ENVIRONMENTAL
Science & Technology

Emphasizing Water, Air, & Waste Chemistry

AUGUST 1967

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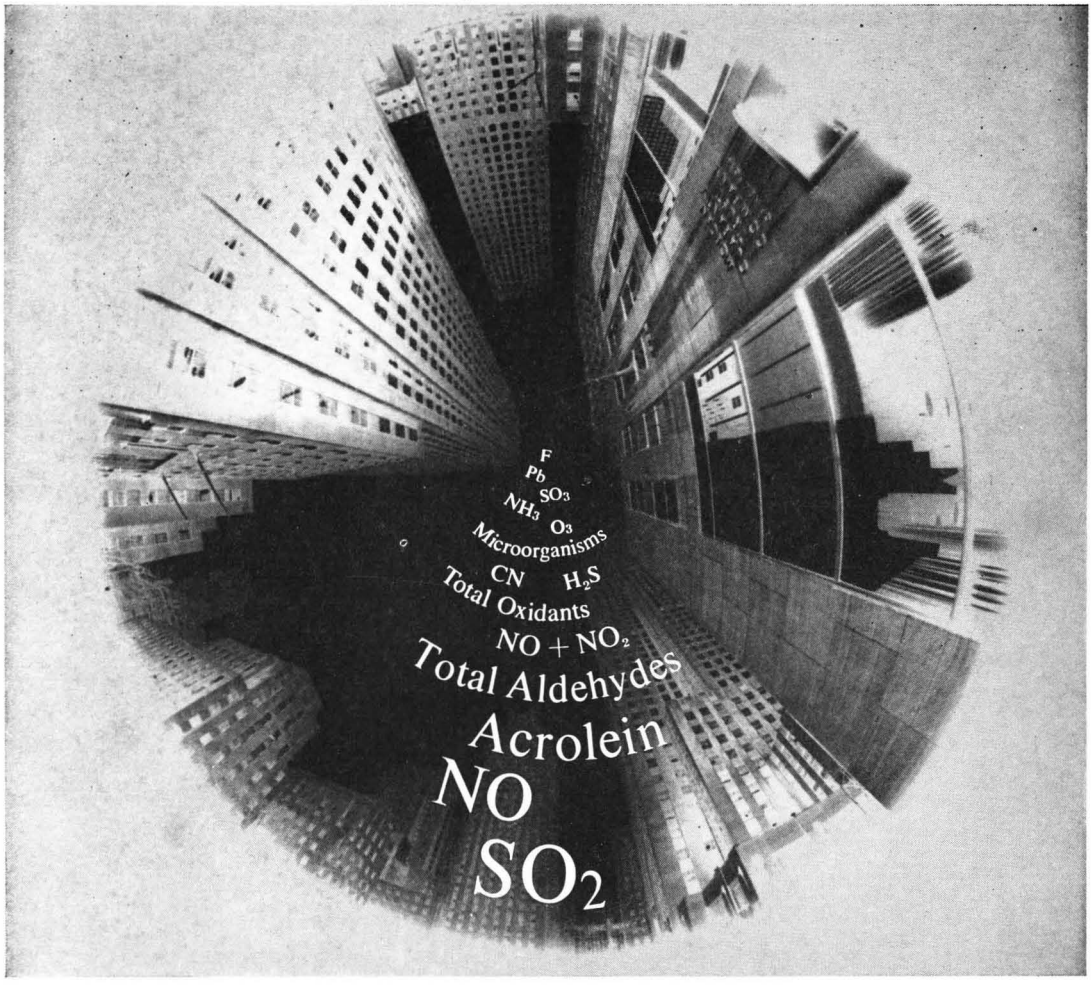

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E. Gjessing and G. F. Lee

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I. H. Suffet, S. D. Faust, and W. F. Carey

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C. R. Thompson, O. C. Taylor, M. D. Thomas, and J. O. Ivie

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H. Horvath

Particulate analysis of air samples from both natural and urban environments reveals a wide variance in the quantity of particles in each environment. Yet the size and shape distribution of particles in the two environments is the same. Using an aerosol spectrometer and counting individual particles with diameters larger than 0.27μ, the authors show that the natural environment has fewer than 300 particles/cm.^{3}, a residential environment fewer than 800 particles/cm.^{3}, and a downtown environment about 5000 particles/cm.^{3}. Furthermore, they show that the urban aerosol is less stable than the natural aerosol.

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A. U. Khan, J. N. Pitts, Jr., and E. B. Smith

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H. H. G. Jellinek and R. J. Kryman

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Nucleation of crystalline phases from sea water concentrates 661

L. H. Shaffer and R. A. Knight

Rapid heating of sea water in a pressure vessel produces a whisker-like crystalline phase at 180° C. If the reaction vessel is cooled immediately, the whiskers redissolve rapidly even at high temperatures. However, if the vessel is held between 140 ° to 180° C., the whiskers form into short-fat needles, which are the anhydrite ($CaSO_4$), shown by x-ray analysis. The authors were not able to isolate or identify the first-formed, whisker-like phase.

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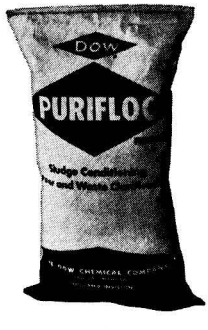

DOW

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EDITORIAL

The world wears a mixed mantle of beauty and grime

Children have a right to expect that the adult world in which they live is the very best of all possible worlds

Moving through the countryside can be an exciting adventure for a family on vacation. It can also be an eye-opener when, as frequently happens on long automobile trips, the books and games pall and the youngsters begin to comment on the passing world around them. Viewed as through the eyes of a child on just such a recent trip, the world takes on a mixed mantle of beauty and grime, of splendor and shabbiness, of freshness and foulness.

It was a simple enough trip, though long. As it began early in the morning, the garbage collectors were filling their noisy, slightly odoriferous machines with their semi-weekly samplings of household wastes. Wisps of trash floated or fell to the street while the trucks groaned, clanked, and whined their trash collection cacophony.

From home it was a short ride to the new throughway. As this superhighway threaded across the mostly verdant hills, the travelers commented on the ugly brown gashes in badly eroded fields. What they could not then see were the washed-away soils making their regular contributions to the mud and silt load that turns nearby streams and rivers into miniature Big Muddies, and fills catchments behind dams, making them old before their time.

The morning air was sweet with the fresh smells of summer and meadow, and the sky was clear. But foul odors and black soot from diesel-engine trucks on the highway created a gray-black stream that seemed to merge with other similar streams to form an air-borne river of pollution. This river moved on to join with the brown "smaze" that hung uninvitingly over the port city at the highway's end. The smaze itself was fed also by a natural meteorological inversion which prevented the escape of effluents from industrial smokestacks, power plants, burning trash dumps, motor vehicles by the thousands, and the myriad other living and working structures that house the city's populace.

A ferry ride offered a brief respite from the day's exertions, but here, too, the polluter was in evidence. A breeze that was pleasant enough at the bow became warm and oily by the time it reached the stern. The boat's stacks thrust their black outpourings out on the sky. Passengers, not to be outdone by mechanical marvels, added to the pollution scene as paper cups, straws, cans, and other debris were hurled over the side into what, unfortunately, was hardly pristine water. As the cars started their engines and prepared to debark, the exhaust fumes reminded the travelers that they, themselves, also were among those major contributors to the pollution problem.

The oil slicks, trash, bottles, papers, smells, highway signs (that threaten fines for littering), junk heaps, garbage pits, and many other evidences of man's presence destroy—or at least detract from—the greatness of his accomplishments.

Perhaps the children of today's adult world will eventually have a cleaner environment in which to mature and live. Children are aware of some of the problems. They usually see the truth—and, as in the *Emperor's New Clothes,* express it publicly.

However, children rely on adults to take the necessary steps to act in their behalf. They may be dazzled by fancy adult explanations and the fixing on others of blame for pollution. But the effect of the ready answers will be temporary, and the children will soon ask for more and better answers. For valid answers. They have that right.

Melvin J. Joseph

Acid Mine Drainage Programs Set

Interior has called on Congress to approve legislation calling for appropriation of $15 million in FY 68 to help curb the problem of acid mine wastes. The new proposal by Interior provides for two demonstration programs. Under the first program Interior could make contracts or grants of $250,000 to demonstrate methods of controlling acid wastes from mining operations. Under the second program, Interior would make matching grants with states to eliminate all acid mine pollution in a drainage area.

Meanwhile, Pennsylvania contracted with Westinghouse Electric Corp. for preliminary engineering and field survey work prior to actual construction of a 5 million gallon per day demineralization plant. The plant, to be located in the Altoona area, will use a flash distillation process which Westinghouse has already shown in the laboratory to be effective in making "ultrapure water" from acid mine water.

Biological Control of Mosquitoes Sought

Because of a growing concern about the effects of pesticides on the balance of nature, research workers have been seeking alternative paths to pest control. One insect species, the mosquito, that has previously eluded the biological control scientists is now under vigorous and effective attack by Dr. George B. Craig and coworkers at Notre Dame University. The attack is coming from several directions as the workers seek to induce sterility in male mosquitoes, to prevent insemination of female mosquitoes, and to distort the sex ratio in mosquito colonies. The research has as its principal goal the eradication of *aedes aegypti,* the mosquito responsible for transmission of yellow fever, and other parasitic and viral diseases throughout the world. The research workers have already had success in their program to induce male sterility by chemical factors. But the workers believe that chromosomal changes resulting in genetic sterility that can be passed from generation to generation is a more effective approach.

Fluorescent Sand Used as Sediment Tracer

A team of water resource experts of the U.S. Geological Survey have injected about 10,000 pounds of fluorescent sand and lead shot into the Atrisco feeder canal about 15 miles north of Albuquerque, N. Mex. The experiment is part of a project to gain better understanding of the movement of sediment in streams. Continuous addition of yellow fluorescent quartz, green garnet, red monazite, and blue-colored lead shot has been followed by collection of sediment samples at varying distances downstream. The heavier particles—monazite and lead—move 5 to 10 feet a day, the studies show; lighter, finer particles such as quartz and garnet move about 200–300 feet a day. "We have been able to gather detailed information that could be useful in predicting how and at what rate solid pollutants will move in a stream," says project coordinator Vance C. Kennedy. Results of the experiments will be published as soon as possible, Mr. Kennedy promises.

FWPCA Testifies on Congressional Directives

"We were, and still are, in complete agreement with the need for and value of the new programs authorized for research and development," said Dr. Leon W. Weinberger, Assistant Commissioner for Research and Development, FWPCA, in recent testimony before the Senate Committee on Public Works, Subcommittee on Air and Water Pollution. But at the same time, he made special reference to earlier subcommittee reports that stressed that emphasis should be given to programs directed to actual applications of new methods, both in pilot plants and in full-scale field evaluations and demonstrations. Then, to emphasize that the FWPCA program was proceeding on all fronts, including research, Dr. Weinberger introduced the following chart to show the scope of FWPCA's R&D program:

RESEARCH AND DEVELOPMENT PROGRAM

SUBPROGRAM ELEMENTS	MUNICIPAL-POLLUTION CONTROL TECHNOLOGY	INDUSTRIAL-POLLUTION CONTROL TECHNOLOGY	AGRICULTURAL-POLLUTION CONTROL TECHNOLOGY	MINING-POLLUTION CONTROL TECHNOLOGY	OTHER-SOURCES-OF-POLLUTION CONTROL TECHNOLOGY	GENERAL POLLUTION CONTROL TECHNOLOGY	WASTE TREATMENT & ULTIMATE DISPOSAL TECHNOLOGY	WATER QUALITY REQUIREMENTS	PROGRAM DIRECTION AND SUPPORT
	Sewered wastes	Metal and metal products	Forestry and logging	Mine drainage	Recreational	Eutrophication	Dissolved nutrient removal	Municipal uses	Program direction
	Combined sewer discharges	Chemicals and allied products	Rural run-off	Oil production	Commercial vessels	Physical-chemical identification of pollutants	Dissolved refractory organics removal	Industrial uses	Grants and contracts adm. management
	Storm sewer discharges	Power production	Irrigation return flows	Uranium	Construction projects	Biological identification of pollutants	Suspended and colloidal solids removal	Agricultural uses	Laboratory research supervision and support
	Nonsewered run-off	Paper and allied products	Animal feed lots	Other mining sources	Impoundments	Source of pollutants	Dissolved inorganics removal	Recreational uses	
	Nonsewered municipal wastes	Petroleum and coal products	Nonsewered rural wastes		Salt water intrusion	Fate of pollutants in surface waters	Dissolved biodegradable organics removal	Fish and other aquatic life	
	Joint wastes	Food and kindred products			Natural pollution	Fate of pollutants in ground waters	Microorganisms removal	Other single uses	
		Machinery and transportation equipment			Dredging and landfill	Fate of pollutants in coastal waters	Ultimate disposal	Multiple uses	
		Stone, clay and glass products			Oil pollution	Water quality control	Waste water renovation and re-use		
		Textile mill products				Water resources planning and resources data	General waste treatment technology		
		Lumber and wood products				Cold climate research			
		Rubber and plastic				Basic research			
		Miscellaneous industrial sources				Great Lakes research			

Also testifying at the hearings was Dr. Allan Hirsch, FWPCA's Assistant Commissioner for Program Plans and Development. Dr. Hirsch noted that a recent survey indicated that between now and 1972, state and local governments would need an additional 5400 scientists, engineers, and related professional personnel for water pollution control purposes and an additional 3900 technicians and 10,000 trained sewage plant operators. And, noted Dr. Hirsch, to this list must be added the substantial needs of consulting engineers, suppliers of chemicals and equipment for waste treatment plants, universities, and federal agencies. Furthermore, as the demands for better controls increase, the skills of those already active in the field must be improved, he warned.

