the environment pro

As an interested layman, let me use this page to throw out a challenge to the professional in the field of environmental quality: *Can modern technology devise a better method of sewage disposal than using scarce and expensive drinking water to transport human waste from the bathroom to the river or the treatment plant?*

Present approaches seem at a dead end—more sewers for more people, more dollars for more treatment plants, more elaborate techniques of primary, secondary, and now tertiary treatment—and still the effluent damages water quality. Is it possible that the very symbol of modern civilization—the flush toilet—was a tragic mistake?

And with present treatment plants barely able to handle current loads, what of the future? The first annual report of the Council on Environmental Quality states: "The waste loads from municipal systems are expected to nearly quadruple over the next 50 years." Later, the report says: "We need to examine alternative approaches to pollution control."

Yes, surely there must be a better method. Visualize a different approach—*the dry method of sewage disposal:*

The gurgling "water closet" is scrapped and ground up into ideal material for road ballast. In its place is a seat over a cabinet containing a removable canister, made of waterproof but biodegradable material. After each visit, the user sprinkles a powder over his deposit until the surface is dry and fully covered. There is no offensive sight or odor for the next user.

Many years ago in the White Mountains, we used pulverized soil in outdoor toilets for this purpose, and the organisms it contained attacked the waste material, breaking it down into humus. Research will find a better material, some active biological agent (including a deodorant) that will begin the decomposition process. No strong-smelling "chemical toilets" with their offensive odors, sights, and sounds.

Twice a week, the householder presses a top tightly over the canister and places it outside for collection. A special truck picks it up, manned by well-paid, respected technicians. Their hands are never soiled and they experience no unpleasant sights or odors. The final stage is a trip to the country, where the city has paid a farmer to make a field available. The topsoil is scraped aside, the canisters are placed in the trench, and the trench is then re-covered. A heavy roller passes over the field to crush the canisters beneath the soil and to hasten their decomposition. When the farmer plants his next crop, the roots sink down into rich nutriment. In several years, the same field can be used again.

Clearly, research will be needed at many stages to make this new process effective: What kind of plastic or other material is best for a degradable canister? What kind of powder should be used? Should the filled canisters be sterilized before burial and, if so, by what process? How deep should they be buried in dry soil?—in wet soil? Are precautions needed to protect groundwater? How soon can a field be reused?—to name just a few questions.

Incidentally, the dry method may solve the nasty problem of using holding tanks aboard pleasure craft. Instead of waiting at marinas for the unappetizing operation of pumping out such tanks, the yachtsmen would take the canisters ashore in a moment or two.

So here is a layman's suggestion—a promising area for research by the new Environmental Protection Agency. Pilot projects might be tested in small towns without sewers that are planning sewage systems and treatment plants, or in a small lake in danger of pollution, where boat owners are reluctant to use holding tanks.

Harold H. Leich is a graduate of Dartmouth College and American University. He has had a life-long interest in outdoor recreation

Readers are invited to respond to Mr. Leich's challenge; address your letters to ES&T.

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environmental currents

EPA's Ruckelshaus announces initial organization

At his first press conference last month, William D. Ruckelshaus said that the initial organization of the Environmental Protection Agency (EPA) is designed with the maximum flexibility for change. Ten interim regional offices were established, all of which the administrator plans to visit beginning this month. Interim commissioners for the five EPA offices include John T. Middleton (air pollution), David D. Dominick (water pollution), Richard D. Vaughan (solid wastes), Ray Johnson (pesticides), and Joe Lieberman (radiation). Not named was the deputy administrator nor the assistant administrators for the three EPA posts established thus far—planning and management; standards and enforcement and general counsel; and research and monitoring. Later this month, an announcement is expected regarding the two pesticides, aldrin and dieldrin.

10 Interim EPA regional coordinators

Lester Klashman, *Boston, Mass.*
Gerald M. Hansler, *New York, N.Y.*
Lloyd Gebhard, *Philadelphia, Pa.*
John R. Thoman, *Atlanta, Ga.*
Francis T. Mayo, *Chicago, Ill.*
Bill V. McFarland, *Dallas, Tex.*
John M. Rademacher, *Kansas City, Mo.*
Donald P. Dubois, *Denver, Colo.*
Paul DeFalco, Jr., *San Francisco, Calif.*
James L. Agee, *Portland, Ore.*

FWQA approves 34 regional programs and recharge grant

Last month, the Federal Water Quality Administration (FWQA) approved water pollution control programs for 31 states and three other jurisdictions for fiscal 1971. "Approval of the programs means these governmental units are eligible for $5,517,800 in federal assistance on a matching-grant basis," says David D. Dominick, FWQA Commissioner. Alaska, the low state, will receive $20,100, while Pennsylvania, the high one, will receive $496,504. In addition, the Virgin Islands, armed with slightly less than a half million dollar FWQA grant, will determine if groundwater can be recharged sufficiently with treated waste water to increase freshwater reserves.

Strong air bill emerges from Congressional compromise

At press time, a House–Senate conference had just agreed to a modified version of the National Air Quality Standards Act of 1970 which corresponded closely to a bill previously passed by the Senate. Conferees imposed on the auto industry an absolute deadline of January 1, 1976, for development of a practically pollution-free engine. Provisions in the Senate version that emerged intact from the conference establish national air quality standards and require new plants to install the best available pollution control equipment. The compromise bill, which is a strong one, was expected to achieve easy passage in both houses of Congress before being sent to the President to be signed into law.

NIPCC reports on mercury, auto hulks, and detergents

Created by President Nixon last April 14, the National Industrial Pollution Control Council (NIPCC), an organization of leaders of American industry, issued its first three reports late last year. In its detergents report, NIPCC notes that every major detergent manufacturer had under way top-priority efforts to formulate a no-phosphate laundry product. Currently, NTA is being used as a trial replacement for phosphate in 15 regional or national granulated laundry brands. Prior to this substitution, two billion pounds of phosphate per year were being consumed by laundry products. By late 1972, the total amount of phosphate in use for detergents will be decreased to approximately 1.3 billion pounds per year, a 35.8% reduction or about 715 million pounds.

Detroit, Atlanta, Cleveland receive 180-day notice

William D. Ruckelshaus, Environmental Protection Agency (EPA) chief, announced the warning to the three cities' mayors, giving them 180 days to stop polluting the waterways or face federal court action. Detroit's Mayor Roman S. Gribbs said he was "happy" to accept the 180-day warning and asked that the federal government take 179 days to "provide the funds (for pollution in Detroit) that they promised and never provided." Cleveland's Mayor Carl Stokes and Atlanta's Mayor Sam Massell denied that their programs were behind schedule.

Mayor Roman Gribbs

New England establishes second air consortium

The New England Consortium on Air Pollution—Boston University, Harvard, Lowell Technological Institute, MIT, Northeastern, Tufts, and the University of Massachusetts—is a pool of training and research talents in the fight against air pollution and other environmental problems. The goal of the group is to enable schools to assist one another in preventing duplicate research effort in areas considered so complicated that no institution could make significant progress on its own. The first Consortium was set up in North Carolina (ES&T, February 1970, page 92).

Permits are required for lagoons in Pennsylvania

The new Sanitary Water Board orders regulate all waste storage impoundments holding dangerous polluting substances. The new rules require plans for waste storage lagoons showing size, location, construction, and contents, and assuring that the impoundments are structurally sound, impermeable, and protected from malicious acts. In addition, a permit system has been instituted for these lagoons. Permits will not be issued for earthen lagoons that hold toxic substances or petroleum products, or those located on flood plains.

New York City strengthens air pollution control code

Hearings were held last month concerning the revision of New York City's Air Pollution Control Code. Final action by the city council is expected in the first quarter of 1971. The revisions include: • Eliminating the use of lead compounds in gasoline by the end of 1973; • Eliminating the use of photochemically reactive solvents by July 1, 1972; • Permitting the New York City EPA to step in to repair or install control equipment at the expense of the owner; • Expanding the need for permits and operating certificates; • Identifying odor sources that must be controlled; • Establishing fines up to $5000 or imprisonment up to 60 days.

Wisconsin issues 64 water pollution abatement orders

The Wisconsin Department of Natural Resources (DNR) issued 64 new abatement orders to municipalities and industrial firms located in the upper basin of the Wisconsin River. DNR estimates that these orders will result in a two-thirds reduction in the present level of organic material discharged into the river and reduction of more than half of the suspended solids. The new orders establish a timetable for compliance that will be completed in 1973 and will produce noticeable improvements by next year.

environmental currents

Franklin Institute to build full-scale trash separator

The Bureau of Solid Waste Management (now part of the Environmental Protection Agency) has awarded a two-year contract to the Franklin Institute (Philadelphia, Pa.) to develop a trash separator rated at 60 tons per hour. The separator, which will be 40-ft long, 30-ft high, and 15-ft wide, will be based on a laboratory setup at the Institute that has been sponsored by Dickson Paper Fibre, Inc. The machine will be able to separate paper, glass, metal, and soft and hard plastics from trash, and the pilot plant will use unseparated trash collected by Philadelphia. The separator will consist of numerous vibrating screens, baffles, paddle wheels, and gravity separators. Shredded trash is used as feed, and the output is conveyed on belts to collecting stations.

PHOSTRIP PROCESS
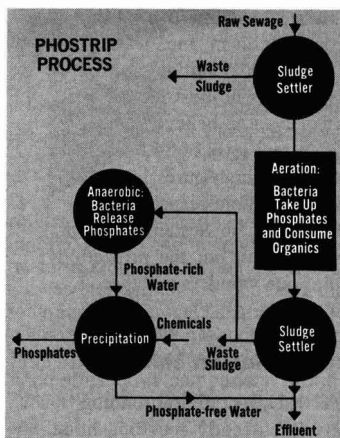
Modified activated sludge process takes out phosphates

By ringing a few changes on the traditional activated sludge sewage treatment process, Biospherics Inc. (Rockville, Md.) has come up with a process that is claimed to remove more than 90% of the phosphate in typical sewage. The process—called PhoStrip by its inventor, Biospherics' president Gilbert Levin—centers on a higher-than-normal aeration rate of the activated sludge–sewage mixtures. Extensive aeration is responsible for the phosphates being taken up by sludge bacteria, which then yield the phosphates in concentrated form in an anaerobic digestion process. Overflow from anaerobic digestion is chemically treated to precipitate the phosphates. The process has been successfully tested in a 15-gph pilot plant.

NAPCA-Ford instrument measures airborne ozone and NO$_x$

The Ford Motor Co. has donated to the National Air Pollution Control Administration (NAPCA) a device that accurately measures the concentrations of NO$_x$ (nitric oxide plus nitrogen dioxide) and ozone in samples of the atmosphere or auto exhaust. The instrument works on the principle that the chemical reaction between NO and ozone produces light, the intensity of which can be determined. Work by NAPCA extended the applicability of the instrument from NO to NO$_x$. Concentrations ranging from 1 ppb to 1 pph can be measured. Response time is about one second. (For a complete review of the reactions that produce photochemical smog, see page 39).

Magnet sweeps up oil in novel spill mop-up method

Scientists in the Systems Division of Avco Corp. (Lowell, Mass.) have hit upon an intriguing use for the magnetic ferrofluids they have been developing since 1963. In small-scale tests, Avco has shown that it is possible to confer magnetic properties to an oil slick by spraying it with a concentrated ferrofluid (a suspension of magnetite—Fe$_3$O$_4$—in light oil). The magnetized oil can then be picked up by a traveling magnet to which is attached a vacuum hose. Although the technique has never been tested on the high seas, it does have the advantage that no water is entrained with the oil, since only the oil becomes magnetic. Avco believes that the technique is preferable to the usual "vacuum cleaner" methods, which typically pick up a mixture containing 99% seawater from which the oil must be separated.

ห้องสมุด กรมวิทยาศาสตร์

environmental currents

Swiss show offers entree into European control market

The U.S. Department of Commerce is currently encouraging U.S. companies with capability in the pollution control field to consider exhibiting at the international trade fair, Proaqua Provita, to be held in Basel, Switzerland, June 8–12. Commerce figures that the European Common Market countries offer excellent prospects for U.S. manufacturers. The Department claims that a trade fair it sponsored in Rome in 1969 resulted in $56 million of new business for the U.S.; West Germany and France are thought to be the best prospects, and American firms already have an upward of 10% of the market for imported pollution control products. But Commerce points out that increasing self-sufficiency of the European countries represents a challenge to U.S. exporters.

Solid waste control to be big business by 1980

The spate of market analysis reports continues. Now come two on the subject of solid waste control, one from Frost & Sullivan, Inc., a firm that has published previous reports on the air and water pollution control markets, and the other from Chem Systems, Inc. As in most recent reports, the projections in these two vary widely. F&S believes that refuse disposal expenditures will rise from a current level of $4.5 billion to over $7 billion by 1980. The corresponding figures in the Chem Systems report are $6.5 billion and $16.5 billion, respectively. A possible reason for the difference could be that Chem Systems talks of solid waste management rather than refuse disposal, but the projections of the two firms for 1980 are so different that one wonders whether optimism or pessimism is more likely to be correct.

U.S. oil industry spent $2 billion on pollution control

1970 antipollution spending by petroleum industry	
	($ millions)
Capital expense	$348.5
Operation and maintenance	134.4
Research and development	36.2
Administration	40.2
Total	$559.3
Source: API	

A survey of 45 companies representing 98% of U.S. crude oil refining capacity reveals that the petroleum industry is currently spending more than $1.5 million a day for pollution control equipment and research and development. In the period 1966–70, according to the American Petroleum Institute survey, the industry spent nearly $2.1 billion, more than half of it in the manufacturing (refining) sector. The expenditures have been about equally divided between air and water pollution control. During the same period, $1.2 billion was spent for capital construction, while $518 million was spent for operation and maintenance of facilities. Expenditures estimated for the year 1970 (see table) more than doubled those for 1966.

Steel exec pushes for pollution control tax incentives

Industry already has enough inducements to get the cleanup job done, Bethlehem Steel Co. chairman Steward S. Cort told the National Association of Manufacturers in December. However, Cort went on to plug hard for an easing of present Internal Revenue Service limitations on tax write-offs for pollution control facilities. The amount that can be written off should not be limited to "any arbitrarily designated portion of a facility's useful life," said Cort. He also attacked a current IRS provision that, to qualify for fast write-off, the facility must be used entirely for the purpose of pollution control and another which disqualifies facilities which recover part of costs by recovery of salable product. Cort did not ask for special tax treatment for operating costs.

Restoration of the Environment

AIR POLLUTION CONTROL
Part I
Edited by WERNER STRAUSS, *University of Melbourne*

A volume in *Environmental Science and Technology, a series of Texts and Monographs, edited by* ROBERT L. METCALF *and* JAMES N. PITTS, JR.

The contributors to this volume examine the exigent dilemma of air pollution, and attempt not only to be comprehensive, but also selective and critical in a constructive sense. They are concerned with the theory, experimentation, and practical applications for its abatement, and cover such topics as dispersion of effluent materials, formation and control of nitrogen oxides, control of sulfur oxides, motor car exhausts, electrostatic precipitation, filtration, and scrubbing.

1970   456 pages $19.95
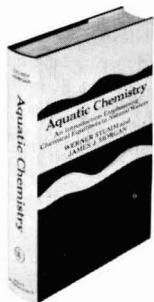
AQUATIC CHEMISTRY
An Introduction Emphasizing Chemical Equilibria in Natural Waters
By WERNER STUMM, *Harvard University and* JAMES J. MORGAN, *California Institute of Technology*

Aquatic Chemistry is addressed to those scientists and engineers who share an interest in, and a sense of responsibility for, the aquatic environment. The two primary goals of this book are to formulate a theoretical basis for the chemical behavior of natural waters and to describe the processes involved in water treatment. The authors give special attention to the chemical processes affecting the distribution and circulation of chemical substances. Since natural waters are characterized by great complexity, and since understanding the pertinent variables is essential, the approach stressed is comparison of the real systems with idealized counterparts or models. These simplified and manageable models clearly illustrate the principal regulatory factors that control the chemical composition of natural waters, and in turn, the composition of the atmosphere.

1970   568 pages $24.95

PRINCIPLES AND PRACTICES OF INCINERATION
Edited by RICHARD C. COREY, *U.S. Department of the Interior*

A volume in *Environmental Science and Technology, a series of Texts and Monographs, edited by* ROBERT L. METCALF *and* JAMES N. PITTS, JR.

"Now, at long last, an editor of outstanding competence has selected informed engineers to write about the various phases of the process in which they are expert. . . . Among the contributors are men who are well known and respected in engineering, combustion, incineration, and allied fields. They have accomplished their tasks in an outstanding and laudable manner.

"The book . . . is one which engineers interested in this subject will find indispensable. . . . Environmental control officials, charged with reviewing plans for incinerator plants, will find it a useful reference."
—Mechanical Engineering

1969   297 pages $14.95

ADVANCES IN ENVIRONMENTAL SCIENCES AND TECHNOLOGY
Volume I
Edited by JAMES N. PITTS, JR., *University of California, Riverside and* ROBERT L. METCALF, *University of Illinois*

"Most elaborate in its scope, arrangement, and coverage by nine outstanding research workers in their respective fields. Each author is expert in his subject. . . . Pitts and Metcalf have chosen well for their contributors and subjects . . ."—*Choice*

This first volume in a particularly relevant new series examines some of the environmental problems that our technology has created. The nine previously unpublished chapters range from an extensive introductory overview of environmental sciences to such diverse topics as the Federal role in pollution abatement, aeroallergens and public health, and more technically oriented considerations of individual pollutants.

1969   356 pages $15.95

ENVIRONMENT, POWER, AND SOCIETY
By HOWARD T. ODUM, *University of Florida, Gainesville*

Environment, Power, and Society offers a macroscopic view of man and his part in the delicate balance of forces that sustains life in the biosphere. To analyze man-made and natural forces, the author discusses the common denominator that unifies these seemingly disparate energetic processes—*power*.

Natural energy such as solar radiation, the hydrologic cycling of the oceans, or the cyclic exchange of carbon, hydrogen, oxygen, and nitrogen can be easily diagrammed in terms of power. But, the author shows that the affairs of man also have quantitative power ratings and that the important issues of man's existence and survival are as fully regulated by the laws of energetics as those of the simple physical and chemical world.

1970   336 pages $9.95

APPLIED STREAM SANITATION
By CLARENCE J. VELZ, *Professor Emeritus, University of Michigan*

A volume in *Environmental Science and Technology, a series of Texts and Monographs, edited by* ROBERT L. METCALF *and* JAMES N. PITTS, JR.

In addition to presenting useful tools for evaluating solutions to water pollution, this book will assist in developing an informed, intelligent appreciation of the complex problem of waste disposal and pollution control. The basis of effective stream sanitation is the phenomenon termed *stream self-purification;* the ability of the stream to assimilate wastes and restore its own quality. The orientation of this book is towards practical application of this waste assimilation capacity of streams, in terms useful not only to the professional potomologist, be he scientist or engineer, but also to the conservationist, economist, lawyer, and administrator.

1970   640 pages $24.95

Simultaneous SO₂ and fly ash removal

Use of granular bed devices makes it possible to remove both pollutants from flue gases

Fly ash and sulfur dioxide (SO₂) removal from flue gas streams has been a problem for years, and various devices have been contrived to eliminate these pollutants. Some are effective but expensive; others are inexpensive but not effective (see "Particulate controls: A must to meet air quality standards," ES&T, November 1969, page 1149). Now one school of thought is centered around removing both the particulate pollutant and the gas in the same process with the same equipment. Generally, each pollutant has been treated separately and with separate facilities.

Early in 1968, the National Air Pollution Control Administration (NAPCA) contracted Avco for a study on granular bed devices with the orientation of looking at simultaneously removing SO₂ and fly ash from large coal-fired power stations. Also, the study required a survey of available information and a technical and economic analysis of the potential of granular bed devices.

Before identifying the various fly ash removal devices, says Ted Schoenberg of Avco Corp., project engineer of this NAPCA study, an explanation of the granular bed is necessary. A granular bed is, in essence, a bed of rocks—fine-mesh sand or particulate matter 0.625, 0.25, 1.5 in., or even larger in diameter. If this bed is used as a dust collector, the dirty gas is passed over it, and the closely packed granules make up the collection surfaces for the filter. With time, this system can lose capacity as the collected fly ash or dust accumulates on the granules and block the spaces between the granules, thus causing the pressure drop to become too high for the same gas rate.

Characteristic of a granular device,
• The bed must have means embodied in it to knock off the accumulated fly ash or to rejuvenate the bed by maintenance of a fresh granular surface for continued collection.
• The closely packed bed can be

fixed or moving (granules in constant motion).
• The bed is not fluidized or a dispersed phase with particles forcibly kept in motion by the gas being treated.

Since "rocks" are used in a granular bed to remove fly ash, why can't a granular sorbent "rock" be used to remove SO₂ also? Schoenberg considered only the synthetic sorbent alkalized alumina for use with the devices reviewed during this study. The granular bed devices operated thus far have not been oriented toward large-scale cleanup of power stations, but are dust collectors for small installations, such as cleanup of fumes from a copper furnace. Their function on large-scale cleanups has yet to be tested.

Granular bed designs

Many granular bed designs are shaft filters or panel filters—a rectangular shaft of any length or depth that contains the granular material. The sides of the shaft contain gas entry and exit louvers (sketch 1). These shaft filters are usually one of three varieties.
• **Crossflow shaft-falling solid design:** a vertical panel filter in which the collecting particles continuously fall through the shaft while the gas flows across the shaft. These filters include the Dorfan Impingo filter, the Consolidation Coal Co. filter, and the Carnegie-Mellon crossflow filter.
• **Intermittent moving-bed type of design:** a fixed-bed device of vertical panels with intermittent movement of granules. In this category are the Squires designs and the Granger filter.
• **Fixed-bed granular filter:** does not move or replace the particles; rejuvenation is achieved by a back flow of clean gas or vigorous shaking. Ducon Co. and Fuller Co. have filters of this type under development, but little information is publicly available. The Lurgi Co., however, has marketed devices of this nature in Europe.

Of the devices for which data was available, the Dorfan and Squires models provide potential for further study.

Dorfan Impingo filter

This filter is an example of the crossflow shaft-falling solid design. The falling particles, contained in two separate filtering shafts, are contacted by a crossflow stream of gas (see sketch 2). The typical 1-ft thick shaft tested has a 9 × 14-ft filtering area with a capacity of 32,000 cfm. Because of the constant falling of the granules, the particles remain in the shaft for 200 minutes.

The Dorfan filter has been used in the collection of dust generated during the drying of asbestos rock, and has a reported collection efficiency of 97% with dust size ranging from 100% through 100 mesh and 60% finer than 10 μ. In this application, the collection granules were raw asbestos rocks ranging from 0.5 to 1.5 in. However, no Impingo filters are known to be still in active service. These plants were using "big rocks," says Schoenberg. To get a system with good gas distribution and continuous operation without blockage is not easy and poses a tough engineering problem.

Squires designs

The Squires designs consist of two panel filter concepts in which the accumulated fly ash is removed periodically through the gas-entry louvers. Both the LS (loose surface) and GSC (gas solid contactor) are intermittent moving-bed filters. The GSC (sketch 3) provides countercurrent contacting of the gas and solid. Two types of granules are used in the 4 × 12-in. shaft—fine sand as the collecting medium and coarse sand for preventing the finer sand from being blown out of the shaft. When used as a dust collector and sorber, the countercurrent gas solid contacting can be maintained by balancing solid and liquid gas flows so that

the sorption front remains within the treating zone. Fly ash builds up on the particles on the gas-entry side and may be removed by a hammer system or puffback system.

The hammer system consists of the gas-entry slats being struck a sharp blow, which would dislodge the front layers of the granular collecting material. More sorbent would then be drawn down from an overhead hopper. The puffback system is comprised of a rapid reverse-pressure surge of gas, which tends to knock the fly ash particles off of the granular collecting material. Not yet tested experimentally, the GSC has been estimated to have a collection efficiency of 99%+ at 10 to 15 ft/min face velocity.

The LS model is simpler than the GSC design in that it contains fewer internal elements (sketch 4). Small-scale tests carried out on the collection efficiency and puffback system of cleaning resulted in 99.7% efficiency. Scale-up of relatively small systems may require further engineering. Practice of principles applicable to small-scale operations may not effectively function when expanded, Schoenberg points out.

Problems

One problem encountered in measuring fly ash collection efficiency is that of agglomeration, both under experimental conditions and in actual use. With a wide distribution of particle sizes, realistic figures are difficult to obtain, especially in experimental conditions with particles being fed into the system.

Another problem encountered with these devices is the theoretical analysis and prediction of their performance. Dust collection theory has been developed for the collection of particulate matter on a single collecting body—a single fiber or a single sphere. Therefore, calculation for an array of collectors in a real situation, with more than one mechanism for accumulation, presents serious obstacles. Simultaneously, direct interception, impingement, diffusion, gravity, and electrostatic effects all influence the entrapment of the fly ash particle. An engineer must also take into account the distribution of particle sizes, the agglomeration in the gas phase, and the agglomeration in the spaces within the granular bed. The simpler task of calculating sorption performance indicates that, at the flow rates recommended under adequate conditions for dust collection, there is no problem getting efficient collection of the SO_2 with a good sorbent.

Cost estimates

The estimation of costs is associated with the installation of granular bed equipment and the modification of existing plants without detailed engineering designs. Also, since over 6 million pieces (estimated for an 800 MW power station) are needed for the Squires units, mass production is a must. Schoenberg says that the cost estimates for the sorption-collection equipment compare well with reported costs for SO_2 removal techniques or for dust collection by electrostatic precipitators, offering both particle collection and SO_2 removal simultaneously.

Future application

"As a result of the preliminary economic analysis, there is relatively little basis to choose between the various granular bed designs. Although a design may appear economically competitive, its true economic value can be determined only when the two questions of efficiency (collection and sorption) and operatability have been experimentally evaluated. But I think if you can get something as simple as a bed of rocks, at the same cost or lower than an electrostatic precipitator and operating at the same efficiencies, real advantages may result, especially with regard to high-temperature operation. But I just don't know; there aren't enough data," summarizes Schoenberg. Enough evidence is available, however, to point to the need and advantage of further work and experimentation in using granular bed devices for removal of SO_2 and fly ash.   CEK

Typical panel filter section

filter particles

gas exit louvers   gas entry louvers

sketch 1

Dorfan Impingo filter

dirty gas

filter particles

clean gas

sketch 2

GSC panel section

fine particles

coarse particles

dirty gas

clean gas

sketch 3

LS panel section

clean gas   dirty gas

filter particles

sketch 4
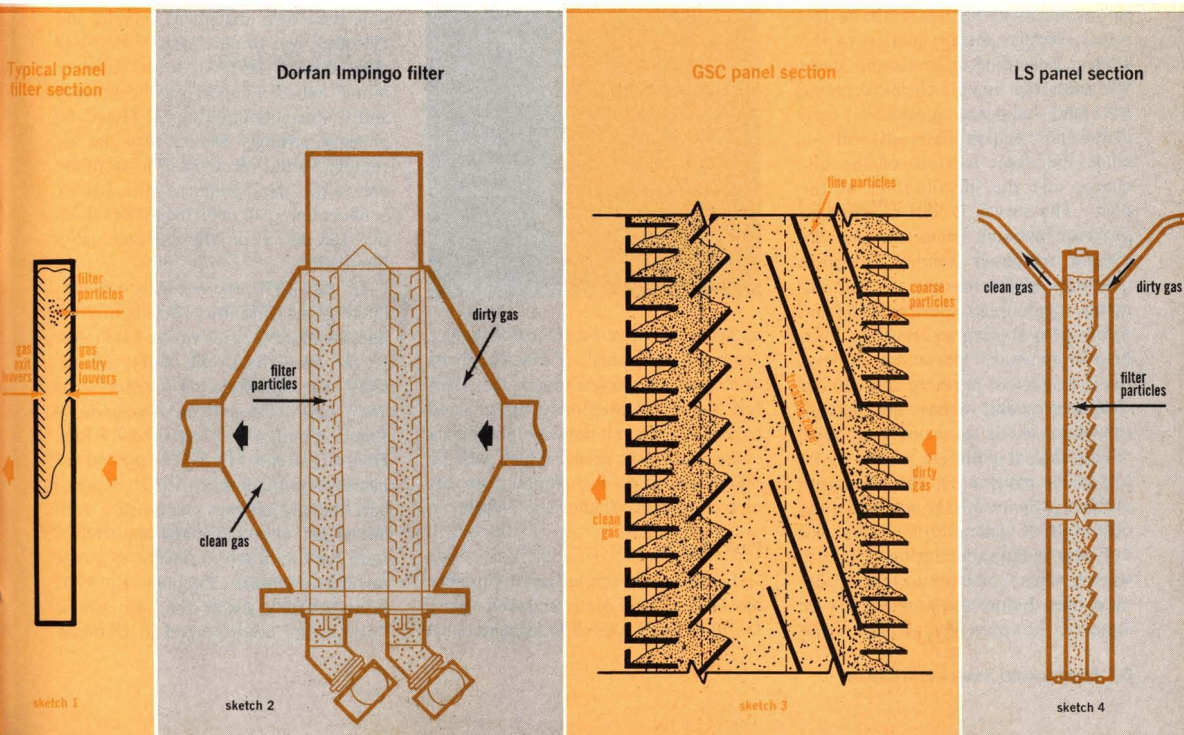
Industrial waste water: FWQA inventory under way at last

*After years of delay, federal officials are now asking industries
to volunteer details of their waterborne discharges*

A majority of government effort and money has, in the past, gone into the treatment and monitoring of municipal wastes. However, the federal government has known for years that industry discharges the largest volume and the most toxic of pollutants. "The volume of industrial wastes is growing several times as fast as that of sanitary sewage," states the 1969 report, "The Cost of Clean Water and Its Economic Impact." Previously, little detailed information was available for industrial waste water, but the Industrial Waste Inventory, undertaken by the Federal Water Quality Administration (FWQA), will show the effects of industrial discharges on the receptive water.

What is the purpose of this inventory? Jesse L. Lewis of FWQA's technical data information branch, explains that the inventory is intended to reveal whether discharges from industrial plants end up in open waters, public sewers, deep wells, or ground reservoirs (where the waste is stored and does not reach the waterways). Besides the destination of the effluent, according to Lewis, this study will show the liquid's chemical, physical, and biological properties. Incidental information obtained will include the exact location of the discharge and the identification of the plant. The survey is also expected to provide economic data for use by FWQA's manpower training and grant programs in determining the requirements for a water cleanup program. Adds FWQA's George Wirth, "In a broader sense, before we can do anything as far as planning a pollution cleanup program, we have got to know something about the cause and effect relationship of pollution." This inventory will survey rather than solve the problem. Obviously, the polluted state of a body of water can be determined by water quality monitoring or by observing waters' inability to support desired uses. Before the problem can be attacked, however, the relation back

What FWQA is looking for: Water quality characteristics

Physical parameters

- flow
- pH
- temperature
- color
- specific conductance

Chemical parameters

- total solids
- total volatile solids
- total suspended solids
- total dissolved solids
- acidity
- alkalinity
- 5-day BOD
- COD
- oil and grease
- chloride
- sulfate
- sulfide
- phenols
- NH_3 (as N)
- NO_3 (as N)
- NO_2 (as N)
- organic N
- Kjeldahl
- ortho-phosphorus
- total phosphorus
- Cr, Cu, Fe, Cd, Pb, Mn, Zn, F, As, Hg

to the cause must be traced—whether industrial, municipal, or other kinds of discharges are going into a stream. "We feel that it is absolutely essential to have this information to provide a cause and effect model which will be the groundwork for planning an attack on pollution," continues Wirth.

Past efforts

The idea for this inventory project has been around for over seven years. In 1963, the House of Representatives' Subcommittee on Natural Resources and Power, chaired by Rep. Robert E. Jones (D.-Ala.), recommended that such an inventory be undertaken. In 1964, an effort was made to initiate the survey, but the project never got off the ground. A main reason for this was that industry objected. Another was that the Bureau of the Budget (now Office of Management and Budget, OMB) would approve the inventory only on a test basis, meaning that the data had to be taken in only one river basin area and that data obtained would be confidential. Under these conditions, the Public Health Service (PHS), which at that time had all water pollution control functions, did not concur, and the project was never executed.

In 1967, the project was submitted again to OMB. But budget officials again deferred action until two other studies affecting industry were completed. (One study was the feasibility of offering industry incentives to initiate their own abatement actions, and the other was to determine the cost of clean water.) In 1968, Jones' subcommittee issued a report on the project, and it was submitted again. However, industry strongly hinted that the inventory would result in little response unless the data obtained was strictly confidential. OMB deferred action pending resolution of the confidentiality question.

In May 1970, the necessity for conducting the inventory through direct questionnaire to firms was re-evaluated. At this time, the House of Representatives' Subcommittee on Conservation and Natural Resources, successor to Jones' committee and chaired by Rep. Henry D. Reuss (D.-Wis.), pushed for hearings on the inventories. In September, the project was once again submitted for approval. OMB approved a form for use in a test mailing to a representative sample (250 plants) of U.S. manufacturing plants that use water. These forms were mailed in October,

and FWQA is currently processing replies.

Procedure

The Industrial Waste Inventory zeroes in on the major water-using industries in the U.S. Categories include blast furnace and basic steel products, motor vehicles and parts, paper mills, textile mill products, petroleum refining, canned and frozen fruits and vegetables, meat and dairy products, and chemicals. An initial goal of 30 days (which ended December 3) was set for

ing. (At press time, 34.5% of the 250 industries contacted had responded to the questionnaire.) Of the 350,000 manufacturing plants in the U.S., only 10,000 use 90% of all water intended for industrial purposes. It is the intent of FWQA to cover these 10,000 plants regardless of the number of questionnaires mailed.

Information requested

The data requested are the characteristics of the effluent just before reaching the receiving water—in other words, at the end of the pipe. For the

vironmental control, and a forecast of funds to be spent in the next five years for abatement facilities and personnel.

The second page asks for data on actual discharges—point of discharge, type of discharge, and various water quality indicators of the intake water and the waste water effluent. The water quality indicators are taken before and after treatment of the intake water and before and after treatment of the waste water effluent (see box). However, industry is asked to furnish only information that they have on hand and can provide. This will give an idea of what is being monitored at the present time.

Industry response

A big question is how industry is responding to the inventory. "We feel that if a government agency needs information about one of our installations, we supply it," says a spokesman for the Du Pont Co. Generally, there is a cooperative attitude prevalent among the large corporations, according to FWQA's Lewis. "These people want to cooperate and fill out the questionnaires." FWQA officials stress that this trial program is strictly voluntary and is not intended to be used against industry. The matter of self-incrimination has been a touchy point in the inventory. But the survey is being taken primarily to give a picture of what is being discharged to the waterways, summarizes Lewis.

Conversely, a spokesman for Reuss' subcommittee stated that there will be strong pressure from the subcommittee for incrimination and prosecution. But, according to another subcommittee aide, this information may merely be used to determine the cost of the pollution cleanup.

Data application

What will the analysis of the data received from the inventory reveal? The information will define the problem of pollution in the nation's waterways and perhaps provide a basis for steps in a cleanup campaign. FWQA officials say that the main goal is to enhance the water quality improvement program, but without harming the industries that volunteered the information. Commissioner Dominick has stated that the inventory is "essential to the carrying out of the President's environmental improvement program." Time alone will reveal whether the inventory will fulfill this mission or just stir up a hornet's nest. CEK
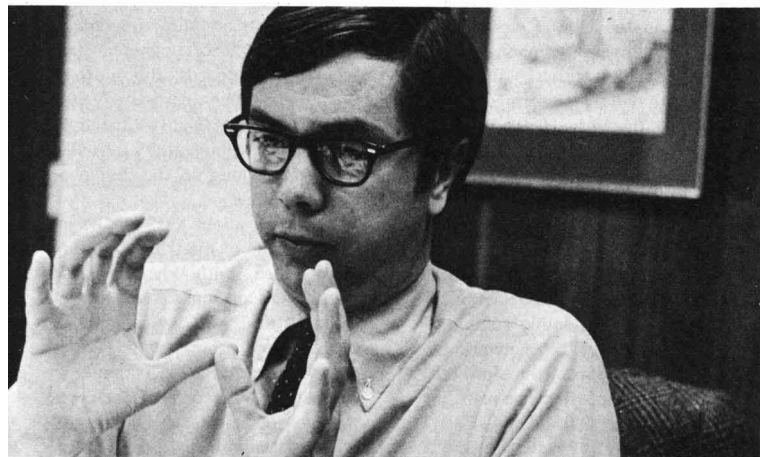
FWQA's Dominick
Requesting industrial cooperation

industries' replies to FWQA's Commissioner David D. Dominick's forwarding letter and preliminary survey. At the end of this initial period, Dominick sent follow-up letters and questionnaires to the firms that had not answered, again allowing a 30-day response period.

At the beginning of this month, FWQA's John Dell'Omo started an overall analysis of the response. After determining the percentage of plants that have answered, the percentage of these that have given replies to specific questions, and the exactness of the replies, FWQA will again meet with OMB to review the results of this test survey. FWQA officials are hoping that OMB will approve the questionnaire for a mass mailing to over 10,-000 industrial plants, which they will be able to begin in April or May.

The preliminary survey will give an idea of the percentage of firms that are likely to respond to any mass mail-

purpose of this survey, FWQA is interested in the quality of the effluent, not the quality of the stream into which the effluent is discharged. Of course, pollution of federal bodies of water is defined as a discharge into a stream that affects the water quality as established by the standards. The effects can always be observed; but without information on the cause, decisions on the approach to nationwide cleanup cannot be made.

The form consists of a two-page questionnaire. The first page has three parts. Part one is mainly for identification purposes and gives an idea of the plant size, including the number of employees, and whether the plant operates on a seasonal or yearly basis. The second part asks for the name and type of the water source as well as the name and type of the body of water that receives the discharge. Part three concerns economic data—existing abatement costs, number of personnel in en-

ORSANCO: Pioneer with a new mission

New roles for 22-year-old water pollution agency add to an impressive list of past achievements

The term "regional approach" has become somewhat of a cliche, so much so that mere utterance of the words tends to conjure visions of the addition of yet another layer of bureaucracy onto a field already long on programs but short on results. This is unfortunate, for although full implementation of regional action is a concept perhaps more honored in the breach than in the observance, the basic concept is a sound one. That it can work has been amply demonstrated by the Ohio River Valley Water Sanitation Com-

Executive director Horton
Not dominated by feds

mission (ORSANCO), the 22-year-old pioneer in interstate cooperation on water pollution problems. ORSANCO is alive and well, and shows no signs of flagging from its original mission—restoration and continued protection of 981 heavily industrialized miles of the Ohio River.

By mere coincidence, the ORSANCO organization dates exactly as far back as the federal government's nationwide water pollution control effort. P.L. 80-845, the first major federal involvement in water pollution abatement, was signed by President Truman on June 30, 1948, the same date that the ORSANCO compact became effective. Because of the coincidence, the temptation to compare ORSANCO's rate of progress with that of the fed-

eral program is strong. However, ORSANCO's track record is strong enough not to require comparisons.

Monitoring

The most well-known and concrete of the Commission's achievements is the monitoring network that has been established on the Ohio River. What began as a rudimentary manual sampling grew rapidly with the development of automatic monitoring equipment, and by the early 1960's had become a showcase for demonstrating remote monitoring and data acquisition and handling concepts.

But the Ohio River's quality, and not monitoring techniques, is the Commission's primary concern, and the trends charted in the *ORSANCO Quality Monitor,* a monthly summary of data generated by the network of sampling stations, shows the slow but inexorable trend of improvement in the quality of the Ohio River. Early in its development, the Commission had established a set of water quality standards for the portion of the river that flows through the boundaries of the eight signatory states—Illinois, Indiana, Kentucky, New York, Ohio, Pennsylvania, Virginia, and West Virginia. Of the 21 chemical and biological criteria that have been adopted for appraising river quality, fully two-thirds are met routinely 100% of the time. To be sure, some of the deficiencies are troubling, including such vital parameters -as dissolved oxygen, coliform density, and pH. But even on these criteria, considerable progress has been charted over the years, and will continue as the compact states continue to implement their abatement plans.