Water Supplies in Northeast Back to Normal

"From a water resource standpoint, the back of the Northeast Drought was broken this spring, and it ended this summer," reports Henry C. Barksdale of the U. S. Geological Survey, who monitored water-supply trends in the northeast states during the 1961–66 period when several critical shortages developed. Except for a few highly isolated and localized pockets, reservoirs, streams, and ground water levels in the northeast states have returned to normal, and now resemble the water-supply situation that existed prior to 1961.

Another reflection of the return to normal is the movement of the *salt front* in the Delaware River. Near-normal fresh-water inflow to the tidal reaches of the Delaware River has resulted in the lowest chloride concentrations for July since 1961 at some points in the river. "Perhaps the most optimistic note of all," says Barksdale, "comes from our field observers, who report that ground water levels are above average in most of the region."

Ecologists Join Movement to Preserve Aldabra

About a quarter of the invertebrates of the island of Aldabra are found nowhere else in the world. Aldabra is located on an uplifted coral atoll 400 miles east of Africa and 260 miles northwest of Madagascar in the Indian Ocean. It is a biological treasure house that has a unique ecosystem with 12 endemic species or subspecies of birds, including the flightless rail, and more than 18 unique species of higher plants.

Both the Royal Society of Great Britain and the National Academy of Sciences have, understandably, reacted passionately against a proposal of the Ministry of Defence of Great Britain to locate an airfield, a transmitting station, and supporting facilities on the island, claiming that the installation would cause "incalculable damage to one of the world's unique resources for scientific investigations." If left undisturbed, the National Academy points out, the island "will provide an ideal location for the scientific study of evolutionary processes in a relatively closed biotic environment."

The Secretary of State for Defence, the Right Honorable Denis Healy, has made the following formal statement: "We had given very careful thought to the possibility of making use of other islands in the Indian Ocean, which are of lesser scientific importance, instead of Aldabra; but it had proved necessary for compelling reasons to rule them out." Despite this pronouncement, the installation remains in the "proposal" stages, and the island of Aldabra may still escape the threat of civilization. But on the chance that it does not, a joint British-American team plans an extensive survey of terrestrial marine ecology for the period of August 1967 to March 1968. The project was set up as a demonstration of concern for "the preservation of unique biotic environments which can serve not only as gene banks for endemic species but also as unique and invaluable areas for future evolutionary studies."

New National Water Quality Laboratory in Duluth, Minnesota

On hand at the dedication (August 11, 1967) of the first and only national research center to be devoted exclusively to the water quality requirements of fresh water, Secretary of the Interior Stewart L. Udall stated that primary emphasis at the facility will be placed on quality requirements of fish and other aquatic life and on the chronic and acute effects of impurities on water life. Over 120 scientists will man the new laboratory, working closely with scientists in universities and industry to provide a scientific base for protecting our water life.

"Water or the lack of it has held the power of life or death over mankind for far longer than history has been written," said Udall in his address. "It still does. But now, at long last, the tables are beginning to turn. We are no longer completely at the mercy of either flood or drought. Through wise management and the application of an expanding technology, we can curb the flood, and we can make the desert bloom. And this is only the beginning." The facility, located at Duluth, Minnesota, is the first national research facility authorized under the Federal Water Pollution Control Act Amendments of 1961. A companion laboratory specializing in salt water pollution problems is planned for Narragansett, R. I. Construction has not yet started on this facility.

Water Standards Approved for Seven More States

Secretary of the Interior Stewart Udall announced recently that he has approved water quality standards, required by the Clean Water Restoration Act of 1966 and its parent Water Quality Act of 1965, for all interstate waters of Arkansas, Idaho, Maryland, Massachusetts, New York, North Dakota, and South Dakota—with the exception of the Bear River Basin in Idaho and the Red River of the North in North Dakota.

On July 19, the Secretary had announced approval of the standards submitted by Georgia and Indiana, and for most of Oregon and the Delaware River Basin in New York. At that time he indicated that standards were substantially satisfactory for Alabama, as well as part of New York, and all of South Dakota. Standards for other states and territories are still in review, Udall stated.

Industrial Designer Predicts Improved Pollution Control

The size of cars, as well as exhaust and safety features, may soon be limited in the public interest, predicts industrial designer W. Dorwin Teague. Speaking at an all-day conference in Teaneck, New Jersey, he noted a trend toward the elimination of automobile traffic in downtown areas to allow for malls, pedestrian walkways, plantings, and pools.
"Pollution can be made to work for us," Mr. Teague proposes. The fertilizing effects of sewage should be utilized, and submarine junkyards should be considered. "Fish like to live in old cars," he states, citing solid waste disposal studies. Other possibilities are home garbage compactors for easier disposal, incinerators with gas and smoke controls, and individual air purifiers.

Ingenuity and Incinerators

Faced with special problems, West German engineers have forged ahead in designing refuse incinerators. Unfortunately, the U.S. can't import all that high-grade technology in toto

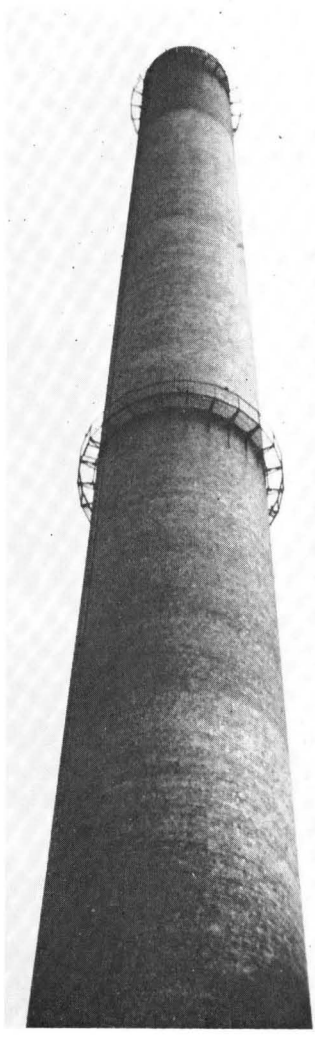
Visitors to West Germany frequently come away singing the praises of the country's postwar achievements. Catching the eye of many an observer are the new, modern refuse incinerators, their plumeless stacks pushed high into the German skies, their heat recovered and used—not wasted as in the U.S. These observers and many of their colleagues in the U.S. raise the question: "Why don't we have such plants in the U.S.?"

"We don't have such plants," says Leo Weaver, just returned from a tour of West Germany, "because our economics are quite different from theirs. Start with the price of coal. Consolidated Edison may pay as little as $5 for a ton of coal in New York; in Munich the price may be $20—and the coal will be inferior to ours. Of course, we can still learn a lot from what they're doing; some of their engineering innovations should be quite useful to us. But, at least under current conditions, their experience has only limited validity for the U.S."

Weaver, recently retired as head of the Public Health Service's solid waste disposal program, made his tour as chairman of a panel sent by the U.S. Government to study West Germany's solid waste disposal practices. The panelists first went to Paris for a meeting of the International Association of Public Cleansing, where they had an opportunity to see Europe's newest equipment and to talk with experts from all over the continent. The panelists then went on to tour West Germany with stops in West Berlin, Frankfurt, Munich, Dusseldorf, Rosenheim, Duisburg, and Schweinfurt.

Weaver's overall impression of the West German refuse incinerators is that the German engineers have come up with some high-grade and ingenious technology to meet the country's special needs. West Berlin's refuse incinerator is a good example of the application of such technology. The city's new incinerator is being built adjacent to a power plant so that by-product steam from the incinerator can be sent to the power plant to help generate electricity. Construction started on the incinerator in late 1964. One furnace unit is now operating; three more will be operating within a year. But the incinerator complex can do no more than supply heat for power generation.

Plumeless. *Efficiently working incinerator stack shows no white plume*



A sintering plant has been built adjacent to the incinerator. There, the nonmetallic part of the incinerator residue can be sintered into aggregate for concrete blocks. Weaver points out that such a plant would not be economically feasible in the U.S.; his German hosts told him it is not economic in Frankfurt. But it is economic in West Berlin, which has no readily accessible countryside from which to get stone for aggregate. The plant also reclaims metals from incinerator residues. Again, such metal reclamation frequently is not economic in the U.S.

U. S. conditions differ

While the state of the U.S. incinerator art may not be as far advanced as in West Germany—and, indeed, Europe in general—all this may change. Weaver explains it this way: "The economics of refuse incineration in the U.S. may change significantly as air pollution regulations get stricter. If an incinerator needs an expensive piece of equipment like an electrostatic precipitator, we may have to reclaim that waste heat. I don't see it being used for

power—atomic power seems to be what all the power engineers talk about. More likely the heat could be used for heating purposes. We've reclaimed very little heat before because it was just cheaper to waste it. Or, perhaps, we haven't tried hard enough to find uses for that heat. We'll have to try harder now."

Weaver feels that some of the West Germany engineering innovations should be applied in the U.S. Some examples he cites: grate design and manufacture, ash handling equipment, and air pollution control equipment. Accordingly, he is recommending that the U.S. send a mechanical engineer to West Germany for extensive study of incinerator design.

U. S.-German cooperative program

The panel's tour was part of a program that evolved during Chancellor Ludwig Erhard's visit to the U.S. in December 1965. At a White House dinner, President Johnson said "We are now watching with great interest the pioneer work that you in Germany are doing to make your cities more livable. We are especially interested in your antipollution programs, which are said to be among the most effective in the world. So, I propose sending a working group, headed by our distinguished Secretary of the Interior, Mr. Udall, to West Germany . . . to view some of your accomplishments firsthand."

The Presidential Mission visited West Germany for a week in March 1966, then drew up a report recommending that teams of experts be set up in five problem areas. Two more areas were added later, making a total of seven now active:

- Water pollution abatement.
- Air pollution abatement.
- Solid waste disposal.
- Urban planning.
- Coal research.
- Noise abatement.
- Electric power.

Weaver feels that West Germany will benefit from U.S. technology picked up when its experts visit the U.S. "West Germany and the U.S. now have different kinds of refuse, and, consequently, different kinds of problems. But they're heading toward our throw-away economy and before long will probably have the same kinds of problems we now have," Weaver notes. A two-man German team is scheduled to visit the U.S., probably at the time of the American Public Works Association meeting in Boston, Oct. 1-5. If the West German budget permits, their solid waste disposal panel will come to the U.S. next spring.

Visits in other problem areas

Exchange visits have also been made by experts in water pollution abatement, air pollution abatement, and coal research. Visits in urban planning and electric power have been set for this fall, according to James A. Slater, director of the program, now known as the U.S.-German Cooperative Program in Natural Resources, Pollution Control, and Urban Development. Visits on noise abatement will probably occur in the spring of 1968.

Slater is pleased with progress of the program to date. He stresses that the purpose is the exchange of information rather than assistance. He sees the program continuing as long as it is mutually beneficial. He also sees it as a way of helping close the technology gap.

Panel Members

The U.S. panels set up under the U.S.-German Cooperative Program in Natural Resources, Pollution Control, and Urban Development draw their members from many non-government sources, with the chairman coming from the government.

Serving with Leo Weaver on the solid wastes disposal panel are: **Norman Hume,** Bureau of Sanitation, Los Angeles, Calif.; **Harold B. Gotaas,** Northwestern University; **Karl Wolf,** American Public Works Association; **James Coulter,** Maryland State Department of Health; **Elmer Kaiser,** New York University; and **William Xanten,** consulting engineer, Washington, D.C.

Modular Desalting Plants Have Wide Utility

According to OSW, the smallest practical unit should be capable of producing 2½ million gallons of potable water per day, enough to support a town of 25,000

Kenneth A. Roe and Henry M. Rose
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The world-wide increase of both people and factories creates a soaring demand for clean, fresh water. Our government predicts that in the U.S. alone, clean water requirements will double by 1985. This demand will be met largely by increasing water reuse through water renovation. In some cities, desalting may be the most economical way to reduce seasonal water shortages. But in the arid coastal deserts of the world, desalting will contribute a much larger share of the water supply.

The economic development of any region of the world is paced by the availability of its water supply. The rate of regional development will always be established by the amount of potable water available on which growth can be planned. When water needs out-distance the classical methods of natural water collection and distribution, potable water becomes a product which can be made and sold.

As the arid regions of the world have been exploited for their natural resources, their military assets, or their resort capabilities, various methods of water production have been used to make this development possible.

Water-short regions, or nations, become "have-nots" in this respect, and the U.S. Department of the Interior, Office of Saline Water (OSW), has developed a system of desalting water technology to help these nations in their economic upsurge. This OSW program envisions a modular desalting plant concept applicable anywhere in the world to satisfy burgeoning regional needs for fresh water. The very broad scope studies made under OSW auspices show that the smallest unit of production ought to produce $2^1/_2$ million gallons of potable water per day. Such a plant would support a population of 25,000 people in a standard of living similar to our own urban centers, where consumption averages 100 to 120 gallons of water per person per day. This plant could support an oil or coal development in an arid area, or a good sized resort area.

The OSW program envisions that this first standard $2^1/_2$ million gallon-per-day plant will be installed in multiples of 1, 2, 3, or 4, up to 10 million gallons per day output. After a period of use and design improvement, industry could probably expand this design into the range of 15 to 20 million gallons per day. For plants larger than this size range, the beginning step in the OSW program is the 17 million gallon-per-day module, the first of which is now being constructed in California.

Basic module

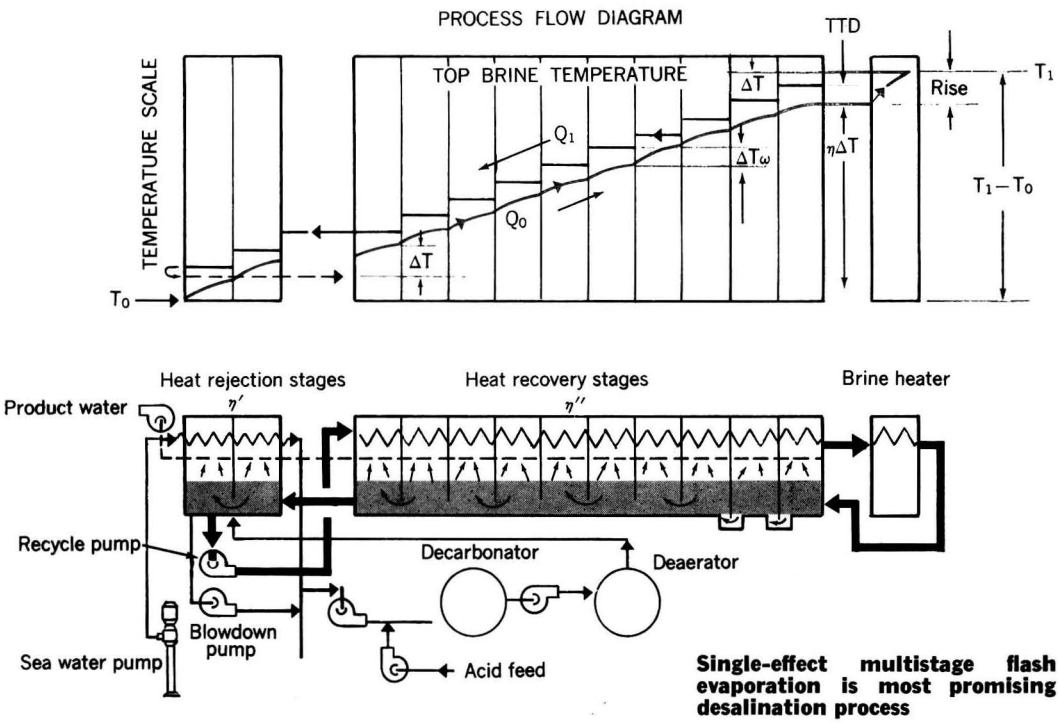
The first and smallest module is the $2^1/_2$ million gallon-per-day unit. Many desalting processes are available for use in the design of such a plant. The development of all these processes constitutes a race for the desalting market, the prize eventually going to the process which can desalt sea water at the least cost. The race is not over, but as of today, flash evaporation has the lead in large size plants for use with sea water as a water source. For this reason, the first universal design is based on a single-effect, multistage, flash evaporator, using horizontal condenser tubes and a recycle brine flow.

Flash evaporation process

In this type of plant, the sea water is heated and allowed to flow through a series of chambers which are maintained at successively lower pressures corresponding to the saturation temperature of the water in each chamber. In each chamber or stage, some of the sea water evaporates rapidly, or flashes into steam. In doing so, it cools, then flows on into the next stage through a flow control orifice. The vapor that flashed off proceeds through mist separators to a bank of condenser tubes where it is condensed and collected in product water trays as it drips from the tubes.

The sea water flows on through the complete series of stages, cooling and giving up fresh water in each stage. The flashing brine stream becomes more saline in each stage. At the end of the flash-down, the cool brine is pumped back through the condenser tubes where it recovers the heat given up by the condensing fresh water.

In addition to heat recovery, this recycling of the brine stream is done to save on water treatment costs. Thus, the recycled brine is progressively heated as it flows through the tubes in each stage until it leaves the first, or highest temperature stage. The brine receives its final heating in the brine heater to give it the temperature dif-



Single-effect multistage flash evaporation is most promising desalination process

ference, or rise, needed to meet the process parameters.

The recycle brine stream leaving the lowest pressure stage cannot be used in the condenser of that same stage because no temperature difference would exist. The cool brine, therefore, is piped to that stage where it can efficiently condense the fresh water vapor, generally bypassing the three lower stages and entering at the fourth stage up from the lowest. The cooling water for the bypassed stages is pumped into the condenser directly from the sea. After cooling these three stages, it is returned to the sea which serves as the system heat sink. Thus, the entire plant is considered as divided into a heat recovery section and the heat rejection section.

Addition of makeup water

The recycling of the brine in this manner causes it to become more and more concentrated each cycle. This higher concentration raises the boiling point, causing reduced efficiency. Because of the increasing salinity, it will certainly cause—due to precipitation of scale forming chemicals—scaling of the tubes of the condenser and brine heater if allowed to continue. Also, as the cycling through the system progresses, the flow is reduced by the loss of the fresh water. This loss must be made up if the cycle is to continue.

In addition to this makeup water, an additional amount of sea water feed is needed to keep the salinity below the value at which tube scaling will occur. As sea water is continuously fed into the evaporator and to maintain the proper brine material balance, concentrated brine is "blown down" to the sea, taking the excess salt with it.

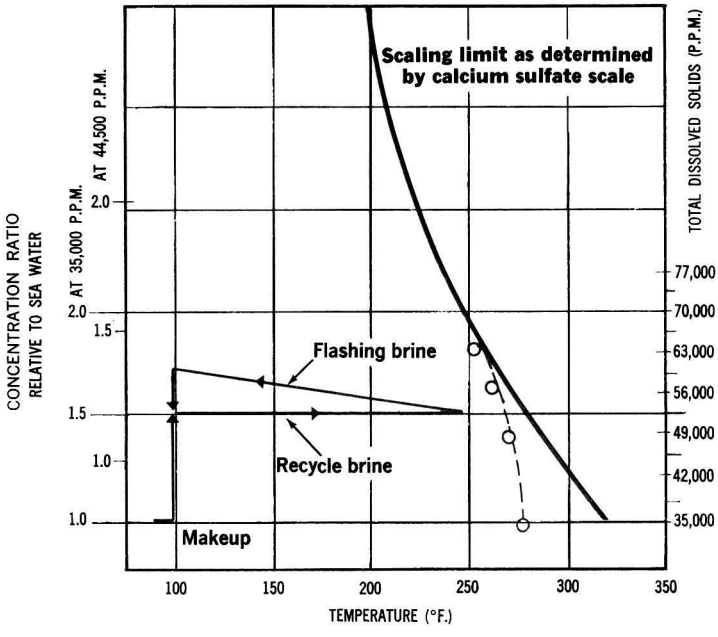
Some of the warmed sea water leaving the condenser is used for this makeup. It is properly treated prior to being fed into the system at some appropriate point.

The thermodynamic laws governing the process dictate that if the output is fixed by demand and the flashing range is fixed by the combination of the sea water heat sink temperature and some maximum brine temperature, then the brine recycle flow is automatically fixed. In most plants, the output and sea water temperature are fixed by conditions at the selected site and by local water requirements. Although the top brine temperature is also limited, it can be varied up to the temperature at which scaling occurs on the brine heater tubes. However, to maximize fresh water output, it is desirable to operate at the maximum possible brine temperature. The selection of the method of makeup treatment governs this maximum temperature.

Scaling prevention

Two commonly used methods of raw sea water treatment were introduced into the design of the universal plant. One is acid treatment and the other is polyphosphate treatment. These two processes suppress scaling in different ways. The troublesome

Concentration of total dissolved solids defines scaling limit



scale-forming substance dissolved in sea water is not the salt, but rather those compounds having an inverse temperature solubility curve such as calcium sulfate, calcium carbonate, and calcium bicarbonate. The recycle brine approaches this limit as it is heated in the evaporator and brine heater. When the water temperature increases to their solubility limit, these compounds start to precipitate, the carbonates first, and then sulfates at higher temperatures of 250° F. to 270° F., depending upon the concentration.

Acid treatment converts the carbonates and bicarbonates to sulfates, liberating CO_2 and water. Polyphosphates act in a different way, acting to take the calcium ions out of circulation, or sequestering the ions. Other such complexing agents may be used, but the proprietary polyphosphate compounds are the most economical.

The maximum brine temperature possible with acid treatment is 250° F., and close to 190° F. with polyphosphate treatment. Because of its greater flashing range, the acid treatment method can obviously produce more water for any given plant. However, the cost differential between acid treatment and polyphosphate treatment is such that there will be locations where the polyphosphate plant will produce water at a lower cost.

Acid vs. polyphosphate treatment

The universal plant design provides for either method of makeup treatment, and different plant designs and water costs result. The makeup brine treatment, whether by addition of acid or polyphosphate, is done prior to its entry into the recycle stream. In the acid treatment process, sulfuric acid is fed into the makeup brine stream, mixed, and then it flows into an atmospheric decarbonator where most of the CO_2 is removed. The makeup brine then is pumped into a low-temperature vacuum deaerator where both air and residual CO_2 are reduced to 10 p.p.b. The pH of this stream is adjusted with caustic and antifoam agents if conditions require. The makeup brine is then ready for mixing with the recycle flow.

The polyphosphate treatment eliminates the decarbonator and some pumping equipment. Acid metering equipment is still required to provide for periodic acid cleaning of the system.

Dual-purpose plants

The potential owner of a water desalting plant must also decide whether the economics of the specific location will reduce the product water costs by integrating his plant with some other process such as electric power production. Whenever some of the facilities of the two plants can be combined, the outputs of each are less costly than if they came from plants built separately.

If a water plant can use low grade steam, such as would come from a back pressure turbine used to generate electric power, it will share the boiler cost and cooling water intake costs to the benefit of both the power and the water costs. This same result will be realized if the brine heater uses waste heat from some other manufacturing process, or as is already being done, from a water-wall garbage incinerating boiler.