Achievements

ORSANCO is a regulatory agency, not a treatment authority, but the pace of treatment plant construction along the Ohio is a direct result of judicious use of the Commission's enforcement powers and coordinating efforts. Twenty-five years ago, prior to the establishment of the Commission,

less than 1% of the population in the Ohio basin was provided with sewage treatment facilities. But today, treatment facilities serve more than 95% of the population with at least primary or intermediate treatment. In its last annual report, the Commission notes that about 30% of the basin's treatment plants require upgrading, mainly as a result of upgraded state water quality standards. But most of these municipalities, particularly the larger cities on the Ohio—Pittsburgh, Pa., Cincinnati, Ohio, and Louisville, Ky.—are well along on the design of improved facilities.

Furthermore, about 87% of the industrial effluents in the Ohio basin are in compliance with the ORSANCO standards, and all but a handful of those industries not yet complying have abatement programs in various stages of design and construction.

With such a record of achievements, even the most cynical critic of the "regional approach" would have to concede that ORSANCO must be doing something right. Just what it has been doing right has been documented by Edward J. Cleary in "The ORSANCO Story," published a few years ago by Resources for the Future. Cleary's book presents considerable detail on the ORSANCO compact: its genesis in the concern of a group of Cincinnati citizens in 1936 over the condition of the Ohio River; the tortuous route of negotiation of the compact, both among the states and with the federal government; and, finally, its rapid growth and implementation. The thoroughness of Cleary's account is overshadowed only by the objectivity of the author who, as ORSANCO's first executive director and chief engineer, was deeply committed to ORSANCO's goals.

Future directions

To assess ORSANCO's future role in the light of a growing federal involvement in water pollution control—three new water quality acts have been passed since the Commission was activated—ES&T visited with Robert K.

Horton, who has taken over as executive director (Cleary still serves the Commission occasionally as a consultant). Horton agrees that ORSANCO's *modus operandi* must change, and in fact has been changing subtly, with changing public attitudes.

Horton points out that the strength of ORSANCO lies in the fact that the original compact, stripped of its organizational provisions, is basically a pledge of "faithful cooperation" by the signatory states. He explains that many people are misled by the fact that the Commission was formed under Congressional authorization, and has three members from the federal government. "We are in no way dominated by the federal government," he says. "ORSANCO simply consists of a mechanism whereby the states can devise compatible actions."

Perhaps because of this "self-policing," the Commission has had to use the enforcement powers delegated to it by the compact only sparingly, and only as a "last resort," according to Horton. For example, when a member state itself has been unable to get satisfactory enforcement from local courts, the Commission, acting as an interstate agency, can bring the ac-

tion to a federal district court. Even so, enforcement can only be brought on agreement by both a majority of the signatory states and a majority of the three members of the delegation from the state involved. In no case, however, has this requirement hindered initiation of interstate agency intervention.

The Federal Water Quality Act of 1965, with its standards-setting provisions, did not create any confusion in ORSANCO's mission, according to Horton. "At the time of the act, the Commission was getting ready to update its standards anyway," says Horton, and the only confusion was over whether the Commission should hold joint hearings on standards. Although the Department of Interior did sanction joint hearings, the Commission opted for unilateral action and submission by separate states. "We lost a little time in ironing out the inconsistencies," says Horton, but he points out that uniform standards have recently been approved by the Commission.

What is ORSANCO's future direction? "A most important thing we are doing, and will continue to do, is our river monitoring effort," says Hor-

ton. "We will continue to become a service agency, coordinating what the states can't do for themselves." With new and upgraded standards to be enforced soon, this mission implies surveying the operation of treatment plants now abuilding and determining where new facilities will be needed; ORSANCO's monitoring network will be the backbone of this operation.

In fact, its river-wide monitoring capability will play a major role in most of ORSANCO's future plans, according to Horton. The Commission has just received a federal research and development grant to define river quality forecasting procedures. Such a capability would offer several advantages.

ORSANCO will soon have a role in long-range planning in the Ohio River basin. The Commission will be a member of the recently formed Ohio River Basin Planning Commission, established under the Federal Water Resources Planning Act. Says Horton: "ORSANCO will be the agency for reviewing water quality aspects of long-range planning in the area. Input from our monitoring system will be a major contribution to the planning commission." PJP

ORSANCO's territory covers parts of eight states
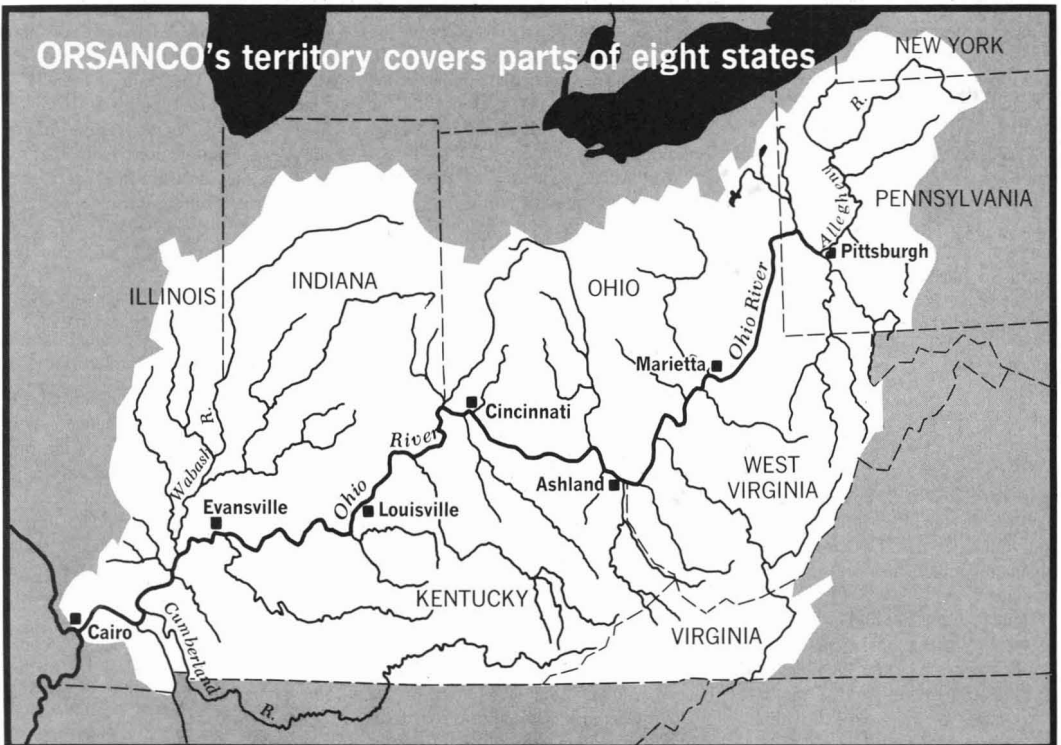
Ion exchangers sweeten acid water

Spanking new treatment plant

in coal region removes mine drainage contaminants

from a community's water supply

A piece of countryside scarred by strip mines is not a pretty sight: a visit to many parts of Appalachia will testify to that. But quite apart from the esthetic destruction that years of grubbing for coal has wrought on the landscape, a more insidious evil has appeared as an unwanted by-product of mining activity—acid mine drainage.

How acids form inside coal mines is a matter of some scientific debate—in the research pages of this publication and in other forums—but it is broadly accurate to say that the sulfur in coal is capable of being oxidized to sulfuric acid in the presence of moisture. In any event, conditions in abandoned mines and within the stripped ground cover left after strip mining machinery has moved on to greener pastures seem to be ideal for acid formation—with unfortunate consequences for any nearby body of water.

The unwanted side products of coal mining have reached such staggering proportions that several states in the eastern U.S. coal belt have been forced to undertake almost Herculean efforts to keep them in check. (See "States make headway on mine drainage," ES&T, December 1969, page 1237.) In Pennsylvania, for example, Operation Scarlift has been launched to spearhead a multipronged attack on mining's legacy of pollution. Pennsylvania voters in 1967 authorized a $500 million bond issue for solution of problems associated with coal mines. The state's Department of Mines and Mineral Industries has $200 million with which to attack problems of mine drainage.

Some of this $200 million has found its way to the small community of Smith Township, some 20 miles west of Pittsburgh, in a part of the state where signs of years of strip mining are all around (the city park and the high school in Burgettstown are built on reclaimed strip mining land). Smith Township is spending $700,-000 to solve a problem it shares with many small communities in Appalachia—you can't drink the water because it is contaminated by acid mine drainage.

Contaminated

Not that Smith Township's water is acid—its pH is in fact around 8, distinctly alkaline. But mine drainage is indeed the cause of the community's undrinkable water. Acid leaching out of mine formations is neutralized by the dolomite, which occurs naturally in this rocky landscape. The result: the township's Dinsmore reservoir is full of water containing a staggering 1000 ppm of sulfates, largely calcium sulfate, and several hundred ppm of carbonates. The water's alkalinity is accounted for by the presence of the smaller quantities of calcium and magnesium carbonates.

Joe Abate, secretary of the Smith Township Municipal Authority, recalls that the community has for years sought ways to reduce the solids content of its water. Studies in the mid-60's conducted in conjunction with the Dow Chemical Co.'s ion-exchange group (then part of Nalco Chemical Co.) initially led the municipal authorities to consider ion exchange as a potential way to clean up their water supply. With the availability of state money in 1968, the township could afford to build a plant embodying an efficient process.

Ion-exchange process

The process that was finally arrived at for the 500,000-gpd Smith Township water treatment plant, now undergoing final shakedown tests, is based on Sul-biSul technology of the Dow Chemical Co. and on a resin handling system developed by Chemical Separations Inc. (Oak Ridge, Tenn.). It employs two ion-exchange steps and an intricate method for regenerating and transporting ion-exchange resins.

In outline, the process operates like this: the incoming raw water is fed to a cation exchanger, where the cations (positively charged ions—Ca^{2+}, Mg^{2+}, etc.) are exchanged for the hydrogen ion in a mixed bed of Dowex HCR-W strongly acidic and Dowex CCR-2 weakly acidic cation-exchange resins. The liquid leaving the cation exchanger contains sulfuric acid and carbonic acid. CO_2 gas is allowed to escape from solution (carbonic acid quickly dissociates) and the liquid, now predominantly composed of sulfuric acid, is passed through the anion exchanger. This exchanger contains Dowex SBR strongly basic anion-exchange resin. The resin is initially in "the sulfate form," and passage of the acid-containing water results in removal of bisulfate ions from the water onto sites on the resin, which then attains "the bisulfate form" (hence, Sul-biSul). The effluent water, when filtered and chlorinated, contains less than 250 ppm of dissolved solids, and doubtless will taste like vintage champagne to those in the township.

Regeneration

While such an overall description illustrates how the ion exchangers work in broad terms, the secret of the process, in practice, almost certainly relies as much on the way the resin beds are regenerated as on the specific ion-exchange properties of the resins themselves. Since, with passage of raw water (through the cation exchanger) and acids (through the anion exchanger), the resins become loaded and lose their effectiveness for further ion exchange, they must at intervals be regenerated.

This means that the hydrogen ion
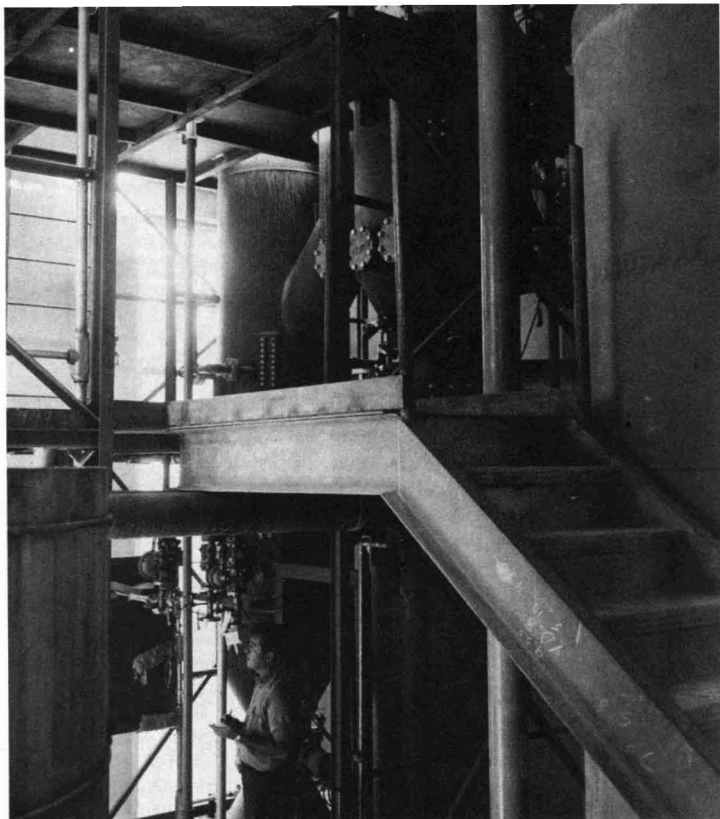
Purification· *Effluent from cation exchanger (not shown) contacts anion-exchange resin in column (far left). Spent resin is regenerated, rinsed, and recycled*

must be put back into the cation-exchange resin, and that the anion-exchange resin must be reconverted from the bisulfate to the sulfate form. Obviously, to stop the whole process while regeneration is carried out would severely limit the overall throughput rate of the whole plant.

What Irwin Higgins, technical director of Chemical Separations, has done is to design a system that regenerates resin in a short cycle during which the resin bed is not being loaded. After regeneration, a brief hydraulic pulse drives the regenerated resin into the loading zone in the ion exchanger (such a pulse is used in both anion and cation exchangers, though not necessarily at the same time, of course).

To achieve complete regeneration and to avoid contaminating product with regenerant, an automatic control and monitoring system is designed into the plant. Work during the plant shakedown period has been aimed at finding exactly the right timing for the regeneration cycle.

Ion exchange would be a very cheap process in many instances were it not

for the necessity to buy regenerating materials. At the Smith Township plant, lime is used to regenerate the anion-exchange resin and sulfuric acid is used to return the hydrogen ion to the cation resins. Both regenerants are fairly cheap—perhaps $20/ton for CaO and $30/ton for H_2SO_4—but, as Higgins explains, some unique wrinkles make the most of the cheap materials. For instance, the Dowex CCR-2 weakly acidic cation-exchange resin is used primarily because of its strong affinity for the hydrogen ion—i.e., its easy regenerability—rather than because it is useful in removing calcium and magnesium cations from the raw water. According to Higgins, presence of this resin in the cation exchanger makes it possible to use sulfuric acid in near stoichiometric amounts for regenerating the mixed-resin bed. Normally, regenerant acid must be used in considerable excess, obviously leading to increased regeneration costs.

To regenerate the anion resin, lime is used, together with a saturated calcium sulfate solution produced as a result of regeneration of both anion and cation exchangers. The calcium

sulfate alone would be sufficient to reconvert the anion-exchange resin to the sulfate form, according to Higgins, but lime is used to neutralize the sulfuric acid produced by regeneration. From the economic standpoint, Higgins points out that only enough lime to neutralize this acid needs to be used. If the acid produced by regeneration could be discarded somehow (back into the reservoir, for instance!), no lime at all would be needed. But, of course, the acid cannot be discharged. Even so, chemical costs will be low: Lou Wirth, Dow's manager of ion exchange, estimates these costs at less than 0.25 cents per 1000 gallons.

The only fly in the ointment that Joe Abate and the Smith Township authorities are concerned with is that their plant, in addition to the potable water, will produce large amounts of calcium sulfate. Although present plans call for the settled calcium sulfate to be trucked away and landfilled, Abate is imbued by the true spirit of ecology: "We'll find a use for that stuff, somehow," he vows.

Economies

The ion-exchange process at Smith Township represents a considerable economy for the community—water treatment costs will be brought down to about 20 cents per 1000 gallons from approximately 50 cents with their old lime and soda ash process, which produced much less drinkable water, as well as being more costly. But when one considers that it costs $700,000 to provide potable water for what amounts to a population of about 10,-000 people, one wonders how much money will have to be spent just to clean up acid-contaminated waters in mining areas. One wonders, too, whether numbers such as the $500 million in the Pennsylvania bond issue may not just be drops in an almost bottomless bucket.   DHMB

Congress makes further progress on antipollution legislation
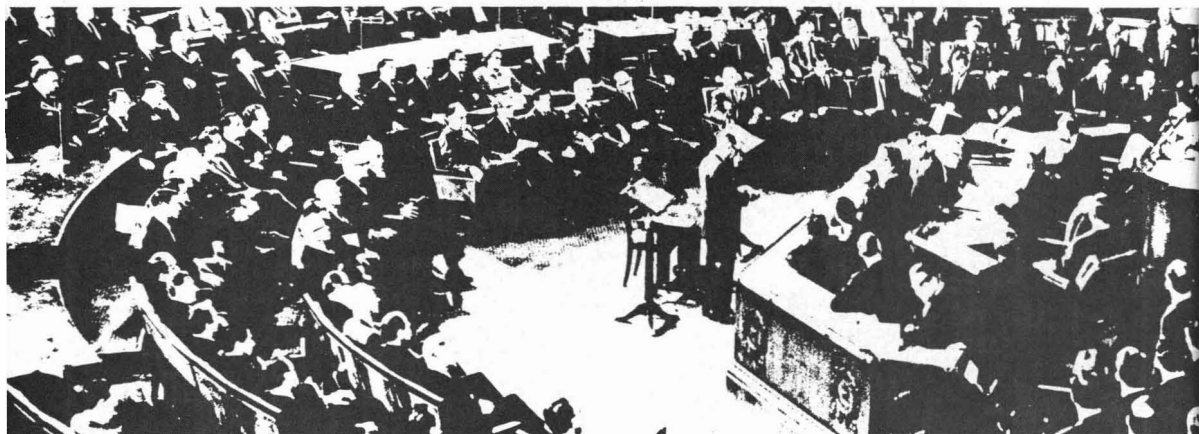
New laws, amendments, and increased appropriations suggest that the nation's lawmakers are paying more than lip service to environmental improvement

Already environment has become a political issue of the 70's. The second session of the 91st Congress will be remembered as the one to hold a lame duck session, the first such session since the late 50's.

On the environmental issue, the session scored high with its amendments to U.S. laws on three environmental fronts—air pollution, water pollution, and solid wastes management. In addition, it will be remembered for its initiation of environmental education and its approval of the reorganization which established the Environmental Protection Agency (EPA). Legislators also voted increased appropriations for federal agencies' environmental programs for fiscal year 1971. Truly, this session set a brisk pace for the nation's antipollution effort.

All in all, there were holding actions as well as gains. But, by any measure, it was a good session. New statutory authority for continuation of the air pollution control and solid waste management programs are certainly gains. Hopefully, these programs will move ahead and their appropriations will not lag the new authorizations. However, in recent years, appropriations for pollution control have consistently fallen short of authorized amounts. For example, $3.4 billion was authorized for construction

of waste water treatment facilities under the 1966 Water Pollution Control Act amendments, but only $1.8 million has actually been appropriated. Similarly, only half of the money authorized by law for air pollution and solid waste management was appropriated.

Conspicuous among the holding actions, the failure to pass new statutory authority for water pollution control is perhaps the biggest disappointment. The Congress, in its wisdom, realized that the statutory authority for air pollution and solid waste expired in fiscal 1970—actually last June 30—and that the water legislation does not expire until fiscal 1971—actually June 30, 1971. So, putting first things first, the air and solid bills were extended. Nevertheless, 14 days of hearings on proposed water amendments were held.

New solid waste law

The Resource Recovery Act of 1970, now P.L. 91-512, is without doubt an important inroad to the nation's solid waste disposal problem, which has been referred to as the poor relation of environmental matters when funds were doled out in the past (ES&T, May 1970, page 384).

Despite the administration's testimony that more federal legislation is not needed and its opposition to solid

waste planning grants (ES&T, November 1969, page 1160), Congress passed the measure. The President subsequently signed it, but what funds are appropriated remain to be seen.

What this solid waste act does, for the first time, is to include funds for:

• Construction of improved solid waste disposal facilities, including innovative facilities.

• Demonstration of areawide resource recovery systems.

Although specific funds for these purposes are deferred till fiscal '72 and '73, some $41.5 million is authorized for grants in fiscal '71 to states as the demand requires. No one state can receive more than 15% of the annual authorization under the law, however.

In addition to the new funds—$80 million for fiscal '72 and $140 million for fiscal '73 earmarked for construction and demonstration purposes—P.L. 91-512 includes $41.5 million in fiscal '71 for grants to states along with $72 million for fiscal '72 and $76 million for fiscal '73 for the remainder of the programs under the Solid Waste Disposal Act (P.L. 89-272).

New water law

The Water Quality Improvement Act of 1970, the biggest disappointment of the first session of Congress,

was signed on April 3. It provided tighter controls on oil and vessel discharges and set the stage for control of hazardous materials and pesticides in the water environment (ES&T, May 1970, page 379).

What the act (P.L. 91-224) did for oil pollution control was to establish the principle of absolute liability for anyone discharging oil into the sea. It empowers the federal government to take emergency action whenever necessary to clean up any spill.

Under P.L. 9-224, the federal government is authorized to take immediate cleanup action in the navigable waters of the U.S., including, for the first time, waters of the contiguous zone, the 9-mile limit beyond the 3-mile limit of the territorial sea. For tankers and barges, the oil-carrying liability is set for $100 per ton, or $14 million maximum; for onshore and offshore facilities, the limit of liability for cleanup is $8 million.

The act also authorized the Secretary of the Interior to set performance standards for sanitation devices on all vessels. By 1972, all new vessels will be required to have certified devices on board; and by 1975, old vessels will be subject to the same requirement.

New air law

The National Air Quality Standards Act of 1970, which was awaiting signature by the President at press time, is certainly the toughest piece of air pollution control legislation ever considered. It has more deadlines per square inch than any other antipollution legislation. The toughest deadline, most probably, is the 1975 deadline for 90% control of automobile exhaust emissions. After much controversy, the Congress stood its ground; automobile manufacturers must now meet the challenge.

Perhaps more important than actual deadlines are the new concepts in air pollution, introduced by the '70 amendments. The new terms include national ambient air quality standards, standards of performance for industrial plants, and certificate of performance, to mention a few.

The public's role is very important under the new legislation. Not only are citizens given the opportunity to instigate action against polluters under certain conditions, but they also can participate in the development of implementation plans. In the past, the public participated in the stan-

dards-setting procedure, under the 1967 Air Quality Act, by commenting at hearings, but its role under the new law is unprecedented.

The term "standards of performance" has not previously appeared in federal clean air legislation. It refers to the degree of emission control which can be achieved through process changes, operation changes, direct emission control, or other methods. It would apply to some 19 stationary emissions sources, including emission standards for 14 selected agents. The standards would become effective in less than two years.

Some of the more important proposals left over from the first session of the 91st Congress (ES&T, February 1970, page 105) also received favorable attention during this session. Perhaps the most important of these is the environmental education bill. Others, namely those pertaining to water amendments, were further sidelined until the new Congress convenes on January 21.

Education act

The Environmental Education Act, now P.L. 91-516, a first in the area of education for environmental matters, establishes an office of environmental education within the Office of Education in the Department of Health, Education, and Welfare, along with a 21-member advisory committee. Financial support to the tune of $45 million in the next three years will provide for the development of multi- and interdisciplinary curricula for levels ranging from preschool to graduate. Further, the curricula for environmental studies will be pilot-tested before they are disseminated.

In the past, environmental education, especially at the elementary and secondary levels, was largely limited

to education in conservation. Environmental education, as defined in P.L. 91-512, is a new umbrella term that covers the educational process dealing with man's relationship to his natural and man-made surroundings. It includes the relation of population, resource allocation and depletion, conservation, technology, and urban and rural planning to the total human environment.

Under the Environmental Education Act, grants will be made available for:

• Preparation and distribution of materials and development of programs suitable for use by mass media.

• Preservice and inservice training programs on environmental quality and ecology.

• Community education programs designed especially for adults.

• Planning of outdoor ecological study centers.

• Initiation and maintenance of environmental education programs at the elementary and secondary school levels (but no support for teaching of environmental studies at the college level).

Another holdover from the first session, S. 3072, the proposal for the procurement of a low-emissions vehicle was included as Section 213 of the new air law, is awaiting signature. This provision authorized the establishment of special low-emission vehicle standards for research and development purposes. More importantly, this section would provide the information needed to determine whether technology is available for a low-emissions vehicle by 1975, the deadline for the automobile industry.

Another item on the environmental fringe was also enacted during this session: The Western Interstate Nuclear Compact, P.L. 91-461, grants approval

New three-year statutory antipollution authorizations

(in millions of dollars)

	Fiscal 1971	Fiscal 1972	Fiscal 1973	Total
Air pollution[a]	$150	$250	$325	$725
Research relating to fuels and vehicles	125	150	175	450
Health effects	15	⟶		15
Noise study	30	⟶		30
Solid wastes (P.L. 91-512)	71	172	239	461
Environmental education (P.L. 91-516)	5	15	25	45

[a] Awaiting signature at press time.

to 13 western states (Alaska, Arizona, California, Colorado, Hawaii, Idaho, Montana, Nevada, New Mexico, Oregon, Utah, Washington, and Wyoming) to engage in peaceful use of nuclear energy. Earlier, on July 1, 1962, Congress approved the southern interstate nuclear compact, P.L. 87-563.

Appropriations

All appropriations for environmental programs of federal agencies show gains over last year's fundings, albeit slim ones. These fiscal 1971 actions serve as strong indicators of Congressional attention to environmental matters. Funds for water pollution in the Public Works appropriations, and for air pollution, solid wastes, radiological health, water hygiene, and pesticides standards, plus research appropriation for the Departments of Labor and HEW—all show gains over last year. Appropriations for Agriculture's pesticides research, AEC appropriations for that agency's environmental radiation standards program, and funding for the Federal Radiation Council form the new focus for environment under the aegis of EPA.

The Public Works appropriation (P.L. 91-439) of $5.2 billion is a slight increase from last year's $4.7 billion, and slight gains are also reported for the specific water pollution control activities of the Federal Water Quality Administration (FWQA). P.L. 91-439 specifies a $1-billion expenditure for construction of waste treatment facilities (up from the $800 million appropriated last fiscal year), and slightly more than a $98-million expenditure for operations and research (up from rather more than $86 million last year) (ES&T, January 1970, page 9).

Traditionally late in gaining final approval, the Labor and HEW appropriations for fiscal '71 call for $112 million for air pollution (up from last year's $102.6 million); $15.3 million for solid waste management (same as last year's funding); $2.3 million for water hygiene; and $16.9 million for radiological health. All increases, however slight, attest to continuing Congressional attention to these matters. Agriculture's appropriations (awaiting signature) of slightly less than $8.1 billion include several items for environmental control. The department's Agricultural Research Service funding for fiscal '71 totals slightly more than $272 million, and includes two components of the EPA: pesticides registration funding for

$5.5 million, and the pesticides monitoring program funded at $746,000.

The foregoing appropriations will all be spent on programs that henceforth will come under the wing of the new EPA, so it is perhaps not surprising that they showed increases over the preceding fiscal year. On the other hand, non-EPA federal environmental activities also showed gains. For example, included in HEW's appropriations is $20.6 million for the National Institute of Environmental Health Sciences (ES&T, April 1970, page 275). Dr. Paul Kotin, NIEHS' first director, told ES&T last April, the institute is dedicated to the establishment of a base of scientific knowledge on which a sound approach to the problems of environmental quality can be built.

Housing and Urban Development's (HUD) appropriations of slightly less than $2.7 billion (awaiting signature) contains three programs with definite environmental quality concerns—HUD's 701 grants programs for comprehensive planning ($50 million), its water and sewer grants program ($350 million), and its open space program ($75 million). In addition, other HUD programs with definite but unquantifiable environmental overtones are its programs for urban renewal ($1.20 billion), its model cities program ($575 million), and its neighborhood facilities grants program ($40 million).

The federal government's attention to noise pollution also shows a slight gain, $34 million in fiscal '71, up from $32 million in fiscal 1970 (ES&T, September 1970, page 720).

Transportation's appropriations of $2.4 billion (not yet finalized) include $210 million (agreed to by House–Senate conferees) for the further prototype development of the Supersonic Transport (SST), which has caused much furor (ES&T, July 1970, page 546). It also contains $35 million for oil spill cleanup, the amount authorized under the Water Quality Improvement Act.

Hearings

Bills on other environmental matters formed the focus of attention for various Congressional committee and subcommittee hearings. Some cleared their respective committees but did not receive floor action; others were acted on by only one house of Congress. These include consideration for the Joint Committee on Environment; House hearings on the Environmental Protection Act, which declares that all

citizens are entitled to a federally guaranteed right to a pollution-free environment; National Environmental Laboratory Act for the conduct of research, development, and analysis of environmental problems; Great Lakes dredging (H.R. 17099) to provide for the construction of contained dredged spoil disposal facilities for the Great Lakes and connecting channels; the motor vehicle emission standards act for used cars; the Intergovernmental Coordination of Power and Environment Act, and the Electric Power Reliability Act (S. 1071).

Next session

No doubt, the statutory authority for water pollution control will be extended by the new Congress when it convenes later this month. Certainly, these proposals will be a number-one priority for the new Congress. No power development act was enacted this session, so the problem of power-plant siting will certainly be another piece of key legislation next session.

Major features of water pollution control bills will include the following proposals:
• New environmental financing authority.
• Effluent charge considerations, earlier introduced by Sen. William Proxmire (D.-Wis.).
• Speeding up the enforcement conference procedures established by existing law, with elimination of the hearing phase (ES&T, November 1970, page 887).
• Inclusion of an effluent discharge requirement as an additional element in a state's implementation scheme to achieve its water quality standard.

With little doubt, other agenda items for the new Congress will include:
• Senate Interior Committee hearings to review activities of the Council on Environmental Quality.
• Sen. Philip Hart's (D.-Mich.) proposal, S. 4496, to set up a national environmental data system.

What actions these issues receive, as they are introduced anew in the next session, will set the continuing pace for the nation's protection of the environment and vital resources—the air, the water, and the land.

The battle between political parties over environmental issues is just simmering; the fighting promises to come to a boil as we move toward the 1972 election. He who wins the title of Mr. Environment may, in fact, turn out to be our next president.   SSM

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22A1

Fuels management in

New criteria for fuels selection, based on environmental awareness,
are replacing the old idea that cheapest is always best

Until the late 1960's, the selection of a fuel for any use was a matter of choosing one with the lowest overall costs, with little regard for its effects on the environment. The rising concern about the environment, however, has changed the traditional concept of what is desirable.

In selecting a fuel, the effects of production, processing, and utilization of each fuel on the land, water, and air must now be considered. This presents a complex situation, since all the principal energy sources—coal, oil, gas, nuclear, and hydro—have differing environmental effects. Moreover, the severity of the pollution trade-offs must be evaluated and decisions must be made as to which fuel is likely to have the least harmful environmental impact.

Two fuels management problems are particularly urgent. The first, automobile fuels, is undergoing rapid change, and little can be done in the short term to replace gasoline as a fuel. The second, generation of electricity, does have much substitutability from competing energy sources. Both pose unique management problems that must be solved if the nation is to benefit from low-cost energy that is produced and used in a manner that does not further degrade our environment.

Energy demand and resources

Energy demand is growing exponentially, and the established trends are expected to continue through 1980. Demand for oil and gas is expected to show the greatest increase in absolute terms; however, in relative terms, the increase in nuclear energy is the greatest. Projecting to the year 2000, many technological, economic, environmental, and political factors will influence the demand and supply for various energy sources. These factors

have been studied by the Bureau of Mines, with the conclusion that demand for each of the most-used fuels—petroleum, natural gas, and coal—will at least double between 1968 and 2000. Uranium, however, will increase by a factor of about 15.

The cumulative requirements for these energy resources are enormous. However, the nation's resource base is adequate to supply the demand through 2000. But, if these demands are to be met, the nation's coal and oil shale resources will have to play an important role, whether they are used to generate electricity or are converted into gases or liquids and used in these more convenient, pollutant-free forms.

The nation's fossil fuel resources are not unlimited, and a maximum of producibility is expected to be reached

early in the next century. Thus, after 2000, the nation's energy demand could set the stage for the emergence of unproved systems, such as nuclear fusion, and the widespread use of solar and geothermal energy.

Imported liquid fuels (crude and residual oils and products) now provide 23% of all liquid petroleum consumed in the U.S. Management of fuel resources to solve environmental problems depends upon policy decisions made with respect to future oil import programs, as well as public land leasing, tax treatment, and prorationing policies which, in turn, are intertwined with other factors of national interest such as military security and balance of payments.

The consumption of fuels must also be considered according to the use—household and commercial, industrial,

U. S. energy consumption is growing by leaps and bounds . . .

1 Quadrillion Btu
Equals 965 Billion cu ft
Gas or 175 Million Bbl
Oil or 38 Million Tons Coal

GAS

NUCLEAR

OIL

HYDRO

COAL

Source: U. S. Department of the Interior
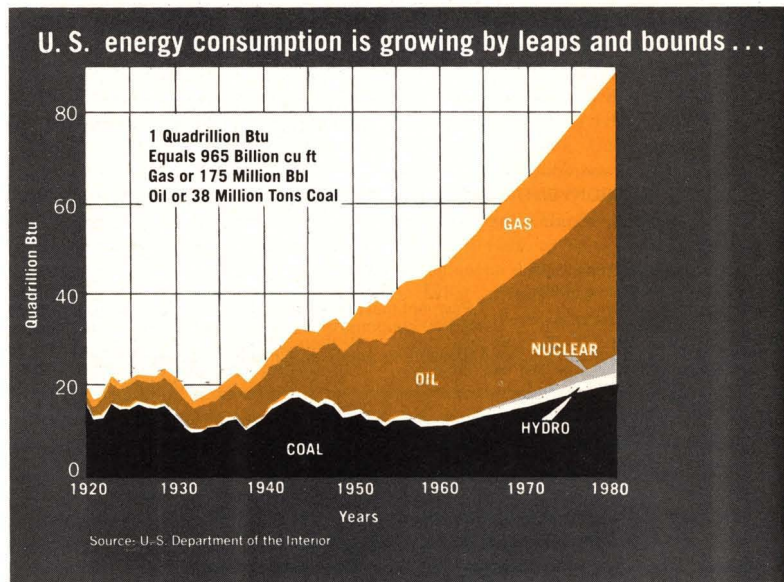
an environmental age

G. Alex Mills and Harry R. Johnson
U.S. Bureau of Mines, Washington, D.C.

Harry Perry
Library of Congress, Washington, D.C.

transportation, or electricity generation. By comparing the expected fuel consumption in the year 2000 with use patterns for 1968 (see table), it can be seen that total gross energy inputs are expected to increase from 62 to 163 quadrillion Btu. Electricity generation will dominate in the future, increasing both absolutely, from 14.0 to 72.3 quadrillion Btu, and as a percent of total gross energy input, from 23 to 44%. Nuclear generation is expected to dominate the generation of electricity, increasing from 0.1 to 38 quadrillion Btu; but coal used for this purpose will increase more than threefold, from 7 to 24 quadrillion Btu.

Consumption patterns of different fuels up to about 1968 are a good indication of the amounts and types of fuels that would be used if environmental problems could be largely ignored. Environmental considerations, however, have begun to alter these supply patterns sharply. For example, sulfur dioxide emission standards in 1969 caused a shift from coal to residual fuel oil at east coast electricity generating plants. By early 1970, the initial penetration of residual oil into the Chicago market had been approved.

The production, processing, and utilization of fuels cause the most environmental problems for the nation. Let us then look at the most significant of these pollution problems, and the impact on land, water, and air.

Land use

About 3.6 million tons of solid wastes are generated each year in the U.S. Agricultural wastes constitute nearly two-thirds of the total, and mineral wastes account for most of the rest. Mineral wastes, not including the large amounts of overburden removed in surface mining but including those wastes generated by mining, processing, and utilization of all minerals and fossil fuels, amount to about 30% of the total wastes. But fuels account for only 125 million tons, or about 3% of all solid wastes generated.

The last complete survey of mining operations in the U.S. indicated that, in 1965, about 3.2 million acres of land had been disturbed by surface mining. Of this total, about 41% resulted from activities associated with coal production.

As yet, only a few tenths of 1% of the total land area of the U.S. has been disturbed by surface mining. Effects of such mining upon the environment, however, vary widely and depend upon such factors as the type of mining, characteristics of overburden, steepness of the terrain, amount of precipitation, and temperature. Where land reclamation is not practiced, water pollution from acid mine drainage and silt damage occur. It is possible, however, to prevent much of this damage through proper land reclamation, adequate drainage, and planting to achieve soil stabilization. In the principal coal mining areas, the average costs of completely reclaiming coal lands range from $169 to $362 per acre, an average cost of 4 to 8 cents per ton.

Underground coal mining can cause subsidence unless the mining systems are designed to prevent deterioration and failure of abandoned mine pillars. Underground fires may weaken or destroy coal pillars that support the surface, causing subsidence with consequent damage to surface structures. An additional threat is the possible collapse of buildings and openings of surface fissures and potholes.

... and all types of consumer are sharing in the increase

figures for 1968 in black; 2000 in color

units are quadrillions of Btu; low fuel use estimates used for year 2000

Consumer	Coal	Gas	Petroleum	Hydro	Nuclear	Gross input	Electricity purchased (sold)	Net input
Household and	0.6	6.5	6.6			13.6	2.5	16.1
commercial		19.1	2.0			21.1	20.0	41.0
Industrial	5.6	9.3	4.5			19.4	2.0	21.4
	2.0	17.5	13.1			32.6	11.0	43.4
Transportation	0.1	0.6	14.5			15.2		15.2
		1.0	35.6			36.6	0.1	36.7
Electricity	7.1	3.2	1.2	2.4	0.13	14.0	(4.5)	
generation	24.2	4.1	0.9	5.1	38.1	72.3	(30.8)	
Totals 1968	13.4	19.6	27.1	2.4	0.13	62.4		52.7
2000	26.2	41.7	51.6	5.1	38.1	162.6		121.1

Source: U. S. Bureau of Mines

Fuel processing also contributes large quantities of wastes during the washing of coal to improve its quality. Over 62% of all coal mined is washed, producing 90 million tons of waste annually. If not returned to the mine, the water accumulates in piles near the plant and mine. At times, these piles ignite and burn for long periods, thus creating air pollution. Rainwater leaches salts and acid from the piles to contaminate nearby streams.

Utilization of coal also produces solid waste in the form of ash and slag. About 30 million tons of these materials are collected each year; an estimated 8 million tons are discharged into the atmosphere.

Uranium mined by either open pit or underground methods creates similar land problems. However, since uranium mining in quantity is a relatively new industry, the volumes and tonnages involved are only 1% of those for coal, and the adverse effects are much smaller. Estimates of the solid wastes from the mining of ore and the subsequent extraction of the desired uranium product are 38 million tons annually.

Solid wastes resulting from nuclear generation of electricity involve only small tonnages of materials, but have a very great potential for environmental damage for long periods because of their radioactivity. As nuclear plants become more numerous, the magnitude of this problem will grow.

Transportation of oil and gas, which is largely by underground pipelines, does not normally produce land problems. However, the special case of transporting oil from Alaska by pipeline raises numerous and, as yet, unresolved land-use problems.

Water problems

Two distinct water problems are of growing concern in fuels management —water quality and water temperature. Questions of quality relate to individual energy sources; thermal problems, however, are common to use of all fuel commodities.

Poor water quality, whether it be through chemical pollution or sedimentation, is a major damage resulting from both surface and underground mining. Available data make no distribution between the two, but it has been estimated that approximately 48% of mine water pollution, primarily sediment, results from surface mining. In the U.S., some 5800 miles of streams and 29,000 surface acres of impoundments and reservoirs are seriously affected by such operations. Acid drainage from underground mines is more difficult to control than that from surface mines, but preventing water from entering the mine and the rapid removal of water which does get into the mine are effective methods for reducing pollution. The effects of acid mine drainage can be reduced by decreasing the amount of acid produced at the source, or by neutralization of the mine water before it is discharged to the streams. The latter technique, though highly effective, is more costly. Erosion and sedimentation from surface mining are serious problems in many areas, but they can be prevented by controlling the surface runoff that follows rainstorms.