The universal design provides for evaluation of single-purpose and dual-purpose plants as well as plants using acid and polyphosphate makeup treatment.

The actual plant design depends on a large number of variable parameters and, of course, the final design details for any given set of design conditions are an optimized selection of the various design features.

Cost factors

The cost of water production is divided into three general classes: fuel cost, fixed charges, and annual operating cost of labor and materials. The thermodynamic parameters are such that minimum water costs can be determined only by using optimizing techniques. These techniques involve the determination of the low point in the summation of the two water cost curves attributable to fuel cost and to fixed charges as they vary with the number of stages in the evaporator.

Very simply stated, the cost of water will increase as the number of stages increases because the fixed charges will go up. However, as the number of stages is increased, the fuel cost will go down due to increased thermodynamic efficiency.

To satisfy the universal concept, it was necessary to design for more than one set of economic parameters. These

are represented by steam cost, power cost, and fixed charge rate. Since these factors are different over the world, the optimization procedure uses a wide latitude in treating these factors.

Design factors

Site factors were reduced to single values wherever possible, using those close to the maximum expected. Sea water temperature and salinity were among these. The amount of makeup water required controls the cost of makeup treatment. Consequently, our design was based on the use of a single maximum brine concentration in the recycle brine leaving the brine heater. Because we had assumed but one sea water salinity, the concentration ratio, the ratio at total dissolved solids leaving the brine heater to the total dissolved solids of the entering sea water, remained constant.

Many other design factors were fixed on the basis of what we considered to be good practice. The in-tube brine velocity, the tube materials, the mist separator thickness, and many similar items were determined by selecting values commonly accepted as producing conservative design.

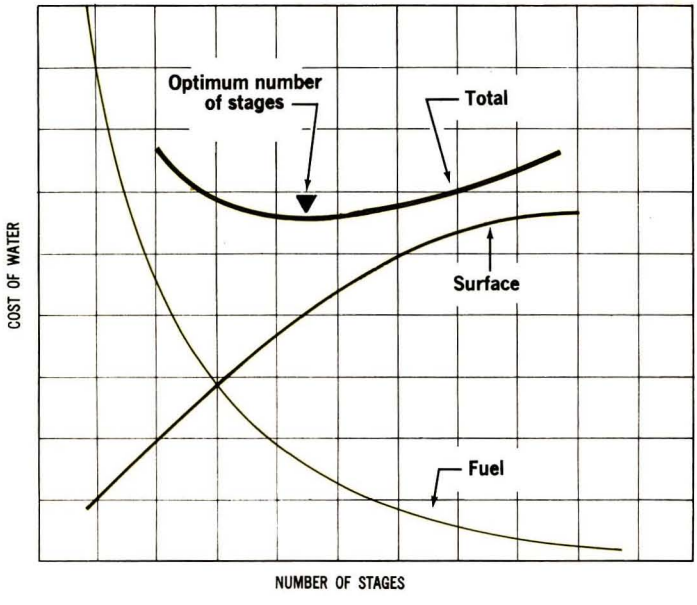
All the plants were assumed to have a 30-year life, with the condenser tubes all replaced during the fifteenth year. A 90% plant capacity factor was used throughout.

Nonvariable capital costs for the acid plant and the polyphosphate plant were computed, and one value only for each plant was used. Variable capital costs were computed in terms of square feet of surface, length and number of stages, and maximum tube length.

Design optimization

The optimum plants were selected by running through a full range of stages and terminal temperature differences for each combination of economic parameters. Some 80,000 cases were examined and about 840 optimum plants were designed. The major effort of determining the optimum plants was done by a computer program which permitted, in addition to electronic summation of optimums, grouping of off-optimum plants varying from the optimum in increments of 0.2% up to 1.5%.

More stages lead to greater fixed charges, lower fuel costs



The several economic parameters and optimizing variables listed below make up a complete matrix. This matrix is considered adequate to meet the expected possibilities that could be encountered by world-wide application of this type of plant. These are:

- Top brine temperature (two temperatures): 250° F. acid—190° F. polyphosphate.
- Power cost (four costs): 5, 8, 11, and 15 mills per kwh.
- Steam cost (seven costs): 10, 20, 25, 30, 35, 40, and 50 cents per million B.t.u.
- Fixed charge rate (four costs): 5, 7, 10, and 14% per year.
- Number of stages (14 cases): 25 to 50 in increments of two stages.
- Initial TTD (30 cases): 4° to 12 ° F. in increments of 0.3° F.

From the 840 designs which the computer output listed as optimum, 11 plants were selected. They were also found to cover all interesting cases from the off-optimum summaries which occurred within the range of ±0.2% off-optimum for the acid plants, and ±0.7% off-optimum for the polyphosphate plants. Therefore, we believe that these 11 plants will produce water at the minimum cost, within a small percentage of the 30-year evaluated cost, at any expected site location in the world and under any expected economic conditions. These plants will all produce 2½ million gallons of water per day with a maximum salinity of 25 p.p.m. and will also produce some water of boiler feedwater quality at 2 p.p.m. for in-plant use.

Certain widely variable site development costs, such as costs of water intake, steam supply, and land could not be included in this computer program because the actual site conditions were not known. This made it necessary to limit the capital costs included in the computer program to those cost factors which would logically occur in every water plant. With further study, a method of including costs which vary with the site could be possible.

Battery limits

A strict limitation of the costs to be included was done by enclosing all the plant to be included in the computer program within a conceptual envelope or battery limits. All plant and equipment external to these limits are not contained in the computer capital costs. These limits are:

• The sea water inlet flange of both the heat rejection module and the vent condenser.

• The sea water discharge at the outlet flange of the flow control valve.

• The steam inlet flange of brine heater and air ejector flow control valves.

• The blowdown discharge flange of the flow meter.

• The product water at the discharge flange of the diversion valves.

• The electrical system at the input bus bar of the 4160 volt switchgear.

• The condensate at the outlet flange of the brine heater hotwell.

• For all equipment, the bottom face of the surface designed to support the weight of the equipment.

Evaporator design

Over many years, the industry and OSW have accumulated all kinds of data on desalting plants using the single-effect, multistage flash evaporators. These data were carefully reviewed, evaluated, and cranked into our design.

In discussing the design factors used in the evaporator, it is convenient to break the cycle into its component streams: recycle stream, flashing brine stream, product water stream, and vent, makeup, and blowdown streams.

Recycle stream

The size of the recycle flow through the condenser tubes is governed by total flashing range and the output required. The in-tube velocity is set by good practice and this fixes the number of tubes and the computer fixes the total area of the tubes. This leaves only the tube diameter and material and the tube bundle configuration to be established.

After a considerable amount of study, condenser tubes of 20 gauge, 90-10 copper nickel alloy (ASTM-B-11-66) having a wall thickness of .035 inch, were selected.

A variety of studies indicates that in tube bundle design, sophistication is not necessary for good operating efficiency, and no laning is provided for the vapor. Because of the relatively high driving forces in most of the evaporator, bundle losses are low. At the low pressure end of the plant where the driving forces approach those in conventional power plant condensers, the tube pitch is increased slightly to reduce the bundle losses. The entire heat recovery section uses a bundle of circular cross section, about 5 feet in diameter with ¾ inch diameter tubes on a 1 inch triangular pitch.

Removal of air and noncondensibles is accomplished by providing an inverted keyhole shaped space, void of tubes, in the center of the bundle and extending to the top of the bundle. Light gauge stainless steel baffle plates are used to assure that the noncondensibles are thoroughly subcooled before reaching a vent.

Flashing brine stream

The design of the flashing brine system must consider the flashing area, the nature of the high and low pressure flashing devices, and the method of control of those devices. The most up-to-date studies of the flashing phenomenon have shown that the stage length is governed, not by the distance required for the flashing stream to reach equilibrium, but by the length of condenser tubes needed to provide sufficient condensing surface. The optimum depth for the flashing brine stream is 12–15 inches, and the width of the stream should be such that it will allow a brine flow rate of about 800,000 pounds of brine per hour per foot of width.

In the high pressure stages, which have interstage pressure differentials of up to 5 feet of water, the interstage flow is controlled by using U-tube flow paths of sufficient height to assure that blow-through will not occur as the interstage pressure differentials fluctuate. In the lower pressure stages, the use of submerged weirs is practical because the interstage pressure differential is low and blow-through seldom occurs. In both cases, butterfly dampers are used to control the brine flow.

The interstage pressure differentials are maintained by the venting system. Noncondensibles are vented externally from stage to stage, cascading down to the lowest pressure stage in each module. Then the gas is removed at an appropriate point by a three-stage steam jet air ejector complex.

In the stages operating above 180° F., the annular clearance space in the stage divider plates between the plate and the tubes, is sealed with polypropylene O-rings.

Evaporator shell

The evaporator shell must enclose the tube bundle, water tray, mist separators, the vapor disengagement height, and the flashing brine stream. This stack of parts totals 10 to 11 feet. A round vessel enclosing this stack would have many advantages over a rectangular shape in ease of construction. However, a circle which encloses the above stack will have a perimeter larger than the rectangular design. There is a difference in the 30-year shell corrosion allowances above and below the mist separator of sufficient amount so that the use of a rolled shell is made even more difficult. Based on all of these considerations, the optimum cross section for the evaporator is a shape having a flat bottom, straight sides, and rounded top. The required cross section is 8 ft. 6 in. wide for the acid plant and 15 ft. 10 in. wide for the polyphosphate plant.

The evaporator could, theoretically, be built in one long structure. Such a structure would be at least 300 and possibly 500 feet long. However, condenser tubes are not yet available in such lengths. So even if the problem of differential thermal expansion could be satisfactorily overcome, it would seem prudent to size the plant into modules of a length approximating the maximum available tube length. Although at this time the maximum tube length available in the United States is 110 feet, to permit bidding by foreign tube mills, the modules have been limited to lengths of 80 feet.

The relatively modest size of this plant, and the probability that it must be fabricated in one part of the world and shipped to its point of use, precludes the use of concrete as a material for the evaporator shell.

Product water stream

The product water vapor after flashing off the brine surface is drawn towards the cool condenser bundle. The disengaging height, three feet of clear space, permits most of the entrained droplets which are too big to be carried by the vapor stream to disengage themselves and fall back into the brine. The droplets which are still vapor-borne pass into the mist separator—a Monel metal mesh device. These droplets agglomerate and fall back into the brine stream. Despite these design pre-

cautions, some extremely small droplets will get through these separators and find their way into the product water. The product water vapor condenses on the tube bundle and falls into the product water tray. This tray is made of copper nickel alloy to assure that no *red water* is produced. The product water available at the exit of each stage flows through U-tube interstage sealing devices, flashing down from stage to stage giving up its heat each time to the recycle flow, and finally is pumped out of the evaporator at the last stage. Control valves in the U-tubes maintain proper flow.

Vent, makeup, and blowdown stream

The venting or air ejector system serves two functions: removal of noncondensibles from the evaporator and removal of air from the deaerator. The various vents from the evaporator are taken directly into the three-stage steam jet air ejector complex. The air from the deaerator and the heat rejection stages of the evaporator, however, must be passed through a large vent condenser in order to remove as much of the water vapor as possible before going to the steam jet air ejectors.

The final area of interest in the plant design is in the fluid supply, transfer, and removal systems. A pump feeds the decarbonator with the brine makeup. A second and separate pump feeds the deaerator. Brine flows from the deaerator to the recycle stream by gravity. The brine recycle flow is caused by a pair of one half capacity brine recycle pumps. Both a blowdown pump and a product water pump are provided for each of these streams. The decarbonator, deaerator, and product water systems are equipped with 100% spare pumps. The pump which takes suction from the last heat rejection stage, and the blowdown and recycle pumps are all vertical, centrifugal, can-type pumps. These pumps take their suction from a plenum chamber located below the last evaporator stage.

This plenum chamber is an innovation dictated by the universal nature of the design. By providing a suitable place to connect all the various streams, the following are accomplished:

- The arrangement of pumps can be very flexible since they can be put on either side or end of the chamber.
- The recycle and makeup water can be mixed properly.
- The makeup can be introduced so that no fresh makeup can become a part of the blowdown.
- A surge volume is always available to handle system transients, particularly since the deaerator sump contributes to the surge volume directly.
- The flows into the blowdown and recycle pumps will have very low velocities, low losses, and the chances of flashing and cavitation in the pump suctions are greatly reduced.
- Space is provided for a vortex suppression device, if required.