In processing uranium ores, some of the potentially hazardous radioactive elements or isotopes, particularly Ra-226 and Th-230, are partly dissolved during the leaching operation used to recover uranium oxide. While most processing plants are located in very isolated areas, steps are taken to avoid pollution of water supplies by radioactive constituents of liquid effluents.

Disposal of the effluent is accomplished principally by impoundment and evaporation, controlled seepage into the ground, and injection through

Most energy sources have significant environmental impacts

Energy Source	Impacts on Land Resource			Impacts on Water Resource			Impacts on Air Resource		
	Production	Processing	Utilization	Production	Processing	Utilization	Production	Processing	Utilization
Coal	Disturbed Land	Solid Wastes	Ash, slag Disposal	Acid Mine Drainage		Increased Water Temperatures			Sulfur oxides Nitrogen oxides Particulate Matter
Uranium	Disturbed Land		Disposal of radioactive material		Disposal of radioactive material	Increased Water Temperatures			
Oil				Oil spills, transfer, brines		Increased Water Temperatures			Carbon monoxide Nitrogen oxides Hydrocarbons
Natural Gas						Increased Water Temperatures			
Hydro									

Recoverable resources are adequate for the next 30 years

Fuel	Fuel consumption per year 1968	Fuel consumption per year 2000	Cumulative demand 1968 to 2000	Estimated recoverable resources
Coal (billions of tons)	0.5	0.9-3.0	27-42	773.5 bituminous coal and lignite 6.5 anthracite
Petroleum (billions of barrels)	4.9	7.3-16.4	195-308	532 crude petroleum 600 shale oil 4 in bituminous rocks
Natural gas (trillions of cu ft)	19.0	34.8-55.7	855-1130	2400
Uranium (thousands of tons)	4.0	61.0-69.0	1190-1540	553 as uranium 527 as thorium (estimate based on approximate current prices)

Source: U. S. Bureau of Mines

deep wells into saline or nonpotable aquifers. Where ore processing plants are adjacent to rivers or streams, the effluents may be released directly to the streams at controlled rates if, after dilution, the concentration is within predetermined limits. During periods of low stream flow, effluents are impounded or may be chemically treated before release.

Onshore oil production, except for accidental occurrences, does not present any difficult pollution problem. Nevertheless, nearly three barrels of brine must be disposed of for every barrel of oil produced. Accidental pollution may occur from blowouts of wells, dumping of oil-based drilling muds, or losses of oil in production, storage, or transportation. At sea, the blowout at Santa Barbara, the oil slicks and the fires and oil spills in the Gulf of Mexico in recent months have demonstrated that these dangers are more than academic in offshore operations. Methods must be found for their prevention and control. Spills and discharges from tankers are also important. However, the greatest, if less dramatic, problem is the contamination of inland waterways and harbors resulting from transfer of oil between or from vessels.

Thermal pollution

By far the most important water problem resulting from fuel use is thermal pollution. Over 80% of all thermal pollution arises from the generation of electricity. The amount of heat rejected to cooling water represents 45% of the heating value of the fuel

used in the most efficient fossil fuel plants, and 55% in nuclear plants. If projected use of electricity is accurate and if nuclear energy, as expected, supplies nearly 50% of the electricity demand, more than 10 times as much heat will be rejected to turbine cooling water in 2000 as is being rejected now. Even with greatly increased use of brines or seawater for cooling, the demands for fresh cooling water will be larger than its supply.

This suggests that the solution is not in treating the heat as a "waste" product. Rather, the heat must be viewed as a resource that can be used. Evolution of such concepts must not be constrained by current uses, for huge amounts of heat may be used in systems not considered practical or feasible at this time. For example, the heating and cooling of whole cities whose environment is controlled by a protective membrane is one possibility.

Air pollution

Nearly 80% of all air pollution in the U.S. is caused by fuel combustion. About 95% of all sulfur oxides, 85% of all nitrogen oxides, and over half of the carbon monoxide, hydrocarbons, and particulate matter are produced by fuel use. Management of fuels, therefore, is critical for the minimization of the nation's air pollution problems.

The most competitive market for fuels is the generation of electricity. Not only do the fossil fuels compete with each other, but they also compete with hydropower and, more recently, with nuclear energy. Obviously,

from an air pollution standpoint, hydropower is the perfect method of electricity generation. During the generation of electricity from fossil fuels, production of oxides of nitrogen or carbon monoxide is not greatly different for any of the fossil fuels used. The production of electricity using natural gas produces no sulfur oxide emissions, but the use of coal and residual oil in electric generating plants is the source of 74% of all the oxides of sulfur emitted into the air.

About seven times as much coal as oil is used in electricity generating plants. For this reason, and because of its relatively high sulfur content, coal accounts for nearly two-thirds of the sulfur oxides emitted to the atmosphere. In addition, nearly one-third of the particulate matter emitted into the atmosphere is from burning coal for generation of electricity.

About one-half of the coal consumed by industry is used to make coke. Part of the sulfur appears in the coke oven gas and, if this is used as a fuel, it eventually appears as sulfur dioxide. The balance of the sulfur remains in the coke and is released as hydrogen sulfide in the blast furnace gas. When the gas is used as a fuel or flared, the sulfur appears as sulfur dioxide.

Local air pollution problems in the vicinity of plants that make coke are severe. Alternatives to the use of coke for the production of pig iron are available, and these processes might reduce the amount of air pollutants released to the air. Uncontrolled surface and underground coal fires emit smoke, fumes, and noxious gases.

About 17% of all the oil consumed in this country is used by industry. Much of it is residual oil, which in most cases is high in sulfur. Moreover, residual oil is difficult to burn efficiently and is usually burned in large equipment at high temperatures. Because of these two factors, industrial use of oil tends to contribute larger amounts of carbon monoxide, hydrocarbons, and oxides of nitrogen than the household and commercial sector, which consume about 25% of the fuel oil.

The largest use of oil is for gasoline to power the nation's 100 million

vehicles. About 42% of each barrel of oil is used in this manner. If we include diesel and jet fuels, about 54% of each barrel of oil is used for transportation.

The use of fuels in transportation causes approximately one-half of all the air pollution in the U.S. There are alternatives to the use of gasoline for automobiles and trucks, such as natural gas and liquefied petroleum gases. But it is doubtful that the massive changeover that would be required by two of the country's largest industries would occur if other solutions could be found to reduce air pollution generated by the transportation sector. Moreover, if a switch to electric cars were made, the total pollution load might actually be increased, although controls would be needed on a relatively few electric power plants, rather than on millions of autos and trucks.

Management problems

Ideally, the management of fuels to satisfy environmental requirements should be guided by a system model that relates energy needs to damage, emissions, and fuel availability. Included in the model would be an assessment of the relative damage among dissimilar pollutants, for example, esthetics of land vs. air pollution, as well as comparisons between a small, constant hazard (nitrogen oxide) vs. a large, infrequent hazard (nuclear). Detailed knowledge of what happens to specific pollutants both geographically and over time would also be included in the model. In addition, economics, supply availability, and the broader question of national security would all need to be examined.

No such model now exists. However, many factors can be approximated so that a number of problems associated with fuel use can be examined. Two such problem areas are the automobile and the generation of electricity.

Autos and air pollution

Much that is written and said about automotive pollution indicates that very little is really being done to change the pollution characteristics of internal-combustion engines. It is alleged that, in fact, little can be done. Such negative views are unwarranted, since both

engines and fuels offer opportunity for modification to reduce markedly the pollution from internal-combustion engines in all applications. Nevertheless, in the long run, other supplementary methods of transporting people may be needed. All of the alternatives proposed to eliminate automobile-caused air pollution have great implications for fuels and materials management.

Some reduction in pollution from the automobile has resulted from federal standards already enacted through 1971. These standards will result in a continuous improvement in air quality through the 1970's as the controlled vehicles comprise an increasingly larger portion of the car population. Unless further progress is made to clean up exhaust emissions, however, an upturn in emission output is expected near the end of the 1970's, as the increasing number of vehicles in use begins to overcome the effects of the standards. Technology is available for continued progress, but lead times of two years or more are required to manufacture and distribute modified fuels and (or) engines. Thus, continued progress will depend upon the decisions made between 1970 and 1975.

The impact of change in fuels and engine design will be far reaching and long lasting. Trends now developing and those established within the next few years will be, in practice, largely irreversible within the next decade. In terms of today's dollar, costs will be higher for each mile driven, and some of the broad options that are now available for fuels manufacture and for designing high-performance engine and fuel systems will be lost.

The types and effectiveness of control methods depend upon the composition of the automobile population in the 1970's. Early in this decade, pre-1968 cars will represent 50% of the automobile population. Even in the last half of the decade, pre-1968 cars will still be a significant part of the population. These vehicles are important, since they generally do not have exhaust-emission controls.

There are options available to reduce pollution from the various automobile populations. Relatively simple engine and fuel-system modifications have been or will be made in 1968–

CO, 63.8
Part., 1.2
SO$_x$, 0.8
HC, 16.6
NO$_x$, 8.1
Transportation
total emissions: 90.5 million tons/year

SO$_x$, 24.4
Part., 8.9
NO$_x$, 10.0
CO, 1.9
HC, 0.7
Fuel combustion in stationary sources
total emissions: 45.9 million tons/year

Part., 7.5
CO, 9.7
SO$_x$, 7.3
HC, 4.6
NO$_x$, 0.2
Industrial processes
total emissions: 29.3 million tons/year

CO, 7.8
Part., 1.1
HC, 1.6
SO$_x$, 0.1
NO$_x$, 0.6
Solid waste disposal
total emissions: 11.2 million tons/year

CO, 16.9
Part., 9.6
SO$_x$, 0.6
HC, 8.5
NO$_x$, 1.7
Miscellaneous
total emissions: 37.3 million tons/year
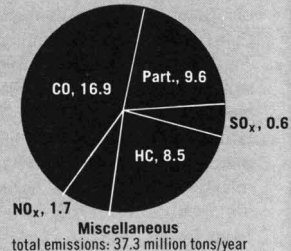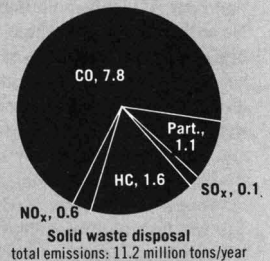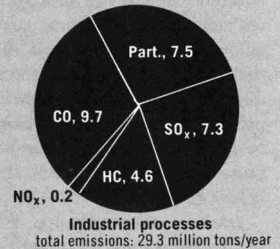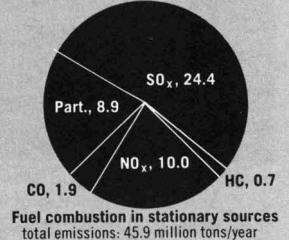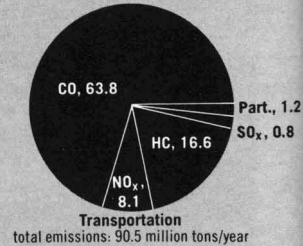
HC — hydrocarbons
CO — carbon monoxide
Part. — particulate matter
SO$_x$ — sulfur oxides
NO$_x$ — nitrogen oxides

Source: CEQ First Annual Report   estimated data for 19

74 model vehicles to meet emission standards. But the major impact of these changes will not be seen until the mid-1970's. Extensive engine redesign and exhaust treatment is expected for the 1975–79 cars. This possibility is widely discussed in the popular press, but the maximum effectiveness of such technology as catalytic conversion of exhaust gases will not be until 1980 or later—a decade away. Gasoline-composition modification is applicable to all cars on the road today, and its effect would be immediate. Engine retuning is mainly for those cars manufactured before 1968, and its effect would also be immediate. Field tests of this control method have met with disappointing public response and, in the absence of compulsory legislation, engine retuning will probably not result in a significant reduction of polluted air.

Changes in the composition of gasoline which limit volatility during the summer months and eliminate C_4 and C_5 olefins would reduce smog by 25% or more, according to recent research by the Bureau of Mines. This is the most rapid solution toward improving air quality, because such modifications can be accomplished quickly and are applicable to all cars now in use, without requiring any changes in the cars themselves. However, the olefins to be replaced have high octane ratings and their removal would make it more difficult to maintain the octane levels of fuels without using lead. Thus, this control method must be carefully coordinated with lead removal if undue losses in engine performance are to be avoided. It has been estimated that the modifications to gasoline can be achieved without significant changes in the product mix from refineries and at a cost to the consumer of less than 1 cent per gallon of gasoline. No estimates are yet available on the cost of accomplishing the same thing with low-lead and unleaded fuels, but the cost should not be significantly higher provided all fuel composition changes are carefully coordinated.

The lead-in-gasoline issue evokes a strange mixture of emotion, politics, and fact. Lead does contribute to the contamination of our environment— nearly 170,000 tons are released an-

Without further restrictions, auto pollution will again increase
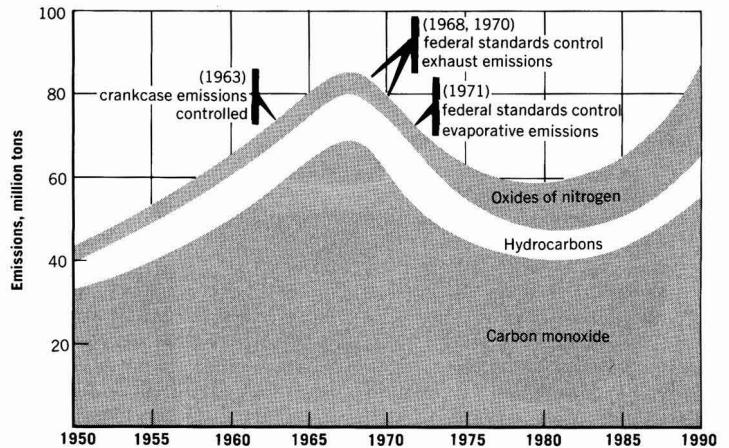
Source: Department of Health, Education and Welfare

nually. It also forms deposits that foul engines and emission-control systems, unless controlled by additives, leading to increased emissions. Of particular importance, it presents difficult problems in developing exhaust-treatment catalysts. For effective use of these advanced control systems, the lead content of gasoline should be near zero.

Any move to modify fuels must be guided by the types of vehicles already in use. Many of these vehicles may have marginal acceptable performance using a low-octane, unleaded gasoline. High-octane unleaded fuels that contain large amounts of aromatics blended into the gasoline could increase the smog-forming potential of the exhaust gases up to as much as 25%, depending on the octane level to be achieved. The cost of manufacturing unleaded gasolines with acceptable octane levels would be reflected in gasoline price increases of 1 to 4 cents per gallon.

The lead issue demonstrates the difficult fuels management problem that has arisen as the result of environmental awareness. For example, if engine compression ratios are lowered to accommodate lower octane unleaded gasoline, the efficiency of the engine may drop and gasoline consumption increase. This would significantly reduce

our already declining petroleum reserves. The manufacture of high-octane unleaded gasoline could set up severe competition for the stocks normally used as raw materials for the petrochemical industry. Significantly greater amounts of new oil may be required, and the needed fractions would be stripped from this oil. In this case, large volumes of oil products without aromatics would need to find a market.

A sweeping change-over to unleaded gasoline would be a massive technical and economic undertaking, the results of which have not yet been adequately delineated. For these reasons, the gradual transition to unleaded gasoline must be encouraged, the timing to depend on the distribution of the existing car population and on the types of vehicles yet to be manufactured.

Materials management will also become vastly more complex in the 1970's. New metal alloys are being developed for use in thermal reactors. A new horizon is opening in the catalytic field—both in refining of modified gasoline and in material for catalytic conversion systems. And, as lead may be removed, a significant jump in the use of additives to maintain engine cleanliness is expected. All of these will have significant impacts on the current use of raw materials.

1970 through 1974

1968-74 cars
50%

pre-1968 cars
50%

1975 through 1979

1975-79 cars
31%

1968-74 cars
54%

pre-1968 cars
15%

. . . but emissions can be controlled on both old and new cars.

Methods of reducing auto emissions	Applicable to	Significant effect beginning
Engine and fuel system modification	1968-74 cars	mid-1970
Engine redesign and exhaust treatment	1975-79 cars	1980 and after
Gasoline composition modification	All cars	Immediate
Engine retune	pre-1968 cars	Immediate

Source: U. S. Bureau of Mines
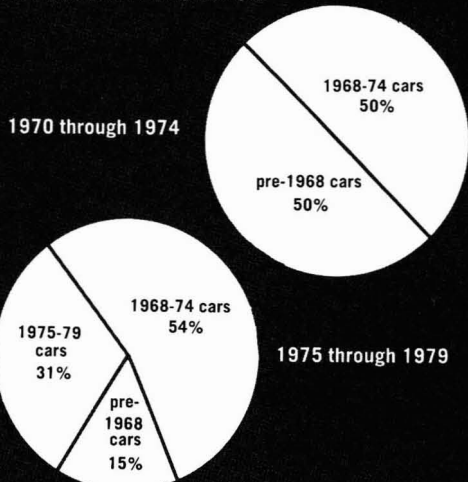
Natural gas (methane) and propane have had wide publicity as substitutes for gasoline. Although these fuels have chemical characteristics that permit cleaner exhausts, the crisis over natural gas supplies, problems of distribution, and the added complexities of the fuel system probably preclude general use by the motoring public. Use of these fuels in urban-operated fleets, however, is feasible and will probably increase in the future. Moreover, synthetic gas from coal or oil shale could be an added source for the needed fuel.

All of the alternatives proposed as substitutes for the internal-combustion engine must meet three key tests: Will there be a significant change in pollution? If so, at what cost? Is near-comparable performance obtained? Ultimately, it may be cheaper to meet air-quality standards by a totally different approach that involves engine systems yet to be developed. Present analyses of all competing systems indicate that, into the 1980's, the best combination of costs, utility, and potential for reduced pollution output is the current gasoline-powered automobile.

The need for further reductions in total pollution output, however, may force a move to limit the size of both the vehicle and the engine. The increasingly severe problem of urban traffic congestion will result in increasing efforts to develop mass-transporta-

tion systems. These pressures may cause a significant reduction in the demand for gasoline. This, when combined with adoption of proven technology that will enable a 95% reduction in all automobile pollutants, indicates that air pollution caused by automobiles can and will be solved. However, the accomplishment of this task will present a challenge of fuels and materials management unexcelled in a peace-time economy.

Sulfur and electricity

The immediate and pressing question concerning fossil fuels for generation of electricity relates to their sulfur content. Of the coals shipped to electric utility plants in the U.S. in 1964, 21% had a sulfur content above 3%, 60% had between 1.1 and 3.0% S, and only 19% had less than 1% S. Regulations being established for sulfur in fuels are based on sulfur dioxide believed allowable in the air. Each community translates its requirements into a certain maximum sulfur content of the fuel. For a number of communities, a 1% sulfur maximum has been established. Obviously, much of the coal being mined and that in the ground cannot meet this requirement. Moreover, some regulations already scheduled call for a fuel having an effective sulfur content not exceeding 0.3%. Such coal is not available, and only exceptional supplies of petroleum

residuum meet this requirement.

The options for solving the sulfur problem are:
- Fuel substitution.
- Fuel preparation (coal).
- Stack gas removal of sulfur oxides.
- Coal and oil shale conversion to low-sulfur fuels.
- New combustion methods.

Substitution of naturally occurring low-sulfur fuel (gas for coal) is not practical in the immediate future since adequate supplies are not available in the U.S. Two promising options for the next several years are removal of sulfur before combustion and removal from the process gases after combustion. Conversion of coal to other low-sulfur fuels and new combustion processes are long-range options.

Fuel preparation

Improvement in coal preparation involves the removal of iron pyrite from coal. Often, the pyrite content accounts for a half of the sulfur in the coal. However, even with improved pyrite removal, it is evident that the degree of sulfur removal necessary to meet anticipated regulations cannot be achieved by this means alone.

Lignitic coal, mostly located in the West, represents a vast national resource, and it typically has a sulfur content of about 0.6%. (The effective sulfur content is a little higher than this, since lignite contains about 7000

Btu/lb, compared with about 12,500 Btu/lb for bituminous coal.) Moreover, lignite is an inexpensive fuel, priced at only about $1.50 per ton, which is equivalent to about 10 cents per million Btu. Lignitic coals should be helpful in certain areas, but obviously do not solve situations where regulations call for 0.3% S. Moreover, lignite deposits are generally far removed from population centers, and shipping costs can be excessive. One possibility is the generation of electricity in huge plants in the West, coupled with a system of long-range, low-cost electrical transmission through a cable cooled to very low temperature.

Stack gas removal

The once-through process for removing sulfur oxides from combustion gases, typified by wet carbonate scrubbing (Combustion Engineering), and being installed in three plants, ranges from 125 to 450 MW. It offers the advantage of relatively low capital investment in plant equipment (perhaps $6 to $13 per kW) and low operating cost ($1.50 per ton of coal). However, it does pose problems in disposal of calcium sulfate (or magnesium sulfate) product—indeed, there is the uneasy fear that an air pollution problem may transform into a land or water pollution problem. It seems likely that with pressure for meeting new regulations, systems such as wet limestone scrubbing will be adopted to some extent in the short-term future.

Regenerative processes for stack gas sulfur removal are expensive to install and to operate. Investments might run from $17 per kW to more than $30 per kW, and operating costs would be in the $3 to $5 per ton of coal range. Such systems involve a solid or liquid which chemically reacts with and removes sulfur oxides. The sorbent is regenerated, in a separate step, usually with the production of sulfur. Included in the "regenerative absorbent" group are potassium bisulfite (Wellman-Lord), magnesia (Chemico), caustic plus electrolytic regeneration (Stone and Webster/Ionic), molten carbonate (North American Rockwell), potassium formate (Consolidation Coal), copper on silica (Houdry), alkalized alumina (Bureau of Mines), and

others. Recently, it was announced that a regenerative-type plant, based on magnesia sorbent and costing $5 million, would be installed in the Boston area.

The conversion-type process is typified by the Monsanto Cat-Ox process. Although well defined, it is relatively costly to install and produces sulfuric acid that may not be desired. Bureau of Mines estimates an investment cost of more than $30 per kW for such a process, and an operating cost of about $4 per ton of coal.

New combustion methods, such as fluidized-bed combustion, offer opportunity for some improvement, if not prevention, of air pollution. However, conversion of a high-sulfur to a low-sulfur fuel appears to present the fundamentally best opportunity for a long-term solution.

Synthetic fuels

From a supply standpoint, natural gas—essentially methane—is now in the most critical stage of all fossil fuels. For the second consecutive year, recoverable reserves have declined—that is, more gas was used than discovered. Yet the use of gas is the most rapidly growing of all the fossil fuels (about 7% annually) compared with a growth rate for energy as a whole of about 3%.

Looking ahead to 1985, projected rates of development will not fulfill the projected need for natural gas, even including importation of gas by pipeline from Canada and Alaska, or by cryogenic tanker from overseas. Anticipating this situation, and in the search for new markets for coal, a vigorous research and development program has been in progress for a number of years to provide processes for conversion of coal to gas. Several processes are currently in advanced stages of development.

Pilot plants are under construction for the Hy-Gas (Institute of Gas Technology) and the CO_2 acceptor processes (Consolidation Coal Co.) under the sponsorship of the Office of Coal Research of the Department of the Interior. Scale-up of the Bureau of Mines steam-oxygen, fluidized-bed coal gasification process has also been initiated.

In the Bureau of Mines process, coal

is reacted with steam and oxygen in a fluidized bed at about 600 to 1000 psi, to produce a mixture of CH_4, H_2, CO, H_2S, and CO_2. After the CO_2 and H_2S are removed, the CO and H_2 are reacted to form additional methane. For a 250-million ft³/day plant, the capital requirement has been estimated to be $160 to $180 million, the manufacturing cost 43 cents/ft³ and selling price 54 cents/1000 ft³ using utility company-type financing. It now appears that if the price of gas increases enough, or if adequate technologic-economic improvement in coal gasification can be made, synthetic gas from coal may soon become a commercial reality.

The price of synthetic pipeline gas noted above is too high to be used by electrical utilities. However, there is a very interesting related possibility—the production of low-Btu gas from coal using air instead of oxygen, followed by sulfur and ash removal, and generation of electricity by gas turbines. In this case, a high-temperature sulfur removal process is needed, to avoid the inefficiency involved in cooling the gas and heating it up again.

Underground gasification of coal and gasification of oil shale offer additional possibilities for gas supply if new technical advances can be achieved. It should be emphasized that all processes contemplated for manufacture of synthetic gases or liquids from coal result in a low-sulfur product.

It is possible to convert coal to liquid fuels, including high-quality gasoline. Moreover, the cost of doing so is approaching the cost of refining gasoline from petroleum. Therefore, probably within the next 15 years, it will be both necessary and economically feasible to make gasoline synthetically.

Another very important possibility which has not yet received emphasis is the conversion of coal to a low-sulfur, low-cost utility fuel. In such a process, coal is contacted with hydrogen and solvent with or without an added catalyst, thus transforming the coal into a new fuel product low in sulfur and ash. It is not important to upgrade the product by removing asphaltenes as in the case of gasoline production. By operation at relatively low pressure and relatively mild tempera-
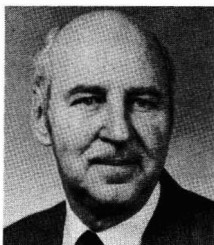
G. Alex Mills, *Chief, Division of Coal, Energy Research, U.S. Bureau of Mines, was until 1968 Director of Research for Houdry Laboratories, Air Products and Chemicals, Inc. Dr. Mills received his degrees from the University of Saskatchewan and Columbia University. He is particularly interested in the conversion of coal to gaseous and liquid fuels.*

Harry Perry *is Senior Specialist in Environmental Policy in the Legislative Reference Service, Library of Congress. Mr. Perry has had a long career in government service, most of it spent in the Interior Department. In 1963, he was made Director of Coal Research in the Bureau of Mines; his last position was Mineral Resources Research Adviser to the Assistant Secretary.*
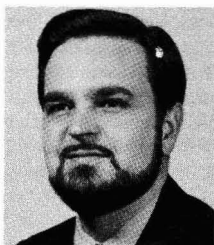
Harry R. Johnson *is a scientific staff assistant to the Chief, Division of Petroleum and Natural Gas, Energy Research, U.S. Bureau of Mines. He is program manager for the Bureau's research program on air pollution from fuel combustion in internal-combustion engines. Mr. Johnson is a graduate of the University of Pittsburgh, majoring in petroleum engineering.*

ture, a minimum of hydrogen is used, so that a low-cost fuel can be manufactured.

Petroleum desulfurization

With new regulations and increased demand, it has become necessary to desulfurize petroleum to achieve a more adequate supply. Fortunately, the petroleum industry has developed effective hydrodesulfurization processes. Of a total of about 14 million barrels of oil produced per day, about 4 million are being desulfurized in the U.S. At present, most desulfurized oils consist of lighter petroleum fractions. Significantly, processes for desulfurizing residua are now coming on stream in different parts of the world. The cost of desulfurization ranges from about 20 to 80 cents a barrel. As an example, for a high-sulfur (2.6%) residuum costing 32 cents per million Btu ($2.00 a barrel), it would cost 4 cents per million Btu for each 0.5% by which the sulfur content were reduced. Desulfurization to 0.5% would thus add 16 cents, bringing the cost to 48 cents per million Btu, a 50% increase over the undesulfurized oil. Costs rise sharply, however, below about 0.5% sulfur.

The natural sulfur content of oil varies greatly. For example, residuum from Algeria is low in sulfur, about 0.5%, whereas that from Venezuela is relatively high, about 3%. No large supply of domestic low-sulfur residuum is available. The importation of a high proportion of utility fuel from abroad poses a problem from the viewpoint of national security since the east coast now imports nearly 94% of its requirements. Part of the current shortage in available residuum is due to its increased initial costs and increased tanker rates.

During the past few years, the substitution of low-sulfur petroleum residuum from abroad for high-sulfur domestic coal has been widely adopted on the east coast, where there is no oil import quota on fuel oil. Moreover, governmental approval recently provided for one plant to use imported residuum in the Chicago area. In this instance, the oil, containing 1% sulfur, will replace coal, at a reported cost of 46 cents per million Btu at that location as compared to about 30 cents for coal. This illustrates forcefully that pollution control is expensive.

New technology

Finally, we should not overlook new energy conversion devices which can become important if certain technological breakthroughs are achieved. Specific cases are fuel cells and magnetohydrodynamics. The former would permit the widespread use of gas for the transmission of energy, followed by generation of electricity, in the home or community.

Management of fuels also should take into account one human habit sometimes not recognized in the fuels system—that is, the production of so-called urban and agricultural refuse. Much of this is organic—for example, urban refuse is about half paper. In the U.S., 7 lb of urban refuse is collected per person per day, and nearly 10 times that amount of agricultural wastes is produced. In the past, urban refuse has been used as landfill or incinerated, causing significant air pollution. Now it is possible to recover energy by controlled incineration, by pyrolysis to make gas and oil, or by hydrogenation to produce a low-sulfur oil. Recent experiments by the Bureau of Mines have shown that heating a ton of garbage to 380°C for 20 minutes in the presence of carbon monoxide and water under high pressure produced over two barrels of low-sulfur oil per dry ton of garbage. Perhaps some such novel means will be necessary for conversion of cellulose, grown by solar energy and discarded by man, into a fuel that can be utilized with less pollution.

Additional reading

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DeCarlo, J.A., Sheridan, E.T., Murphy, Z.E., "Sulfur Content of United States Coals," Bureau of Mines Information Circular 8312, 1965.

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Photochemical Aspects of Air Pollution: A Review

Aubrey P. Altshuller and Joseph J. Bufalini

Division of Chemistry and Physics, National Air Pollution Control Administration, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio 45226

■ The photochemical aspects of air pollution are reviewed through 1964. The topics covered include: nitric oxide oxidation and inorganic reactions, atomic oxygen and ozone reactions, singlet oxygen and its importance to air pollution, aldehyde and ketone photolysis, sulfur dioxide photolysis, synergistic effects, photooxidation of commercial solvents, product formation with emphasis on hydroperoxides, nitric acid and peroxybenzoyl nitrate, reactivity measurements including hydrocarbon consumption, nitric oxide oxidation, oxidant formation and eye irritation, aerosols, natural pollution, and actinometry. The effects of photochemical pollutants on plants are not covered. Suggestions for future research are also given.

Effluents from auto exhaust and stationary sources undergo interesting photochemical reactions, and the manifestations of these reactions in the form of photochemical smog have been observed in many large metropolitan areas throughout the world. Considerable progress has been made in understanding this photochemical smog. With this understanding, some measures for controlling emissions into the atmosphere have been undertaken.

Several reviews have been written on the photochemistry of air pollution and air pollution in general. The classic test of Leighton (1961) is an excellent example of the former; the three-volume treatise edited by Stern (1968) exemplifies the latter.

Our most recent review covered the literature through 1963 (Altshuller and Bufalini, 1965). Since that time, considerable progress has been made, and this paper critically reviews the literature on photochemical smog that has appeared. The older work, pre-1964, is cited only in relationship to the more recent literature.

Photochemical Mechanism

Inorganic Reactions. The photochemical mechanisms applicable to air pollution can be categorized as those involving inorganic and organic substances. Both types of mechanisms were discussed in the earlier review.

Some of the rate constants for the photochemical mechanism for inorganic substances are shown in Table I. These values are different from those given in the earlier review because recent investigations and reinterpretation have doubled the atomic oxygen–molecular oxygen rate constant.

The mechanism for inorganics involves the thermal oxidation of nitric oxide, a product of the combination of N_2 and O_2 in high-temperature combustion processes. The mechanism for oxidation of nitric oxide to nitrogen dioxide was discussed earlier (Altshuller and Bufalini, 1965). Several papers on the oxidation have appeared since. Solc (1966) investigated the oxidation at partial gas pressures between 1 and 50 mm. mercury and found that the formal third-order rate constant calculated from reaction rates near the starting point of the reaction depends upon reactant composition and presence of a third body, M. Morecroft and Thomas (1967) investigated the oxidation at low and high partial gas pressures. Their investigation resulted from an earlier work (Tipper and Williams, 1961) showing that the reaction was pressure dependent. Morecroft and Thomas found the rate constant independent of the O_2:NO ratio and independent of the partial gas pressures at 478° K. At 529° and 593° K., the rate constant was also independent of O_2, NO, and N_2. Greig and Hall (1966)

Table I. Rate Constants for Atomic Oxygen and Atmospheric Pollutants

Reaction	Rate constant at 300° K.	Reference
$O + O_2 + M \rightarrow O_3 + M$	1.5×10^8 l.^{2} mole^{-2} sec.$^{-1}$	Benson and Axworthy (1957)
		Jones and Davidson (1962)
		Kaufman and Kelso (1964)
		Zaslowsky, Urbach, et al. (1960)
$O + NO_2 \rightarrow NO + O_2$	5.3×10^9 l. mole^{-1} sec.$^{-1}$	Schuck, Stephens, et al. (1966b)
$O + NO_2 + M \rightarrow NO_3 + M$	4.2×10^{10} l.^{2} mole^{-2} sec.$^{-1}$	Schuck, Stephens, et al. (1966b)
$O + NO + M \rightarrow NO_2 + M$	2.3×10^{10} l.^{2} mole^{-2} sec.$^{-1}$	Schuck, Stephens, et al. (1966b)
$O + SO_2 + O_2 \rightarrow SO_3 + O_2$	2.7×10^9 l.^{2} mole^{-2} sec.$^{-1}$	Mulcahy, Steven, et al. (1967)

also found the reaction to be second-order with NO and first-order with oxygen. Morrison, Rinker, *et al.* (1966) found that the oxidation of nitric oxide is autocatalytic—*i.e.*, the presence of nitrogen dioxide increases the rate of oxidation of nitric oxide. However, Heicklen and Cohen (1966), in their excellent critique on nitric oxide, pointed out an error in the mechanism proposed by Morrison *et al.*, and observed that the reaction is not autocatalyzed. The nitrogen dioxide, a strong ultraviolet absorber, dissociates back to nitric oxide and atomic oxygen. In the absence of hydrocarbons, nitric oxide and nitrogen dioxide are in equilibrium. This equilibrium is dependent upon uv light intensity (Bufalini and Stephens, 1965), as shown in Equation 1.

$$\frac{(NO)}{(NO_2)} = \sqrt{\frac{2k_3k_a\phi}{k_6k_9(O_2)^2(M)}} \tag{1}$$

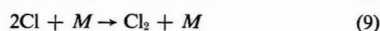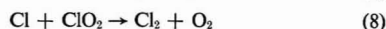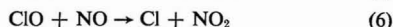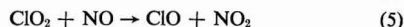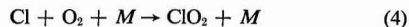where k_3 is the rate constant for atomic oxygen and NO_2, $k_a\phi$ is the primary dissociation constant for NO_2, k_6 is the atomic oxygen–molecular oxygen and third-body (M) rate constant, and k_9 is the thermal rate of oxidation for nitric oxide.

If an atmosphere were polluted with only oxides of nitrogen, the oxidation of nitric oxide would be described by Equation 2.

$$\frac{d(NO_2)}{dt} = k_9(O_2)(NO)^2 - \frac{2k_3k_a\phi(NO_2)^2}{k_6(O_2)(M)} \tag{2}$$

During the period of darkness, the second term in Equation 2 is the only important term and nitric oxide oxidizes at rates shown in Figure 1. At sunrise, the light intensity begins to increase and the third term in Equation 2 begins to contribute. Depending upon the magnitude of the light intensity and the amount of nitrogen dioxide present, the nitric oxide may be oxidized at a lower rate, as shown by the lower curves in Figure 1 $\{[d(NO)/dt] = [-d(NO_2)/dt]\}$ or nitric oxide may be formed by the dissociation of NO_2. The latter will occur if the ratio is less than that prescribed by the equilibrium condition of Equation 1. The atmosphere polluted with only the oxides of nitrogen can be described by two curves, one for nitric oxide, the other for nitrogen dioxide. At night, the dioxide increases to a maximum while nitric oxide decreases to a minimum. During daylight hours, the dioxide is at a minimum and the nitric oxide at a maximum.

An interesting mechanism is put forth by Pierrard (1969) on the photochemical decomposition of lead halides from auto exhaust. Since Hirschler, Gilbert, *et al.* (1957) suggest that one half of lead aerosols is lead bromochloride, Pierrard arrived at bromine and chlorine production rates of 0.2 and 0.1 p.p.b. hr.$^{-1}$, respectively, for Los Angeles (based upon 30 μg. m.$^{-3}$ of lead bromochloride). Halogen atoms can participate in the oxidation of nitric oxide. The chemical mechanism suggested for nitric oxide oxidation is

$$Cl_2 + h\upsilon \to 2Cl \tag{3}$$
$$Cl + O_2 + M \to ClO_2 + M \tag{4}$$
$$ClO_2 + NO \to ClO + NO_2 \tag{5}$$
$$ClO + NO \to Cl + NO_2 \tag{6}$$
$$2ClO \to Cl + ClO_2 \tag{7}$$
$$Cl + ClO_2 \to Cl_2 + O_2 \tag{8}$$
$$2Cl + M \to Cl_2 + M \tag{9}$$

This mechanism can obviously be extended to include hydrocarbons. Perhaps chlorinated and brominated lachrymators will be found in heavily polluted urban areas.

The primary photophysical processes and the quenching reactions of the first excited singlet and triplet states of SO_2 have been studied by Rao, Collier, *et al.* (1969). These investigators determined the fluorescence and phosphorescence rates of SO_2 excited by 2875 Å radiation. The quantum yields of excited SO_2 with biacetyl, CO_2, and O_2 were also determined. Rate constants for various reactions are given. This work is cited not because their results are immediately applicable to air pollution but because the photochemistry for the SO_2 removal mechanisms is virtually unknown in air pollution. Although this work by Rao and coworkers obviously needs to be extended, it is a step in the right direction.

Hydrocarbon Photooxidation Mechanism. The mechanisms for oxidation of nitric oxide in the presence of hydrocarbons and for oxidation of hydrocarbons have been discussed by many investigators. This review does not present the mechanisms, but instead describes more recent additions or modifications of those postulated earlier. These include ozone and atomic oxygen–hydrocarbon reactions, singlet oxygen–hydrocarbon reactions, aldehyde and ketone–hydrocarbon reactions,
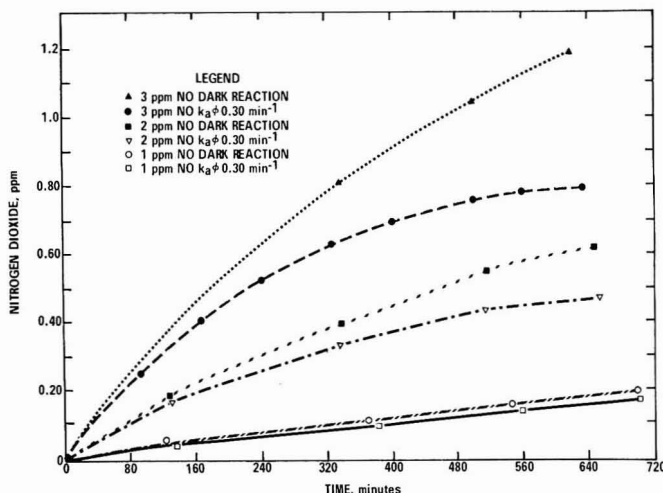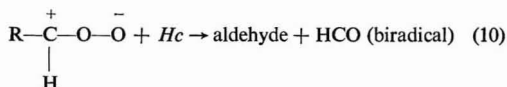

Figure 1. Oxidation of nitric oxide in the absence and presence of ultraviolet light

influence of water vapor on hydrocarbon photooxidation, and SO_2 photolysis in the presence of hydrocarbons.