None of the pumps for these systems pose any unusual technical problems, and they are made of the materials commonly in current use for hot salt water service.

The balance of the desalting plant equipment, such as vent condensers, jet air ejectors, brine heater, deaerator, decarbonator, chemical feed systems, and the auxiliary electrical equipment pose no unusual technical problems. Each of these systems is specified to meet equipment criteria that are well-known and widely used for the services involved.

Final design package

The final design of this plant is quite a package. Three volumes of data and 65 drawings provide all the information necessary to select a plant for any site, and to compute the actual cost of product water.

Volume I contains the User's Manual. It is in two parts, the first having the explanatory text, and the second the computer outputs and water cost factors for all eleven plants. This manual explains how one of the eleven plants is selected, and how, in detail, the actual water costs can be calculated for the site in question.

Volumes II and III are the bidding and technical specifications for the entire plant within the battery limits.

The 65 drawings show the detail design of the evaporator modules.

This design package takes into account many design, cost, and output factors and, by optimizing them into 11 plant designs, facilitates selection of the one design which will produce potable water at minimum cost at any spot in the world.

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Henry M. Rose *is chemical engineer with Burns & Roe, Inc. Previously (1960–65), he was design superintendent for the Celanese Plastics Co. (Newark, N.J.), plant engineer (1945–51 and 1953–60) with Congoleum-Nairn, Inc., and chief engineer (1951–53) with Lovell-Dressel Co. Mr. Rose received his B. S. (1940) in mechanical engineering from Cornell University. Mr. Rose served (1940–45) in the U. S. Navy, attaining the rank of Lieutenant Commander. Since joining Burns & Roe in 1965, Mr. Rose has been engaged in the design and application, and system cost analysis, of controlled flash evaporator applications to boiler feedwater supply and potable water supplies, as well as various desalination plant proposals to private utilities—including removable tube bundles and selection of plastic material for chutes. He is a member of American Nuclear Society, U. S. Naval Institute, and Tau Beta Pi.*

Effective Water Pollution Control Requires Accurate Data

Careful determination of the quality of a water system provides data on the nature and sources of pollutants

Dwight G. Ballinger

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Effective water pollution control is dependent upon having objective and accurate scientific data on existing water quality. These data must identify specific pollutants, define their concentrations, and describe their effects on present and potential water uses. Such information is essential to the assessment of conditions, the planning and attainment of abatement, and for legal action to secure compliance with water quality standards.

A discussion of analytical chemistry in water pollution control must begin where the analysis begins—with the sample. A sample of polluted water is an extremely complex mixture, containing many chemical and biological entities. Some of the constituents are highly significant to the evaluation of water quality, while others serve only as troublesome interferences. It is readily apparent that a complete chemical analysis is next to impossible and probably of little value in any case. The analyst must select his parameters by consideration of both the past history of the sample and the planned or desired uses of the water body. He must choose those determinations required to characterize the sample and reject those which are of academic interest. The first consideration, then, is the selection of tests to be performed.

Typical determinations

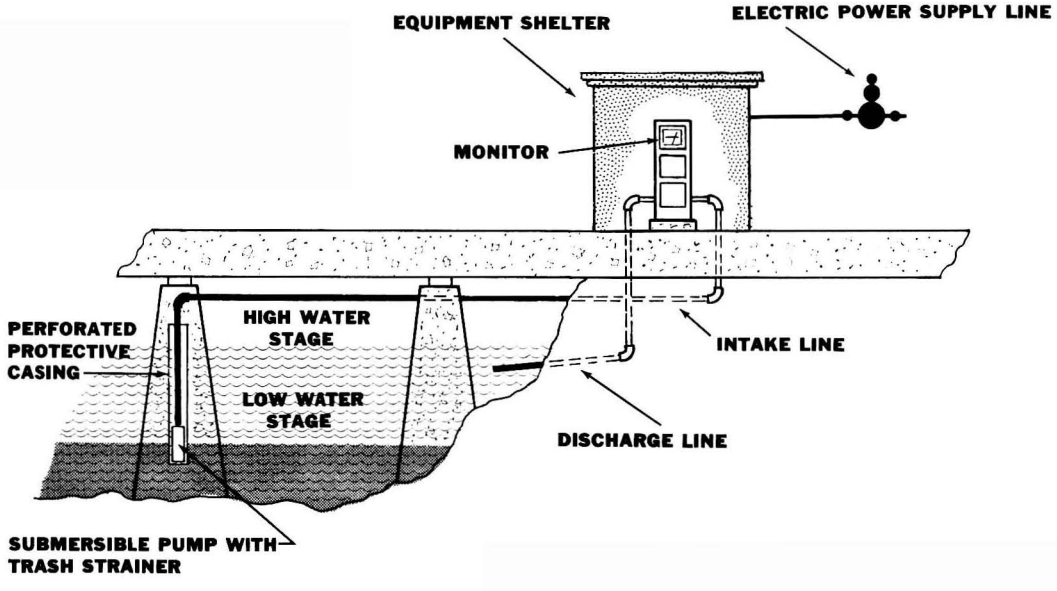
The chemical determinations or tests applied to water and waste samples can be divided into two general classes:

- Specific pollutants which may be present.
- Water quality characteristics.

The choice of specific pollutants to be determined depends upon the known or probable types of waste discharge. Organic carbon, grease, nitrogen forms, phosphorus, suspended matter, and surfactants are contributed by domestic sewage, while heavy metals and cyanides are often discharged by metal plating plants. The pattern of pollutants present suggests the probable sources of the waste.

For example, domestic sewage effluents having very high concentrations of grease and organic nitrogen may indicate appreciable packing house wastes, while the presence of high cyanide levels without accompanying metals would point to chemical manufacturing rather than plating operations. In each case the laboratory results should correlate with the engineering survey of pollution sources. On occasion the chemist may uncover a waste source previously undetected.

The presence of pollution is re-



flected in changes in water quality characteristics, since sewage will increase the oxygen demand and decrease the dissolved oxygen, while metal plating wastes will increase acidity, decrease alkalinity, and lower the pH. The interrelationship of the water quality characteristics is useful in judging the reliability of analytical results. An increase in oxygen demand without a corresponding decrease in dissolved oxygen suggests a faulty test.

In reviewing analytical data, the analyst should be able to spot inconsistencies, because of the cause and effect relationship of the various factors. Satisfactory analyses, therefore, must include both the pollutants present and the changes in character caused by those pollutants. Also, the relationships of the various results must fit a logical pattern.

Because of the complex nature of water and waste samples, preliminary treatment of the sample often is required to eliminate interfering substances or to isolate the desired constitutent. In the colorimetric determination of heavy metals, the organic matter must first be destroyed by combustion or wet oxidation. Phenols and ammonia nitrogen are isolated by distillation, while cyanides and arsenic are converted to gaseous forms to remove them from the interfering substances. Complexing agents, such as EDTA or tartrate, are often employed to tie up extraneous metals. Isolation of the desired element by precipitation and filtering is rarely used because of the minute quantities involved. On the other hand, samples that are turbid or highly colored must be clarified and decolorized before beginning the analysis.

Dynamic systems

In addition to being a complex mixture, a water sample is also a dynamic system. Most polluted water contains millions of microorganisms, which continually consume available food materials and, thus, significantly alter the water's chemical constituents. The analyst must be aware of the effect of biological action on the sample and make adequate provision to account for it. He must determine immediately the analyses to be made, the preservative measures which will stabilize certain entities, and the constituents which are stable enough for later determinations. For example, dissolved oxygen will be held in solution without change for a few hours if the sample is refrigerated at 4°C.; 1% nitric acid will prevent the precipitation and adsorption of most metals; and chloroform will stabilize phosphorus compounds for weeks. Calcium and magnesium, on the other hand, are relatively stable in most waters.

Since most laboratories cannot complete all the required analyses immediately, the sample must be subdivided, preserved as needed, and analyzed according to a predetermined schedule.

Required sensitivity

Just as all the constituents of the sample are not equally significant, so the relative concentrations of the chemical entities may vary in importance. For certain pollutants, extreme analytical sensitivity is needed to adequately identify and quantify the substance.

The sensitivities required to detect the presence of toxic materials can present more than the usual analytical difficulties, because of the wide range of concentrations encountered. Often the analyst must measure a constitutent in the waste discharge where it occurs at high concentration, and also in the receiving water where it occurs at levels near the lowest detectable limit. The difference may be several orders of magnitude. Dilution of the waste sample can be made, but occasionally two procedures must be used to cover the anticipated range of concentration.

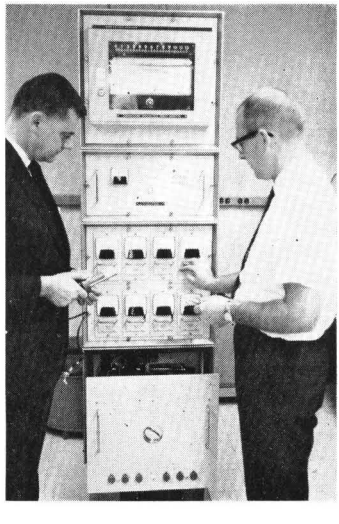
Precision and accuracy

Precision and accuracy are also important considerations in water pollution analyses. An accompanying table shows the precision and accuracy reported by 64 laboratories participating in a round robin study conducted by the Analytical Reference Service of the U.S. Public Health Service in 1962. In general, the performance of the overall group appears to meet satisfactorily the requirements of the analytical program. Since the reported results are the mean of all participating laboratories, it is obvious that some of the laboratories did not perform as well as shown in the table, while others were able to secure precision and accuracy greater than shown in the table. Weaknesses are especially apparent in the aluminum methods, indicating, at least in the case of aluminum, a need for a search for more reliable procedures.

In water pollution studies the *sample to batch* ratio is statistically staggering. To illustrate: the Detroit River flows at the rate of 200,000 cubic feet per second, or 5.4×10^9 gallons per hour. If a sample collected once each hour is considered to represent the water flowing past the sampling point during the previous 60 minutes, a one gallon sample has a sample to batch ratio of one in 5.5 billion. If we consider that the usual sample aliquot is rarely more than 100 ml., the true ratio becomes one in 205 billion. Thus, an analytical determination of 0.01 mg./l. in the copper test represents 450 pounds of copper in the river.

Because of the presence of many other chemical substances, analytical methods in water pollution control must be highly specific. A procedure

Monitor. *Continuous sampling techniques are very effective for measuring water quality*



which yields a value for total organics, for example, is useful only as a gross indication of water quality. Whenever possible, methods are selected which give concentrations of specific chemical elements, functional groups, or compounds.

Occasionally, however, separation of a group into specifics is too tedious and difficult. The determination of phenols, for example, gives a total value for most hydroxy substituted benzene compounds, without identification of the particular aromatics present. Similarly, the grease determination lumps together all hexane soluble substances. When it becomes necessary to pinpoint the source of a waste, however, procedures are used which can separate petroleum products from animal fats, or chlorinated phenols from cresols.

Analytical methods

To obtain the necessary sensitivity, accuracy, and specificity, a variety of analytical techniques are utilized. Since colorimetric methods are usually very sensitive, they are more often applied than titrimetric procedures. Gravimetric methods are not applicable in the microgram range and are restricted, therefore, to the measurement of suspended matter and grease. Instrumental methods (not to be confused with instrumental devices used in colorimetric or titrimetric tests) are available for many determinations, and I shall discuss some of them in detail later.

Many of the colorimetric tests involve three steps:

- Isolation of the measured constituent.
- Color formation by means of an organic reagent.
- Concentration of the colored complex by organic solvent extraction.

Phenols, for example, are determined by distillation from the original sample (after pH adjustment and complexing of sulfur with copper), and addition of 4-amino antipyrine for coupling at the para position. If the concentration of phenol is greater than 0.10 mg./1. the color is measured in the aqueous phase. With extraction in chloroform the detection limit may be extended down to 1 μg./l. Similarly, cyanide is evolved as HCN, absorbed in alkaline solution, and the resulting sodium salt is titrated with silver nitrate or measured as a colored complex with pyridine-pyrazolone reagent. Greater sensitivity can be obtained by extracting the color with butyl alcohol.

Cadmium may be determined colorimetrically as the dithizonate, by polarography, or by atomic absorption. In the case of cadmium, the choice depends largely upon the availability of instruments rather than the concentration in the sample.