Ozone and Atomic Oxygen–Hydrocarbon Reactions. The chain-initiating step in the photooxidation of hydrocarbons in the presence of nitrogen dioxide is the atomic oxygen–hydrocarbon reaction. Atomic oxygen arises from the photodecomposition of nitrogen dioxide. Ozone is formed by the rapid reaction between atomic oxygen and molecular oxygen. The chain-initiating step is taken as the atomic oxygen–hydrocarbon reaction and not the ozone–hydrocarbon reaction, since Wei and Cvetanovic (1963) observed 1-to-1 stoichiometry with ozonization reactions involving olefins in the presence of nitrogen but not in the presence of oxygen. This finding strongly suggests that the Criegee zwitterion formed from the dissociation of the initial ozone–olefin addition product does not react further with the olefin—*i.e.*, Reaction 10 is unimportant (Bufalini and Altshuller, 1965).

$$
\begin{array}{c}
\overset{+}{\text{R}}-\text{C}-\text{O}-\overset{-}{\text{O}} + Hc \rightarrow \text{aldehyde} + \text{HCO (biradical)} \quad (10) \\
\mid \\
\text{H}
\end{array}
$$

where Hc = hydrocarbon.

After the initial reactions of atomic oxygen and ozone with the hydrocarbon, several reactive intermediates must be postulated to explain the very rapid rate of disappearance of the hydrocarbon. Since Wei and Cvetanovic found 1-to-1 stoichiometry with the ozone reactions, the free radicals responsible for the so-called "excess-rate" must arise from the atomic oxygen–hydrocarbon reactions.

Some rate constants not shown in the earlier review involving atomic oxygen are shown in Table II. Hydroxyl radical reactions are also shown, since these radicals appear to be responsible for at least part of the excess rate (Bufalini, 1969; Heicklen, Westberg, *et al.*, 1969).

Stephens (1966) investigated the role of oxygen atoms in atmospheric reactions and concluded that no free radicals partake in hydrocarbon consumption. His conclusion is based upon rate ratios—the rate of hydrocarbon consumption divided by the rate calculated for atomic oxygen–hydrocarbon reaction. These rates were obtained from the photooxidation of one olefin in the presence and absence of another olefin, and the difference in rates of reaction in the two systems was noted. However, Stephens observes that these rate ratios are larger early in the reaction when two olefins are present. Also, calculated values for O-atom reactions with propene and butene-1 are about one-tenth those observed. On the basis of these observations, we conclude that Stephens' hypothesis that olefins react only with O-atoms, in the presence of NO, is unjustified.

Some rate constants for ozone–hydrocarbon reactions are shown in Table III. Many of these rate constants are shown not because they differ greatly from those given in the earlier review, but because Williamson and Cvetanovic (1968) recently re-evaluated some of the rate constants. The rate constants obtained by these investigators, as seen in Table III, agree well with those obtained earlier by Cvetanovic and coworkers (Vrbaski and Cvetanovic, 1960; Wei and Cvetanovic, 1963). The rate-constant values of Schuck, Doyle, *et al.* (1960) are slightly larger than those obtained by Cvetan-

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Table II. Rate Constant for Atomic Oxygen and Hydroxyl Radicals with Some Organic Compounds

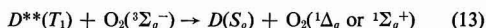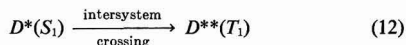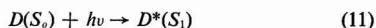| Reaction	Rate constant at 300° K	Reference
O + CH$_3$CHO	4.6×10^8 l. mole^{-1} sec.$^{-1}$	Combined from Cvetanovic (1956) and Elias and Schiff (1960)
	2.4×10^8 l. mole^{-1} sec.$^{-1}$	Cadle and Powers (1967)
O + CH$_4$	3.3×10^6 l. mole^{-1} sec.$^{-1}$ in O$_2$ at 295° K.	Cadle and Allen (1965)
	0.085×10^6 l. mole^{-1} sec.$^{-1}$ in N$_2$ at 295° K.	Cadle and Allen (1965)
O + CH$_4$	0.7×10^4 l. mole^{-1} sec.$^{-1}$ at 298° K.	Westenberg and deHaas (1967)
O + C$_2$H$_6$	5.6×10^5 l. mole^{-1} sec.$^{-1}$ at 298° K.	Westenberg and deHaas (1967)
O + n-C$_4$H$_{10}$	3.3×10^7 l. mole^{-1} sec.$^{-1}$ with O$_2$ present	Allen and Cadle (1965)
	2.5×10^7 l. mole^{-1} sec.$^{-1}$ without O$_2$	
	1.44–1.59×10^7 l. mole^{-1} sec.$^{-1}$ at 307° K.	Herron and Huie (1969b)
O + n-C$_5$H$_{12}$	4.02–4.72×10^7 l. mole^{-1} sec.$^{-1}$ at 307° K.	Herron and Huie (1969b)
O + n-C$_6$H$_{14}$	6.19–6.87×10^7 l. mole^{-1} sec.$^{-1}$ at 307° K.	Herron and Huie (1969b)
O + HCHO	2.1×10^7 l. mole^{-1} sec.$^{-1}$	Niki (1966)
	9×10^7 l. mole^{-1} sec.$^{-1}$	Herron and Penzhorn (1969)
	2.1×10^8 l. mole^{-1} sec.$^{-1}$	Bufalini and Brubaker (1969)
OH + HCHO	$\geq 4 \times 10^9$ l. mole^{-1} sec.$^{-1}$	Herron and Penzhorn (1969)
	6×10^7 l. mole^{-1} sec.$^{-1}$	Avramenko and Lorentzo (1949)
OH + C$_2$H$_6$	1.76×10^8 l. mole^{-1} sec.$^{-1}$	Greiner (1967)
OH + C$_3$H$_8$	8.2×10^8 l. mole^{-1} sec.$^{-1}$	Greiner (1967)
OH + iso-C$_4$H$_{10}$	1.28×10^9 l. mole^{-1} sec.$^{-1}$	Greiner (1967)

Table III. Comparison of Relative Rates of Ozonation of Olefins

Olefin	Vrbaski and Cvetanovic (1960)	Wei and Cvetanovic (1963)	Bufalini and Altshuller (1965)	Williamson and Cvetanovic (1968)	Schuck, Doyle, et al. (1960)
1-Hexene	1.0	1.0	1.0	1.0	1.0
1-Pentene	0.8	0.9		1.1	
Isobutylene	0.8	0.8	2.0	1.3	1.3
cis-2-Butene	2.9	2.7	29	2.1	4.3
2-Hexene	2.7	2.9		1.9	
Trimethylethylene	2.5	2.8	65	2.2	
Tetramethylethylene	3.0	3.8		2.6	
Cyclopentene				2.6	
trans-2-Butene	2.2		38		14.5

ovic's group, but not as large as those obtained by Bufalini and Altshuller (1965). The reason for this large discrepancy is not clear. Bufalini and Altshuller employed lower concentrations ($\sim 10^{-8} M$) than Cvetanovic's group ($\sim 10^{-3} M$), but some of the rate constants obtained by the two groups differ by more than an order of magnitude. Also interesting is that the disagreement is only with the 2-olefins. Williamson and Cvetanovic suggest that this problem may be resolved if a systematic study is made of the dependence of rates of reaction on reactant concentration over several orders of magnitude.

Singlet Oxygen–Hydrocarbon Reactions. An interesting and intriguing explanation of at least part of the reaction of atmospheric hydrocarbons has been put forth by Khan and coworkers (1967), by Kummler, Bortner, et al. (1969), and by Pitts, Khan, et al. (1969). This explanation involves the role of singlet oxygen in the production of photochemical air pollution. The possibility that singlet oxygen may be important to air pollution was first discussed by Leighton (1961), but was discarded since singlet oxygen undergoes very rapid depletion reactions and its rate of production was too low to be important. However, the mechanism that had been assumed for production of singlet oxygen involved absorption in the A and B bands of ground-state oxygen. Since absorption is so weak in this region (7590 to 7660 Å and 6870 to 6920 Å), it was concluded that singlet oxygen could not be important in photochemical smog.

Khan and coworkers (1967) avoided the problem of small concentrations of singlet oxygen produced by direct absorption of radiation. They accomplished this by proposing that a high yield of singlet oxygen can be obtained in a system in which solar radiation is absorbed not by direct absorption by oxygen but by energy transfer. The mechanism was presented as

$$D(S_o) + h\nu \rightarrow D^*(S_1) \tag{11}$$

$$D^*(S_1) \xrightarrow[\text{crossing}]{\text{intersystem}} D^{**}(T_1) \tag{12}$$

$$D^{**}(T_1) + O_2(^3\Sigma_g^-) \rightarrow D(S_o) + O_2(^1\Delta_g \text{ or } ^1\Sigma_g^+) \tag{13}$$

The donor molecule in the mechanism may be any one of a variety of organic compounds that absorb solar radiation beyond the atmospheric cutoff near 3000 Å. The compounds considered as donor are polynuclear aromatics, aldehydes, and ketones. Kummler and Bortner (1969) recently substantiated this mechanism for singlet-oxygen formation by irradiating benzaldehyde–oxygen mixtures with ultraviolet light. A 1.27-μ emission due to $O_2(^1\Delta_g)$ was detected, but unfortunately their experimental apparatus could not determine the concentration of $O_2(^1\Delta_g)$ generated by this mechanism. Formaldehyde–oxygen and acetaldehyde–oxygen mixtures

were also irradiated, but no 1.27-μ emission due to $O_2(^1\Delta_g)$ was detected.

Snelling (1968) also observed the 1.27-μ emission by irradiation of benzene–oxygen mixtures. He assigned this emission to $^1\Delta_g$ oxygen. Kearns, Khan, et al. (1969), and Wasserman, Kuck, et al. (1969) observed the generation of $O_2(^1\Delta_g)$ by paramagnetic resonance with the irradiation of naphthalene and naphthalene derivative with oxygen, respectively. These workers obtained a high concentration of $^1\Delta_g$ oxygen, Kearns reporting 0.5 for the quantum yield. Since these investigators (Kummler and Bortner; Kearns, Khan, et al.; and Wasserman, Kuck, et al.) did not exclude high-energy radiation—i.e., associated with wavelengths below 3000 Å—it is difficult to assess the value of their work in relation to atmospheric conditions.

Kummler, Bortner, et al. (1969) put forth another approach for the generation of singlet oxygen involving the Hartley photolysis of ozone in polluted atmospheres. The photolysis of ozone in the Hartley region (3200 to 2000 Å) is shown in Equation 14.

$$O_3 + h\nu \rightarrow O_2(^1\Delta_g \text{ or } ^1\Sigma_g^+) + O(^1D) \tag{14}$$
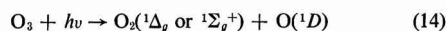
The presence of ground-state molecular oxygen may form more singlet oxygen by an energy-transfer process

$$O(^1D) + O_2(X^3\Sigma) \rightarrow O_2(^1\Delta_g \text{ or } ^1\Sigma_g) + O(^3P) \tag{15}$$
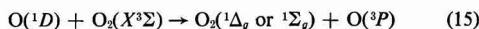
Ozone can then be regenerated by the very fast reaction

$$O(^3P) + O_2(X^3\Sigma) \xrightarrow{M} O_3 \tag{16}$$
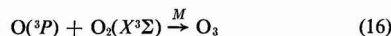
The formation of $O_2(^1\Delta_g)$ by this mechanism requires energy associated with wavelengths below 3100 Å. From the absorption coefficient of ozone and the solar energy available below 3100 Å, Kummler calculated that as much as 3.2×10^{-14} mole/liter of $O_2(^1\Delta_g)$ can be generated when the ozone concentration is 2×10^{-8} mole/liter. Obviously, a different oxygen concentration will be obtained if different ozone concentrations, cloud coverage, and solar zenith angles are considered. Pitts, Khan, et al. (1969) suggest still another mechanism for generating singlet oxygen through the highly exothermic reaction between nitric oxide and ozone.

$$NO + O_3 \rightarrow NO_2 + O_2(^1\Delta_g) \tag{17}$$
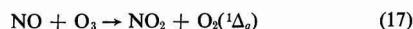
Rao, Collier, et al. (1969) suggest that singlet oxygen can be formed through the spin inversion of SO_2 through the reaction

$$^1SO_2{}^v + O_2(^3\Sigma) \rightarrow {}^3SO_2 + O_2(^1\Delta, {}^1\Sigma) \tag{18}$$
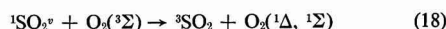
The vibrationally nonequilibrated excited singlet molecule ($^1SO_2{}^v$) is formed by irradiation with 2875 Å energy. It is doubtful that this reaction is a significant source of $O_2(^1\Delta_g)$ in the atmosphere.

The evidence very strongly favors the presence of singlet oxygen $O_2(^1\Delta_g)$ in polluted atmospheres. The problem seems to be the measurement of quantities as minute as 10^{-14} mole/liter.

If the concentration of $O_2(^1\Delta_g)$ is within an order of magnitude of 10^{-14} mole/liter, one must wonder if this concentration is sufficient to be of any importance in the reactivities of olefins and aromatics present in the atmosphere. Kummler, Bortner, et al. (1969), using the "DASA Reaction Rate Handbook" (1967), suggest that the reaction of ethylene with $O_2(^1\Delta_g)$ is the same as that of atomic oxygen, 1.7×10^8 liter/mole sec. If the rate constant is indeed this large, then the rate of reaction of olefins with singlet oxygen is at least as important as their reaction with ozone. Arnold (1966) reported the removal of $O_2(^1\Delta_g)$ by a series of olefins; she found 2,3-dimethylbutene-2 very effective in removing $O_2(^1\Delta_g)$ and obtained a rate constant of $\sim 10^8$ liter/mole sec. for this compound with $O_2(^1\Delta_g)$. Broadbent, Gleason, et al. (1968) obtained a rate constant of 2.5×10^5 liter/mole sec. for the removal of 2,3-dimethylbutene-2 with $O_2(^1\Delta_g)$. This value is considerably lower than Arnold's estimate. Even if one assumes that Arnold's rate constant is correct, the relative rate of reaction of $O_2(^1\Delta_g)$ with ethylene is much lower than for 2,3-dimethylbutene-2 $k_{\text{TME}}/k_{\text{ethylene}} \approx 300$) (Arnold, 1966). This implies that the rate constant for $O_2(^1\Delta_g)$ and ethylene is much lower than 10^8, as assumed by Kummler. A more reasonable value is probably $\sim 10^6$ liter/mole sec. This places the $O_2(^1\Delta_g)$ and ethylene rate constant between those for the atomic oxygen–ethylene and ozone–ethylene reactions—i.e., 1.7×10^8 liter/mole sec. and 2×10^3 liter/mole sec. At an $O_2(^1\Delta_g)$ concentration of $\sim 10^{-14}$ mole/liter, the rate of reaction with ethylene is about 1000 times less important than the ozone–ethylene reaction.

If Broadbent's value of 10^5 liter/mole sec. is chosen and if the relative values of Arnold are valid, then the $O_2(^1\Delta_g)$–ethylene rate constant would be $\sim 10^3$ liter mole^{-1} sec.$^{-1}$ At a recent symposium on air pollution, both Herron (1969) and Pitts (1969) pointed out that the $O_2(^1\Delta_g)$–olefin rate constants are close to the ozone–olefin rate constants. Herron and Huie (1969a) have recently found the rate constant between $O_2(^1\Delta_g)$ and TME to be 10^6 liter/mole sec. Ackerman, Pitts, et al. (1970) found the rate constant between TME and $O_2(^1\Delta_g)$ to be 3×10^5 liter/mole sec. and 1.1×10^3/liter/mole sec. for the ethylene–$O_2(^1\Delta_g)$ reaction. Under actual atmospheric conditions the reaction between $O_2(^1\Delta_g)$ and ethylene would be 10^{-6} that of O_3 and ethylene [again assuming the concentration of $O_2(^1\Delta_g)$ is 10^{-14} mole/liter].

The concentration of $O_2(^1\Delta_g)$ may, of course, be much greater than that assumed by Kummler (10^{-14} mole/liter). If the concentration is $\sim 10^{-9}$ mole/liter, then the reaction of olefins with $O_2(^1\Delta_g)$ may still be important in air pollution. However, it would appear that the 6340 Å emission between two $O_2(^1\Delta_g)$ molecules or the 1.27-μ emission of $O_2(^1\Delta_g)$ would have been observed at such high concentrations.

The reactions considered earlier were energy transfer, Reaction 13, and ozone photolysis, Reaction 14. Both of these reactions cannot be important, since the rate of disappearance of an olefin can be described by the ozone–olefin reaction late in the reaction. If an aldehyde or ketone product is absorbing energy for the energy transfer, more singlet oxygen would result late in the reaction, since more of this product is observed then. However, since olefin disappearance is adequately described by its reaction with ozone, one must conclude that no energy transfer is occurring, or if an energy transfer is occurring, it is much too slight to be important.

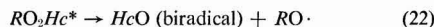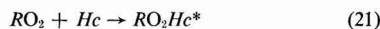There still is the possibility that singlet oxygen is important

in the moderately rapid nitrogen–oxide-induced photooxidation of aromatic hydrocarbons. However, the rate constant for aromatics–atomic oxygen is at least an order of magnitude lower than that for olefins and atomic oxygen, whereas the ozone-aromatic rate constant is two orders of magnitude lower than that for ozone–olefin reactions. It is reasonable to assume that singlet oxygen–aromatic reactions are at least one order of magnitude lower than the atomic oxygen–olefin reactions. If so, singlet oxygen–aromatic reactions would contribute little to the observed overall rates of nitrogen–oxide-induced photooxidation of aromatic hydrocarbons.

All evidence strongly suggests that singlet oxygen is not important in the photooxidation of olefins and aromatics in model laboratory systems. The validity of the foregoing discussion depends, of course, on how well laboratory studies can be extrapolated to actual atmospheric conditions.
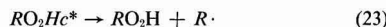
Aldehyde–Hydrocarbon Reactions. As stated earlier, an energy transfer from an aromatic aldehyde to oxygen can produce $O_2(^1\Delta_g)$ that may react with hydrocarbons. However, photodecomposition of aldehydes also can result in free radicals, as shown in these reactions.

$$RCHO + h\nu \rightarrow RCHO^* \tag{19}$$

$$RCHO^* \rightarrow R\cdot + \cdot CHO \tag{20a}$$

$$\rightarrow RH + CO \tag{20b}$$

This mechanism was explored by Altshuller, Cohen, et al. (1966) in the photooxidation of propionaldehyde and by Johnston and Heicklen (1964) with acetaldehyde. The alkyl and formyl radicals will either react with oxygen to produce peroxyalkyl and peroxyformyl radicals or, as is much less probable, will react with olefins and aromatics directly. If the alkyl or formal radicals react first with molecular oxygen, the resulting peroxyformyl and peroxyalkyl radicals can react with an olefin or aromatic

$$RO_2 + Hc \rightarrow RO_2Hc^* \tag{21}$$

$$RO_2Hc^* \rightarrow HcO \text{ (biradical)} + RO\cdot \tag{22}$$

or

$$RO_2Hc^* \rightarrow RO_2H + R\cdot \tag{23}$$

In either case, a chain-propagating step or steps are occurring and the photodecomposition of aldehydes should facilitate the reaction of hydrocarbons. Some of the reactions of methyl and methoxy, as well as ethoxy radicals, were discussed by Hanst and Calvert (1959) and Dever and Calvert (1962).

Altshuller, Cohen, et al. (1967) showed that aliphatic aldehydes, when photooxidized in air with radiation of 3400 Å or lower, will produce intermediate species that react with olefinic and aromatic hydrocarbons. These reactions, even at low concentrations, proceed at significant rates in the absence of nitrogen oxides. These reactions were investigated both with sunlight fluorescent lamps ($E_{\text{max}} = 3100$ Å) and natural sunlight; data are shown in Tables IV and V. Although conversions of aldehyde and olefin mixtures in natural sunlight are shown to be low, the amounts consumed are significant. Comparisons of the rates of reaction of olefins under these conditions with those involving oxides of nitrogen are difficult. Altshuller and coworkers state that the rate of reaction of ethylene is approximately 10 times higher in the presence of nitrogen oxides than its rate of reaction with aldehydes. This comparison was made under the most favorable conditions of $Hc : NO_x$ ratio and with natural sunlight.

Table IV. Photooxidation of Aldehyde-Hydrocarbons in Air Mixtures by Sunlight Fluorescent Lamps

Aldehyde and hydrocarbon	Initial concentration, p.p.m. by volume	Percent reacted with irradiation by hour			Other products identified
		1	2	3	
Formaldehyde	13	66	70	79	Methyl ethyl ketone
2-Methylbutene-1	10	11	23	33	
Formaldehyde	30	57	71	74	Oxidant
2,3-Dimethylbutene-2	10	29	54	74	
Formaldehyde	10	50	62	71	
1,3,5-Trimethylbenzene	10	8	20	29	
Acetaldehyde	32	33	61	74	
2-Methylbutene-1	10	5	20	38	
Propionaldehyde	22	53	79		Acetaldehyde, ethyl hydroper-
Ethylene	10	2	6		oxide, hydrogen peroxide
Propionaldehyde	22	53			Acetaldehyde, ethyl hydroper-
trans-2-Butene	11	9			oxide, hydrogen peroxide
Propionaldehyde	20	49	76	89	Acetaldehyde, methyl ethyl
2-Methylbutene-1	10	7	21	38	ketone, ethyl hydroperoxide
Propionaldehyde	22	51	76	89	Acetone
2,3-Dimethylbutene-2	10	12	32	53	
Propionaldehyde	18	49	75	88	Acetone, methyl ethyl ketone,
2-Methylbutene-1	10	1	8	15	ethyl hydroperoxide, hydro-
2,3-Dimethylbutene-2	10	8	21	36	gen peroxide
Propionaldehyde	18	50		88	Formaldehyde
1,3,5-Trimethylbenzene	10	8		34	

Table V. Photooxidation of Aldehyde-Hydrocarbons in Air Mixtures by Sunlight

Aldehyde and hydrocarbon	Initial concentration, p.p.m. by volume	Percent reacted with irradiation by hour		Other products identified
		5	6	
Formaldehyde	15	61		Oxidant, hydrogen peroxide
2,3-Dimethylbutene-2	10	36		
Acetaldehyde	5	12		Oxidant
2-Methylbutene-1	10	4		
Propionaldehyde	19		25	Acetaldehyde, methyl ethyl ketone,
2-Methylbutene-1	10		10	oxidant, hydrogen peroxide

Ketone-Hydrocarbon Reactions. Another group of oxygenates, the aliphatic ketones, should also contribute to the reaction of hydrocarbons. The primary quantum yield for the photodissociation of acetone at 3130 Å has been reported as 0.9. Acetone dissociates as shown below

$$CH_3COCH_3 + h\nu \rightarrow CH_3CO + CH_3 \quad [I]$$
$$\rightarrow 2CH_3 + CO \quad [II]$$

(24)
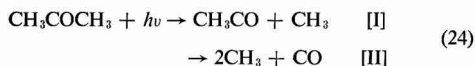
where $\phi_{II}/(\phi_I + \phi_{II}) = 0.07$ at 3130 Å and ambient temperature. Purcell and Cohen (1967a) irradiated acetone and diethyl ketone in the presence of 2-methyl butene-1 and sunlight fluorescent lamps for periods ranging from 1 to 3 hr. Table VI shows the rates of reaction of the olefin and the products resulting from such an irradiation.

Effect of Water Vapor on Hydrocarbon Photooxidation. The effect of water vapor on photochemical reactions pertaining to air pollution was first observed by Haagen-Smit and Bradley (1953). They stated that water vapor was essential for reaction, but gave no data to substantiate this statement.

Ripperton and Jacumin (1963) noticed that humidity has an effect on the photochemical production of oxidant. They irradiated 1-hexene–NO_2 mixtures in air at five different humidities (0, 5.4, 10.8, 16.3, and 21.7 mm. H_2O) and three

different temperatures (14°, 25°, and 35°C.). The highest oxidant concentration was observed when the humidity was 16.3 mm. H_2O for all temperatures except 25°C. At that temperature, the maximum oxidant was observed at 10.8 mm. H_2O.

Dimitriades (1967) reported that humidity affected photochemical processes to a significant degree. Table VII presents data from a series of experiments in which ethylene was irradiated in the presence of NO. These data indicate that the rate of NO oxidation is very sensitive to changes in relative humidity. The formation of formaldehyde is also dependent upon the amount of water vapor present. The increase in oxidant as discussed by the author is partly due to an increase in NO_2 concentration from the more rapid oxidation of nitric oxide in the presence of large quantities of water vapor.

Dimitriades reinvestigated (1969) the effect of humidity on an olefin and extended the studies to include aromatics and two aldehydes. His data are given in Tables VIII to XI. These data show differences but these are not systematic, and one cannot conclude that a humidity effect occurs. Indeed, Dimitriades states that the random influences can be caused by variation in NO_2 to NO_x ratio in the initial charge and by dark reactions occurring after irradiation and during analysis.

Table VI. Photooxidation of Ketone-Hydrocarbon in Air Mixtures by Sunlight Fluorescent Lamps

Ketone and (or) hydrocarbon	Initial concentration, p.p.m. by vol.	Amount reacted during irradiation (percent) time, min.					Other products identified, time, min.		
		38	60	120	150	180	60	120	180
Acetone	10		12.4	23.3		31.9	Total oxidant[a] (0.14)	Formaldehyde[b] (1.82) Hydrogen peroxide[c] (0.03) Methyl hydroperoxide[d] ($T\ ^1/_2 = 33$ min.) Total oxidant (0.267)	Formaldehyde (2.88) Total oxidant (0.352)
Acetone	5		10.2	22.4		34.7			Formaldehyde (0.93) Total oxidant (0.29)
2-Methyl-1-butene	10		2.3	7.0		11.3			
Acetone	10		11.4	23.8		32.4			Formaldehyde (1.8) Total oxidant (0.49) Slow oxidant ($T\ ^1/_2 =$ 32 min.)
2-Methyl-1-butene	10		4.5	8.6		15.8			
Acetone	20		12.2	23.6		33.5			Formaldehyde (3.84) Total oxidant (0.84)
2-Methyl-1-butene	10		7.8	17.6		28.7			
Diethyl ketone	3	17.3	24.7		69.3	76.7	Ethyl hydroperoxide ($T\ ^1/_2 = 50$ min.)		

[a] Ferrous thiocyanate method (absorbance per 1-liter sample).
[b] Chromotropic acid method (p.p.m.).
[c] Titanium-8-quinolinol method.
[d] Kinetic colorimetry with molybdate-catalyzed KI.

Table VII. Reactivity Levels from Irradiation of 1.65 p.p.m.C Ethylene + 0.50 p.p.m. NO in the Presence of Various Water-Vapor Levels

H_2O (mm. Hg)	Relative humidity at room temp. (77° F.), (%)	Relative humidity at chamber temp. (93° F.), (%)	Reactivity level			Max. oxidant level (p.p.m.)	Max. oxidant formation rate (p.p.m./min.)
			R_{NO_2} (p.p.m./min.)	Oxidant (p.p.m. $\times$ min.)	HCHO (p.p.m. $\times$ min.)		
0.5	2.0	1.5	0.00193	23.7	123.9	0.23	0.0014
3.9	16.4	11.7	0.00265	28.9	121.9	0.27	0.0017
7.2	30.2	21.6	0.00351	42.4	145.4	0.28	0.0021
11.8	49.6	35.4	0.00482	48.6	171.7	0.27	0.0022

Table VIII. Reactant Disappearance and Product Formation in Photooxidation of Propionaldehyde at Different Humidity Levels

Ambient Temperature, °F.	Test no. 1 58		Test no. 2 45		Test no. 3 63	
Absolute humidity, %	<0.03	0.90	<0.03	0.90	<0.03	1.21
Aldehyde consumption, %	12.0	9.5	39.6	35.7	60.0	60.0
Formaldehyde, p.p.m.					0.005	0.006
PAN, p.p.m.	0.009	0.03	528[a]	408[a]		
MeONO$_2$, p.p.m.						
PPN, p.p.m.	0.3	0.40	776[a]	376[a]		
EtONO$_2$, p.p.m.	0.019	0.019				

[a] The data represent peak heights rather than p.p.m. concentrations. Calibration of analytical system was omitted.

Table IX. Reactant Disappearance and Product Formation in Photooxidation of *iso*-Butyraldehyde at Different Humidity Levels

Ambient temperature, °F.	Test no. 1 85		Test no. 2 65		Test no. 3 67		Test no. 4 50	
Absolute humidity, %	<0.03	1.75	<0.03	0.90	<0.03	0.90	<0.03	0.90
Aldehyde consumption, %	31.9	29.4	36.8	31.8	39.5	40.4	50.0	44.9
Formaldehyde, p.p.m.	trace	0.3						
Acetone, p.p.m.							2.7	2.8
PAN, p.p.m.								
MeONO₂, p.p.m.					0.001	0.001		
PPN, p.p.m.					0.01	0.01		
EtONO₂, p.p.m.					0.001	0.001	0.005	0.003
i-PrONO₂, p.p.m.					59.0[a]	62.5[a]	57.2[a]	58.5[a]

[a] The data represent peak heights rather than p.p.m. concentrations. Calibration of analytical system was omitted.

Table X. Reactant Disappearance and Product Formation in Photooxidation of Propylene at Different Humidity Levels

Ambient temperature, °F.	Test no. 1 76		Test no. 2 85	
Absolute humidity, %	<0.03	1.75	<0.03	1.75
Olefin consumption, %	66.8	66.2	78.6	78.4
Formaldehyde, p.p.m.			5.5	5.5

Shortly after the appearance of Dimitriades' article on the photooxidation of ethylene and the effect of water vapor on such an oxidation, Bufalini and Altshuller (1969) studied the effect of water vapor on several systems. Tetramethylethylene, *n*-butane, butene-1, and mesitylene were investigated at relative humidities of 5 and 50%. Neither the rate of hydrocarbon reaction, nitric oxide oxidation, nor ozone production increased with increasing water vapor. Since no effect was observed with the four hydrocarbons mentioned, the work was repeated with ethylene, since Dimitriades observed a water vapor effect with this compound. At an $Hc:NO_x$ ratio of 1:40 with relative humidity at 13%, after 3-hr. irradiation ($ka\phi = 0.24$ min.⁻¹), 13.1 and 15% of the ethylene reacted in two replicate runs. With an $Hc:NO_x$ ratio of 1.36 and relative humidity of 48%, approximately 16% of the olefin reacted. At a higher $Hc:NO_x$ ratio of 2.7, the amount of hydrocarbon reacted was 13.5% when relative humidity was 48.5%. Therefore, no water vapor effect was observed with the photooxidation of ethylene when the humidity was increased from 13 to 48%.

Wilson and Levy (1969) recently investigated the effect of water vapor on the photooxidation of 1-butene and NO_x mixtures. Some of their data are shown in Figure 2. Both the maximum oxidant and steady-state oxidant concentrations are lower at the higher relative humidities. The olefin seems to react more quickly in the presence of large quantities of water vapor, but the steady-state concentration is higher, an indication that less olefin has reacted. Especially interesting is that an increase in relative humidity in this system caused a decrease in oxidant production. Dimitriades (1967) reported an opposite effect for ethylene–NO_x mixtures.

It is difficult to account for an increase in reactivity by the addition of water vapor. It does not appear likely that the water molecule would partake in the free radical mechanism for hydrocarbon photooxidation. The observations that have been reported may have resulted from very reactive walls on the reaction chamber. A large portion of the free radicals produced in the photooxidation of hydrocarbons may be destroyed by the walls of such a chamber. Introducing a large quantity of water vapor may deactivate these sites on the walls of the reactor, extending the lifetime of the free radicals and thus enabling them to react further with the hydrocarbons.

Another approach does not involve hydrocarbon free radicals

$$NO + H_2O + NO_2 \rightarrow 2HNO_2 \qquad (25)$$
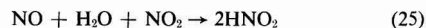
The equilibrium constant for this reaction is $K = 1.65$ atm.⁻¹ Leighton (1961) calculated the amount of nitrous acid formed when $NO_2 = 10$ p.p.h.m., $NO = 1$ p.p.h.m., and $H_2O = 2 \times 10^6$ p.p.h.m. (63% relative humidity at 25° C.). The calculated rate is only 0.5 p.p.h.m. hr.⁻¹, and the equilibrium concentration of HNO_2 is only 0.6 p.p.h.m. This value seems to be much too low to be of any importance in photochemical reactions. Had the reaction been more rapid, the HNO_2 formed could act as a hydroxy-free radical source upon photodecomposition. This would facilitate hydrocarbon reaction.

Another possibility for water-vapor effect is the reaction

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (26)$$

Table XI. Reactant Disappearance and Product Formation in Photooxidation of *m*-Xylene at Different Humidity Levels

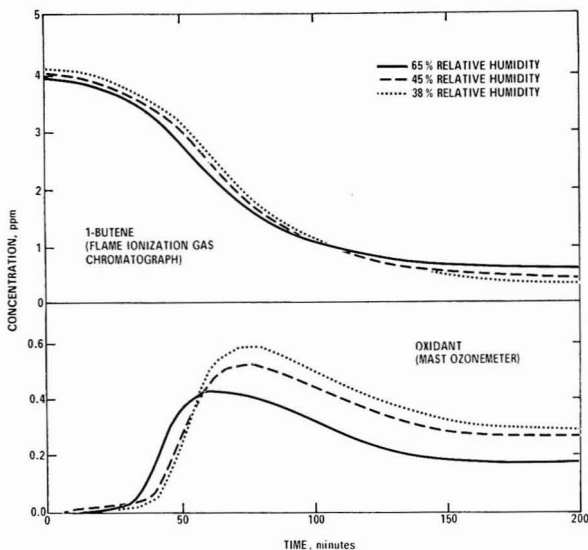| Ambient temperature, °F.	Test no. 1 86		Test no. 2 78		Test no. 3 77		Test no. 4 50	
Absolute humidity, %	<0.03	1.75	<0.03	1.75	<0.03	0.90	<0.03	0.90
Xylene consumption, %	22.2	21.1	30.9	26.5	38.3	39.0	44.0	39.0
Formaldehyde, p.p.m.	0.34	0.34	trace	0.4				
PAN, p.p.m.					0.55	0.40	0.85	0.81
MeONO₂, p.p.m.					0.002	0.002	0.004	0.004

Figure 2. 1-Butene (4 p.p.m.) irradiated with 1 p.p.m. of nitric oxide at three relative humidity levels

The N_2O_5 can presumably arise from the reaction of nitrogen dioxide with NO_3, the latter formed by the reaction of either ozone or atomic oxygen with NO_2. There is some basis for Reaction 26 since nitric acid has been observed as a photo-oxidation reaction product (Gay and Bufalini, 1969). However, Reaction 26 does not really aid in explaining the increase in reaction rate for the photooxidation of hydrocarbons. Nitric acid has a low absorption coefficient ($\alpha = 1$ liter mole^{-1} cm.$^{-1}$) at 3000 Å (Leighton, 1961). This reaction will therefore render the oxides of nitrogen inactive for photolytic processes and give the effect of increasing the $Hc:NO_x$ ratio. In the photooxidation of ethylene in the presence of nitric oxide, Dimitriades worked with an $Hc:NO_x$ ratio of 3.3:1. According to the work of Altshuller and Cohen (1964), the minimum half-life for ethylene consumption should occur at an $Hc:NO_x$ ratio of 5:1. Since Reaction 26 removes NO_x, the $Hc:NO_x$ ratio probably more closely approaches 5:1 and the ethylene reaction should increase. The importance of this argument can be verified by observing the rates of consumption of NO_x at high and low relative humidities and initiating the reaction at $Hc:NO_x$ ratio of 5:1 for ethylene. No definitive statements can be made concerning the role of H_2O in photooxidation reactions involving hydrocarbons and NO_x until these measurements are made and the role of surface sites eliminated.

SO_2 Photolysis with Hydrocarbons. The photolysis of SO_2 in the presence of hydrocarbons and other materials was investigated by Urone and coworkers (1968). They found a rate of 1 to 3% per hour for SO_2 in the presence of hydrocarbons but only 0.1% in their absence. Water vapor did not affect the reaction rate except when the relative humidity was 100%, at which high value the rate of SO_2 disappearance increased.

The reaction of SO_2 with inert solids such as sodium chloride and calcium carbonate was slight. Heterogeneous reaction rates with iron oxide were much greater than homogeneous photooxidation reactions for SO_2. The heterogeneous reactions were complicated by the tendency for absorption of SO_2 by the particles of high specific surface area. In this respect, the heterogeneous reaction work is of questionable value.

This work of Urone and coworkers is unfortunately largely empirical. No mechanism is put forth that would extend our knowledge of SO_2 photooxidation beyond the work of Schuck and Doyle (1959) and Renzetti and Doyle (1960). Also, it is doubtful whether 10-min. irradiations are comparable to "more than an hour of noonday sunlight." Employing a light intensity seven times greater than noonday sunlight does not necessarily result in reaction rates seven times greater.

Recently, Calvert, Gall, *et al.* (1969) investigated the photo-oxidation of azomethane in the presence of SO_2. The reaction between methyl radicals and SO_2 was complex, with the data showing a third-order nature. This work should be extended to the RO_2 and SO_2 reaction to obtain the oxygen atom transfer reaction ($RO_2 + SO_2 \rightarrow RO + SO_3$).

Photooxidation of Commercial Solvents. Studies of the kinds and quantities of solvents in the atmosphere have been made in Los Angeles County (Brunelle, Dickinson, *et al.*, 1966; Hamming, 1967). These studies indicate that emissions of organic solvent vapors have increased from 445 tons per day in 1963 to an estimated 590 tons per day in 1966. The studies also indicate that emissions from various organic solvents averaged about $1/6$ lb. per person annually for Los Angeles County and that total emissions would increase with increasing population. Solvent emissions account for over 20% of the total hydrocarbons.

The results of the surveys show that the reactivities of commercial solvents can be listed in the following decreasing order:

> Xylenes and heavy aromatics
> Isophorone
> Toluene
> Methyl isobutyl ketone
> Trichloroethylene
> Naphthene
> Mineral spirits
> VMP solvent
> Stoddard solvent
> Isoparaffin mixtures
> *n*-Paraffin mixtures

Benzene, perchloroethylene, chloronated saturated hydrocarbons, and acetone were virtually unreactive.

Especially interesting in the list is trichloroethylene (TCE). Kopczynski (1968) briefly studied this compound and found it moderately reactive; the data are summarized in Table XII. Values for ethylene and propylene are also shown for comparison. On the basis of NO_2 formation, rate of oxidant formation, maximum oxidant concentration, oxidant dosage, and rate of disappearance of the compound, TCE must be considered to be between propylene and ethylene in reactivity.

Formaldehyde is not produced from the irradiation of trichloroethylene (Table XII). No formaldehyde would be expected, since the fragmentation products do not contain a sufficient number of hydrogens to form formaldehyde. However, the eye irritation index is higher for TCE than for either propylene or ethylene. Since no formaldehyde was observed, it must be concluded that another more potent type of eye irritant is formed. Although this irritant has not been identified, it is reasonable to assume that it is phosgene, another known eye irritant.

Wilson, Doyle, et al. (1969) also observed eye irritation from the photooxidation of TCE but to a lesser extent than that observed by Kopczynski. Wilson observed an eye irritation index of 0.58 for TCE after 6.3 hr. irradiation; for ethylene, the value was 0.71 after 5.4 hr. Wilson observed the nitrogen dioxide maximum for TCE at 2 hr. and for ethylene at 1 hr., whereas Kopczynski's data show 113 min. for TCE and 150 min. for ethylene. Both investigators observed that TCE reacted more quickly than ethylene after 6 hr. irradiation.

It is difficult to understand why Wilson observed lower eye-irritation levels. The photooxidation of trichloroethylene, as stated earlier, should produce phosgene and probably formyl chloride; both of these compounds should be very strong eye irritants.

Synergistic Effects in the Photooxidation of Organic Substances

A synergistic effect is one in which the reactivity or the amount of product produced by a given compound is affected by the presence of a second. Some indications of this effect were observed by Nicksic, Harkins, et al. (1964) with the photooxidation of ethylene. When ethylene was irradiated in the presence of oxygenates and certain aromatics, more formaldehyde was produced. This occurred not because more formaldehyde was produced per molecule of ethylene reacted, but because more ethylene reacted. Thus, we notice in Figure 3 that when 5 p.p.m. of acetone was added to the base run (5 p.p.m. ethylene + 6 p.p.m. NO_2) the amount of ethylene reacting increased from 53 to 83%. These data do not show whether the increase in reactivity was due to a decrease in $Hc:NO_x$ ratio; that is, it would not be at all surprising to note an increase in reactivity of ethylene if the $Hc:NO_x$ ratio were increased from 5:6 to 5:3. Synergistic effects were more apparent in the presence of other olefins; however, even in these cases, the effects were partly due to changes in the $Hc:NO_x$ ratio. Thus, with $Hc:NO_x$ ratios of 6:1, 1:1, and 1:4, the amount of ethylene reacted was approximately 40%. When 5 p.p.m. of propylene was added to 7 p.p.m. of ethylene with 1, 6, or 24 p.p.m. of NO, the amounts of ethylene reacted were 43, 65, and 52%. When 5 p.p.m. of trans-2-butene was added to approximately 6 p.p.m. of ethylene with 1, 6, or 24 p.p.m. of NO, the amounts of ethylene reacted were 24, 50, and 47%. When both 5 p.p.m. of propylene and 5 p.p.m. of trans-butene-2 were added to 6 p.p.m. of ethylene, the amounts of ethylene reacted increased to 27, 47, and 75%. The nitric oxide concentrations were again 1, 6, and 24 p.p.m.

The low reactivities of ethylene in the presence of 5 p.p.m. of trans-butene-2 (24%) and in a mixture of 5 p.p.m. of trans-butene-2 and 5 p.p.m. of propylene (27%) must be due

Table XII. Reactivities of Trichloroethylene, Propylene, and Ethylene

Reactivity measurement		Trichloroethylene	Propylene	Ethylene
NO_2 formation rate for $1/2$ conversion of NO, p.p.b./min.		15	29	14
Time for NO_2 max., min.		113	55	150
NO_2 dosage, p.p.m./min.		360	155	291
NO_x reacted at 6 hr., p.p.m.		1.32	1.51	1.49
NO_x reacted at 6 hr., %		88	88	92
Oxidant formation rate[a] =	KI	2.1	8.9	2.4
$\dfrac{\text{oxidant, max.,}}{2\,T_{1/2}}$ p.p.b./min.	Mast[b]	2.4	4.1	2.0
Max. oxidant, p.p.m.	KI	1.02	1.23	0.99
	Mast[b]	1.21	0.98	0.90
Time to max. oxidant, min.	KI	360	123	340
	Mast[b]	360	360	360
Oxidant dosage, p.p.m./min.	KI	122	333	153
	Mast[b]	138	215	117
Max. CH_2O formed, p.p.m.		0	2.0	1.7
Eye irritation index at 6 hr. (clean air = 0.25)		1.89	1.38	1.14
Organic reacted in 6 hr., %		94	100	74
$1/2$ Time for organic disappearance, min.		157	69	225
$1/4$ Time for organic disappearance, min.		74	49	104

[a] Corrected for NO_2.
[b] Mast values multiplied by 1.5.
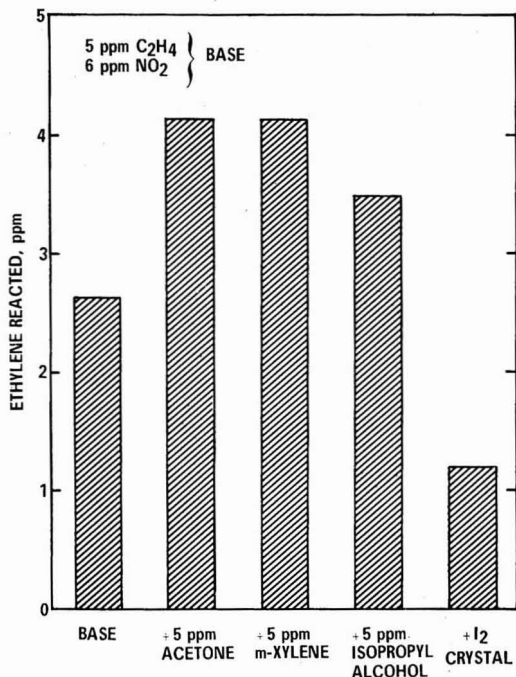
Figure 3. Effect of other compounds on the amount of ethylene reacted

ated alone and 0.25 p.p.m. when irradiated with other olefins. The same percentage reacted, with different starting concentrations.

Dimitriades (1969) observed a synergistic effect in the photooxidation of 1-butene-1-C^{14} in the presence of added hydrocarbons and aldehydes. These data are shown in Table XIII. The amount of formaldehyde-C^{14} and CO^{14} formed from 1-butene-1-C^{14} apparently is independent of added hydrocarbons. The mechanism for oxidation and subsequent fragmentation of 1-butene-1-C^{14} probably is not altered by the presence of other reactive hydrocarbons. Note the inhibitory effects of acetaldehyde on the photooxidation of butene-1. Acetaldehyde apparently alters the mechanism by which butene-1 undergoes reaction. In this connection, notice also the high concentration of CO_2^{14} formed.

We (Bufalini and Altshuller, 1967) have also investigated synergistic effects in the photooxidation of mixed hydrocarbons. Figure 4 shows the half-life of butene-1 as a function of NO_2 concentration. Both the half-life and the shape of the curve for butene-1 consumption are shifted significantly with *trans*-butene-2. Similar results obtained with mesitylene are shown in Figure 5.
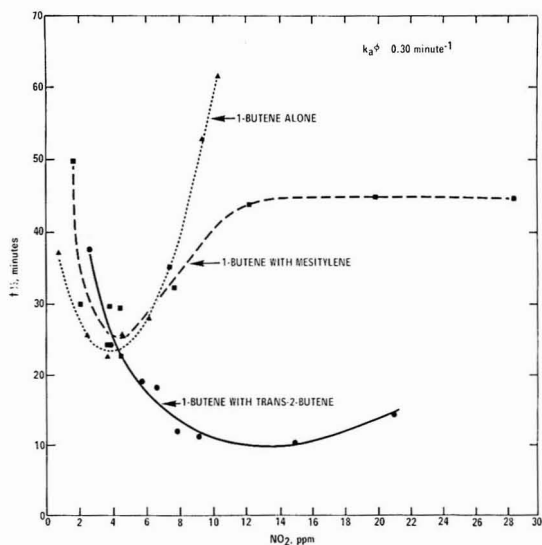
Figure 4. Half-life of 9.6 p.p.m. of 1-butene both alone and in the presence of either *trans*-2-butene or mesitylene

to the high $Hc:NO_x$ ratio since the nitric oxide concentration in both experiments was only 1 p.p.m. The nitric oxide is probably consumed very early in the reaction by the more reactive hydrocarbon. At the 6-p.p.m. level of NO, the reactions in both cases were greater than that when only ethylene and NO were present. This indicates that a synergistic effect is taking place and that some product (or products) is being formed from the more reactive olefins, a product that reacts further with ethylene.

Altshuller, Klosterman, et al. (1966) also investigated the photooxidation of ethylene; their results essentially agree with those of Nicksic, Harkins, et al. (1964). When 0.5 p.p.m. ethylene and 1 p.p.m. of NO were irradiated alone or in a multicomponent olefin–nitric oxide system, the amount of ethylene reacted was between 27 and 29%. Whether synergistic effects were occurring in this system is difficult to determine. The ethylene concentration was 0.51 p.p.m. when irradi-

Table XIII. Extents of Reaction and Product Yields from NO_x-Sensitized Photooxidation of 1-Butene-1-C^{14} in Presence of Added Hydrocarbons or Aldehyde

Hydrocarbon reactants[a]	Extent of butene[b] reaction, %	Product yield[c]	
		(HCHO + CO)[b]	CO_2[b]
Butene[b]	33.7 ± 0.4	1.00 ± 0.02	0.021 ± 0.002
Butene[b] + 1-butene	66.9 ± 1.1	1.00 ± 0.04	0.026 ± 0.002
Butene[b] + propylene	72.7 ± 0.3	1.00 ± 0.03	0.024 ± 0.002
Butene[b] + *trans*-2-butene	75.1 ± 0.3	0.99 ± 0.03	0.025 ± 0.003
Butene[b] + *m*-xylene	46.1 ± 0.6	0.99 ± 0.03	0.028 ± 0.004
Butene[b] + mesitylene	55.8 ± 0.5	0.99 ± 0.02	0.028 ± 0.001
Butene[b] + acetaldehyde	14.3 ± 0.5	0.95 ± 0.02	0.056 ± 0.019

[a] Initial reactant charge consisted of purified air containing the designated hydrocarbons or aldehyde each at 1 p.p.m., and NO_2 at 1 p.p.m.
[b] Designates C^{14}-labeled products.
[c] Yield was defined as moles of produced product per mole of reacted butene[b]. Each datum of the table represents results from five or six replicated runs. Confidence intervals were computed at the 95% probability level.
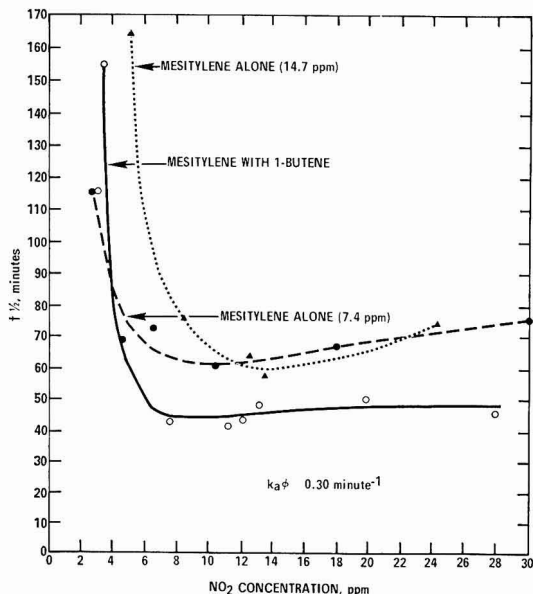
Figure 5. Half-life of 7.4 and 14.7 p.p.m. of mesitylene alone and 7.4 p.p.m. of mesitylene in the presence of 1-butene

The influence of one hydrocarbon upon another in photooxidation reactions involving oxides of nitrogen is really quite difficult to evaluate. The $Hc:NO_x$ ratio is altered, and thus the reactivity of a particular hydrocarbon changes. In many instances the two hydrocarbons do not convert nitric oxide to nitrogen dioxide at the same rate. The rate of reaction of a particular hydrocarbon may increase only because the nitrogen dioxide concentration increases. A better method of determining synergistic effects in photooxidation reactions involving mixed hydrocarbons is to calculate the contribution of the increased nitrogen dioxide concentration to the reaction rate. Some observed and calculated values are shown in Table XIV. Butene-1 at three light intensities shows

values of 6.6×10^{-2}, 13×10^{-2}, and 14×10^{-2} p.p.m. per minute. In the presence of *trans*-butene-2, the rates are 8×10^{-2}, 35×10^{-2}, and 45×10^{-2} p.p.m. per minute. The differences between these sets of numbers represent the magnitudes of the synergistic effect.

Although the rate of reaction of butene-1 depends strongly on the presence of other hydrocarbons, the formation of the major product, propionaldehyde, is unaffected. Approximately 0.59 p.p.m. of propionaldehyde is formed for every p.p.m. of butene-1 reacted when the butene is irradiated in the presence or absence of *trans*-2-butene.

The presence of *n*-butane in the photooxidation of toluene apparently has a suppressing effect (Altshuller, Kopczynski, *et al.*, 1970). In a 6-hr. irradiation period, the average consumptions of toluene at 4.5, 3.0, and 1.5 p.p.m. were 40, 48, and 50%, respectively. When 3 p.p.m. of *n*-butane were added, only 32% of the toluene reacted at the 1.5-p.p.m. level.

Saturated hydrocarbons are apparently unaffected by the presence of more reactive hydrocarbons. Altshuller, Kopczynski, *et al.* (1969) observed a 16% reaction of 3 p.p.m. of *n*-butane when irradiated with different concentrations of nitric oxide. When 3 p.p.m. of *n*-butane was irradiated in the presence of either propylene or toluene, the same amount of *n*-butane reacted, 16%. These observations are difficult to understand. The photooxidation of *n*-butane must take place with the presence of free radicals since calculations show that the rate of reaction of this compound with atomic oxygen is much too slow to explain its rate of photooxidation. The only rationalization left to explain the lack of a synergistic effect may be that the particular free radicals formed in the presence of olefins and aromatics are unreactive to saturated hydrocarbons. We are suggesting that the free radicals responsible for saturated hydrocarbon reactions are different from those responsible for olefins and aromatics. We can only speculate on the nature of the free radicals involved in the photooxidation of saturated hydrocarbons and those involved with olefins and aromatics. Hydroxy radicals look particularly attractive for the case of saturated hydrocarbons; OH, RO_2, and RCO_3, for olefins and aromatics.

Table XIV. Differences in Observed and Calculated Rates of Photooxidation for 1-Butene and Mesitylene under Various Conditions

Hydrocarbons	$k_a\phi$	NO_2[a]	$R \times 10^{2b}$	$R \times 10^{2c}$	$D \times 10^{2d}$	t^e
1-Butene	0.06	4.0	13	6.4	6.6	30
	0.21	3.4	23	10	13	24
	0.30	3.7	25	11	14	19
1-Butene with *trans*-2-butene	0.06	10	18	10	8	10
	0.21	13	45	9.6	35	3
	0.30	14	67	12	45	2
1-Butene with mesitylene	0.06	3.7	8.0	4.9	3.1	60
	0.21	5.3	25	11	14	26
	0.30	4.0	18	15	3	18
Mesitylene	0.06	8.3	2.0	0.06	1.9	120
	0.21	6.4	8.0	0.11	7.9	75
	0.30	11	8.6	0.20	8.4	45
Mesitylene with 1-butene	0.06	6.4	3.7	0.03	3.7	80
	0.21	6.4	9.3	0.19	9.1	30
	0.30	11	11.2	0.80	10	0

[a] Initial nitrogen dioxide concentration, p.p.m.
[b] Maximum observed rate, p.p.m./min.
[c] Calculated rate at maximum observed rate, p.p.m./min.
[d] Difference between observed and calculated rates, p.p.m./min.
[e] Time in minutes at maximum rate (of first hydrocarbon listed when two are present).

Altshuller, Kopczynski, *et al.* (1969) studied the effects of propylene addition on maximum oxidant concentration produced in the photooxidation of an *n*-butane–ethane–nitrogen oxide system. Results are shown in Figure 6. The maximum oxidant level did not vary significantly with addition of propylene to *n*-butane–ethane–nitrogen oxide mixtures at the lower nitrogen oxide concentration (0.3 p.p.m.). The addition of 0.25 to 0.75 p.p.m. of propylene to 3 p.p.m. of ethane in the presence of 0.3 p.p.m. of nitrogen oxide caused a marked increase in oxidant level.

Addition of toluene to the *n*-butane–nitrogen oxide system caused an increase in the maximum amount of oxidant formed at the higher nitrogen oxide levels but a decrease at the lowest nitrogen oxide level (0.3 p.p.m.), as shown in Figure 7. Addition of 3 p.p.m. of *n*-butane to 1.5 p.p.m. of toluene increased the maximum oxidant formed at all nitrogen oxide levels.

The importance of synergistic effects in actual atmospheric conditions has not been determined, not because of lack of effort but from lack of sufficiently good data from both atmospheric samples and laboratory measurements. Some data obtained from the irradiation of atmospheric samples are shown in Table XV. The data of Kopczynski, Lonneman, *et al.* (1969) and of Stephens and Burleson (1967) are the result of irradiating Los Angeles air samples; the data of Heuss and Glasson (1968) and Schuck and Doyle (1959) are from the irradiation of pure components. The data of Leach, Leng *et al.* (1964) are from the irradiation of diluted auto exhaust. The data of Schuck and Doyle seem to disagree markedly with other data. The single-component data are the only data in which synergistic effects are absent. If we ignore the data of Schuck and Doyle, the remaining values show that *n*-butane, *sec*-butylbenzene, and the olefins react more quickly when irradiated in multicomponent mixtures. Equally apparent is that the reactivities of toluene and the xylenes are essentially unchanged. It is not obvious why the data of Schuck and Doyle do not agree with any of the other data. More information is needed before definitive conclusions can be reached on synergistic effects in polluted atmospheres.
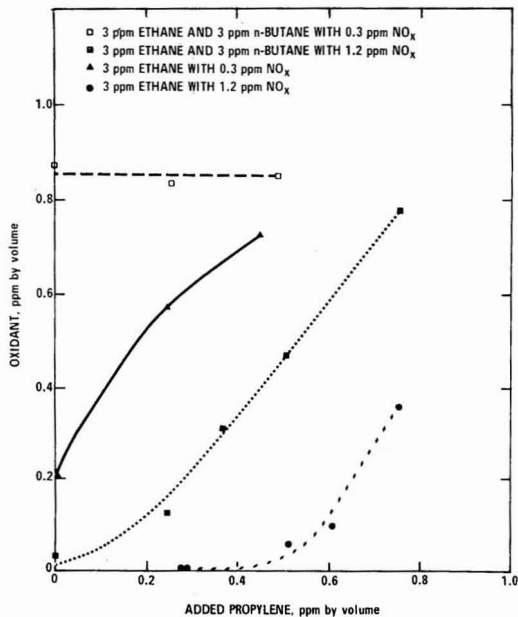
Figure 6. Oxidant concentrations produced as a function of addition of propylene to 3 p.p.m. ethane or to 3 p.p.m. *n*-butane plus 3 p.p.m. of ethane at two nitrogen levels

Product Formation

The major products formed from photooxidation of hydrocarbons in the presence of oxides of nitrogen are aldehydes, ketones, carbon monoxide, carbon dioxide, organic nitrates, ozone, and organic oxidants. We are not giving a detailed table of products formed from particular hydrocarbons, since product formation was presented in the earlier review.

Although the structure of compound X (peroxyacetyl nitrate) has been fairly well established, two significant
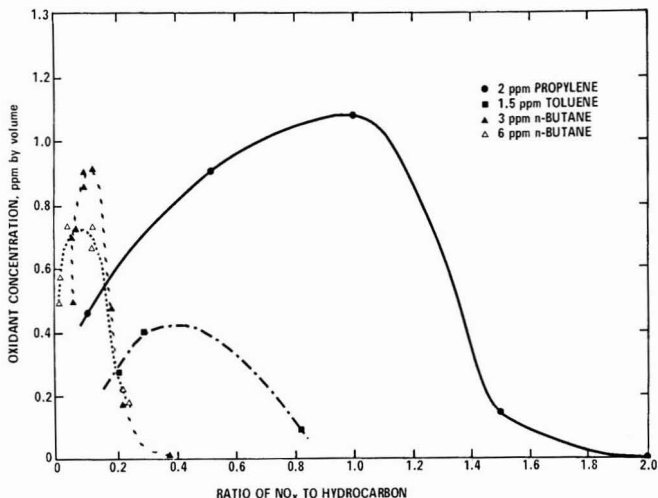
Figure 7. Oxidant concentrations produced as a function of nitrogen oxide concentration in the presence of *n*-butane, toluene, or propylene

Table XV. Relative Reaction Rates of Selected Hydrocarbons Averaged over 4-hr. Irradiation (Ethylene = 1.00)

Hydrocarbon	Kopczynski et al. (1969)		Stephens and Burleson (1967) (4-hr. irradiation)	Heuss and Glasson (1968) (6-hr. irradiation)	Leach et al. (1964) (auto exhaust)	Schuck and Doyle (1959)
	Relative rate	Standard deviation				
Ethane	0.06	0.09	0			
Propane	0.16	0.09	0.18			
n-Butane	0.27	0.13	0.37	0.11	0.3	
Isobutane	0.24	0.26	0.33			
n-Pentane	0.37	0.07				0.037
Isopentane	0.43	0.13	0.58			0.037
2,4-Dimethylpentane	0.99	0.27				
Acetylene	0.14	0.07	0.17			
Ethylene	1.00		1.0	1.00	1.00	1.00
Propylene	2.33	0.42	2.5	1.6	1.95–2.50	12.6
1-Butene	1.62[a]	0.52	2.5	1.9		9.7
2-Methyl-2-butene	9.39[b]	1.99		2.1		60
Toluene	0.56	0.34		0.87	0.59	
m-Xylene	1.14	0.45		1.2	1.13–1.59	
o-Xylene	0.70	0.28		1.2	0.74–1.27	
sec-Butylbenzene	1.25[c]	0.45		0.47		

[a] Contains isobutylene.
[b] Averaged over first hour of irradiation.
[c] Contains 1,2,4-trimethylbenzene.

publications have appeared on its structure since 1965. Nicksic, Harkins, et al. (1967) have made nuclear magnetic resonance, infrared, and chemical studies on the elusive compound X. The n.m.r. absorption peak occurred at 137.5 cycles/sec. downfield from tetramethylsilane in CCl₄. The resonance position was found to be consistent with an acetyl methyl attached to a group less electronegative than chlorine but more electronegative than —OOH.

In the chemical analyses these investigators found that PAN in the presence of sodium hydroxide converts to acetate ion and nitrite ion; they conclude that either the compound contains a nitrite group or nitrite is in some way formed, accompanied by the evolution of oxygen. The direct oxygen analyses indicated that the molecule contains at least five atoms of oxygen, but the data were inconclusive.

Conclusive data for oxygen were obtained by Stephens (1967). Stephens conducted alkaline hydrolysis of PAN directly in a gas chromatograph, in which one column contained aqueous NaOH. By passing the decomposition products over a molecular sieve column, Stephens found that PAN produced one molecule of oxygen for every PAN molecule decomposed. The structure of PAN is then

$$CH_3-\overset{\overset{\textstyle O}{\|}}{C}-O-O-NO_2$$
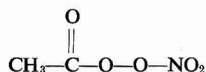
We consider that three important developments have occurred with respect to product formation. These relate to the formation of hydroperoxide, peroxybenzoyl nitrate, and nitric acid.

Hydroperoxide Formation. A number of analytical techniques were used to identify ethylhydroperoxide as a major product of the photooxidation of propionaldehyde by sunlamps (Altshuller, Cohen, et al., 1966; Cohen, Purcell, et al., 1967). Figure 8 shows results from the photooxidation of propionaldehyde. Almost all of the two-carbon fragment from propionaldehyde results in ethylhydroperoxide. However, the yield of ethylhydroperoxide relative to propionaldehyde decreased slowly with increasing irradiation time.

Altshuller, Cohen, et al. (1966) also investigated the photooxidation of acetaldehyde, which photooxidized at about two-thirds the rate of propionaldehyde to form a peroxy-type substance and formaldehyde as the two major products. The peroxy compound was identified as methyl hydroperoxide, a finding that agrees with that of Johnston and Heicklen (1964). Their measurements showed a marked increase in methyl hydroperoxide formation relative to methanol, formic acid, and acetic acid when acetaldehyde was photooxidized at low partial pressures. The lower partial pressure range is closer to that employed by Altshuller and coworkers.

The mechanism described by Altshuller and coworkers for hydroperoxide formations involves the reaction of two free radicals.

$$C_2H_5O_2 + HO_2 \rightarrow C_2H_5OOH + O_2 \qquad (27)$$

Although this reaction seems plausible, the hydrogen abstraction reaction

$$C_2H_5O_2 + C_2H_5CHO \rightarrow C_2H_5O_2H + C_2H_5CO \qquad (28)$$

seems to be the more reasonable reaction from bond–energy considerations. Also, H_2O_2 should be formed early in the reaction from the reaction

$$HO_2 + C_2H_5CHO \rightarrow H_2O_2 + C_2H_5CO \qquad (29)$$

if hydroperoxy radicals were actually present. Hydrogen peroxide was observed only later in the reaction. This seemed to arise from the photooxidation of formaldehyde.

Since photooxidations of propionaldehyde and acetaldehyde produced ethyl and methyl hydroperoxide, respectively, it is reasonable to assume that photooxidation of formaldehyde produces H_2O_2. Purcell and Cohen (1967b) found hydrogen peroxide when formaldehyde was photooxidized at low partial pressures. The amount of H_2O_2 formed from the photooxidation of formaldehyde was much less than the amount of hydroperoxide produced from the photooxidation of propionaldehyde. Purcell and Cohen showed that the
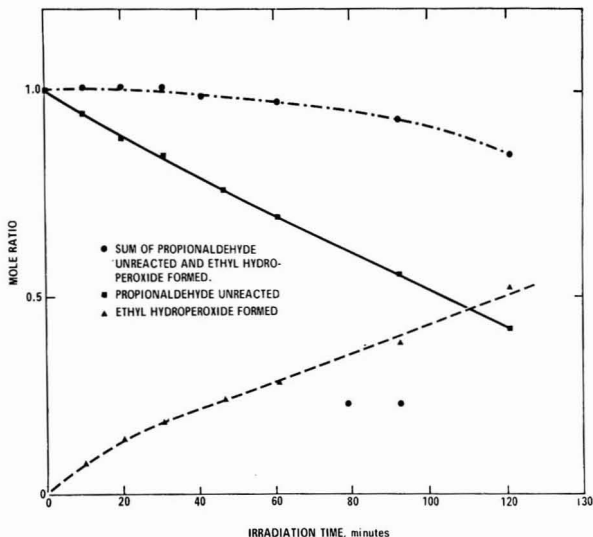
Figure 8. Moles of propionaldehyde unreacted or ethyl hydroperoxide formed per mole of propionaldehyde initially present

reaction product depended strongly on surface effects, essentially the same observation reported by Norrish and Thomas (1966) on the gas-phase oxidation of formaldehyde. These workers found that no H_2O_2 was produced when surfaces were very clean. Preconditioned surfaces allowed H_2O_2 to build up. The propagation steps for H_2O_2 formation given by Norrish and Thomas and by Purcell and Cohen are similar, with HO_2 radicals abstracting a hydrogen atom from formaldehyde.

Bufalini and Brubaker (1969) investigated the photooxidation of formaldehyde in the presence and absence of oxides of nitrogen. Their data are shown in Figure 9. The amount of H_2O_2 formed by the photooxidation of formaldehyde in the presence of oxides of nitrogen is less than when formaldehyde is photooxidized alone. The explanation put forth for this decrease is the reaction

$$HO_2 + NO \rightarrow NO_2 + OH \qquad (30)$$
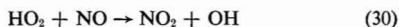
Formic acid, performic acid, and peroxyformic acid were not detected in the photooxidation. This finding agrees with that of Dimitriades (1969), who attempted to synthesize peroxyformyl nitrate (PFN) with no apparent success. Dimitriades

tried to synthesize PFN by photooxidizing methyl nitrite, by irradiating ethylene with NO_2, and by photooxidizing formaldehyde and NO_2. The latter experiment was conducted both in air and in nitrogen containing 100 p.p.m. of O_2.

The carbon-containing products from formaldehyde must result in formation of CO and CO_2.

$$HCO + O_2 \rightarrow HCO_3 \qquad (31)$$

$$HCO_3 \rightarrow CO + HO_2 \qquad (32a)$$

$$\rightarrow CO_2 + HO \qquad (32b)$$
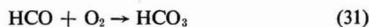
If peroxyformyl radicals were stable, performic acid and PFN would be formed. The molecule HCO_3 is apparently too small to accommodate the excess vibrational energy resulting from reaction. It would be academically interesting to irradiate formaldehyde and NO_2 at very low temperatures to note whether PFN can be produced.

Since no one has found hydroperoxides in polluted air, the applicability of aldehyde photooxidation to real conditions can be questioned. We are not aware, however, that anyone has looked for hydroperoxides in the atmosphere.
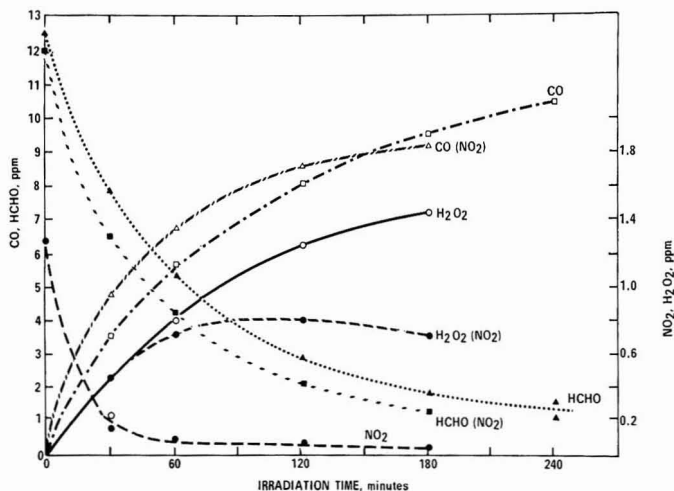
Figure 9. Formaldehyde irradiated with and without NO_2 in the presence of fluorescent sunlamps

Nitrogen Balance. One explanation for the lack of nitrogen balance could be the formation of a carbon–nitrogen polymer on the walls of the reaction vessel. Since the carbon balance was generally less than 100%, this appeared to be a logical possibility. In the photooxidation of ethylene and NO_x, Altshuller and Cohen (1964) found that as much as 100% of the carbon could be accounted for as CO, CO_2, and formaldehyde. In a more recent study, Altshuller, Kopczynski, *et al.* (1967) observed that in the photooxidation of propylene with nitric oxide, approximately 90% of the carbon can be accounted for as observable products early in the reaction (~60 min. irradiation). With continued irradiation, the carbon balance steadily decreases until after 6 hr., 75% of the carbon is accounted for as observable products. The nitrogen oxide concentration remained constant until the nitrogen dioxide reached a maximum. After formation of peroxyacetyl nitrate began, the nitrogen balance was dependent on the initial level of oxides of nitrogen. When the initial nitrogen oxide level was low, 0.2 p.p.m., all of the nitrogen oxide consumed could be accounted for as peroxyacetyl nitrate; when the initial nitrogen oxide level was between 0.2 and 0.5 p.p.m., 50 to 90% of the nitrogen oxide could be explained as PAN; with initial nitrogen oxide levels between 0.5 and 1.5 p.p.m., only 35 to 70% of the nitrogen oxide appeared as PAN. The exact fraction was dependent upon the $Hc:NO_x$ ratio. Methyl nitrate accounted for a small fraction of the nitrogen. No other nitrogen-containing product was observed. On the basis of these observations, the possibility that a nitrogen-containing polymer is formed was abandoned.

Bufalini and Purcell (1965) put forth a mechanism for the formation of molecular nitrogen with the photooxidation of ethylene and nitrogen dioxide. This work was repeated recently by Gay and Bufalini (1969), and their data do not confirm the earlier findings. They could detect neither molecular nitrogen nor N_2O by gas chromatography or infrared. Instead, they did observe nitric acid on the walls of the reaction vessel. Their findings seem to indicate that nitric acid is formed not by gas-phase reactions but by wall reactions. Although a complete mechanism for nitric acid formation was not put forth, a reaction was suggested

$$N_2O_5 + H_2O \text{ (wall)} \rightarrow 2HNO_3 \text{ (wall)} \qquad (26)$$

and

$$OH + NO_2 \rightarrow HNO_3 \qquad (33)$$

The N_2O_5 is presumably formed by the reaction of NO_3 with NO_2 during the course of the irradiation. Hydroxyl radicals can be produced by H-atom abstraction by atomic oxygen.

The formation of nitric acid from ethylene is not unique, since nitric acid was also observed (Gay and Bufalini, 1969) in the photooxidation of 1,3-butadiene-NO_x mixtures. Heuss and Glasson (1968) also observed hydrogen nitrate as a product in the photooxidation of benzaldehyde–NO_2–ozone mixtures, although they apparently made no quantitative measurements for HNO_3.

Peroxybenzoyl Nitrate. In their investigation of hydrocarbon reactivity and eye irritation, Heuss and Glasson (1968) found that the chemical measures of reactivity correlated very well with one another but not at all with eye irritation responses. Figure 10 shows the striking observation. The most potent precursor to eye irritation, shown at the top of Figure 10, is 1,3-butadiene. This observation is not unexpected since the photooxidation products arising from 1,3-butadiene are formaldehyde and acrolein, two very strong eye irritants. However, the next strongest eye irritants produced were

the monoalkylbenzenes. Since these compounds do not form large quantities of formaldehyde or PAN (another known eye irritant), Heuss and Glasson concluded that another product must be present that is responsible for the strong eye irritation. After several screening experiments, they found that 0.5 p.p.m. of styrene when irradiated with 0.25 p.p.m. of NO caused eye irritation after the NO_2 maximum appeared. Since benzaldehyde, a major product, was not a strong eye irritant, they deduced that cleavage occurs at the double bond and that the eye irritant was similar in structure to benzaldehyde. Since Tuesday (1961) demonstrated that PAN can be prepared from acetaldehyde–N_2O_5 mixtures, Heuss and Glasson reacted benzaldehyde with ozone and NO_2 in the dark. (Ozone and NO_2 react to form N_2O_5.) They found a rapid decrease in benzaldehyde concentration and concluded that a reaction product such as PAN was formed. Their suspicions were confirmed by study of infrared spectrum of the product. The spectrum was very similar to that observed by Stephens, Darley, *et al.* (1961) and by Stephens (1964) for PAN. After several tests, which included ultraviolet spectrometry, mass spectrometry, nuclear magnetic resonance, and the titration method of Nicksic, Harkins, *et al.* (1967) on PAN, Heuss and Glasson concluded that the mysterious eye irritant was peroxybenzoyl nitrate (PBN), having the structure

$$\langle \bigcirc \rangle\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!O\!-\!O\!-\!NO_2$$
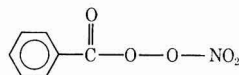
Reactivity Scales

Although hydrocarbons are essential to the formation of photochemical smog, not every hydrocarbon produces the manifestations such as eye irritation, plant damage, and visibility reduction that are usually associated with smog. The reason for this is the differences in reactivity and chemical structure of hydrocarbons. The available literature indicates
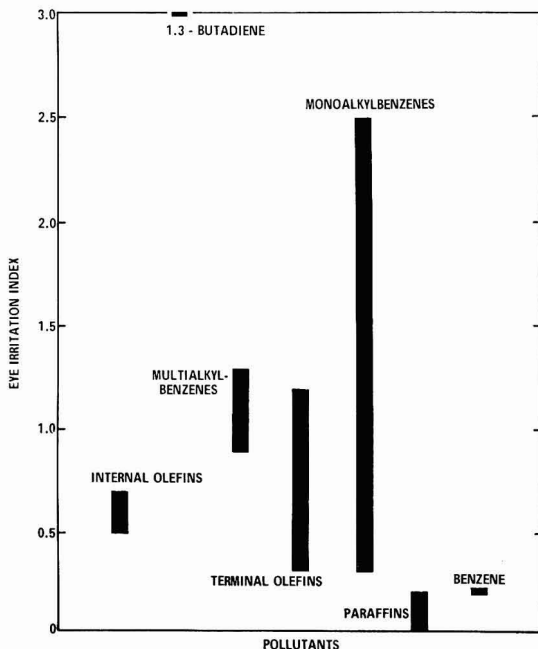

Figure 10. Effect of hydrocarbon structure on eye irritation index

clearly that several measures of reactivity must be considered in determining which hydrocarbons are to be controlled.

The reactivities of hydrocarbons for producing photochemical smog can be evaluated with the use of experimental data. These include, but are not limited to, the following: hydrocarbon consumption, nitric oxide oxidation, oxidant formation, aerosol formation, eye irritation, and plant damage. Aerosol formation is discussed separately; plant damage, as stated earlier, is not covered in this review.

Hydrocarbon Consumption. Rates of reaction or times for partial consumption of various hydrocarbons and aldehydes have been reported in a number of studies. The scale appearing in Tables XVI and XVII is an arbitrary one in which the most reactive compound is rated at 10 (>95% reacted).

Since the experimental conditions in which the rates have been measured by the various investigators are different, the rating of the scales are not completely compatible with each other. Despite these limitations, the rankings of organic substances of many of the compounds are quite consistent. Branched or straight-chain olefins with internal double bonds, such as 2,3-dimethyl-2-butene or *trans*-2-butene, form the most reactive class. The trialkylbenzenes, tetraalkylbenzenes, and olefins with terminal double bonds (except ethylene) rank next, followed by the dialkylbenzenes, aldehydes, and ethylene. Toluene is less reactive than ethylene, and the paraffinic hydrocarbons, acetylene, and benzene are less reactive than toluene. This ordering of hydrocarbon consumption

from laboratory measurement was confirmed in solar irradiations of atmospheric samples (Kopczynski, Lonneman, *et al.*, 1969).

Nitric Oxide Oxidation. The reactivities of nitric oxide and several hydrocarbons, as measured by Glasson and Tuesday (1965) and by Altshuller and Cohen (1963), are shown in Table XVIII. Although slight differences are apparent, the agreement is generally good. The ranking of the hydrocarbons follows the same general order as that obtained from rates of hydrocarbon consumption. This measure of reactivity is no better, but it is quite simple, involving the use of only a few chemicals and a colorimeter.

Oxidant Formation. In air pollution studies, the term "oxidant" refers to the group of substances that can oxidize potassium iodide or some other chemical reagents. These oxidants therefore include ozone, nitrogen dioxide, peroxyacyl-type nitrate compounds, possible other types of organic peroxy and hydroperoxide compounds, and H_2O_2. Because the relative responses of the various oxidant methods or instruments to these different materials vary, the concentrations of oxidant measured by various procedures should not necessarily agree. Data obtained by two methods considered relatively specific for ozone are shown in the first two columns of Table XIX. One is based on rubber cracking, the other on infrared absorption. Note that the two sets of data do not agree. The ozone yields from irradiations of the terminal double-bonded monoolefins and nitrogen oxide overlapped those from the irradiations of internally double-bonded monoolefins and nitrogen oxide. This result does not agree with

Table XVI. Ranking of Reactivities of Hydrocarbons when Photooxidized in Presence of Nitrogen Oxides under Static Conditions

Hydrocarbon	Ranking of hydrocarbons		
	Schuck and Doyle (1959)	Stephens and Scott (1962)	Tuesday (1963)
Tetramethylethylene	10	10	10
trans-2-Butene	6		8
cis-3-Hexene		6	
Isobutene	1.5	2	2
1,3-Butadiene	1		
Propylene	1	2	1
m-Xylene		1	
p-Xylene	0.5	0.5	
Ethylene	0.1	0.3	
Hexanes, octanes	<0.1		
Pentanes	<0.01		

Table XVII. Ranking of Reactivities of Aromatic Hydrocarbons when Photooxidized in Presence of Nitrogen Oxides under Static Conditions

Aromatic hydrocarbons	Ranking of reactivities[a,b]
1,2,3,5-Tetramethylbenzene	10
1,3,5-Trimethylbenzene	8
1,2,4-Trimethylbenzene	6
1,2,3-Trimethylbenzene	6
m-Xylene, 3-methylethylbenzene	3
o-Xylene	1.5
p-Xylene, *p*-diethylbenzene	1.5
Toluene, ethylbenzene, isopropylbenzene	1
Benzene	0.5

[a] Based on percent consumed in first hour of reaction.
[b] Kopczynski (1964).

Table XVIII. Reactivities of Hydrocarbons Based on Ability to Participate in Photooxidation of Nitric Oxide to Nitrogen Dioxide[a]

Hydrocarbon	Ranking	
	Altshuller and Cohen (1963)	Glasson and Tuesday (1965)
2,3-Dimethylbutene-2		10
2-Methyl-2-butene		3
trans-2-Butene	2[a]	2
Isobutene	1	
Propylene	1	0.5
Ethylene	0.4	0.3
1,3,5-Trimethylbenzene	1.2	1.2
m-Xylene	1	0.9
1,2,3,5-Tetramethylbenzene	0.9	0.7
1,2,4-Trimethylbenzene	0.6	0.7
o- and *p*-Xylene	0.4	0.4
o- and *p*-Diethylbenzene	0.4	0.4
Propylbenzenes	0.3	0.2
Toluene	0.2	0.2
Benzene	0.15	0.04
n-Nonane	0.15	
3-Methylheptane	0.15	
n-Heptane		0.2
Methylpentanes	<0.1	0.2
Pentanes		0.2
2,2,4-Trimethylpentane	0.15	0.15
Butanes		0.1
Ethane		0.03
Methane		<0.01
Acetylene	0.1	

[a] Arbitrarily adjusted to the same ranking as *trans*-2-butene on Glasson and Tuesday's scale to permit comparison of other hydrocarbons.