Dissolved oxygen has classically been determined by the Winkler titration, involving oxidation of a manganous salt, production of equivalent iodine from iodide, with final titration by means of thiosulfate. The method is being superseded by a modified solid electrode polarograph, in which a gas permeable Teflon membrane limits electroreduction to gaseous oxygen.

The analytical requirements of research studies in water pollution control are basically similar to those in pollution survey work. The same tests are required and the same analytical procedures are used, although maximum sensitivity often is required, since the research investigator is looking for subtle differences. In toxicological studies the analytical group may be hard pressed to provide adequate sensitivity to match the toxicity thresholds. Fortunately, the work load is generally less than in the survey laboratory, permitting more involved methods.

Field laboratories

It is well to recognize that water pollution control analyses must often be performed away from a large, well equipped laboratory. Samples for certain tests, such as biochemical oxygen demand, cannot be preserved adequately at present, so analysis must begin within a few hours of sample collection. Further, it is wise for the investigator to make exploratory tests to confirm the presence of pollutants before embarking on a full scale sampling program.

To help him carry out such exploratory tests, the analyst has a wide variety of mobile laboratories or field test kits at his disposal. The mobile laboratory is essentially a small version of the fixed lab, since standard facilities and equipment are used. In these mobile labs the more compact models of the analytical instruments are especially desirable. Field kits are useful for on-site analyses in remote areas, but generally the kits provide only semiquantitative results because of limitations in measurement of reagents and inferior colorimetry equipment.

Legal aspects

Because the analytical results may be needed in enforcement actions, we should take a brief look at the legal aspects of laboratory analyses. The methods used in most water pollution control laboratories are found in a volume called *Standard Methods for the Examination of Water and Wastewater* published jointly by the Water Pollution Control Federation, the American Waterworks Association, and the American Public Health Association. The selection of methods in the volume is based on committee activity similar to that of the Association of Official Analytical Chemists and the American Society for Testing and Materials, though, unfortunately, not on the excellent referee system characteristic of those organizations.

For many years ASTM, through its Committee D-19, has published the *Manual on Industrial Water and Industrial Waste Water*. While prepared from the industrial viewpoint, this manual has some procedures identical to those in *Standard Methods*, not surprising since several of the country's foremost water and waste analysts assist in the preparation of both volumes. To date, analytical procedures prescribed by *Standard Methods* have been accepted without challenge in pollution control hearings and court actions. Since the proper method does not necessarily ensure a correct result, the better laboratories have instituted extensive quality control programs as well.

Data handling

An interesting phase of the use of analytical data is the storage and retrieval of the information. To provide for maximum utilization of water quality data, the Federal Water Pollution

Control Administration has established a storage and retrieval system called STORET. Electronic computers in Washington, D.C., receive and store data from cooperating laboratories throughout the country. Potential users of water quality information can obtain data in printed form on any water course covered by the system. In addition to the actual laboratory results, the computers can provide calculations of monthly and annual averages and trends, comparisons between results at different sampling stations, and correlations between such different water quality parameters as dissolved oxygen, waste load, temperature, and the like. This computer repository of accessible information can serve as the basis for an evaluation of existing water quality and comprehensive planning for pollution control.

Water quality determinations

Specific Pollutants	Characteristics
Heavy metals	Acidity
Organic carbon	Alkalinity
Chloride	Hardness
Cyanide	Color
Grease	Oxygen demand
Lignin	Dissolved oxygen
Ammonia nitrogen	pH
Nitrate nitrogen	Turbidity
Organic nitrogen	Temperature
Phenol	Specific conductance
Phosphorus	
Suspended matter	
Surfactants	

Instrumental analyses

In water pollution control work, as in most chemical analyses, we are moving toward increased automated instrumentation. Automatic instruments provide speed, sensitivity, and better data presentation.

The atomic absorption spectrophotometer has been a great step forward in the analyses for heavy metals. Because this instrument measures aqueous solutions, little or no preliminary sample preparation is required. Often the sample can be aspirated directly from the sample container. At present, sensitivity of atomic absorption spectrophotometer methods is not quite satisfactory for drinking water analyses, but solvent extraction or ion exchange provides an easy means of concentrating the metals.

The emission spectrograph, though not widely used, offers simultaneous rapid scanning for as many as 60 elements. While the advantages of the emission spectrograph are obvious, the relatively high cost of a complete instrument package and the skill required to obtain reliable results may restrict this equipment to only the largest water laboratories.

The Technicon AutoAnalyzer has been adapted to a wide range of colorimetric determinations in the water pollution control laboratory. The unat-

Precision and accuracy of metals determinations

Standard deviation mg./l.	Mean Error mg./l.
Al ± 0.10	0.35
Cr ± 0.01	0.04
Mn ± 0.03	0.03
Cu ± 0.01	0.01
Fe ± 0.06	0.22
Cd ± 0.01	0.02
Zn ± 0.07	0.04
Pb ± 0.04	0.02

Some sensitivity requirements for water analyses

Element or Compound	Detectable Limit, μg./l.
Arsenic	5
Cadmium	10
Calcium	1000
Cyanide	50
Lead	10
Ammonia nitrogen	10
Phenol	1
Phosphorus	10
Endrin	0.001

Note: Test procedures will be dictated by these significant concentrations. Endrin, for example, is significant at 0.001 μg./l., while lead is probably insignificant below 10 μg./l.

Analytical methods in water pollution control

Colorimetric	Titrimetric	Gravimetric	Instrumental
Ammonia	Acidity	Grease	Chloride
Color	Alkalinity	Suspended matter	Conductance
Cyanide	Chloride		Dissolved oxygen
Lignin	Dissolved oxygen		Metals
Metals	Hardness		Organic carbon
Nitrate			pH
Organic nitrogen			Temperature
Phenols			Turbidity
Phosphorus			
Surfactant			

tended operation is both a boon and a danger, since the robot is not able to detect the abnormal sample and adjust accordingly. This type of instrument is most applicable to a large number of repetitive analyses on samples having essentially the same chemical characteristics.

Many of the titrations utilize potentiometric endpoints and, therefore, can be performed with an automatic titrator. One model now available provides automatic sample changing and digital tape printout.

Recently, potentiometric electrodes sensitive to single cations or anions have become available. Their application to water analyses is being explored and they appear to have some promise, particularly for rapid sorting of samples into concentration ranges. As additional electrodes become available, these will be tested in laboratories of the Federal Water Pollution Control Administration.

Continuous monitoring

A rapidly expanding area of instrumental analysis in water pollution control is the continuous monitoring of waste effluents, rivers, and tidal estuaries. Many of these monitoring instruments are now installed at various sites throughout the country, measuring dissolved oxygen, pH, temperature, conductivity, chloride, turbidity, oxidation-reduction potential, and solar radiation. The data are recorded on multi-point recorders, punched paper, or magnetic tape—or the data are telemetered to computer centers. Present measurements are generally of water quality characteristics rather than of specific pollutants. Because of this limitation, as well as the cost and difficulty of installation and maintenance, this type of analytical measurement will probably remain as a supplement to the regular laboratory program rather than a replacement for it. But the potential for a continuous finger on the pulse of the river and the possibility for automatic feedback to treatment control systems are attractive plus values for the system.

Research needs

The research needs of the water pollution control analyst are basically the same as those of all other analytical chemists and include the development of tests that yield greater specificity and greater sensitivity or that may be designed for automatic analyses, including automatic sample changing, digital data presentation, and automatic printout.

In addition to these needs, however, there remain the nagging little problems and weaknesses in the analytical methods now in use. Among the methods needed are the following: a simple, reliable, specific test for hydrogen sulfide in water (not total sulfide, but the gas and its ionic forms), an instrumental method to replace the archaic Jackson candle technique for turbidity, an uncomplicated procedure to separate the lignins in paper mill effluents from the tannins resulting from forest land drainage, an organic nitrogen method to replace the procedure published by Kjeldahl in 1883, and a method for measuring the oxygen demand of undisturbed lake bottoms.

Analytical chemistry in water pollution control is almost unique because of the nature of the sample, the extremely low levels of many of the measured constituents, the economic and legal significance of the laboratory results, and the variety of analytical techniques used. The procedures are characterized by preliminary removal of many interferences, isolation of the desired substance, and sensitive colorimetric or instrumental measurements. Trends toward increased instrumentation, including remote monitoring, are apparent. Research needs in analytical chemistry include greater specificity, greater sensitivity, and increased automation.

Dwight G. Ballinger *is assistant director for laboratories of the Division of Pollution Surveillance, Federal Water Pollution Control Administration, U. S. Department of the Interior. He has recently completed his 26th year in the service of the Federal Government program of water pollution control and continuing surveillance of water quality in the nation's rivers, lakes, and estuaries. Mr. Ballinger received a B.Ph. degree (1956) in chemistry from the University of Cincinnati. He is the author of many publications in the analytical chemistry of water and wastes, dealing chiefly with instrumental analysis. Mr. Ballinger is a member of ACS, Water Pollution Control Federation, and American Water Works Association, serves on several of the subcommittees in the preparation of* Standard Methods for the Examination of Water and Wastewater, *and is a member of Committee D-19 for Water of the American Society for Testing and Materials.*

QUOTE . . .

PEOPLE MIGHT ENJOY CITY LIFE

Almost all of the inhabitants of the U.S. in the year 2000 will be living in cities. If, as at present, population densities of cities continue in the neighborhood of 15,000 persons per square mile, we can look forward to adding some 10,000 square miles of new urban development by the year 2000 and over 30,000 new square miles of urban development in another one hundred years.

Our increasing per capita needs for raw materials, our growing per capita energy consumption, and our growing volume of waste products, including waste heat, will place increasingly severe limitations on the sizes of cities and will place certain geographic regions in more favorable positions for city development than others. I suspect that the strains placed upon existing cities will continue to build up rapidly and that as time goes by, it will become ever easier to build new cities than to attempt to patch up the old ones.

In the light of this rapidly changing situation, where lies the destiny of our cities? Clearly if we continue our present procedures of waste disposal, we will poison ourselves, the end result conceivably being death. In my opinion we must create a situation where all wastes, except heat, are reclaimed—where we learn how to live in a closed system, much like that in which the astronaut finds himself in space.

What would this mean in terms of our present way of life?

It would mean that all noncombustible waste would be reclaimed—as distinct from the small fraction of such waste which is reclaimed today.

It would mean that biological wastes would be returned to the soil or fed to chemical plants.

It would mean that only carbon dioxide would be returned to the atmosphere as waste.

It would mean that wastes not easily transformable into useful products, such as waste heat and surplus soluble salts, would be returned to the sea.

I also believe that it should be possible for us to create new cities in which such goals are automatically included in the design specifications.

I believe our cities as they now exist both physically and politically are doomed. I believe further that technological developments can greatly change this picture. These developments include our learning how to build a self-contained city, which will not grow under any circumstances beyond a certain size. This city will feed on the oceans, air, rock, and the soils which surround it. It will be mainly nuclear powered. It will recycle all wastes, including water. It will border upon being a self-contained unit.

And above all, people might even enjoy living there!

Harrison Brown

Professor of Geochemistry and Science and Government, California Institute of Technology, Pasadena, before the U.S. Senate Subcommittee on Intergovernmental Relations which was holding hearings on the creation of a Select Committee on Technology and the Human Environment, March 20, 1967

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Thermal Pollution of Water Systems

Recognized as a problem since World War II, heat pollution of water systems is amenable to modern environmental, mathematical analysis

Burton Davidson and Robert W. Bradshaw
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Temperature alterations in the aquatic environment have become the latest industrial pollution syndrome. In common parlance, this syndrome is called thermal or heat pollution (Carr, 1966; Hoak, 1961; and Moore, 1958). Historically, the term thermal pollution has been used as a siren call whenever normal ecological conditions in a stream have been disrupted by dint of man-made thermal discharges (Laberge, 1959). This connotation has implied that relatively hot effluents have a deleterious effect upon stream purification capacity.

Whereas the thermal pollution terminology is more pithy than platitudinous, the stigma should be studiously avoided because it engenders a misguided sense of understanding of the problem. We do not want to infer, however, that the thermal pollution stigma has not served a useful purpose. Since World War II, the continual use of this terminology has alerted people to the potential hazards of heated discharges from industrial plants. As a consequence, temperature effects in the aquatic environment have been extensively researched and the findings seem to suggest a rather interesting paradox.