Table XIX. Ozone or Oxidant Yields from Photooxidation of Organic Substance–Nitrogen Oxide Mixtures

Organic substance	Static irradiations			Dynamic irradiations, Altshuller, Klosterman, *et al.* (1966) (p.p.m. by volume)
	Haagen-Smit and Fox (1956), cracking depth (mm.)	Schuck and Doyle (1959) (p.p.m. by volume)	Altshuller and Cohen (1963) (p.p.m. by volume)	
1,3-Butadiene	12	0.65		0.72
2-Alkenes	8	0.55–0.73		
1,3,5-Trimethylbenzene	7		1.1	0.87
Xylenes	6–7	0.18	0.65–1.0	
1-Alkenes	5	0.58–1.00		0.4
Methanol, ethanol	5			
Formaldehyde	4			1.05
Propionaldehyde	4		1.0	0.80
3-Methylheptane	3			
n-Nonane	3		0.2	
Ethylene	2	1.1		0.69
Hexanes, heptanes	1	~0.2		0.0
Toluene	0.6		0.5	0.36
Acetylene	0.5		0.0	
C_1–C_5 paraffins	<0.2	0.0–0.2		

data obtained by rubber cracking. The rubber cracking method indicated that more ozone was produced by irradiating internally double-bonded monoolefins with oxides of nitrogen. Also, the ethylene system gave the highest ozone concentration, which caused less rubber cracking than other olefin mixtures.

Table XX presents a classification of hydrocarbons according to ability to produce ozone or oxidant. Although the table shows that little or no oxidant is produced with C_1–C_5 paraffins, this is not exactly correct; it has been shown (Altshuller, Kopczynski, *et al.*, 1969) that as much as 0.9 p.p.m. of oxidant (mostly ozone) is produced when 3 p.p.m. of *n*-butane is photooxidized with 0.3 p.p.m. of oxides of nitrogen. Similar results were obtained with ethane. When 3 p.p.m. of ethane was photooxidized with 0.3 p.p.m. of NO_x, 0.2 p.p.m. of oxidant was observed. Therefore, it appears that almost every hydrocarbon except methane can produce some oxidant when photooxidized in the presence of high enough ratios of hydrocarbons to oxides of nitrogen. Oxidant concentration as a measure of reactivity is very complex since it is very dependent

upon $Hc:NO_x$ ratio and irradiation time. No oxidant was observed in earlier work on C_2–C_5 paraffins, apparently because the $Hc:NO_x$ ratio was too low.

Relatively long laboratory irradiations of diluted auto exhaust mixtures with hydrocarbon (carbon p.p.m.) to nitrogen oxide ratios of 2 to 1 do not produce oxidant (Altshuller, Kopczynski, *et al.*, 1967). However, these mixtures contain considerable amounts of olefin and alkylbenzenes. No oxidant would be observed if only gaseous paraffinic hydrocarbons and traces of olefin were emitted, except at very high ratios, which would not be anticipated under normal atmospheric conditions.

Eye Irritation. Eye irritation as it occurs in areas exposed to the photochemical type of air pollution is an aggravating effect. No clinical condition has been associated with this effect. In recent years laboratory measurements have been confined to obtaining subjective responses of human panelists to irritation of their eyes by various mixtures.

The principal methods for measuring eye irritation in air pollution studies were reviewed by Wayne (1967). These may be categorized as intensity methods, threshold methods, and response delay methods. Intensity methods rate the severity of the irritation after the subject has been exposed for a specific time. Threshold methods are based on determination of a minimum amount of irritant with which the panelist can detect irritation. The response delay method involves determination of the time that elapses between exposure of the subject and onset of the irritation sensation.

The technical problems associated with these types of measurements are concerned with consistency of the responses of the subjects. Subjects are often suspicious of the potency of a particular irritant and may give unreliable values for the pollutants. Suggestibility regarding the potency of the pollutant must be kept at a minimum.

Aside from the problems, there is also some question of the validity of eye irritation measurements as a measure of hydrocarbon reactivity. The earlier work of Schuck and Doyle (1959) showed that atmospheric measurements of eye irritants were almost an order of magnitude lower than laboratory concentrations that resulted in equal eye irritation. A rationalization of this disagreement resulted in the postulate that free

Table XX. Ranking of Various Organic Compounds by Ozone or Oxidant Formation (0-to-3 Scale)

Substance	Ozone or oxidant	Ozone[a]
C_1–C_5 paraffins	0	1[b]
C_6^+ paraffins	0–1	1
Acetylene	0	
Ethylene	2	2
1-Alkenes	3	3
Internally double-bonded olefins	3	3
Benzene	0	0
Toluene or other monoalkylbenzenes	2	2
Other aromatics	3	3
Aldehydes	2–3	

[a] Heuss and Glasson (1968).
[b] *n*-Butane.

radicals and aerosols were present in the atmosphere and that these probably increased the degree of irritation. However, Schuck and Doyle pointed out that eye irritation persists indoors and it is unlikely that free radicals have a half-life long enough to exist any period of time indoors. Also, Doyle, Endow, et al., (1961) showed that aerosols, when mixed with other pollutants, decrease rather than increase eye irritation.

A re-examination by Schuck, Stephens, et al. (1966a) of eye irritation response to formaldehyde indicated that a linear relationship between eye irritation responses and formaldehyde concentration does not hold when formaldehyde concentration is below 0.3 p.p.m. Subjects may experience equal eye irritation when concentrations of the irritant differ by an order of magnitude. This finding has not been confirmed by others.

The data on eye irritation reactivity are shown in Table XXI and also in Figure 10. Comparison of hydrocarbon reactivity with eye irritation reactivity shows that the two scales do not agree. Heuss and Glasson (1968) found very poor correlation between chemical measurements and eye irritation. These investigators arrived at an eye irritation reactivity scale based upon the average threshold response time. This scale is based on the equation

$$\text{Eye irritation scale} = \frac{(240 - t) \times 10}{240}$$

Reactivities for the various hydrocarbons, based on the scale from 0 to 10, are shown in Table XXI. As pointed out earlier, the high eye irritation potential associated with alkylbenzenes is highly important. This result also was reported recently by other investigators (Altshuller, Kopczynski, et al., 1969).

Aerosols

The mechanism by which photochemical aerosols are produced in the atmosphere is still not clear. A considerable amount of work has been published on size distribution of aerometric aerosols (Wagman, Lee, et al., 1967; Ludwig and Robinson, 1968; Lee, Patterson, et al., 1968); aside from the work of Goetz and coworkers (Goetz and Olgierd, 1967; Goetz and Pueschel, 1967), very little has been published on the photochemical production of aerosols.

Goetz and Pueschel (1967) conducted over 1000 tests under various conditions to elucidate the various parameters important to aerosol formation. Following are some principal findings of their work. In the absence of SO_2, the aerosols generated by photooxidation of olefins with NO_2 always produce the highest degree of light scattering in the low-humidity range (15 to 30%). In the presence of defined nucleating centers, aerosol formation follows the same pattern, but on a higher level. Light scattering varies with the sequence in which the NO_2 and hydrocarbon are introduced into the reactor chamber. In the absence of nucleating centers the effect is small, but in their presence the sequence in which NO_2 is introduced first seems to produce the greatest amount of light scattering. This seems to be independent of humidity. The presence of small amounts of SO_2 reduces light scattering (aerosol formation) drastically when stable centers are absent. This inhibiting effect of small SO_2 concentrations is greater at high humidity levels, being 10-fold higher at 50% relative humidity than at 15%. Greater SO_2 concentrations eventually reverse the trend. The presence of reaction centers does not alter the effect of initial reduction with low SO_2 concentration. The effect of humidity in this latter case seems to be the same, high humidity giving less light scattering. However, the presence of reactive centers did affect the sequence; when SO_2 was first put in contact with the reactive centers, the decrease was much lower.

The reason for the decrease in aerosol formation by small amounts of SO_2 is not obvious. Goetz and Pueschel suggest some interaction between SO_2 and NO_2 to inhibit the subsequent photolysis of the reactant combination, particularly at higher humidities.

The role of SO_2 in visibility reduction was investigated by Harkins and Nicksic (1965). By employing radioactive propylene and ethylene in the presence and absence of SO_2, they showed that the total tracer count for the aerosols was the same. Sulfur dioxide consistently caused the formation of aerosol, but these aerosols did not contain any organic matter. These experiments showed that SO_2 does not provide condensation nuclei for organic aerosols. This finding is consistent with some earlier work of Doyle and Jones (1963).

In the irradiation of auto exhaust Harkins and Nicksic found an inverse correlation between relative humidity and SO_2-induced aerosols. The aerosol counts steadily decreased when the relative humidity was increased from 20 to 75%. This decrease, however, as the investigators point out, may be

Table XXI. Eye Irritation Reactivity[a]

Hydrocarbon	Eye irritation reactivity	Hydrocarbon	Eye irritation reactivity
n-Butane	0	m-Xylene	2.9
n-Hexane	0	1,3,5-Trimethylbenzene	3.1
Isooctane	0.9	...	...
tert-Butylbenzene	0.9	1-Hexene	3.5
Benzene	1.0	Propylene	3.9
Ethylene	1.0	Ethylbenzene	4.3
1-Butene	1.3	Toluene	5.3
Tetramethylethylene	1.4	n-Propylbenzene	5.4
cis-2-Butene	1.6	Isobutylbenzene	5.7
Isopropylbenzene	1.6	n-Butylbenzene	6.4
sec-Butylbenzene	1.8	1,3-Butadiene	6.9
2-Methyl-2-butene	1.9	α-Methylstyrene	7.4
trans-2-Butene	2.3	Alkylbenzene	8.4
o-Xylene	2.3	β-Methylstyrene	8.9
p-Xylene	2.5	Styrene	8.9

[a] Based on a scale of 0 to 10.

due to an increase in particle size. As the relative humidity increases, larger particles may be formed that are less effective in scattering light; or these particles may drop out of the reaction chamber. Another possibility is that the scattered light is due to sulfuric acid agglomerated by H-bonding. Water might interfere by occupying the available H-bonding sites and thus preventing agglomeration. Thus, the particles would remain small, and light would be scattered less effectively. In some earlier work on pure components, Schuck, Doyle, *et al.* (1960) found that an increase in relative humidity increased the light scattering. The work of Harkins and Nicksic does not agree. Comparisons are difficult, since the earlier work was on pure components whereas the work of Harkins and Nicksic was on auto exhaust.

Recent laboratory experiments on model systems, along with work showing large amounts of nitrate aerosol in irradiated auto exhaust (Lee, Patterson, *et al.*, 1970) emphasize the rapidity of conversion of nitrogen dioxide to nitric acid and particulate nitrate. In view of the large amounts of both ammonia and nitrogen oxides available in the atmosphere, the rate of atmospheric particulate nitrates needs immediate evaluation.

Natural Air Pollution

The haze observed in large cities and surrounding areas can be ascribed to the presence of appreciable quantities of submicron aerosols. These aerosols are partially a result of the presence and photooxidation of the many compounds arising from human activity. It has been suggested (Went, 1960) that the origin of the blue haze usually observed over vegetation-containing land masses is similar to that of haze over large cities. The aerosols in the nonurban areas would arise from photooxidation of organic material emanating from plants. Rasmussen and Went (1965) measured organic volatiles emanating from plants and identified such compounds as α- and β-pinene, myrcene, and isoprene. They conclude that the worldwide production of volatile substances released to the atmosphere by plants is approximately 4.38×10^8 tons per year.

Rasmussen (1969) and Ripperton, White, *et al.* (1967) recently strengthened the suggestion proposed by Went. Rasmussen provides some experimental evidence that the same types of products are obtained from the photooxidation of isoprene that are observed in the photooxidation of auto exhaust. Ripperton and coworkers studied the rate of reaction between ozone and α- and β-pinene. The rate constants were very high (0.8×10^5 liter mole^{-1} sec.$^{-1}$ and $\sim 0.25 \times 10^5$ liter mole^{-1} sec.$^{-1}$, respectively). They also found that the reaction is nonstoichiometric—*i.e.*, more pinene than ozone is consumed, usually 2 to 50 times as much. They also observed some aerosol formation and concluded that some polymerization of pinene occurs. They further suggested that the original estimate of Rasmussen and Went of 4.38×10^8 tons per year of terpenes is low by a factor of 2 to 10. This conclusion is based upon the natural abundance of O_3 in the atmosphere and the rates of reaction between O_3 and terpenes. Since the reaction is so rapid, the terpenes are lost through their reaction with O_3 and their concentrations are underestimated.

To our knowledge, no one has measured or described the products arising from photooxidation of terpenes present in nonurban, vegetation-laden areas. Terpenes, not being light absorbers (3000 to 4000 Å), need to be oxidized by the photodecomposition of nitrogen dioxide. Probably enough NO_x is present, either brought by air movements from urban areas or by natural bacterial action, to facilitate the photo-oxidation of terpenes. If terpenes are photooxidized in this fashion, the resulting products would be very similar to those observed in photochemical smog in urban areas. Went (1960) mentioned "weather fleck" on tobacco plants during hazes formed in dense heat well away from human activities. It seems reasonable to assume that this physiological disturbance is a result of some oxidant arising from the haze. This is only speculation, however, and more work is needed.

Actinometry

Our earlier review criticized contributors to the literature who do not state the light intensity employed in laboratory studies. It is well known that light intensity is an important parameter in analysis of photochemical smog. To obtain meaningful data in the laboratory or in the field, some method for measuring light intensity is highly desirable.

Schuck and Stephens (1966) evaluated the quantum yield of the photolysis of NO_2 and its use as an actinometer. They concluded that NO_2 can be used as an actinometer for photochemical air pollution work.

In our laboratories, we have found the photodissociation of NO_2 in nitrogen to be a convenient and rapid method for measuring relative light intensity (Tuesday, 1961). However, this method, while giving a measure of the energy available between 3000 and 4000 Å, favors the longer wavelength region, since the absorption coefficient for NO_2 is greater in this region (Hall and Blacet, 1952). This method is satisfactory if the energy distribution of the lamps remains constant. If it is altered, the value of the first-order dissociation constant, kd ($kd = 1.45$ $ka\phi$) will not be very meaningful. We have observed, for example, that the photooxidation of formaldehyde in the presence of oxides of nitrogen proceeded more rapidly at a kd value of 0.14 min.$^{-1}$ with the use of sunlamps than at a kd value of 0.32 min.$^{-1}$ with the use of blacklamps (Bufalini and Brubaker, 1969). The reason for this observation is obviously a result of the photodissociation of formaldehyde by the higher energy emitted from the sunlamps. Therefore, it seems reasonable to assume that in the photooxidation of hydrocarbons in the presence of oxides of nitrogen, their photooxidation rate may be higher at lower light intensities as measured by the kd value of nitrogen dioxide. This may be caused by the further dissociation of the original products, such as aldehydes, accompanied by synergistic effects. In light of our observations with formaldehyde and possible interaction by photodissociation of the initial products of photooxidation of hydrocarbons, we suggest that if light intensities are measured by the kd value method, the number and types of lamps be stated or the energy distribution given.

Another method that measures relative light intensity makes use of the photoisomerization of o-nitrobenzaldehyde (Pitts, Cowell, *et al.*, 1968; Pitts, Vernon, *et al.*, 1965). The reaction for the isomerization is

$$\text{(34)}$$
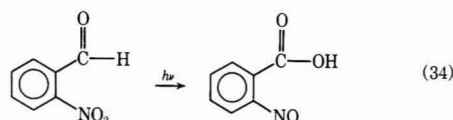
The photorearrangement of the compound proceeds with a quantum yield of 0.5 between 3100 and 4000 Å, and is constant whether in a solution, a solid, or a gas. Thus, as stated by Pitts and coworkers, the use of o-nitrobenzaldehyde as an actinometer offers some unique advantages for photochemical air pollution studies. It can be used as an actinometer in any

phase and has the absorption onset at 4000 Å; further, since the atmosphere does not transmit energy higher than 3000 Å, the actinometer becomes a natural indicator for all energy between 3000 and 4000 Å. An added advantage is that the method can be employed with ordinary laboratory instruments; the only instrumentation required is a pH meter. Its main disadvantage is that the absorption coefficient is not constant between 3000 and 4000 Å. The absorption coefficient increases some two orders of magnitude from 4000 to 3000 Å. This naturally weights the shorter wavelengths more strongly than the longer wavelengths. McCormick, Vernon, *et al.* (1967) consider 3670 Å as the average wavelength to be taken if one desires to average energy measured by the actinometer for natural sunlight.

Other methods for measuring sunlight are the filter-photocell method (Nader and Smith, 1967) and the filter phototube method (Stair, Waters, *et al.*, 1965).

In a joint study sponsored by the Public Health Service, several methods, including those already mentioned, were evaluated for measurement of ultraviolet radiation in the Los Angeles area. Figure 11 shows data obtained on an Eppley filter uv detector during various days of smog in downtown Los Angeles in 1965. Figure 12 shows data obtained on a filtered phototube for the same period. Figures 13 and 14 show data obtained by photolysis of NO_2 and by photoisomerization of ONBA, respectively, for the same period. Note that values given by the Eppley and the NBS instruments (filter phototube) agree within 17%, the Eppley giving the higher values. According to Nader, this discrepancy may be due to differences in adherence to the cosine response for the various instruments, since disagreement is greatest at low angles of elevation. The data given by the two chemical methods agree in a very general way with those obtained by the physical methods. Both NO_2 photolysis and the ONBA give higher energy values than those observed by the physical instruments. This brings out a very important point with respect to uv radiation available to a volume in space. Several aerometric measurements from the wings of light aircraft have indicated that a significant amount of energy is reflected back into the atmosphere. These data are shown in Figures 15 and 16. If the solar energy were uniformly distributed throughout space, then values given by the chemical methods should read approximately six times those of the physical Eppley instrument. However, from anisotropic distribution the factor is
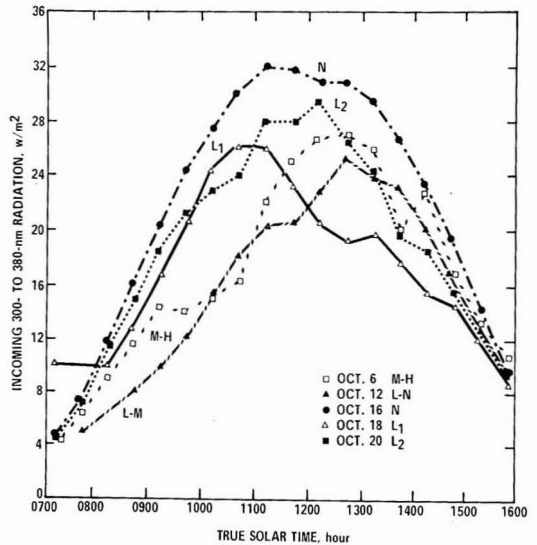
Figure 12. NBS wide band filter measurements of average incoming radiation in downtown Los Angeles for 30-min. intervals as a function of time of day in October 1965

less than six. Calculations of the ratio of volumetric measurements to horizontal measurements show a value between 2.6 and 4.8. The ratio of the ONBA to the Eppley is 3 for a nonsmog day. Also of interest, although not surprising in Figures 15 and 16, is the increase in outgoing radiation on a polluted day as compared to a nonpolluted day. The outgoing radiation is apparently a combined measure of the incoming radiation scattered by the polluted atmosphere and radiation reflected from ground level, whereas the data for nonsmog days indicate only the reflectivity from ground level.

Concluding Comments

Many problems cited in the earlier review are still very much with us. Little progress has been made in elucidating which reactive intermediates are responsible for the excess rate. We (Bufalini and Altshuller, 1967) postulated that RO_2 and RCO_3 radicals partake in the photooxidation of olefins;
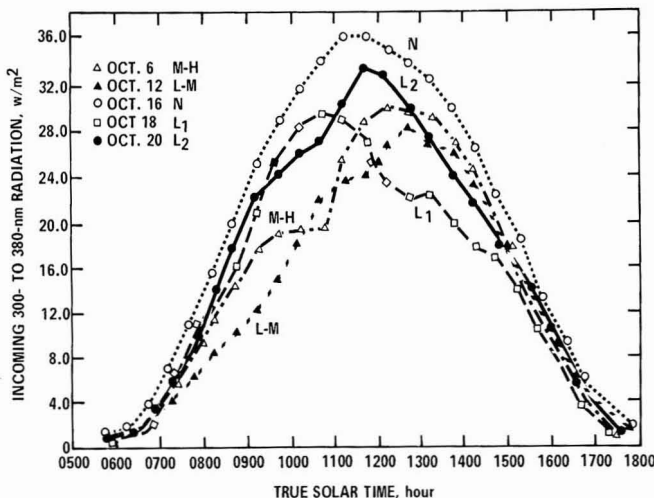
Figure 11. Average incoming 300 to 380 nm. radiation for 30-min. intervals as a function of time of day on various days of smog in downtown Los Angeles in 1965

Figure 13. Incoming 300 to 410 nm. radiation as a function of time of day for various days of smog in downtown Los Angeles
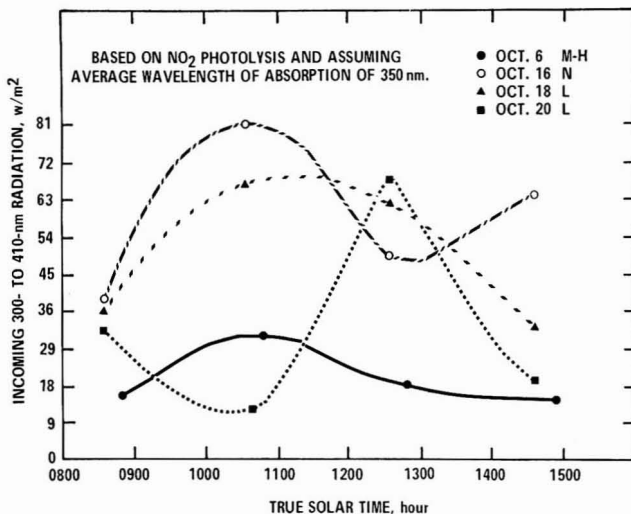
Figure 14. Incoming 300 to 400 mm. radiation as a function of time of day for various days of smog
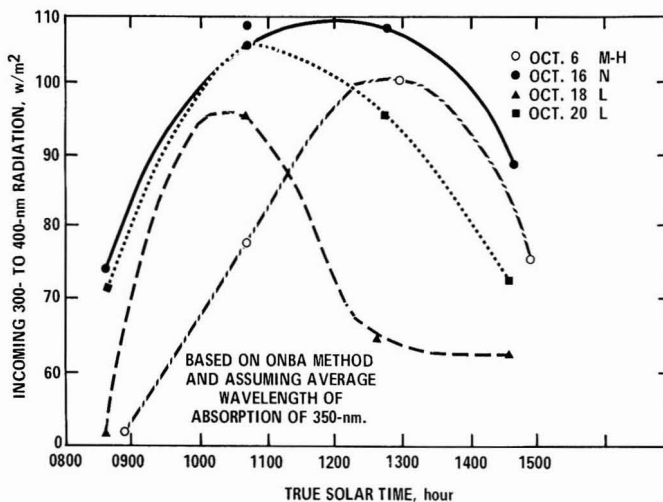
Figure 15. Outgoing 300 to 380 nm. radiation as a function of time of day for various elevations over Los Angeles, October 16, 1965 (no-smog day)
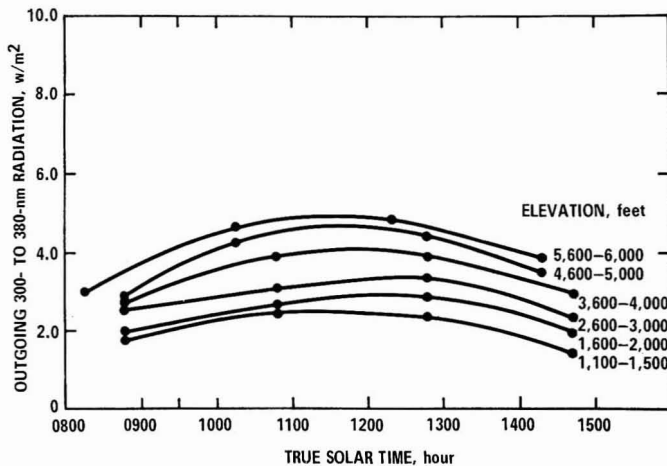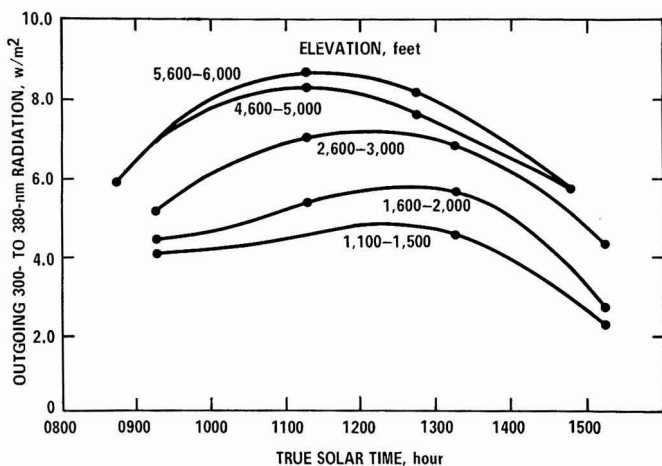
Figure 16. Outgoing 300 to 380 nm. radiation as a function of time of day for various elevations over Los Angeles, October 6 (M–H smog)

however, in view of the rate constants estimated by Benson (1965) this hypothesis seems incorrect. Benson calculated activation energies of 6 and 14 kcal. per mole for the addition and H atom abstraction reaction of an RO_2 radical with an olefin. Since the pre-exponential factor is $10^{8.5}$ liter mole^{-1} sec.$^{-1}$ for both reactions, the rate constants appear to be too low to make the reactions important. The same is probably true for RCO_3 radical. The RO radical reaction with ethylene was estimated by Thynne (1964) and found to be $10^{8.5}$ exp $(-6000/RT$ liter mole/sec.$^{-1})$. This reaction also appears too slow to be of importance in air pollution. Reactions of hydroxy radicals with olefins do appear to be sufficiently rapid to be of importance (Avramenko and Kolesnikova, 1964; Greiner, 1967). The number of free radicals that facilitate reactions of hydrocarbons in the atmosphere is clearly limited if the estimated rate constants are correct. More work is needed to verify the estimated values, particularly for reactions involving hydroxy radicals.

A good or even adequate understanding of the role of hydrocarbons in the oxidation of sulfur dioxide in model systems is lacking. To typify this, Altshuller, Kopczynski, et al. (1968) found no effect of SO_2 on the rate of oxidation of propylene and oxidant formation when SO_2 was added to a propylene–NO_x–$h\nu$ system. Ripperton, Decker, et al. (1965) showed that the amount of oxidant decreased with the addition of SO_2 to a hexene–NO_x system. Wilson and Levy (1968) showed that the effect of SO_2 on these systems is more subtle. They observed that the maximum ozone concentration depends not only on the amount of SO_2, but also on the relative humidity. Thus, in a dry system the ozone concentration increased with increasing SO_2 when 1-butene was irradiated with nitric oxide. At a relative humidity of 65% the ozone concentration decreased with increasing SO_2. Obviously, there is a degree of relative humidity in this system at which the addition of SO_2 does not affect oxidant production. Determination of the degree of interaction of sulfur dioxide in reactions producing photochemical smog manifestations is urgently needed.

Observations of the effect of water vapor on photooxidation reactions are confusing and contradictory. A detailed study of the effect is clearly needed, with careful consideration given to maintaining a proper $Hc:NO_x$ ratio. Such results are needed to evaluate humidity effects on atmospheric reactions in our urban atmosphere.

The carbon balance in many model systems is poor. Very little progress has been made since the last report. To our knowledge, no one engaged in air pollution studies is currently conducting research along this line. The undefined products may well have significant importance in terms of biological activity or contribution to aerosol formation.

We need more information about the fate of pollutants in the atmosphere. Olefins and arenes from combustion sources and terpenes from natural sources apparently are photooxidized, and ultimately transformed to submicron aerosol particulates; these particulates in part are eventually removed from the atmosphere by rain washout and natural deposition, but they also may contribute to increases in atmospheric turbidity on a global scale. The natural deposition suggested by Went (1960) may ultimately have some relation to petroleum formation. Methane is apparently the only unreactive hydrocarbon that does not eventually undergo gas-phase oxidation. Since only about 10% of the methane based on loading estimate of 310×10^6 tons per year (Koyama, 1963) can be transported to the stratosphere to be oxidized by high energy reactions (Bainbridge and Heidt, 1966), there must be a natural sink for methane in the biosphere. Rabinowitch (1945) identified a number of bacteria that are methane reducers; no other scavenging processes have been identified. The fate of CO is still unknown. It has been estimated that approximately 2×10^{14} g. of CO are introduced into the atmosphere each year. Since the amount of CO in the atmosphere is approximately constant at ~ 0.15 p.p.m., the residence time for CO is 2.7 years. Stevens (1969) has measured the C^{13}:C^{12} ratio for CO in the atmosphere. His results suggest that a large portion of the CO may not arise from technological sources. This suggests that large natural sources of CO must be operative. The 2.7-years residence time for CO is then much too long. This finding is compatible with the work of Weinstock (1969). Radiocarbon measurements put a lower limit of 0.1 year for the residence time of CO. Because of the low solubility of CO in water, rain washout and ocean solubility can be ruled out. Also, the ocean appears to be a source rather than a sink for CO (Swinnerton, Linnenbom, et al., 1969), with chemical reactivity also apparently too slow to be of importance. Perhaps the biosphere is a sink for the CO (Rabinowitch, 1945).

Other pollutants, such as SO_2, H_2S, NO_2, and NH_3, are involved in oxidative processes. The SO_2 and H_2S are oxidized in a few days to sulfate aerosols. The NH_3 can either be oxidized like NO_2 in part to nitrate aerosol to form NH_4NO_3 or be combined with sulfate to form $(NH_4)_2SO_4$, which has been found in the atmosphere as a natural aerosol. But we have little in the way of experimental results to describe such

processes. These submicron aerosol species are also likely contributors to increases in atmospheric turbidity.

We know very little about the fate of organic and inorganic chemical species on a global scale. In view of the importance of a long-term increase of atmospheric turbidity as it affects global radiation balance, it is imperative that we rapidly learn more about atmospheric chemistry on a global scale.

Progress in data analysis and mathematical modeling related to experimental work with chemically reactive atmospheres has not been discussed. These efforts are most important, but since they are still in preliminary stages, a detailed discussion of results would be premature. Some general observations are appropriate, however.

There has been an unfortunate tendency to assume 1-to-1 relations between pollutants from various sources of emissions. For example, we lack measurements that tell us how much a ton of organics from solvent operations or a ton of nitric oxide from a power plant contributes to total atmospheric pollution in comparison with a ton of organics and nitric oxide emitted concurrently from vehicles. The emissions from the solvent operation and the power plant begin to participate as they mix with each other or with vehicular emissions. Dilution occurs during an undetermined time interval before reaction starts to occur. As a result, the advantages of controlling various sources of pollution may be different in different urban complexes. Thus, our ability to determine the effectiveness of controlling a number of pollutants is likely to depend on our measurements and modeling of individual urban complexes with respect to distribution of source strengths, reaction rates, trajectories, inversion heights, and other meteorological parameters. Only by jointly applying chemistry, physics, meteorology, and mathematics are we likely to produce the evaluations we need. Without such evaluations, continued control efforts will be blind attempts to improve atmospheric conditions without realistically evaluating the consequences of controls.

In related ways we need to learn more about the chemical and physical consequences of pollution on regional and continental scales. Results obtained at Riverside and other outlying areas in the Los Angeles Basin and also in agricultural areas in the eastern U.S. give ample evidence that ozone formation proceeds with concurrent extensive dilution over long air trajectories. These trajectories may be at least of the dimensions of air quality regions. As a consequence, the levels of ozone formation may be seriously underestimated when monitoring is confined to core urban areas. The slow oxidation of moderately reactive inorganic and organic pollutants to aerosol products over long distances may contribute appreciably to haze formation on a regional or continental basis.

Over long time scales, we are uncertain as to the contribution of pollutants to global pollution. However, we have increasing evidence that the accumulation of submicron particulates adversely affects turbidity on a global scale. In particular, the high global levels of particulate sulfate can be attributed in part to urban pollution. We know little about the processes leading to accumulation *vs.* fallout or rainout of various particulate species on a global scale.

Without measurements on these larger scales of distance and time, it is difficult to judge the net advantages of such steps as moving thermal power plants out of core urban areas to rural locations. The effects of large combustion installations in nonurban sites on regional visibility and global turbidity and the more localized biological effects on flora and fauna need much more experimental evaluation.

In conclusion, air pollution control does not stop at the stack or the tailpipe. As long as undesirably high levels of pollutants are emitted, it is critical that we properly evaluate the consequences of proposed control measures. This evaluation can be accomplished only by the coordinated application of the physical and biological sciences to the earth's atmosphere on scales ranging from the thin layer over the core areas of our cities to the entire atmosphere of the planet earth. These efforts must be supported by laboratory photochemical measurements designed to investigate variation of experimental parameters meaningfully related to atmospheric problems.

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Characterization of Crude and Residual-Type Oils by Fluorescence Spectroscopy

Alfred D. Thruston, Jr. and R. W. Knight

Southeast Water Laboratory, Federal Water Quality Control Administration,
U.S. Department Interior, Athens, Ga. 30601

■ The ability to pinpoint the source of an oil spill on water is vital to the enforcement of water pollution control procedures and to the reduction in frequency of spills. The usual approach to identifying the source of a spill is the analysis of numerous parameters that can be used to compare samples of oil from the spill to those from suspected sources. A method was developed to determine fluorescence intensities and wave number ratios for comparing various crude and residual-type oils. The method was applied to samples from an actual oil spill and confirmed results of infrared and metals analyses.

T he ability to pinpoint the source of oil in an oil spill on a beach, a river, or a harbor is vital to the enforcement of water pollution control procedures. Many oil spills are not discovered until days after they occur, at which time it becomes difficult to locate and identify the sources. The usual approach to identifying the source of a spill is a systematic analysis of the physical and chemical parameters of the polluting oil and comparing the data for these parameters to those from suspected sources. These time-consuming methods require infrared absorption techniques (Kawahara, 1969), metal analyses (Gamble and Jones, 1955), percent sulfur (ASTM, 1962), and others.

By using the intensity at chosen wave numbers of the fluorescence emission spectrum of an oil, a new, rapid method has been developed for the comparative identification of crude and semirefined oils.

All crude and semirefined oils fluoresce when excited by ultraviolet light. This fluorescence results from the radiations of many organic compounds, the major ones being the poly-aromatic and heterocyclic compounds (Riecker, 1962). Parker and Barnes (1960) used the intensity of the fluorescent spectrum for determining oil mist in air collected from filter traps of an air compressor. Riecker (1962) used changes in the fluorescent wavelength to trace the extent of migration of crude oil in oil fields. Schuldiner (1951) found that oil spills in harbors could be matched with known samples by comparing the shape and color of oil spot chromatograms on filter papers when viewed under ultraviolet light.

The fluorescence emission spectrum of an oil in solution is dependent on concentration because of absorption effects when measured with a spectrophotofluorometer; as an oil in solution is diluted, this absorption effect becomes negligible. Each oil reacts differently upon dilution, not only in peak intensity, but also in the shape of the entire spectrum. This method utilizes these properties for the comparative identification of oils.

Experimental

The fluorescence emission and excitation spectra of a typical fuel oil when diluted 1:10,000 with cyclohexane are shown in Figure 1. The fluorescence excitation spectrum of this fuel oil, measured with the emission monochromator at 386 nm., has a maximum around 340 nm. When excited at its excitation maximum of 340 nm., there is a maximum in the emission spectrum at 386 nm., with two slight shoulders around 405 and 440 nm. This spectrum maximum and general shape are similar in all crude or semirefined oils examined in this laboratory. However, the intensities of the maximum and shoulders are different for each type of oil.

Figure 1. Emission and excitation spectra of Humble no. 6 fuel oil diluted 1:10,000 with cyclohexane

Six different oils were examined

1. American Bunker C
2. Hess no. 6 fuel (2.0% sulfur)
3. Hess no. 6 fuel (0.7% sulfur)
4. Humble Bunker C no. 278 TK
5. Gulf no. 6 fuel (Field A)
6. Gulf no. 6 fuel (Field B)

Samples of oil, each weighing exactly 200 mg., were diluted with cyclohexane to a wt.:vol. of 1:10,000, 1:20,000, and 1:100,000.

Figure 2 shows the fluorescence spectra of these samples at an excitation wavelength of 340 nm. The American sample was the most highly fluorescent of the group, so for each concentration, the instrument slits and sensitivity controls were adjusted so that the American sample read maximum recorder response. All samples at the same concentration were recorded without changing these instrument settings. Diluted samples were stored away from light until the measurement was made.

Each oil shows a maximum of about 386 nm., a peak or slight shoulder at 405 nm., and a slight shoulder at 440 nm. All the oils except the Humble Bunker C show a decrease in relative intensity upon dilution. The fluorescence of the Humble sample is quenched in the most concentrated solution, causing the maximum intensity to be at 405 nm. instead of about 386 nm. The ratio of the intensity of the shoulder at 440 nm. to the maximum peak intensity also decreases with dilution for each sample.

To show the reproducibility of this technique, the emission spectra of five 200.0-mg. samples of each of these six oils are summarized in Table I. American no. 1 was used to set the maximum recorder response for each of the three dilutions.

Some of these differences in maximum intensities and intensity ratios between samples seem minute, but they are reproducible within a narrow range. One has to examine all the data to distinguish differences between similar samples. For example,

The shape of the emission spectrum of an oil can be expressed by comparing the ratio of the maximum intensity at 386 nm. with the shoulder intensity at 440 nm. This ratio gives an identification parameter for each oil. When a solution is diluted 2- to 10-fold, the maximum intensity and shape ratio change, giving another identification parameter.

All spectra were recorded on a Perkin-Elmer MPF-2A spectrophotofluorometer in the ratio mode, with a sensitivity setting at 1 or 2, and slits at 6 mm. The cell was 1-cm. square.

The fluorescence emission of a variety of oils collected from several different sources was investigated spectrophotofluorometrically to determine if this property could be used to distinguish between residual-type oils with reproducible results.

Figure 2. Fluorescence emission spectra from 360 to 440 nm. of six oils diluted with cyclohexane; excitation at 340 nm. The circled fraction is the intensity ratio of 440 nm.:386 nm. max.

Curve A—1:10,000 dilution
Curve B—1:20,000 dilution
Curve C—1:100,000 dilution

Table I. Reproducibility of Fluorescence Emission Intensities of Fuel Oils

Five different 200-mg. samples of each oil, diluted
1 : 10,000, 1 : 20,000, and 1 : 100,000 with cyclohexane

	No.	Maximum intensity at 386 nm.			Intensity ratio 440 nm./max. at 386 nm.		
		Dilution 10,000	Dilution 20,000	Dilution 100,000	Dilution 10,000	Dilution 20,000	Dilution 100,000
American	1	100.0	100.0	100.0	0.706	0.589	0.491
Bunker C	2	100.0	101.0	97.5	0.711	0.590	0.515
	3	99.5	100.7	101.2	0.701	0.594	0.496
	4	100.1	99.8	102.4	0.705	0.594	0.517
	5	99.8	98.9	99.4	0.708	0.586	0.493
Hess	1	74.6	61.5	52.9	0.591	0.531	0.487
No. 6 fuel,	2	76.0	63.4	51.6	0.593	0.536	0.492
2.0% sulfur	3	76.0	62.7	53.4	0.588	0.527	0.482
	4	76.2	61.6	52.5	0.589	0.537	0.501
	5	75.1	62.9	53.4	0.585	0.527	0.480
Hess	1	65.2	52.0	42.2	0.585	0.538	0.491
No. 6 fuel,	2	66.0	49.5	40.1	0.576	0.541	0.492
0.7% sulfur	3	67.8	53.1	43.4	0.606	0.554	0.513
	4	66.0	52.1	41.5	0.584	0.539	0.506
	5	66.0	49.6	42.8	0.580	0.537	0.487
Humble	1	69.4[a]	81.3	96.6	0.856	0.742	0.618
Bunker C	2	72.3[a]	80.0	96.5	0.860	0.733	0.624
No. 278 TK	3	70.4[a]	79.9	96.5	0.857	0.731	0.626
	4	72.4[a]	84.0	97.6	0.860	0.729	0.630
	5	71.0[a]	79.0	96.3	0.866	0.732	0.624
Gulf	1	51.8	48.9	42.5	0.665	0.580	0.564
No. 6 fuel,	2	51.8	47.4	41.7	0.663	0.598	0.566
Field A	3	53.4	47.7	42.8	0.655	0.591	0.563
	4	53.0	48.6	43.4	0.659	0.572	0.556
	5	52.1	47.9	43.4	0.669	0.604	0.556
Gulf	1	51.7	53.6	50.2	0.723	0.638	0.579
No. 6 fuel,	2	51.5	52.0	50.6	0.724	0.634	0.583
Field B	3	53.1	52.5	51.6	0.714	0.638	0.585
	4	52.1	52.8	51.9	0.725	0.647	0.588
	5	51.1	53.0	52.0	0.729	0.645	0.589

[a] Maximum is at 405 nm. instead of 386 nm.

in the Gulf Field A and Gulf Field B oils, there are no maximum intensity differences at the 1:10,000 dilution; however, the 440 nm.:386 nm. ratios are significantly different. At the 1:100,000 dilution there is a difference in maximum intensity but no significant difference in the ratios.

The Hess 2.0% sulfur and Hess 0.7% sulfur show no significant differences between any of the ratios for any of the dilutions; however, all the maximum intensities are different.

Depending on the type of oil, other dilutions, such as 1:1000 or 1:50,000, may also be used for a wider spread of identification parameters.

Weathering Effects

To apply this method to oil pollution problems, weathering conditions that may affect an oil slick floating on top of water must be considered.

The evaporation of low-boiling fractions is a type of weathering that affects oil in spills. The six samples previously mentioned were residual-type oils with no volatiles at room temperature. To test the effect of volatilization of low-boiling fractions on this fluorescence technique, five different crude oils, each containing about 30% volatiles, were examined

1. Humble Louisiana–Mississippi Crude 187 TK
2. Humble East Mississippi Crude 271 TK
3. Humble South Louisiana Crude 192 TK
4. Humble North Louisiana Crude 188 TK
5. Humble Citronelle Crude 264 TK

Two 1-g. samples of each oil were prepared. Sample 1 of each oil was diluted with cyclohexane to 1:10,000 (wt.: vol.). Sample 2 was heated on a steam bath until all volatiles had evaporated; then the residue was reweighed and diluted to the same volume as Sample 1. Weight losses ranged from 28 to 39%.

The fluorescence emission was determined by using the same instrument settings for each sample. Humble Louisiana–

Mississippi Crude had the highest maximum intensity and was used to set maximum recorder response.

The fluorescence maximum intensities and intensity ratios of these oils are presented in Table II. The evaporation of low-boilers from crude oil produced no detectable change in the emission spectrum. Maximum intensities and ratios remained unchanged by removal of volatiles by evaporation on a steam bath. Since steam bath evaporation is the means by which extractant is separated from pollution and suspect oil samples prior to analysis (samples are cleaned and dried by dissolving in methylene chloride and filtering) this characteristic is vital to reliable comparison of oils by fluorescence spectrometry. It also indicates that evaporation losses before sampling may not be significant.

Decomposition by sunlight is another weathering problem encountered in oil pollution analysis. This effect was studied by exposing these crude oils to sunlight and determining fluorescence decomposition after four days of exposure.

Five 2-liter glass beakers were filled with water to within an inch of the top. The area of the surface was approximately 160 cm.[2] Approximately 3 ml. (equivalent to about 2 g. non-volatile oil) of a crude oil was floated on the water in each beaker. Each oil was spread uniformly over the water surface, giving a thin, opaque, black film with the exception of the South Louisiana crude, which gave a transparent film with a deep amber color. The beakers were then set in the sunlight and wind for four days.

The change in odor indicated that most of the light volatiles of each oil had evaporated by the end of the first day.

On the fourth day, the oil was skimmed off the water surface and the sides of each beaker with a Teflon spatula, and washed into a separatory funnel with methylene chloride. The methylene chloride–oil solution was filtered through glass wool prewet with methylene chloride into a beaker. The methylene chloride was slowly evaporated on a steam bath.

For comparison, 3 ml. of each unweathered crude oil was added to individual beakers, approximately the same volume of methylene chloride added, and each solution was slowly evaporated on a steam bath.

After evaporation, exactly 200 mg. each of the unweathered and the sun-weathered oil was diluted 1:10,000 with cyclohexane. Figure 3 shows the effect sunlight weathering had on the spectra of different oils. The fluorescence of the exposed oil decreased in maximum intensity, and the shape of the spectrum also was changed.

The maximum intensity and the 440 nm.:386 nm. ratio parameters changed slightly for the dark, opaque-type oils, while the fluorescence spectrum of the amber-colored, transparent South Louisiana crude oil changed beyond recognition. This emphasizes the importance of prompt sample collection after a spill occurs if adequate identification of the oil is to be made.

Oil Spill Samples

An oil spill in an estuary in the southeast, during January 1969, offered an excellent opportunity to test this method in a field situation and to compare the results with other identification parameters.

Table II. Effect of Loss of Volatiles from Crude Oil

Samples 1 and 2 are identical samples made to the same dilution. Sample 2 had volatiles removed first

| Humble oils | Sample 1 | | Sample 2 | | |
	Max. intensity at 386 nm.	Intensity ratio 440 nm./ 386 nm.	Max. intensity at 386 nm.	Intensity ratio 440 nm./ 386 nm.	% Lost as volatiles
La.–Miss.	100	0.55	98	0.56	28
East Miss.	87	0.64	85	0.64	39
South La.	89	0.47	87	0.47	37
North La.	71	0.59	72	0.59	28
Citronelle	63	0.68	64	0.68	36
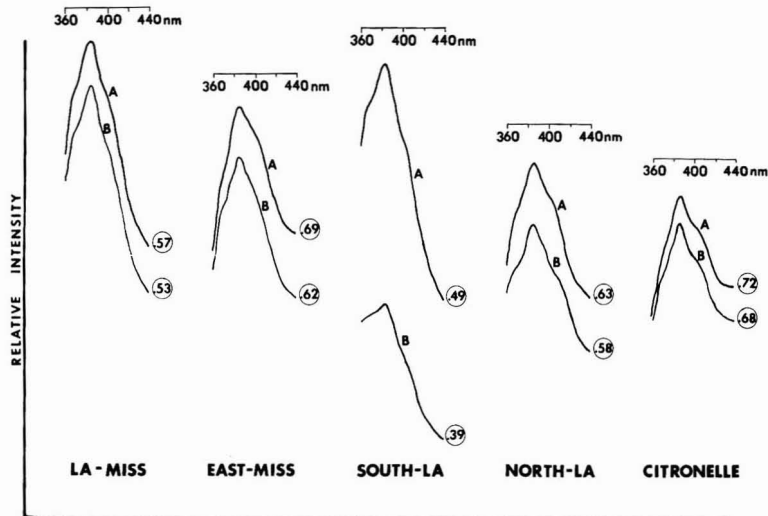
Figure 3. Effect of sunlight on fluorescence emission spectra of crude oils

Curve A—unweathered oil
Curve B—oil weathered in sunlight for four days

The source and exact date of the spill were unknown. The slick covered an area of about a square mile. The oil was in clumps instead of a uniform film, indicating a heavy viscous oil. Four pollution samples, Numbers 1 to 4, were collected at widely separated points in the spill area and six suspect samples, Numbers 5 to 10, were taken from oil depots, ships, and industries surrounding the spill area.

Pollution and suspect samples were cleaned and dried by dissolving in methylene chloride and filtering through glass wool. The methylene chloride was slowly evaporated on a steam bath.

All pollution and suspect samples were analyzed fluorometrically and by four other analytical procedures: (1) percent sulfur; (2) nickel–vanadium ratios; (3) infrared ratios; and (4) a simple color comparison under uv light. These analytical procedures have been applied to other oil spills with varying degrees of success.

The different parameters were compared to determine whether all the pollution samples came from the same source and which, if any, of the suspect samples were identical to the pollution samples.

Fluorometric Procedure. The pollution and suspect samples were each diluted (wt.: vol.) 1:10,000, 1:50,000, and 1:100,000 with cyclohexane.

The emission spectra of the 10 samples were recorded for each concentration with an excitation wavelength of 340 nm. Sample 10 had the highest maximum intensity and was used to set the maximum recorder response for each concentration.

The fluorescence maximum intensity and intensity ratios are summarized for the 10 samples in Table III.

By use of this fluorescence emission technique, the four pollution samples appear to come from the same source. Of the suspect samples, only Sample 5 is indistinguishable from the pollution samples in fluorescence spectral intensity and shape.

Other Analytical Procedures. PERCENT SULFUR. Sulfur was determined gravimetrically, using the oxygen bomb method (ASTM, 1962).

NICKEL AND VANADIUM. Two-gram samples were coked and ashed by the method of Gamble and Jones (1955). The ash was dissolved in HCl, and nickel and vanadium were determined by atomic absorption.

Nickel and vanadium are trace impurities common to the origin of an oil, and the Ni:V ratio is usually unchanged by weathering.

COMPARATIVE RATIOS OF INFRARED ABSORBANCES. Infrared analyses were done by the method described by Kawahara (1969). Comparative ratios of selected infrared absorbances show distinct differences between oils and may be used for comparative identification.

COLOR COMPARISON UNDER UV LIGHT. Smears of the pollution samples and suspect samples were placed on porcelain spot plates and compared visually under ultraviolet light. This is a quick, yes-no test for comparative screening of different crude oils.

These analytical procedures are summarized for the 10 samples in Table IV.

These analyses agree with the fluorometric procedure; the various parameters all indicate that the four pollution samples come from the same source and that only suspect Sample 5 is indistinguishable from the pollution samples.

Summary

This method for measuring fluorescence emission intensities of an oil is a rapid and precise method for the comparative identification of crude and semirefined oils. With samples from an actual oil spill, it was demonstrated that the results of this fluorescence method were in agreement with those of four other oil identification methods.

Low-boiling volatiles found in crude oils showed no fluorescing properties in the crudes tested, and no analytical problems resulted when volatiles were removed by evaporation before analysis.

It should be emphasized that immediate sampling of an oil spill is very important because prolonged exposure to sunlight can affect fluorescence properties of the oil. Also, enough samples should be taken to establish variabilities of

Table III. Oil Spill Samples
Fluorescence spectra

Sample no.	Maximum intensity at 386 nm.			Intensity ratio shoulder at 440 nm./386 nm. max.			Parameters that agree
	Dilution 1:10,000	Dilution 1:50,000	Dilution 1:100,000	Dilution 1:10,000	Dilution 1:50,000	Dilution 1:100 000	
			Spill samples				
1	70	77	72	0.67	0.60	0.54	
2	65	81	90	0.70	0.61	0.55	
3	66	72	76	0.71	0.63	0.55	
4	72	72	75	0.67	0.61	0.53	
Range of spill samples	65–72	72–81	72–90	0.67–0.71	0.60–0.63	0.53–0.55	
			Suspect samples				
5	67	81	90	0.71	0.63	0.55	6 of 6
6	50	60	64	0.62	0.55	0.47	0 of 6
7	73	68	65	0.57	0.53	0.45	0 of 6
8	78	76	71	0.58	0.52	0.45	1 of 6
9	50[a]	73	99	0.82[a]	0.72	0.59	1 of 6
10	100	100	100	0.56	0.51	0.44	0 of 6

[a] Maximum is at 405 nm. instead of 386 nm.

Sample no.	% Sulfur	Ni/V	$\dfrac{720\text{ cm.}^{-1}}{1375\text{ cm.}^{-1}}$	$\dfrac{3050\text{ cm.}^{-1}}{2925\text{ cm.}^{-1}}$	$\dfrac{810\text{ cm.}^{-1}}{1375\text{ cm.}^{-1}}$	$\dfrac{810\text{ cm.}^{-1}}{720\text{ cm.}^{-1}}$	$\dfrac{1600\text{ cm.}^{-1}}{1375\text{ cm.}^{-1}}$	uv Colors	Parameters that agree
					Infrared ratios				
1	[a]	[a]	0.28	0.023	0.24	0.88	0.13	yellow	
2	2.59	0.31	0.29	0.020	0.27	0.94	0.15	yellow	
3	2.78	0.38	0.34	0.034	0.36	1.09	0.18	yellow	
4	2.62	0.29	0.31	0.026	0.26	0.86	0.16	yellow	
Range of spill	2.59–2.78	0.29–0.38	0.28–0.34	0.020–0.034	0.24–0.36	0.86–1.09	0.13–0.18	yellow	
5	2.65	0.31	0.29	0.023	0.27	0.95	0.16	same yellow	8 of 8
6	2.30	0.19	0.19	0.023	0.25	1.34	0.15	darker (brown)	3 of 8
7	2.56	0.27	0.33	0.023	0.20	0.60	0.09	lighter (yellow)	2 of 8
8	2.02	0.21	0.26	0.017	0.21	0.82	0.11	lighter (yellow)	0 of 8
9	2.08	0.61	0.35	0.041	0.47	1.36	0.27	darker (brown)	0 of 8
10	1.68	0.24	0.16	0.034	0.26	1.66	0.14	lighter (yellow)	

[a] Sample no. 1 did not contain enough oil for sulfur, nickel, or vanadium analysis.

parameters within an oil slick. For a comparative identification, it is virtually impossible to tell if oil "A" is the same as or different from oil "B" unless a sufficient number of replicate samples of both is obtained.

This method might be applicable to other types of oils with use of other fluorescence excitation and emission maxima.

Acknowledgment

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COMMUNICATIONS

Pyrolyzed Sewage Sludge: Its Production and Possible Utility

John M. Beeckmans and Park C. Ng

Faculty of Engineering Science, University of Western Ontario, London, Ont., Canada

■ Filtered sludge from a municipal activated sludge plant was pyrolyzed in a continuous-feed, multiple-hearth furnace. The carbon content of the pyrolysate under optimum operating conditions was 14.1%. The pyrolysate was crushed 70 to 100 mesh, and its ability to adsorb COD and the dye crystal violet was measured. Parallel adsorption tests were made with fly ash and activated coconut charcoal. The pyrolysate was found to be intermediate in its adsorbing capacity between fly ash and activated coconut charcoal for both adsorbates, suggesting that it could prove useful as a tertiary treatment agent in waste water renovation.

Considerable interest has been shown in recent years in the use of activated carbon and other carbonaceous adsorbents such as coal for the reduction of residual oxidizable material in the effluent of waste water treatment plants (Johnson *et al.*, 1965; Parkhurst *et al.*, 1967; Shannon and Silveston, 1968). Coal is advantageous in that it has essentially zero cost, since it can be used as an adsorbent without affecting its later usefulness as a fuel. However, it has a disappointingly low absorbing capacity, and in some cases, it may even have a negative adsorbing capacity—*i.e.*, it increases the BOD of the water in contact with it (Johnson *et al.*, 1965). Fly ash is available from the incineration of the sewage sludge, but it also

has a low absorbing capacity. Activated carbon has been found to be useful as an adsorbent in the tertiary treatment of waste water (Parkhurst *et al.*, 1967), but its initial cost is high.

The present study investigates the possibility of producing a pyrolysate with an appreciably higher adsorbing capacity than fly ash, by the pyrolysis of the sewage sludge. The potential economic benefits acruing from the production of a suitable adsorbent from the sludge itself as opposed to the use of activated carbon are obvious, provided that the adsorbent has a reasonable capacity with respect to residual BOD, and provided that the capital and operating costs of the pyrolysis unit do not excessively exceed those of the sludge incinerator which it would replace.

Pyrolysis of Sewage Sludge

The sludge was obtained as a partly dewatered cake from the filtration house of the Greenway Pollution Control Center at London, Ont. This plant uses a conventional activated sludge process, treating approximately 22 m.g.p.d. of domestic sewage. The sludge contained 85% moisture, and analyzed 47% ash and 32% carbon on a dry basis.

The pyrolysis unit consisted of a closed, vertical stainless steel cylinder, with internal dimensions of 8-in. diameter by 18-in. high, containing six equally spaced hearths. The sludge was introduced continuously at the top of the unit by means of a feed screw, and the pyrolysate was continuously removed from the bottom by a vertical exit tube dipping into water. The sludge was processed through the unit by the raking action of off-center pairs of rabble arms attached to a central rotating shaft, with one pair of arms per hearth. The motion of the rabble arms pushed the sludge toward the periphery of the unit and toward its center, on alternate hearths. Suitably placed holes in the hearths then permitted the sludge to fall onto the next hearth beneath. The residence time of the sludge could be controlled by the angular velocity of the central shaft, and the feed rate of the sludge could be controlled by adjusting the speed of the feed screw.

A controlled flow of oxygen-deficient gas (generally below 2% O_2) was maintained in the furnace by drawing in the combustion products of a propane flame through an opening through the side near the top. This was accomplished by a suction pump which was connected, via a condensate trap and a condenser, to the bottom of the unit. The flow of gases was thus concurrent with the sludge. This arrangement was designed to encourage depletion of the oxygen content of the gases through partial oxidation of the volatiles in the upper portions of the unit, thereby minimizing oxidation of the carbon residue in the pyrolysate. The oxygen concentration of the combustion products admitted to the furnace could be varied within limits by adjusting the propane flame, and the flow of gases through the furnace was controlled by a screw clip on the rubber hose connecting the pump to the condensate trap. The temperature at the top, center, and bottom of the unit was monitored by thermocouples, and provision was also made for sampling the gases at these locations. The furnace was heated on the bottom by Bunsen burners, and was insulated along the sides and at the top. The temperature at the bottom of the unit was controlled by adjusting these burners.

The results of the experiments on sludge pyrolysis are presented in Tables I to III. The principal conclusions drawn were that, for maximum carbon content in the pyrolysate, the oxygen content of the furnace gases should not exceed 2% at the top of the furnace, that the sludge residence time should be approximately 90 min., that the sludge feed rate should be approximately 12.5 g./min. (wet basis), and that the input gas

Table I. Effect of Oxygen Concentration in the Purge Gas on the Carbon Content of the Pyrolysate[a]

O_2 in inlet gas, %	C in pyrolysate, %
2.0	10.2[b]
4.2	4.6[b]
10.0	0.2[b]

[a] Input air flow, 25 liters/min.; residence time, 120 min.; sludge feed rate, 9.4 g./min.; bottom temperature, 1290°F.
[b] Average of five runs.

Table II. Effect of Residence Time and Sludge Feed Rate on Carbon Content of the Pyrolysate[a]

Input air flow, liter/min.	Residence time, min.	Sludge feed rate, g./min.	C in pyrolysate, %
25	50	22.0	Pyrolysis incomplete
25	90	12.5	14.1[b]
25	120	9.4	10.2[b]
25	150	7.6	8.7[b]
15	90	12.5	10.7[b]
15	120	9.4	8.5[b]
15	150	7.6	8.4[b]

[a] Oxygen in inlet gas, 2%; bottom temperature, 1290°F.
[b] Average of four runs.

Table III. Effect of Purge Gas Flow Rate on Carbon Content of the Pyrolysate[a]

Input air flow, liter/min.	C in pyrolysate, %
15	8.5[b]
25	10.2[b]
30	8.4[b]
60	4.1[b]

[a] Oxygen in inlet gas, 2%; residence time, 120 min.; bottom temperature, 1290°F.
[b] Average of four runs.

flow rate should be approximately 25 liters/min. Under these conditions, the carbon content of the pyrolysate averaged 14.1% at 1290°F. At 920°F., pyrolysis was incomplete, and residual extractable material was present. It was also concluded that contact with oxygen should be minimized, since the carbon content of the pyrolysate diminishes with increasing oxygen content of the purging gases, with an increase in sludge residence time beyond the optimum 90 min., and generally with increasing purging gas flow, although for an unexplained reason carbon content decreased when the purging gas flow was reduced below the optimum 25 liters/min. Approximately 25% of the carbon in the sludge appeared in the pyrolysate when the latter contained 14.1% carbon.

Adsorption Experiments

Samples of 14.1% carbon pyrolysate, together with fly ash obtained from the incinerator of the Greenway plant, and activated coconut charcoal (Fisher Co., catalogue no. 5-690), were pulverized, and in each case the portion passing 70-mesh and retained on 100-mesh was retained for the adsorption tests.

Effluent from the Greenway plant was used for the experiments designed to measure the capacity of the adsorbents and with respect to removal of residual organic material. The

effluent was first filtered, then heated to 180°F. for 10 min. to stabilize it biologically. The runs were made with 200 ml. of effluent and 1 g. of adsorbent in shaken Erlenmeyer flasks over 24 hr. at room temperature. The contents of the flasks were allowed to settle, and samples of supernatant solution were withdrawn, filtered, and their COD determined. Results of these experiments are presented in Table IV.

The dye crystal violet was selected for the decolorization tests. The dye concentration before and after adsorption was calculated from optical adsorbance measurements at 585 μ. The calibration curve was linear over the concentration range encountered in the adsorption tests. Preliminary tests indicated that adsorption equilibrium was essentially attained after 5 hr. Decolorization runs were made in shaken Erlenmeyer flasks containing 100 ml. of dye solution having an initial concentration of 3×10^{-3} g./liter of dye, and various weights of adsorbate. The results are shown in Figure 1. Residual adsorbent was removed from the samples by centrifuging before taking spectrophotometer readings.

Discussion

The results of both sets of adsorption experiments indicate clearly that pyrolyzed sewage sludge is intermediate in its adsorbing capacity between fly ash and activated carbon. The data represented in Figure 1 are best fitted by an equation of the Freundlich-type—namely, one in which the weight of adsorbate adsorbed per unit weight of adsorbent is proportional to the equilibrium concentration raised to a constant fractional power. This type of equation does not permit the calculation of a nominal monolayer adsorption, and it is therefore difficult to compare quantitatively the relative adsorptive capacity of the three adsorbents. The COD reduction tests also did not permit the determination of a quantitative measure of adsorptive capacity, since these tests resulted in different equilibrium concentrations for the different adsorbents. The general trend of the results is unmistakable, however, and it implies that pyrolyzed sewage sludge has a considerably greater adsorbing capacity with respect to both the dye crystal violet and residual oxidizable organic material in sewage plant effluent than has fly ash, although not surprisingly, its capacity was found to be less than that of activated charcoal. The potential use of this material in the tertiary treatment of renovated waste water will be determined by further studies on its production and adsorbing properties.

Table IV. Results of COD Adsorption Tests,[a] Initial COD 53.5 mg./liter

Adsorbent	Activated carbon	Pyrolyzed product, % C				Fly ash
		14.3	13.25	10.7	5.3	
Final COD, mg./liter	10.2	32.6	32.9	36.1	41.4	49.8
Removal, %	81.0	39.1	38.5	32.5	22.5	6.8

[a] Contact time, 24 hr.
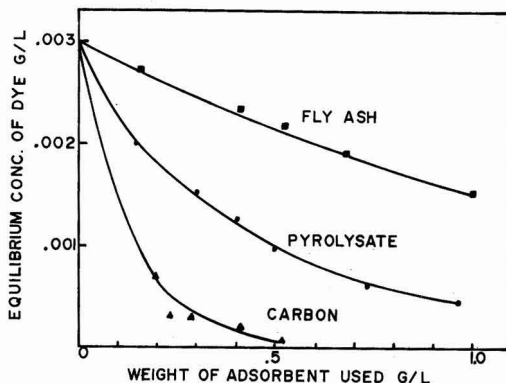
Figure 1. Adsorption of the dye crystal violet

Equilibrium dye concentration *vs.* weight of absorbent used (100 ml of solution used per run)

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Removal of Lead from Automobile Exhausts by Molten Salts

Shang-I Cheng, Harris Pitlick, and Robert Siegel
The Cooper Union for the Advancement of Science and Art, New York, N.Y. 10003

■ An exploratory study has been made on the removal of lead particulates from automobile exhausts by means of molten salts. The variables investigated were the type of salt, screen size, and the temperature of the salt. The experimental data indicate that the efficiency of lead removal increases with the temperature of scrubbing and decreases with the screen-hole size. Although concrete conclusions with regard to the optimum operating conditions of this process are difficult to draw because of limited data, it is apparent that molten salts have the ability to remove lead particulates from automobile exhausts. The higher than expected efficiency suggests to the authors that the particular removing process might involve a polarization phenomenon.

Lead is usually added to gasoline in the form of tetraethyl lead (TEL) to improve the efficiency of fuel combustion in high-compression engines. Chlorides and bromides are also added to gasoline as "scavengers" to prevent lead from building up inside the engine. The principal lead compound exhausted into the atmosphere is lead chlorobromide, which can form complexes with ammonia and phosphorous oxides. These compounds are in the form of small particles, 90% of which are less than 1 to 60 μ in diameter, 75% less than 0.90 μ, and 60% less than 0.45 μ (First, 1965). In New York City 2560 p.p.m. of lead was found in street sweepings as compared to 16 p.p.m. for the average lead content of the earth's crust (McCaldin, 1965).

The problem of whether lead compounds exhausted from automobiles affect human health remains a controversial issue. While there are claims that the case for control of lead emissions has not been strong enough to justify immediate action, and that airborne lead pollutants do not have adverse effects on health, there are supporting studies (HEW, 1959; Mackenzie, 1966) that show lead compounds are poisonous to the catalysts in the after-burners required by law in some states to be attached to the exhaust to convert products of incomplete combustion to harmless oxides. Therefore, without consideration of health problems, the removal of lead compounds from automobile exhausts might still be beneficial to the air pollution abatement program as a whole. Some exploratory work in the use of molten salts for this purpose is reported here.

Experimental

Apparatus. The experimental apparatus is shown in Figure 1, and a detailed drawing of the salt kettle is shown in Figure 2. The inlet to the train of four adsorption flasks was connected to the exhaust of an idling 1964, 6-cylinder Falcon gasoline engine, and the engine was connected to a dynamometer. The gasoline used was Mobil regular, each gallon containing 2.40 to 2.55 g. of TEL and 1 equivalent of chloride and 0.5 equivalent of bromide as scavengers. The engine was operated at 600 r.p.m., with the rate of gasoline consumption of about 1.02 gal. an hour. The total flow rate of exhaust gases was 12.4 ft.^{3} per min. Only a part of the flow (0.20 to 0.34 c.p.m.) was allowed into the scrubbing device, the rest vented directly into the atmosphere. The engine exhaust gases were first passed through a condenser to be cooled to near room temperature, and then passed through a train of four 500-ml. flasks. The first three flasks each contained 200 ml. of 5% nitric acid solution. The fourth flask contained 200 ml. of 4% caustic solution to prevent any acid from getting into the meter flow. The depth of the molten salt in the kettle was 6 in. above the bottom. A stainless steel screen was placed 4 in. below the
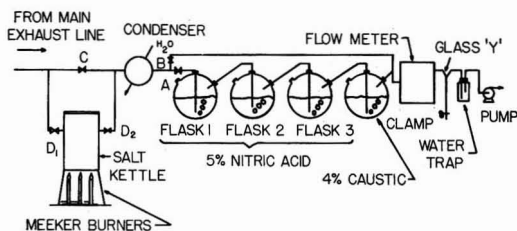
Figure 1. Apparatus used for lead removal
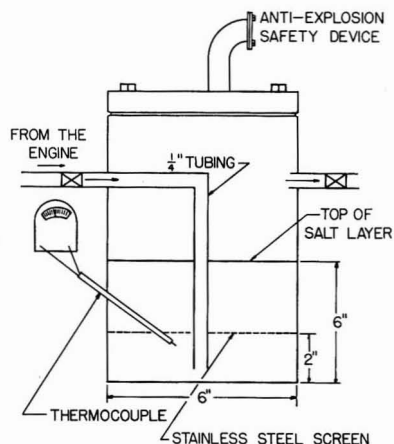
Figure 2. Salt kettle

surface of the molten salt. The suction at the end of the adsorption train was adjusted so that the pressure in the salt kettle was maintained at atmospheric pressure.

Procedure. The engine was run for 30 min. to reach a steady concentration of lead in the exhaust. When the engine was started, lead deposits built up in the engine from prior operation were blasted off, therefore the quantity of lead in the exhaust was not uniform. Before taking samples the gaseous contents of the bypass and kettle were vented through valve B with valve A closed. Untreated exhaust was sampled through valve C with valves D_1 and D_2 closed. After 5 ft.[3] of untreated exhaust gas was passed through the adsorbing train, a 10-ml. sample of acid solution was taken from each flask for analysis of its lead content. The contents of each of the first three flasks were replaced with 200 ml. of fresh 5% nitric acid. Five cubic feet of molten salt-treated exhaust gas was passed through the absorbing train through valves D_1 and D_2 with valve C closed. Ten milliliters of acid solution was taken from each of the first three flasks for lead analysis.

Method of Analysis

The analysis of the lead adsorbed by the acid was performed by taking a 10-ml. sample from each flask and diluting to 50 ml. The pH of the solution was adjusted to 8.5 to 10.0. Ten milliliters of the diluted unknown, 10 ml. of ammonium cyanide–sulfite solution, and 10 ml. of dithizone–carbon tetrachloride solution were added into a separatory funnel, in that order. The mixture was shaken vigorously for a few minutes and allowed to settle. The absorbance of the carbon tetrachloride layer at a wavelength of 520 mμ was determined immediately with a Beckman electronic 20 spectrophotometer. The lead content of the acid solution was determined by comparing the absorbance with a nonlinear standard curve. The solutions used for the analysis were prepared according to Sandell (1959) as follows:

Dithizone solution, 25 mg. dissolved in 1 liter of carbon tetrachloride.

Nitric acid solution, 5% by volume in distilled water. Ammonium cyanide–sulfite solution, add 30 ml. of 10% potassium cyanide solution to 725 ml. of 8.0M ammonium hydroxide. Dilute to 1 liter and dissolve in 1.5 g. of sodium sulfite.

Calculations

The percentage of lead removed by molten salt treatment was calculated by the following equation:

$$\% \text{ lead removed} = \frac{\dfrac{AD_1}{E_1} - \dfrac{BD_2}{E_2}}{\dfrac{AD_1}{E_1}} \times 100\%$$

where

A = total lead content of 10 ml. diluted absorbing solution used for treated exhaust gas, in micrograms.
B = total lead content of 10 ml. diluted absorbing solution used for treated exhaust gas, in micrograms.
D_1 and D_2 = dilution factors for untreated and treated cases, respectively.
E_1 and E_2 = collection efficiencies of absorbing trains for untreated and exhaust gases, respectively.

In our case,

$$D_1 = D_2$$

and

$$E_1 = E_2 = \text{efficiency of lead removal}$$
$$\text{for each flask}$$

Sample calculation: run no. 3

Analysis of absorbing solutions for untreated exhaust gas

Sample from flask no.	Absorbance	Wt. of Pb/10 ml. diluted solution
1	0.145	6.10
2	0.075	3.25
3	0.600	2.70

Total lead content per 10 ml. of diluted solution = 12.05 μg.

Analysis of absorbing solutions for treated exhaust gas

Sample from flask no.	Absorbance	Wt. of Pb/10 ml. diluted solution
1	0.090	3.90
2	0.059	2.70
3	0.032	1.50

Total lead content per 10 ml. of diluted solution = 8.10 μg.

Percentage of lead removed =

$$\frac{\dfrac{12.05 \times 50}{E_1} - \dfrac{8.10 \times 50}{E_2}}{\dfrac{21.05 \times 50}{E_1}} \times 100\% = 33.1\%$$

Results

The variables investigated were the type of salt, screen size, and the temperature of the salt.

Potassium thiocyanate and potassium nitrate were tested. The sizes of the stainless steel screens used were 20- to 30-mesh. The temperature range was from 180° to 300°C. Lead content in the untreated exhaust gas was determined under the same conditions twice to check the reproducibility of the method. Table I shows in detail the results of the analysis of lead content of the untreated gas. The closeness of the two results indicates that the reproducibility of the experiment was good. The overall results of the investigation are shown in Table II.

The results indicate that the efficiency of lead removal increases with the temperature of scrubbing and decreases with the screen-hole size. No conclusion can be made on the effect of the type of salt used or its efficiency because of insufficient

Table I. Analysis of Lead Content of the Untreated Exhaust Gas

Run no. 1 Flask no.	Absorbance	Lead per 10 ml. of diluted absorbing solution (μg.)
1	0.145	6.10
2	0.075	3.25
3	0.060	2.70
		12.05 Total
Run no. 2 Flask no.		
1	0.139	5.90
2	0.082	3.50
3	0.062	2.75
		12.15 Total

Table II. Overall Results of Lead Removal by Molten Salts under Different Experimental Conditions

Run no.	Molten salt	Kettle temperature, °C.	Flow rate of exhaust gas through scrubbers, c.f.m.	Screen-size, mesh	% Pb removed
3	KCNS	180–190	0.34	20	32
4	KCNS	210–220	0.34	20	44
5	KCNS	180–190	0.34	30	34
6	KCNS	210–220	0.34	30	62
7	KNO_2	300	0.20	30	72

data. Due to limitations imposed by the melting points and decomposition temperatures of various salts, comparison of the performance of the two salts in the same temperature range was not made.

Conclusion and Discussion

Since molten salts are fluid and have low vapor pressures at elevated temperatures, they are logical scrubbing agents for the removal of particulates where the cooling of polluted gases is not permitted and the use of water or aqueous solutions for scrubbing is not adequate. The authors expected that lead particulates, once captured and wetted by molten salts, would be prevented from re-entraining back into the gas stream due to the relatively high surface tension of molten salts. Although concrete conclusions with regard to the optimum operating conditions of the process cannot be made because of limited data, it is apparent that molten salts have some ability to remove lead particulates from automobile exhausts. The efficiency observed is higher than expected. It indicates the possibility of a polarization phenomenon. Since particles at high velocities and temperatures usually possess some electrical charges, the lead particulates in automobile exhausts may also have charges. When gases containing charged particles are bubbling through molten salts which have relative

high conductances, they may polarize the salt melt. Electrical charges opposite to those particulate matters tend to gather at the vicinity of gas bubbles and an electrical field is built around them. The speedup of the movement of lead particulates toward molten salts under the influence of a force field might be the reason for the increase in collection efficiency.

The electrical charges may be acquired by the particles through several mechanisms: Since the exit velocities of automobile exhausts are relatively high, pulverization and abrasion among particles and between the particles and container may produce charges. Because these particulates are formed at relatively high temperatures, electric charges may be formed by thermionic emission. Another factor which may account for the occurrence of electrical charges on the lead particulates is the settling of gaseous ions and electrons upon particles in suspension (Fuks, 1964).

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Activation Analysis of Airborne Selenium as a Possible Indicator of Atmospheric Sulfur Pollutants

K. K. Sivasankara Pillay, Charles C. Thomas, Jr., and James A. Sondel

Western New York Nuclear Research Center, Inc., Buffalo, N.Y. 14214

■ Neutron activation analysis is used to measure the selenium content of air pollutants. These results are compared with total sulfur content of air pollutants determined by gravimetric analysis. The Se/S ratios of airborne pollutants from Buffalo, N.Y., monitored during 1968–69, range from 0.5 to 1.6×10^{-3}. These results are contrasted with the Se/S ratios in fossil fuels reported earlier. The selenium contents of both particulate and gaseous pollutants have been separately determined and reported. Knowing the Se/S ratio of air pollutants in a region, neutron activation analysis of selenium may be used for an estimate (an order of magnitude or less) of the sulfur content of air pollutants.

The isomorphism of selenium and sulfur has long been recognized. The close analogy of the properties of selenium and sulfur has been used to determine the main features of the geochemistry of selenium in the earth's crust. Indeed, most of the natural sources of selenium are from sulfur-bearing minerals. The distribution of selenium (Lanche, 1965) and sulfur (Ambrose, 1965) in the lithosphere is reported to be approximately 0.09 p.p.m. and 900 p.p.m., respectively. In addition, Rankama and Sahama (1950) and Sindeeva (1964) have reported certain constancy in selenium/sulfur ratios in various geochemical minerals. Pillay *et al.* (1969) reported certain constancy in the Se/S ratios of fossil fuel samples.

Since the major source of sulfur pollutants in the air is from the combustion products of fossil fuels, it is reasonable to expect that the Se/S ratio in airborne pollutants should be representative of the fossil fuel consumption pattern in a geographic area. This paper reports the results of selenium/sulfur ratio analysis of air pollutants in Buffalo over a one-year period.

Air Sampling

All air pollutant samples were collected from four different air sampling stations in the Buffalo area. Samples were collected with sequential air samplers (Gelman Model 24001) modified to use 500-ml.-capacity Greenburg-Smith impingers for liquid traps. The air sampling cycle involved a 2-hr. sampling per filter paper with a 10-min. interval between samples. The air passing through the filter paper is bubbled through the liquid trap (containing dilute solutions of lead acetate). Each of the sequential samplers had 12 sampling positions, consisting of a filter paper and liquid trap. At the end of one cycle (12 samples or 26 hr.), the sampler was recycled. This sequence continued over a period of at least one week. The filter papers were either Millipore EHWPO4700 or Dexter X-1215 (47-mm. diameter), and had a filter efficiency of nearly 100% for particulate matters 0.1 μ or greater. Both filter paper and the liquid samples were used in the analysis of sulfur and selenium. Half the samples from each set were used for the analysis of sulfur and the other half were used for selenium analysis. For the gravimetric analysis of sulfur, the six samples from a set were combined together, whereas, for the neutron activation analysis of selenium, individual samples were used.

Sulfur and Selenium Analysis

For the analysis of sulfur, the filter papers containing air particulate pollutants were digested in 0.1N sodium hydroxide solution. The liquid samples corresponding to the filter papers were added to the filter paper digest. Bromine water was added to the warm solution to oxidize sulfur compounds to sulfates. The solution was kept warm until the excess of bromine was removed. Subsequently, the solution was acidified with dilute hydrochloric acid and sulfates precipitated and determined gravimetrically as barium sulfate (Vogel, 1961).

For the analysis of selenium, liquid samples were reduced to a minimum volume by a flash evaporator (Buchler Model PF-9GN) under reduced pressure. The samples were quantitatively extracted and sealed in quartz vials. The filter papers containing the air particulates were also encapsulated in separate quartz tubes. These samples, along with selenium standards, were arranged in a rotating sample irradiator and exposed to a thermal neutron flux of about 3×10^{13} neutrons cm.$^{-2}$ sec.$^{-1}$ for 20 hr. in the PULSTAR reactor facility. After a week's decay, the samples were removed and frozen in Dry Ice before opening the quartz capsules. The samples were extracted with warm, dilute nitric acid, and after adding 40 mg. of selenium carrier, the solution was evaporated to about 15 ml. and then ashed into a mixture of perchloric acid and nitric acid, 5 ml. each. The solution was then warmed to remove the excess nitric acid. Heating was continued until dense white fumes of perchloric acid appeared. The mixture was allowed to cool before being transferred to a distillation flask. The selenium was separated by extractive distillation as halides and reduced by sulfur dioxide to elemental selenium with the procedure described by Pillay *et al.* (1969) for the separation of selenium from fossil fuels. Selenium is determined by gamma spectrometry of the prominent gamma rays

(265, 136, 280, and 121 Kev) from the long-lived ^{75}Se activity with use of a 4 in. $\times$ 4 in. well-type NaI(Tl) detector and a 400-channel pulse height analyzer. The selenium content of the samples were calculated with Schoenfeld's (1966) ALPHA-M computer program. A limited number of samples were also analyzed using the short-lived [81m,81]Se activity.

Results and Discussion

A series of air pollutant samples containing known amounts of radioactive selenium was analyzed to assess the adaptability of the selenium separation method and the accuracy of analysis. Fourteen samples (both particulate and liquid trapped) were spiked with 0.05 to 1.0 μg. of selenium containing [75]Se. The analysis of these samples by extractive distillation and subsequent gamma-ray spectrometry showed a standard deviation of $\pm 10\%$ for the particulate samples and $\pm 14\%$ for the liquid samples.

Simulated filter paper and liquid trap samples containing soluble sulfides and sulfates were analyzed for sulfur by using the gravimetric analysis procedure discussed earlier. The analyses of six samples containing known amounts of sulfur (about 5 mg.) showed a standard deviation of $\pm 3.8\%$, with a precision of better than 6%.