The beneficial and adverse effects of heated or cooled effluents on stream ecology are found to be in approximately equal proportions on a broad spectrum over a 12 month cycle. Any attempt to define a temperature index for stream pollution, therefore, will tend to apply to a restricted area of the spectrum rather than to the entire range. The effects of temperature change on stream dissolved oxygen is one type of syndrome whereas fish kills due to thermal shocks are quite a different kettle of fish.

Mathematical analysis

In addition to accepting our civic duty to help provide knowledge about thermal pollution, we are also concerned with educating people about the power and pitfalls of modern environmental, mathematical analysis. The analytical powers of a multidisciplinary approach that synthesized basic concepts in biochemistry, plant physiology, transport phenomena, biokinetics, computers, and optimization theory, no matter how tenuously derived, is a step in the right direction.

If the indicial formulation is well set, marginal corrections can be added as more information is processed. The gathering of basic information from the separate disciplines and the amalgamation of this information into a viable mathematical simulation is a two-way street which requires continual repaving by those involved.

In this article, we will discuss the thermal pollution problem in two rather diversely related parts. In the first section we shall discuss the syndrome qualitatively and broadly, whereas in the second, we shall treat a specific aspect of the problem quantitatively and in depth using the systems analysis or mathematical approach.

Source of the problem

The enthalpy balance of a polluted stream, along with the upstream boundary condition, defines the downstream temperature field, which, in turn, causes disturbances in the entire aquatic environment. If a normal stream temperature field is roughly defined as the temperature field of the stream that prevails in the absence of population and industry, then any source of effluent at the upstream boundary location that alters the normal downstream condition can be construed as abnormal enthalpy modifi-

Heated effluent. *At the Chalk Point, Md., generating station of the Potomac Electric and Power Co., heated water from coolant systems is pumped 2 miles upstream (canal shown at center of photo) before being discharged to the Patuxent River*

cation and a likely candidate as a pollution contributor.

We make no distinction at the onset between hot or cold sources of effluents. Abnormal enthalpy modification can arise from either source, depending on whether the enthalpy of the receiving stream at the boundary is greater or lower than the enthalpy of the effluent itself.

An effluent of low enthalpy value (the product of flow rate, heat capacity, and temperature above a datum plane) might originate from releasing hypolimnion water from the bottom of a deep reservoir during a period of low flow augmentation (Feigner, 1963). On the other hand, an effluent of relatively higher enthalpy value is usually associated with the cooling water discharges from surface condensers of steam-electric generating plants (Edinger and coworkers, 1965). We have based the comparison between low and high enthalpy effluents on equal flows. In other words, specific enthalpy or enthalpy per pound is proportional to temperature for dilute, aqueous solutions.

Cooling water discharge

In recent articles (Cadwallader, 1964; Dysart and coworkers, 1965) on thermal pollution, the authors estimated that for each kwh. (3412 B.t.u.'s) generated in a modern, coal-fired power plant, approximately 6000 B.t.u.'s must be dissipated by means of cooling water in heat exchangers. The cooling water discharges often range from 11° to 17° F. higher than the temperature of the water in the stream. Nuclear reactors are less efficient, wasting approximately 10,000 B.t.u.'s per kwh. generated. At the Chalk Point steam generating plant in Maryland, for example, 500,000 g.p.m. of heated cooling water, which at times is equal to or greater than the fresh water inflow, is released into the Patuxent estuary.

Since World War II, the electric utility industry load requirements have doubled each decade, and approximately 75% of these loads were generated in thermal plants. Shore (1967), of the Federal Power Commission, predicted that future power developments for the North Atlantic region in the next six years, which amount to approximately 30 Mkw. or two thirds of what we have today, will be only 32%

POLLUTION EFFECTS OF TEMPERATURE

• Changes in temperature cause gases, such as carbon dioxide, which are dissolved in the water and are present throughout a fish's environment, to change their selective toxicity toward fish. At 1° C., the CO_2 concentration considered lethal to carp is 120 mg./l. whereas with a rise in water temperature to 30° C., the lethal concentration decreases to 55-60 mg./l. (MacNamara, 1966; Westman, 1967; and Wurtz and coworkers, 1965).

• Fish, in general, depend on temperature changes, in specific amounts, to act as a signal for such things as migration and spawning. Distribution is also related to temperature changes. The upsetting of seasonal temperature cycles may upset the entire life cycle of fishes involved (MacNamara, 1966; Westman, 1967; and Wurtz and coworkers, 1965).

• Oxygen consumption by aquatic vertebrates doubles for every 10° C. rise in stream temperature (MacNamara, 1966).

• Different species of fish have different thermal death points (t.d.p.). Even within species, this may vary depending on the temperature acclimation. A flathead minnow acclimated to 10° C. has a t.d.p. of 28.2° C., whereas the same species acclimated to 20° C. has a t.d.p. of 31.7° C. A point is soon reached where the acclimation temperature and the t.d.p. are nearly the same (MacNamara, 1966; Westman, 1967; and Wurtz and coworkers, 1965).

• Trout eggs will not hatch if incubated in water warmer than 14.4° C. (MacNamara, 1966; Westman, 1967; and Wurtz and coworkers, 1965).

• Cold water from hypolimnion reaches in the Fontana Reservoir (N.C.) has drastically altered fish environments in the Little Tennessee River downstream. Once-productive warm water fisheries existing in these waters were largely eliminated by temperature changes (MacNamara, 1966; Westman, 1967; and Wurtz and coworkers, 1965).

• The saturation value of dissolved oxygen (DO) decreases as temperature increases. Although this phenomenon is interesting in itself, it does not apply directly to the ultimate value of dissolved oxygen in a stream because it is an equilibrium factor. The supply and removal of stream DO are rate processes and the saturation value of DO is only part of one of the terms in the DO budget equation (Burkart, 1967).

• All biological processes are to some extent thermochemically controlled by the Van't Hoff-Arrhenius condition. The biological oxygen demand (BOD), with its subsequent demand upon DO, increases over a restricted range with temperature rise (O'Connor, 1967).

• Algal respiration and benthic BOD are also influenced by temperature. Their subsequent demand upon stream DO is increased as temperature of the stream increases (O'Connor, 1967).

• Physical expulsion of supersaturated DO follows a rate law which is roughly proportional to the negative of the DO deficit (DO, minus saturated DO). The expulsion of DO increases as temperature increases.

• Density stratified flow, resulting from incomplete enthalpy mixing of the effluent and receiving streams, may cause serious inhibition of DO reoxygenation from photosynthetic and reaeration sources (Dysart *et al.*, 1965).

conventional steam, 43% nuclear, 13% internal combustion engines, and 12% pump storage. There will be practically no conventional hydro development. The enormous power demands predicted for 1973 and later will be largely nuclear energy with peaking needs fulfilled by pump storage and internal combustion devices.

Since the cooling water requirements will be so enormous, the bulk of the new power installations will have to be near the shores of the sea or the Great Lakes. If they are not so located some of the rivers in the U.S. could reach their boiling point by 1980, and may even evaporate by the year 2010 (Dysart and coworkers, 1965). The Mahoning River in Ohio, for example, at one time reached 140° F. before constraining actions were taken (Carr, 1966).

Pollution effects of temperature

The literature on temperature effects in the aquatic environment is voluminous and only a sampling of results is presented in this article. We have classified enthalpy modification or temperature alterations dichotomously into categories of pollution effects and purification effects. The presentation is necessarily annotated and somewhat disjointed.

A temperature pollution index

The difficulty of dealing with a particular facet of the thermal pollution problem is complicated by the fact that stream enthalpy or temperature changes ineluctably with the time of year and with the time of day (Leclerc, 1964). The ubiquity of the temperature field in a stream and the many opposing mechanisms of its effects upon stream ecology tend to make the problem of even defining a thermal pollution index (an index comparable in stature to BOD) a formidable task, if not an impossible one. A thermal or temperature purification index is perhaps more central to the issue.

If an index is defined too broadly, its interpretation by law-enforcing agen-

cies becomes a hardship. An index defined on too small a scale cannot satisfy the great portion of water users. Yet, there is a basic need to provide pollution control agencies with a quantitative figure of merit or demerit for enthalpy modification of streams. The merit figure should be a function of both the receiving stream and the source of effluent. It is undesirable to base an index for thermal pollution on only the effluent state or only the stream condition.

The DO factor

As a first approach, we recognize that dissolved oxygen (DO) is a necessary factor for the proper survival and propagation of fish and other aquatic inhabitants. DO concentration is measurable, controllable, and amenable to mathematical analysis. We propose to lay aside all tangential effects (thermal death physiology in fish, and the like), and follow a course which centers around maximizing stream DO concentration as the pertinent objective function.

The DO budget equation or material balance is composed of *source* terms or reoxygenation factors and *sink* terms or deoxygenation factors. All source and sink terms are temperature sensitive and their specific temperature response characteristics are obtainable from information derived from the separate disciplines, such as biology, sanitary engineering, and environmental science (O'Connor, 1967).

It is possible, in principle, to derive theoretically the *best* temperature profile for a polluted stream which causes the source and sink terms in the DO budget equation to respond in a direction that produces the maximum DO concentration at each point in the watercourse downstream from a source of organic pollution.

Enthalpy pollution/purification

If, for practical considerations, DO stream temperature and the rate of stream temperature change must be

PURIFICATION EFFECTS OF TEMPERATURE

- A four-year study on the Delaware River, above and below a thermoelectric generating plant, showed that most varieties of fish were almost eliminated from the most heated zone during the warm months, but an extended period of feeding activity occurred in heated waters during the cold months (MacNamara, 1966; Westman, 1967; and Wurtz *et al.*, 1965).

- Most fish can tolerate and adjust to gradual changes in temperature, but sudden change in temperature should be avoided (MacNamara, 1966; Westman, 1967; and Wurtz *et al.*, 1965).

- On Lake Erie and in the Potomac and Delaware Rivers, at least in stretches where pollutants are not too concentrated, fishing is best where power companies return their once-through cooling water. The warmer water apparently stimulates the growth of fish food (Carr, 1966).

- Certain species of game fish stop eating entirely when stream temperatures drop to less than 54° F. (MacNamara, 1966; Westman, 1967; and Wurtz *et al.*, 1965).

- In the winter time, heated coolant water may be very beneficial in natural stream purification. It may prevent ice from forming in a large section of potentially ice-locked body of water, providing for an otherwise nonexistant air-water interface for oxygen transfer (Strandberg, 1962).

- The natural reaeration coefficient in the aeration term of the DO budget equation is influenced by surface tension, density, viscosity, and mass diffusivity. When grouped together, these variables cause the reaeration coefficient to increase with temperature rise (Churchill, 1964).

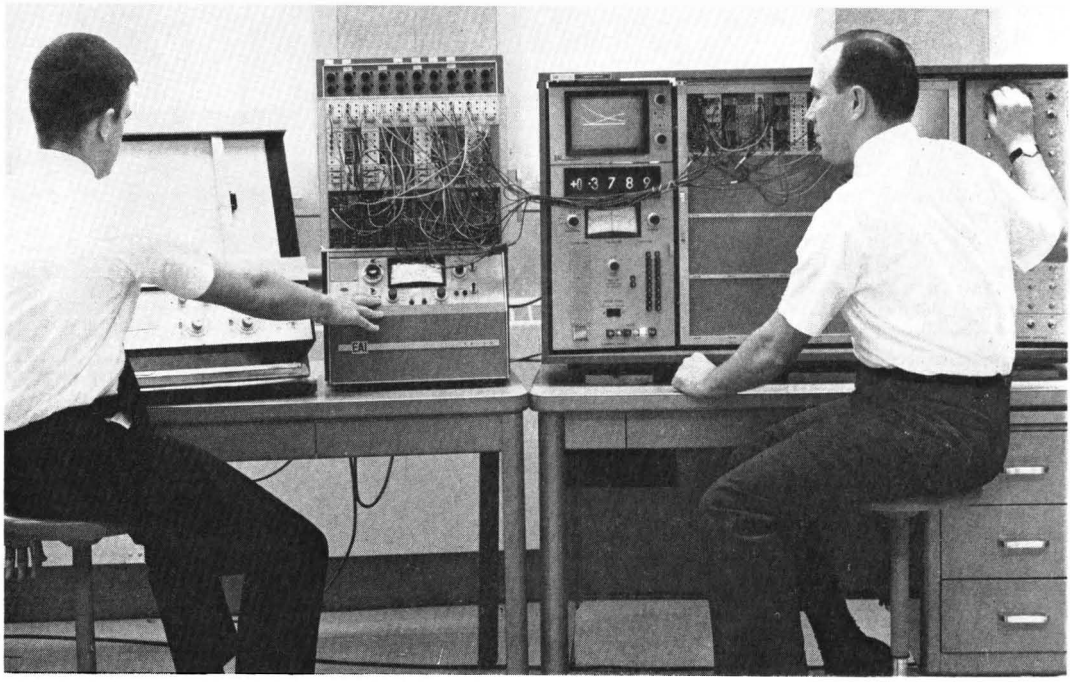
- Reoxygenation from phytoplankton photosynthesis increases with temperature over a restricted range, if other factors like light intensity and nutrient levels are held constant (Edwards, 1964; Fogg, 1965; Hull, 1964; O'Connor, 1960; and Warinner *et al.*, 1966).