Periodic sampling of air pollutants in the Buffalo area was done over a one-year period. The samples were analyzed for both sulfur and selenium content. The results of gravimetric analysis of sulfur and neutron activation analysis for selenium of these samples are presented in Table I. The selenium/sulfur ratio of each set of samples was calculated to determine whether a constancy in this ratio exists. The results show that most of the values of the selenium/sulfur ratio in the atmosphere of Buffalo varied in the range of 0.5×10^{-3} to 1.6×10^{-3} (average, 0.9×10^{-3}) for the period of study.

At the present time the only published work available to compare these results with is the study made by Hashimoto and Winchester (1967) in the New Haven and Cambridge areas. However, their studies were mainly done on falling snow, rain, and ice, with a limited number of air samples. The average value of the selenium/sulfur ratios in these samples was 1×10^{-4} (range, 1×10^{-5} to 4.4×10^{-4}).

Recent work (Pillay *et al.*, 1969) on the selenium/sulfur ratios of about 130 fossil fuels showed that in the majority of the coal samples, the average value of the selenium/sulfur ratio is 2.9×10^{-4} (range, 0.5×10^{-4} to 5×10^{-4}), whereas in the majority of crude oils, the average selenium/sulfur value is 0.5×10^{-4} (range, 0.1×10^{-4} to 0.6×10^{-4}). Erion *et al.* (1960) reported the selenium content of sulfur samples recovered from refinery gases and hydrogen sulfide in natural processing showing a selenium/sulfur ratio of less than 10^{-7}.

According to the results published by the U.S. Public Health Department (1968), the severity of air pollution in the Buffalo and New Haven areas are comparable. Further inquiry into the fuel consumption patterns of New Haven and Buffalo revealed the following information. According to the Connecticut Department of Health (Romano, 1969), the use of coal as a fuel in New Haven, Conn., is very rare. The two large power stations in the area use no. 6 fuel oil, nearly 80% of the domestic heating is by no. 2 fuel oil, and the remaining 20% is mostly by natural gas. On the other hand, according to the Erie County Health Department (Hoekstra, 1969), the sulfur pollutants from coal are about 10 times the level resulting from oil in Buffalo. During 1968, about eight million tons of coal and coke were used in Buffalo. Also, it is known that the Bethlehem steel plant near Buffalo uses 1.3% sulfur coal while the power station uses 2 to 2.5% sulfur

coal. These facts about fuel consumption patterns might account for the difference in the selenium/sulfur ratio between the air pollutants in Buffalo and the environmental samples from New Haven. From the fuel consumption patterns and the known selenium/sulfur ratios in coal and crude oil, it is reasonable to expect the selenium/sulfur ratio in the air pollutants to be higher in Buffalo when compared with New Haven. There is, however, an observable difference (increase) in the selenium/sulfur ratio of the environmental samples when compared with the selenium/sulfur ratio of coal and crude oil. This may be due to the selenium source in the atmosphere not being solely from the combustion products of fossil fuels and (or) the residence time of selenium in the atmosphere may be longer than that of sulfur. It is, however, significant that, in a given geographic area, the measured selenium con-

tent of air pollutants can be a useful indicator of total sulfur levels in the atmosphere, once the selenium/sulfur ratio is reliably established.

During this investigation, we have separately determined the amounts of selenium retained on filter materials and in the liquid trap past the filters. The results presented in Table II show that on the average, about 56% of the selenium was not retained by the filter materials capable of retaining nearly 100% of all particulates 0.1 μ or greater. Since sample sizes were limited, separate gravimetric analysis of sulfur content of particulates and gaseous pollutants corresponding to the selenium values reported in Table II were not possible during this investigation. Moreover, it is hard to distinguish between fine aerosols and gaseous pollutants by ordinary air monitoring methods.

Table I. Concentrations of Airborne Selenium and Sulfur

Sample no.[a]	Vol. of air sampled (m.³)	Selenium $\mu g./m.^3$	Sulfur	Se/S $\times 10^3$	Sampling period
M1	201	9.5×10^{-3}	6.0	1.6	Oct. 1968
M2	269	5.8×10^{-3}	11.5	0.5	Nov.
M3	352	5.1×10^{-3}	4.0	1.3	Nov.
M4	578	5.4×10^{-3}	5.4	1.0	Nov.
M5	323	5.6×10^{-3}	3.7	1.5	Dec.
M6	222	8.2×10^{-3}	5.9	1.4	Dec.
K2	249	7.3×10^{-3}	7.3	1.0	Jan. 1969
K5	599	3.6×10^{-3}	7.2	0.5	Apr.
N5	631	6.1×10^{-3}	8.7	0.7	Apr.
D1	347	7.9×10^{-3}	7.2	1.1	May
D2	541	5.0×10^{-3}	7.2	0.7	May
D3	541	6.1×10^{-3}	8.7	0.7	June
D4	558	5.6×10^{-3}	11.1	0.5	July
D6	790	3.7×10^{-3}	6.1	0.6	Aug.
D7	465	5.3×10^{-3}	8.8	0.6	Oct.
D8	474	7.4×10^{-3}	10.8	0.7	Oct.
D9	694	9.7×10^{-3}	12.1	0.8	Nov.
D10	615	9.1×10^{-3}	10.1	0.9	Nov.

[a] M, Museum of Science, Buffalo, N.Y.; K, Lackawanna, N.Y.; N, State University Campus, Buffalo, N.Y.; D, New York State Air Monitoring Station, Dingens St., Buffalo, N.Y.

Table II. Selenium Content of Atmosphere

Sample no.[a]	Vol. of air monitored (m.³)	Selenium retained				Total concn of Se, $\mu g./m.^3 \times 10^3$
		On filter paper		In liquid trap solutions		
		$\mu g.$	%	$\mu g.$	%	
M1	201	0.69	36.9	1.18	63.1	9.5
M2	269	0.70	50.0	0.70	50.0	5.8
M3	352	0.80	43.7	1.03	56.3	5.1
M4	578	1.31	43.5	1.70	56.5	5.4
M5	323	0.70	39.5	1.02	60.5	5.6
M6	222	0.74	39.8	1.12	60.2	8.2
K2	249	0.80	43.0	1.06	57.0	7.3
K5	599	0.85	38.8	1.34	61.2	3.6
N5	631	1.66	44.5	2.07	55.5	6.1
D1	347	1.12	42.6	1.52	57.4	7.9
D2	341	1.24	42.9	1.65	57.1	5.0
D3	541	1.76	56.2	1.37	43.8	6.1
D4	558	1.32	41.4	1.87	58.6	5.6
D6	790	1.52	52.1	1.40	47.9	3.7
Av.	...	...	43.9	...	56.1	6.1

[a] M, Museum of Science, Buffalo, N.Y.; K, Lackawanna, N.Y.; N, SUNY/AB Campus, Buffalo, N.Y.; D, New York State Air Monitoring Station, Dingens St., Buffalo, N.Y.

Conclusions

The results of this investigation indicate the possibility of using neutron activation analysis of selenium in the atmosphere as an indicator of the levels of total sulfur pollutants. Selenium/sulfur ratio measurements can be used to distinguish the sulfur pollution caused by combustion products of coal from that of crude oil.

With a knowledge of the Se/S ratio of air pollutants in a geographic area, the neutron activation analysis of selenium can be used as a fast and reliable method for estimating total sulfur pollutant levels. The advantage of this method arises from the fact that the neutron activation analysis of selenium can be performed on samples collected by monitoring about 10 to 20 cubic meters of air; whereas, for the gravimetric analysis of total sulfur, at least 150 to 200 cubic meters of air sampling is necessary. The total duration required for selenium analysis can be further reduced by use of the short-lived ^{81,81m}Se isotopes for activation analysis.

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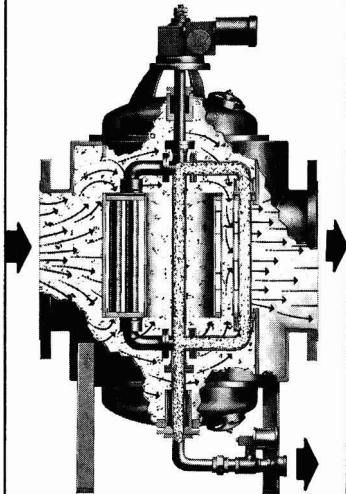
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industry trends

Sun Oil Co. (Philadelphia, Pa.) has developed a Fortran computer program to calculate pollutant concentrations at various distances from a source of emission. Sun Oil will provide the program free to state and local regulatory agencies and, for a small fee, to industrial companies. A detailed manual will also be provided.

AMF Cuno Maxim (Meriden, Conn.) will construct two 47,000-gpd radioactive liquid waste concentration systems under a contract with the Sacramento (Calif.) Municipal Utility District. The systems will be installed at a new power plant. The concentrated wastes will be stored for later disposal by contractors licensed by the AEC. Boric acid, also to be removed, will be reused in the plant.

Monsanto Biodize Systems has been awarded a contract by Blue Ridge-Winkler Textile Co. to design and construct a plant to remove dye pollutants from a textile plant in Bangor, Pa. The plant will treat 750,000 gpd and remove 95% of the BOD. Biodize has six other water treatment plants for customers either built or under construction.

Masonite Corp. is in the second phase of a $10-million pollution control program at its Laurel, Miss., hardboard plant. In this phase, a biological treatment plant will be built to handle 360,000 gph from two separate waste streams. Excess sludge will be electrolytically dewatered and mixed with wood solids to yield a product salable as a soil conditioner.

Kimberly-Clark Corp. has installed a fiber recovery system at its tissue products plant in Neenah, Wis. A suspension containing 4% cellulose fibers is concentrated to about 30% in a modified wine press. The recovered water is recycled and the fibers are mixed with earth for use as cover at a local landfill.

CF&I Steel Co. (Pueblo, Colo.) plans to complete a water pollution abatement system at its New Jersey Roebling plant by the end of this year. The project, estimated to cost $2 million, involves neutralization of spent acids, separation of oils and solids, and the retention of soap solutions.

Babcock & Wilcox Co. has received a $3-million order from Hoerner-Waldorf Co. to provide a control odor recovery unit and to convert a recovery boiler to a control odor design. The work will be done at H-W's Missoula, Mont., pulp mill, a plant that has frequently been in the news for its air pollution that caused vociferous public outrage. The contract is part of the $11-million second phase of H-W's air emission control program.

The Swindell-Dressler Co. (Pittsburgh, Pa.) will construct a mine water treatment plant in Philipsburg, Pa., under a contract with the Pennsylvania Department of Mines and Mineral Resources. The plant will utilize ion exchange (see also this issue, page 24) and will cost $1.9 million. It will supply reservoirs with additional potable water of 500,000 gpd.

Commonwealth Associates, Inc. (Chicago, Ill.) has acquired an exclusive western hemisphere license to offer a German sulfur oxides removal process. The Chemiebau process is based on dry adsorption of the sulfur oxides on char, which is regenerated to yield the oxides in concentrated form. Facilities using the process will be able to produce activated carbon as a side stream, the licensee claims.

Armco Steel Corp. (Middletown, Ohio) has formed a subsidiary company, Armco Environmental Engineering. The new firm will perform surveys, sampling services, process development, and design engineering. It will draw on the experience of its parent company with environmental control systems. Main customers for the new subsidiary are expected to be the smaller firms that cannot afford their own pollution control staffs.

Universal Oil Products Co. (Des Plaines, Ill.) will install a demonstration sulfur removal process at Commonwealth Edison's generating station in Hammond, Ind. The process, which will cost about $4 million, is based on wet scrubbing of flue gases. Gases at 80,000 cfm will be treated in the unit, to be built by Procon, Inc. UOP plans to license the process.

new products
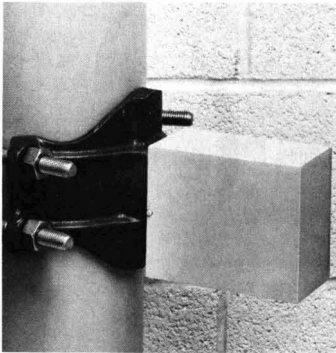
Sludge density meter

A self-cleaning device for the measurement and monitoring of waste water treatment plants constantly reads the density of the sludge, thus providing the operator with information for controlling the plant's operation efficiency. The instrument provides continuous information saving laboratory analysis, and is sensitive over a wide range of sludge and mixed liquor concentrations. It overcomes the waste water equipment problems of slime formation and clogging. The sampling chamber cleans its optical surfaces four times per minute to ensure its accuracy and reliability over long periods. Biospherics Inc.   **61**

Sludge press

A new sludge dewatering multiroll press (MRP) produces higher solids concentration in sludge. The solids content of the dewatered product from the MRP ranges from 15 to 45% dry solids by weight. Developed to treat sanitary sewage, the MRP has also been successfully applied to a wide variety of industrial sludge dewatering requirements. Permutit Co.   **62**

Water monitor boat

Installed on a trailerable 21-ft, fiberglass work boat with diesel power, this water quality monitoring system includes high precision in situ conductivity, salinity, temperature and depth sensors, submersible pump system, dissolved oxygen and pH sensors, and recorders. CM², Inc.   **63**

Air pollution analyzer

A new quadropole mass spectrometer, developed for qualitative and quantitative measurement of air pollutants, measures oxides of carbon, nitrogen and sulfur, ozone, and hydrocarbons. Features include a broad-ranged search for the simultaneous identification of several unknowns, high sensitivity, and rapid measurement. Environmental Instruments Co.   **64**
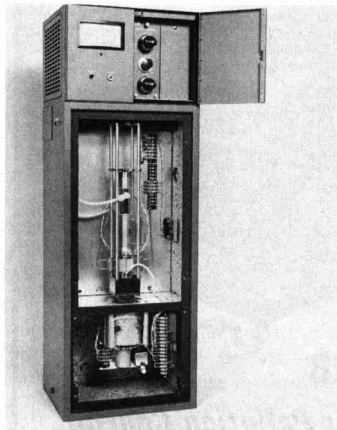
Infrared analyzer

The unit is designed for continuously measuring a single gaseous component in mixed-gas streams. The analyzer combines two functions: sensing the infrared-absorbing gases and sensing all infrared-absorbing gases except the one being measured. Both generate a signal which is picked up by differential thermopiles in a detector. Leeds & Northrup Co.   **65**

Fish pollution testing

Industrial water quality standards can be implemented through use of live fish as testing media. Companies engaged in clarification of their effluent or influent can maintain biological checks by adding treated wastes, in ppm, to laboratory fish tanks having raw or polished waters pumped through fish tanks on a 24-hr cycle, and establishing outdoor fish ponds stocked with multiple-fish populations through which treated effluent is passed. Bioquatic Industries   **66**

Roto-shredder

This machine shreds sewage sludge, household refuse, animal wastes, and other solid waste products. Two to three hundred tons of material can be processed per hour. Wastes are dumped in windrows. The Roto-shredder straddles the windrow and travels its length, aerating and mixing the material. This aeration supports aerobic bacteria, which decompose organics quickly. Machine can be used by the farmer, race track owner, canner, meat packer, and other producers of animal or vegetable organic wastes. Roto-shredder Co.   **67**

Chemiluminescent ozone monitor

The REM Ozone Monitor has the following characteristics: (1) measures ozone specifically, (2) no atmospheric interferences, (3) instantaneous response to ozone, (4) gas-phase chemiluminescent reaction (ozone and ethylene), (5) range of monitor is 0 to 200 pphm with higher ranges available, (6) digital data display, (7) solid-state electronics, and (8) analog and BCD outputs for data recording. NAPCA report available on this instrument. REM Inc.   **68**

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

Butterfly valves

TFE butterfly valves provide positive control of even the most corrosive fluids employed or generated by pollution control operations. These GAR-SEAL valves range from 2 to 20 in. or more. All wetted surfaces are completely protected by molded, void-free, virgin TFE with a minimum thickness of 3/32 in. GAR-SEAL valves provide leakproof control of any liquid or gas at pressures from a vacuum of 30 in. mercury and temperatures as low as −130°F up to operating pressures of 150 psi and temperatures to 400°F. Garlock Inc. **69**

No-pollutant cleaners

The Magic Genie family of nonpolluting cleaning products includes a biodegradable laundry detergent, dishwashing liquid, and an all-purpose disinfectant cleaner. These products contain no phosphates, enzymes, NTA, or any other pollutants. United States Environmental Research, Inc. **70**

Odor control

CAIROX(R), potassium permanganate, is used in solution in the wash water of wet-air scrubbers where it acts as a rapid oxidant, destroying odors completely or rendering them inoffensive. Controls odors caused by sulfides, mercaptans, phenols, starch, cooking, animals, and manure (which may be emitted from chemical companies), food processors, rendering plants, manufacturers of building materials, paint and varnish manufacturers, laboratories, grain-drying operations, textiles manufacturers, and restaurants. Municipalities use CAIROX(R) to overcome odors from digestors in waste treatment plants, sewer lines, and wetwalls. Carus Chemical Co., Inc. **71**

Mercury analyzer

This system determines mercury in solids and solutions, organic or inorganic, or air. Model MAS-50 gives a direct meter reading in micrograms of mercury and %T. With a sensitivity of 0.01 μg of mercury, the instrument has a range of 0 to 9 μg of mercury without dilution. Useful for local governments and antipollution organizations for routine checks of water, soil, air, fish, fowl, game, produce, and the like. Coleman Instruments **72**

Fluoride measurement

Model 409 Water Fluoride Measuring System senses fluoride in drinking water by an electrode. Concentration is read either from the 0.1 to 10 ppm scale or the expanded 0.5 to 2 ppm scale. Color-coded instrument panel, meter face, and standards greatly simplify the operation. Distillations, weighings, and calculations are eliminated, and there is no need to recalibrate when switching scales. Orion Research Inc. **73**

Aluminum can flattener

This tool has a fabricated type of hinge which holds the can in place and then creates enough pressure to flatten the can quickly and with ease. With the aluminum can flattener, 1000 flattened aluminum cans can be put in three bushel baskets—scrap value approximately five to six dollars —in a form acceptable to scrap yards. Features include portability, one-operation simplicity, and its low cost. Falcon Products, Inc. **74**

Manhole pumper

A new trailer-mounted, 1000-gal. manhole pumper operates at street level and completely eliminates the need for personnel to enter manholes or septic tanks. The pumper will handle up to 250 gpm, will pass solids up to 2.875-in. diameter, and is powered by a 12-hp gasoline engine. The pumper is also equipped with an internal flushing system. Rockwell Manufacturing Co. **75**

Flue gas sampler

After insertion at any point along duct work, a sample of the flue gas stream is drawn through a 1.5-in. diameter stainless steel tube in series with a replaceable filter bag. The unit is complete with a control valve, a thermometer well, and draft gauge connections for flow measurements. Universal Oil Products Co. **76**

new literature

Nuclear power and ecology. Two reports describe the ecological effects of nuclear power facilities upon the surrounding environment. "Millstone Point—Its Land and Air" details a variety of hydrological, ecological, and radiological studies begun over the past several years in anticipation of the start-up of the 650,000 kW first-generating unit at Northeast Utilities' Millstone Power Station on Long Island Sound in Waterford. "A River and a Nuclear Plant" describes in lay language a still-continuing study of the lower reaches of the Connecticut River that was begun before the 600,000 kW Connecticut Yankee Atomic Power Station began operating in 1968. Northeast Utilities **91**

Abatement incentives. "Pollution Abatement Incentives for Industry" is a directory of federal and state tax laws containing special tax provisions concerning pollution control investments by companies. These take the form of accelerated amortization on income taxes and exemptions from sales and property taxes. National Association of Manufacturers **92**

Air and water monitors. The "Capsulogue of Precision Scientific Laboratory Apparatus" describes several models of air and water monitors. There are seven different monitoring instruments for various pollution detection and assessment operations: continuous NO_2 monitor, sequential sampler, automatic tape sampler/recorder, tape spot evaluator, high-volume sampler, SO_2 dustfall monitoring stations, and sulfation plate holders. The three water pollution monitoring instruments include the AquaRator for COD tests, Model 805 for BOD measurement, and an analyzer for dissolved oxygen. Precision Scientific Co. **93**

Incineration. Reprint 142 is a guide for plant owners and plant engineers to help them decide when and how to use combustion to dispose of solid, liquid, or gaseous wastes in a pollution-free manner. Also available is a new six-page, two-color brochure with photographs of 14 different installations, showing successful solutions to gas, liquid, and solid waste disposal problems through the use of North American burners. "Pollution Prevention by Combustion" offers safe, simple, and economic conversion of many waste materials to CO_2 and water. North American Manufacturing Co. **94**

Air pollution. "Engineered Equipment for Efficient Control of Air Pollution" is an eight-page catalog describing the products and services of a wide line of customized venturi scrubbers. The brochure also describes other low-energy scrubbers—impactors, absorbers, and spray types, as well as water solids separator equipment. A special feature is a description of venturi scrubbing, the most efficient method for controlling air pollution and recovery of materials from gas streams. Air Pollution Industries, Inc. **95**

Sulfur oxide emissions. Publication describes the abatement of sulfur oxide emissions from stationary combustion sources. Outlines a government-industry program for research, development, and demonstration of potential control processes for sulfur oxide emissions into the atmosphere, primarily from electricity generating stations. $3.00. Clearinghouse, U.S. Department of Commerce, Springfield, Va. 22151 (Write direct)

Plastic waste. "The Plastics Industry and Solid Waste Management" is a comprehensive position statement by the nation's plastic industry on solid waste disposal problems. The 12-page statement discusses methods of waste disposal, the polyvinyl chloride issue, reuse and recycling, and the solid waste management activities of the Society of Plastics Industry. The Society of the Plastics Industry, Inc., 250 Park Ave., New York, N.Y. 10017 (Write direct)

Steel design. Eight-page brochure explains rules and procedures for the 1970–71 Design in Steel Award Program. Product categories include environmental enhancement and control equipment. American Iron and Steel Institute, Design in Steel Program, 201 E. 42nd St., New York, N.Y. 10017 (Write direct)

Pyrolysis. Bureau of Mines Report 7428 is titled "Conversion of Municipal and Industrial Refuse into Useful Materials by Pyrolysis." Report covers analysis of municipal and industrial refuse, the pyrolysis pilot plant and test procedures, and the yields of products from pyrolysis of refuse. Bureau of Mines, Branch of Publications Distribution, 4800 Forbes Ave., Pittsburgh, Pa. 15213 (Write direct)

Pesticides and water. A panel on pesticides was developed to clarify the situation regarding the use of pesticides, particularly in and near water resources. "The Effects of Pesticides on Water Resource Developments" consists of papers and presentations by the panel. General Harold Parfitt, Chairman, Arkansas-White-Red Basins Inter-Agency Committee, 1114 Commerce St., Dallas, Tex. 75200 (Write direct)

Mine drainage. This manual, issued by the Federal Water Quality Administration, aims to help states apply for grants that will demonstrate the feasibility and practicability of mine drainage pollution control methods. "Feasibility Study Manual—Mine Water Pollution Control Demonstrations" was developed to fulfill the new provisions of the Federal Water Pollution Control Act. 65¢. Government Printing Office, Washington, D.C. 20401 (Write direct)

Ocean dumping. "Ocean Dumping—A National Policy" is a report to the President prepared by the Council on Environmental Quality. Topics covered include ocean dumping and its alternatives, ocean pollutant, legislative control of ocean dumping, and international aspects of ocean disposal. 55¢. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 (Write direct)

Three new advisors for ES&T

Morgan

Editor Dr. James J. Morgan has made three new appointments to the ES&T *editorial advisory board. Dr. Russell F. Christman, Dr. George M. Hidy, and Dr. Perry L. McCarty will each serve a three-year term that will end in December 1973. Members whose tenure on the board expired at the end of 1970 are Dr. Richard D. Cadle, Dr. Donald J. O'Connor, and Dr. Walter J. Weber, Jr. Other members of the advisory board who will continue to serve are:*

Terms expire 1971

Dr. C. E. Moser
Dr. Ulrich Merten
Dr. E. D. Palmes

Terms expire 1972

Dr. J. C. Morris
Dr. P. K. Mueller
Dr. J. N. Pitts, Jr.

Dr. Russell F. Christman is special assistant to the Provost for Environmental Affairs at the University of Washington, Seattle. He has held the position of associate professor of Applied Chemistry, Department of Civil Engineering, University of Washington, since 1963.

Dr. Christman received his B.S. (1958), M.S. (1960), and Ph.D. (1962) from the University of Florida. He is a member of ACS, AWWA, WPCF, AAAS, Sigma Xi, and Alpha Chi Sigma.

Dr. Christman's research interests are in the identification of organic compounds in water systems, with emphasis on the chemical characteristics of color-producing substances. In his new position, he is responsible for coordinating and planning the University of Washington's environmental programs.

Dr. George M. Hidy is a member of the technical staff at the Science Center of North American Rockwell in Thousand Oaks, Calif. Previously, he was with the National Center for Atmospheric Research (1962–68) and Procter & Gamble Co. (1958–59). During his university years he spent two summers with the Linde Co.

Dr. Hidy has A.B. (1956) and B.S. (1957) degrees from Columbia University, an M.S.E. (1958) from Princeton University, and a D.Eng. from The Johns Hopkins University. By profession, he is a chemical engineer. He is a member of ACS, APS, AGU, American Meteorological Society, Tau Beta Pi, Sigma Xi, and Phi Lambda Upsilon.

Dr. Hidy's research interests are in the fields of aerosols and atmospheric science, and in wave action on water surfaces.
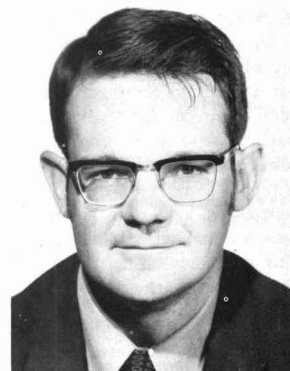
Dr. Perry L. McCarty is professor of Environmental Engineering at Stanford University, a position he has held since 1967. Previously, he was associate professor of Sanitary Engineering at Stanford (1962–67) and assistant professor of Sanitary Engineering at MIT (1958–62). While at MIT he was also an associate with Rolf Eliassen Associates.

Dr. McCarty has a B.S. (1953) in civil engineering from Wayne State University, and S.M. (1957) and Sc.D. (1959) degrees in sanitary engineering from MIT. He belongs to ASCE, WPCF, AWWA, ASEE, American Society of Limnology and Oceanography, Tau Beta Pi, Omicron Delta Kappa, Kappa Mu Epsilon, and Sigma Xi.

Dr. McCarty's particular interests concern biological treatment of wastes and removal of nutrient constituents.

Christman

Hidy

McCarty

bookshelf

Water Utility Accounting. Leon E. Hay, D. J. Grinnell. xviii + 235 pages. American Water Works Association, 2 Park Ave., New York, N.Y. 10016. 1970. $12.50, hard cover.

"This new work is much more than a revision of 'Water Works Accounting,' a basic textbook published in 1938 and designed so that laymen could use accounting procedures," says the American Water Works Association. Written with the formally trained accountant in mind, the book presents all pertinent data on the subject and reflects the increase in complexity that has taken place in accounting procedures. ∎

Environmental Law Review. 704 pages. Sage Hill Publishers, Inc., 435 Hudson St., New York, N.Y. 10014. 1970. $29.95.

Environmental law has been a rather nebulous area for most people because of the fragmented and incohesive nature of the subject. This book is the first attempt to centralize vital information on legal aspects of the rapidly changing field of environmental control. A collection of the best periodical writings of the year in the environmental law field, this volume is the first of an annual production and contains material published in 1970, 1969, and significant articles of 1968. ∎

Reverse Osmosis. S. Sourirajan. xix + 580 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1970. $25.00, hard cover.

The purpose of this book is to point toward a new and versatile field of separation technology in chemical process engineering by application of this general separation technique for the separation, concentration, and fractionation of inorganic or organic substances in aqueous or nonaqueous solutions in the liquid or gaseous phase. The application of reverse osmosis in the field of water treatment and saline water conversion is of tremendous engineering, economic, and social significance, says the author. "Even more significant is the possibility of developing the technique as a general process for the separation of any substance in solution." ∎

Master Planning the Aviation Environment. Angelo J. Cerchione, Victor E. Rothe, James Vercellino, Eds. xv + 208 pages. University of Arizona Press, P.O. Box 3398, College Station, Tucson, Ariz. 85700. 1970. $10.00, hard cover.

The editors say, "In establishing the aviation-environment master-planning symposium series, it became our goal to offer an opportunity for a diversity of viewpoints to be heard. Aviation and the people it serves must not be led as gladiators into an arena to hack each other to death." The book represents an assessment of the aviation environment as the U.S. enters the 1970's. Future plans and public communication are detailed. ∎

Sanitary Landfill Facts, 2nd ed. Thomas J. Sorg, H. Lanier Hickman, Jr. 30 pages. U.S. Government Printing Office, Washington, D.C. 20402. 1970. $1.00, paper.

This publication presents general, pertinent information on the state of the art of the one basic, acceptable, and effective method of solid waste disposal—the sanitary landfill. In clear language, the booklet examines the planning, design, operation, and public health aspects of sanitary landfills. The purpose is to present information to aid the growing number of people involved with planning and development of solid waste management. ∎

Systems Analysis of Regional Solid Waste Handling. Norman Morse, Edwin W. Roth. U.S. Government Printing Office, Washington, D.C. 20402. 1970. $2.50, paper.

"This study develops a systems analysis methodology for regional solid waste management. Although this initial effort is far from comprehensive, it can serve as a model for planners in the application of quantitative techniques for establishing more efficient solid waste systems," says Richard D. Vaughan, director of Bureau of Solid Waste Management. Since the scope was regional, the authors found it sufficient to look toward short-to-medium range problems during these first stages. ∎

Desalinization by Reverse Osmosis. John McDermott. vi + 209 pages. Noyes Data Corp., Park Ridge, N.J. 07656. 1970. $35.00, paper.

The detailed information in this book is based on U.S. patents relating to the production of freshwater from salt or brackish water by reverse osmosis. This publication supplies detailed technical information that can also be used as a guide to the U.S. patent literature in this field. The table of contents is organized to serve as a subject index as well. Other indices by company, inventor, and patent number help to provide easy to obtain information. Included in this book is the summarization of all the patent literature through June 1970, relating to reverse osmosis processes with particular emphasis on membrane technology and equipment design. ∎

Air Pollution Control Primer. 35 pages. Environmental Sciences Services Corp., 750 Summer St., Stamford, Conn. 06902. 1970. $5.00, paper.

Beginning with an air pollution glossary and definition of terms, this publication explains the causes and effects of air pollution as well as going into the legal aspects, automobiles, fossil fuels and lead, and solutions. The book presents pertinent facts in an unconfusing and informative manner. ∎

The Case for Extinction: An Answer to Conservationists. Morton Stultifer. 88 pages. Dial Press, 750 Third Ave., New York, N.Y. 10017. 1970. $4.95, hard cover.

Professor Stultifer's contentious text is supplemented by many witty, repellent line drawings. In the face of the enthusiasm for the preservation of our natural resources and the protection of our wildlife, the author satirically speaks out against conservation. The professor asks if conservationists ever stop to consider such repugnant and undesirable beasts as the tube-nosed fruit bat, the rufous harewallaby, or the giant chicken-eating frog when they talk about saving endangered species. Many of these evolutionary blemishes would be better off extinct! ∎

meeting guide

January 11–15
American Society of Civil Engineers
National Water Resources Engineering Meeting

Phoenix, Ariz.

"Water: Key to Survival" will feature presentations from major government and industry figures on how to solve many aspects of the nation's mounting water resources problem. Contact: Robert C. Esterbrooks, General Chairman, Maricopa County Highway Department, Phoenix, Ariz.

January 20
Water Resources Coordinating Committee of Pa., and Water Resources Center at Penn. State Univ.
Seminar on Systems Applications and Optimization in State Water Planning

Hershey, Pa.

The seminar will feature speakers of national prominence and discussion of the various regional and statewide aspects of water resources planning. Write: Dr. Archie J. McDonnell, Water Resources Research Center, 108 Research Unit A, Penn. State Univ., University Park, Pa. 16802

January 21
Washington Academy of Science, and the American Ordnance Association
Science and the Environment—Lead in Gasoline, Good or Bad?

Washington, D.C.

A panel will explore the effects of leaded gasoline on the environment and whether these effects are lessened by the substitution of other additives which are required to retain the octane rating of the gasoline. Contact: Dr. Alphonse Forziati, President, Washington Academy of Science, 9650 Rockville Pike, Bethesda, Md.

January 25–27
Cooling Tower Institute
Annual Meeting

Houston, Tex.

Program will include technical papers, an operating seminar, and committee working sessions. Attendees include manufacturers and suppliers of cooling towers and related equipment, industry and utility plant personnel, pollution control officials, and air conditioning manufacturers, suppliers, and users. Contact: CTI Office, 3003 Yale, Houston, Tex. 77018

January 28–30
The University of Wisconsin—Green Bay College of Community Sciences, and the Bureau of Community Environmental Management of USPHS
Conference on The Ecology of Human Living Environments

Green Bay, Wis.

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

January 31–February 3
University of Georgia School of Forestry, and others
Symposium on the Role of Trees in the South's Urban Environment

Athens, Ga.

Purpose of the symposium is to point out the profound effect that trees have upon the total environment. For additional information, contact: Dr. Leonard Hampton, Center for Continuing Education, University of Georgia, Athens, Ga.

February 3–5
American Chemical Society
Sixth Middle Atlantic Regional Meeting

Baltimore, Md.

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

February 8–10
Cyrus Wm. Rice Div., NUS Corp.
17th Annual Water Seminar

Pittsburgh, Pa.

Seminars for management, engineering, and operating personnel with water management and quality control. Registration fee: $300. Write: Cyrus Wm. Rice Div., NUS Corp., 1910 Cochran Rd., Pittsburgh, Pa. 15220

February 10–12
Cornell University
Agricultural Waste Management Conference

Syracuse, N.Y.

Conference will emphasize the application of current concepts, research results, and field experiences to the operational problems of agricultural waste management. Contact: Prof. Fred N. Swader, Conference Chairman, 149 Emerson Hall, Cornell University, Ithaca, N.Y. 14850

Courses

January 11–15
University of Tulsa
Short Course on Design of Refinery Waste Treatment Processes

Tulsa, Okla.

Emphasis will be on design methods and will include relevant case histories in all aspects of waste treatment. Enrollment is limited. Fee: $200. Contact: Chemical Engineering Department, University of Tulsa, 600 S. College, Tulsa, Okla. 74104

January 25–28
Louisiana State University
LSU Symposium on Air Pollution

Baton Rouge, La.

The theme "Air Pollution and Its Problems" is to be discussed by NAPCA and other government officials, as well as representatives from universities and research institutions. Fee: $15.00. Contact: Dr. J. W. Robinson, Department of Chemistry, Louisiana State University, Baton Rouge, La. 70803

January 28 and 29
Coulter Electronics Industrial Division
Fourth Annual Particle Characteristics Course

Newark, N.J.

Emphasis will be placed on practical approaches to particulate problems, measuring particle parameters, and correcting particle problems. Write: Shepard Kinsman, Industrial Applications, Coulter Electronics, Industrial Division, 590 W. 20th St., Hialeah, Fla. 33010

Special notices

1st ACS Environmental Improvement Exposition
In conjunction with the Washington, D.C. fall meeting and chemical exposition, September 12–17, 1971, the American Chemical Society will sponsor its first environmental improvement exposition. The exposition will feature products and services for pollution control and environmental management and will be held in the Sheraton Park Hotel. Exhibitors can obtain full details from: A.T. Winstead, Meetings and Expositions Office, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036

University of Colorado
Graduate Training and Research in Water Resources

An interdepartmental program has been developed to provide in-depth training in water resources engineering and the chemical and biological aspects of water resources. Contact: Dr. J. Ernest Flack, Director, Water Resources Training Program, Engineering Center, OT4-34, University of Colorado, Boulder, Colo. 80302

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Great Britain and Western Europe . . . Brayton Nichols, The American Magazine Group, 44 Conduit Street, London, W. 1, England, Telephone—Regent 4714

Japan . . . Sumio Oka, International Media Representatives, Ltd., 1, Shibe-Kotohiracho, Minatoku, Tokyo

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BUSINESS: ☐ Other _____

We're taking the bugs out of your waste treatment plant.

Calgon's physical-chemical Polysorb Process* cleans up wastewater better than a biological plant... in less space and at lower capital cost.
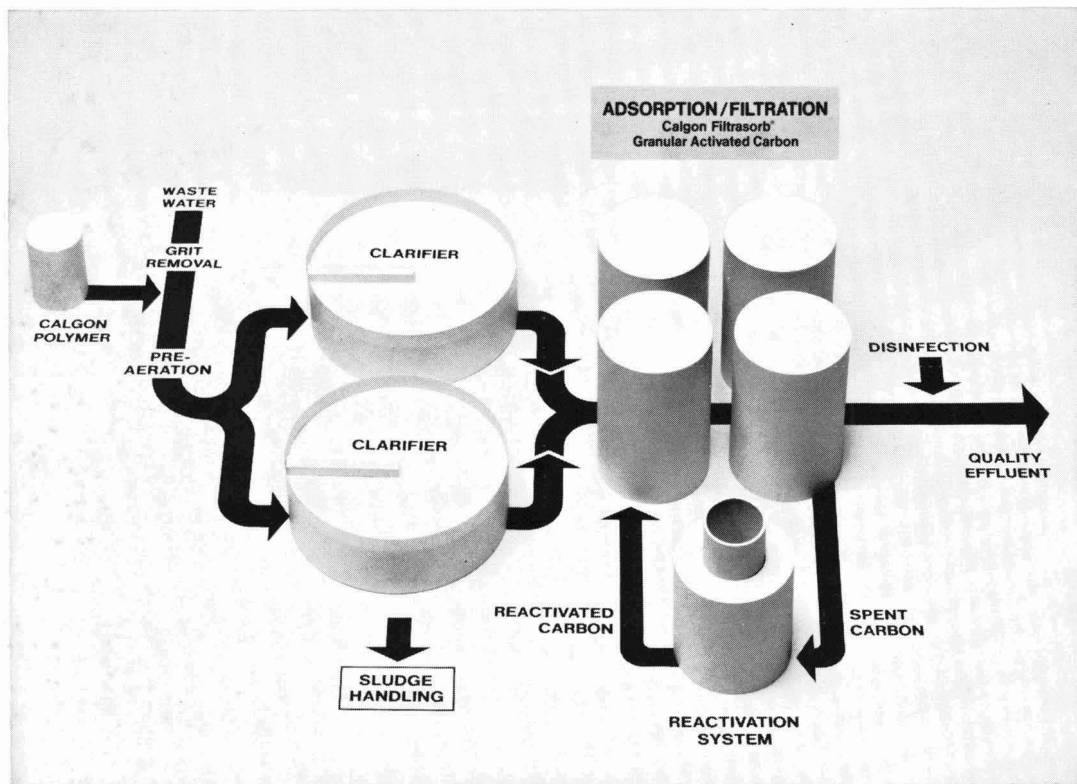
The Polysorb Process from Calgon can upgrade your wastewater by removing a wide range of troublesome organics which can't be handled by conventional treatment systems.

The heart of the Polysorb Process is Filtrasorb® granular activated carbon. Filtrasorb adsorbs dissolved organic contaminants that would throw a biological plant out of action. These include insecticides, chlorinated hydrocarbons, dyes, phenol and others. Suspended solids in the wastewater are removed prior to adsorption by clarification with highly effective Calgon polymer coagulants.

The system is easy to operate, has a wide range of application, and has reserve capacity to handle sudden overloads. The Filtrasorb carbon can be reactivated and used over and over again. In many cases, the upgraded effluent can be recycled to save on water intake.

Each Polysorb Process plant is tailored to your exact requirements. Working with your engineering group, Calgon Corporation can accept responsibility for any phase of your wastewater treatment plant—up to and including a turnkey contract. Plant startup and training of operating personnel can be included. For further details, call J. L. Rizzo at (412) 923-2345. Or write Water Management Division, Calgon Corporation, P.O. Box 1346, Pittsburgh, Pennsylvania 15230.

*Polysorb Process is a Service Mark of Calgon Corporation.

CALGON
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SOLUTIONS
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