- In municipal water treatment plants, the lower the temperature of the water entering the plant, the less efficient sedimentation and filtration become. For each 10° C. rise in water temperature, the cost of chemicals is lowered by 30 to 50 cents per million gallons treated (Hoak, 1961).

- BOD removal is enhanced by temperature rise. Considered by itself, this can be a purification factor.

- Density stratified flow, under special conditions, can offer the fish community a choice of warm or colder pathways for survival, migration, and propagation. Slugs of perfectly mixed warmer or colder waters from thermoelectric power plants or from impoundments offer no escape routes for fish inhabitants as the waves of thermal slugs move downstream.

- A downstream navigational user is benefitted by upstream thermal discharges from power plants during potentially ice-locked conditions in the winter.



Simulations. *An analog computer was used in the simulation of DO, temperature, and BOD. The unit consists of a fully expanded TR-20, a partially expanded TR-48, an X-Y plotter, a five place digital voltmeter, and a repetitive display scope*

limited to protect aquatic life and to ensure their survival and propagation, constraints can be set on these variables. Unencumbered by temperature or DO constraints, a mathematical derivation of a preliminary figure of merit for thermal pollution can be obtained.

Any enthalpy modification of a stream which produces a temperature profile different from the theoretical or optimal one is termed *enthalpy pollution*. On the other hand, any man-made alteration in the abnormal or suboptimal temperature profile in the direction of the optimal state, defined by the optimal temperature profile, is termed *enthalpy purification*.

The enthalpy energy balance is used primarily to establish an implementation program for the optimal temperature profile dictated by the DO and BOD material balance relationships and their corresponding boundary conditions.

Creating a model

BOD and DO material balance equations that are applicable for all streams under all conditions of thermal loading, organic pollution, meteorological stresses, and the like, are impossible to derive. Recognizing that stochastic effects (Thayer and coworkers, 1966), as well as diurnal variations, are the rule rather than the exception, we can set up, nevertheless, meaningful mathematical expressions for BOD and DO. These expressions possess dependable factors and interactions so that the basic idea of temperature profile optimality can be examined without undue complications.

In this discussion we have resorted to one-dimensional, steady-state modeling, in deterministic form, for our derivations. Our analyses have been restricted to slowly-moving, medium-sized streams under summer conditions with idealized, plug flow velocity.

Our analyses seek to uncover the important optimization variables and their interactions. Furthermore, if the problem formulation proves to be well set, marginal corrections for such items as stratified flow, variable stream velocity, diurnal variations, transient conditions, and the like, can be added to the basic formulation in a natural way and the results re-examined using the same optimization algorithm.

Pontryagin model

A relatively new optimization algorithm by Pontryagin and others (Fan, 1966; Horn, 1967; and Pontryagin, 1962) is particularly well suited for calculating the optimal temperature profile required in the maximization of stream DO concentration. In the broadest sense, a polluted stream or river and a tubular reactor behave similarly. Many useful results in chemical reactor design problems have resulted from simplified analysis (Aris, 1961).

The assumptions of steady-state, plug-flow, and first-order kinetics have not been too restrictive in certain cases where the optimization result was of uppermost importance. The manifestation of optimal temperature profiles in chemical reactors and in polluted streams are really the same problem (Burkart, 1967). In order to avoid any misunderstandings, reference to the use of a Pontryagin model hereafter signifies an optimization problem composed of three main elements:

- Continuous, deterministic performance equations (BOD and DO equations) and initial or boundary conditions.
- A piecewise continuous decision vector function and constraints (stream temperature, 0° C. to 60° C.).
- An objective function (maximization of stream DO).

Performance equations. Following the basic work of O'Connor and Dobbins, the appropriate material balance expressions for BOD and DO are:

Performance equations. Following the basic work of O'Connor and Dobbins, the appropriate material balance expressions for BOD and DO are:

$$\frac{dL}{d\tau} = \left\{\begin{matrix} -K_r L \text{ when } C > 0 \\ 0 \text{ when } C = 0 \end{matrix}\right\} \quad 1$$

with $L = L_0$ at $\tau = 0$

and

$$\frac{dC}{d\tau} = \left\{\begin{matrix} +K_a(C_s - C) \text{ when } C_s > C > O \\ -K_a(C - C_s) \text{ when } C > C_s > O \\ +K_a C_s \text{ when } C = 0 \end{matrix}\right\} + \left\{\begin{matrix} -K_d L \text{ when } C > 0 \\ 0 \text{ when } C = 0 \end{matrix}\right\} + \overline{P - R} \quad 2$$

with $C = C_0$ at $\tau = 0$

where C = DO concentration, mg./l.
C_0 = initial DO concentration, mg./l., at $\tau = 0$
C_s = DO concentration at saturation, mg./l.
τ = residence time, in days, from source of pollution
K_a = reaeration coefficient, day^{-1}
K_r = BOD removal coefficient, day^{-1}
K_d = deoxygenation coefficient, day^{-1}, usually taken to be equal to K_r.
L = BOD concentration, mg./l.
L_0 = initial BOD concentration, mg./l. at $\tau = 0$
$\overline{P - R}$ = time smoothed, photosynthesis minus respiration, mg./l. day

In equation **1**, we have accounted for the fact that normal BOD removal is zero under anaerobic conditions. Moreover, we have assumed that organic decomposition under anaerobic conditions is small relative to aerobic rates. In equation **2**, we introduce several modifications which have not been used in ordinary BOD and DO analyses. First, we observe that the natural reaeration term is a three-prong factor depending on whether $C_s > C > 0$, $C > C_s > 0$, or $C = 0$.

In the first case, we have a condition of normal reaeration, but in the second case, we assume that supersaturated DO is physically expelled by a rate process which is characterized by the negative of the rate law for normal reaeration.

In case three, we assume that normal reaeration is only proportional to C_s under anaerobic conditions. The deoxygenation term, with $K_r = K_d$, is assumed to function mathematically like the BOD removal term in equation **1** (O'Connor, 1967).

The last term, $\overline{P - R}$, deserves special attention. Photosynthetic production of oxygen can be approximated by

$$P = \left\{\begin{matrix} P_m \sin \frac{\pi}{p} t \text{ when } 0 \leq t \leq p \\ 0 \quad \text{when } P \leq t \leq 1 \text{ day} \end{matrix}\right.$$

where P_m = maximum value of P during daylight hours
p = the period, equal to ½ day in a one day cycle
t = fractional time of day

The average value of P is calculated to be $\frac{P_m}{\pi}$. Consequently, the average value of the photosynthesis minus respiration term, $\overline{P - R}$, is found to be simply, $\frac{P_m}{\pi} - R$. Letting $P_m = \alpha R$, we finally arrive at $\overline{P - R} = \frac{(\alpha - \pi)}{\pi(\alpha - 1)}(P_m - R)$. The value of α is usually found to be $1 < \alpha < 10$.

Information in an article by McCombie (1966) served as a basis for obtaining $(P_m - R)$ as a function of temperature. The article discusses the relationship between light intensity, concentration of nutrients, and temperature on the metabolism of algae. McCombie's data corroborated our use of a parabola to represent $(P_m - R)$ as a function of stream temperature. Thus,

$$P_m - R = 25.0 - 0.028(T - 303)^2$$

where T = temperature of stream in degrees Kelvin.

Consequently, the final value of $\overline{P - R}$ is given by

$$\overline{P - R} = \frac{\alpha - \pi}{\pi(\alpha - 1)} \times [25 - 0.028(T - 303)^2] \quad 3$$

In a similar fashion, the reaeration coefficient can be modeled empirically from information obtained from cognate work (Churchill, 1964; and O'Connor, 1967). Thus,

$$K_a = a \exp[b(T - 273)] \quad 4$$

where T = stream temperature, °K
a = 0.430 day^{-1}
b = 0.0250° K^{-1}

Similarly, C_s can be approximated by

$$C_s = a' \exp[-b'T] \quad 5$$

where a' = 4,000 mg./l.
b' = 0.0210° K^{-1}

The BOD removal coefficient and the deoxygenation coefficient can be represented by

$$K_r = K_d = a'' \exp[b''T] \quad 6$$

when $a'' = 2.35 \times 10^{-7}$ day^{-1}
$b'' = 0.0464°K^{-1}$
$Q_{10} = 1.59$

The performance equations can be written in shorthand form as

$$\frac{dL}{d\tau} = f_1(L; T) \quad 7$$

$$\frac{dC}{d\tau} = f_2(C; L; T) \quad 8$$

Decision variable. The decision variable in equations **7** and **8** is the stream temperature, T° K. Ordinarily, stream temperatures have significant variability with depth in the body of water, but in our analysis, perfect thermal mixing is assumed in the model which precludes consideration of thermoclines.

Objective function. The objective function is defined by a condition wherein a decision variable profile (temperature profile) is specified so that the stream DO concentration is maximized throughout the downstream course of the stream for a specified upstream boundary condition.

Optimization algorithm. The Maximum Principle of Pontryagin for our continuous, deterministic system can be summarized in the following theorem (Fan, 1966).

Theorem. Let $T(\tau)$, $0 \leq \tau \leq \tau^*$ be a piecewise continuous vector function satisfying the constraint, $273 \leq \tau^*(\tau) \leq 333°$ K. In order that the scalar function, $C(\tau^*)$, may be a maximum for a process described by equations **7** and **8**, with initial conditions at $\tau = 0$ given, it is necessary that there exist a nonzero continuous vector function $z(\tau)$ satisfying

$$\frac{dz_1}{d\tau} = -\frac{\partial H}{\partial L} \text{ and } \frac{dz_2}{d\tau} = -\frac{\partial H}{\partial C} \quad 9$$

where $H = z_1 f_1 + z_2 f_2$ and **10**

$$z_1(\tau^*) = 0; z_2(\tau^*) = 1 \quad 11$$

and that the vector function $T(\tau)$ be so chosen that H, the Hamiltonian function, is a maximum for every τ, $0 \leq \tau \leq \tau^*$. If the optimal decision function,

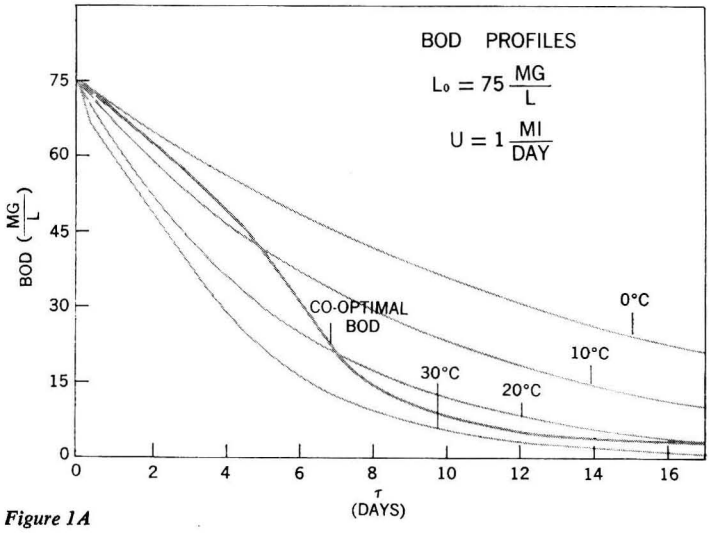


Figure 1A

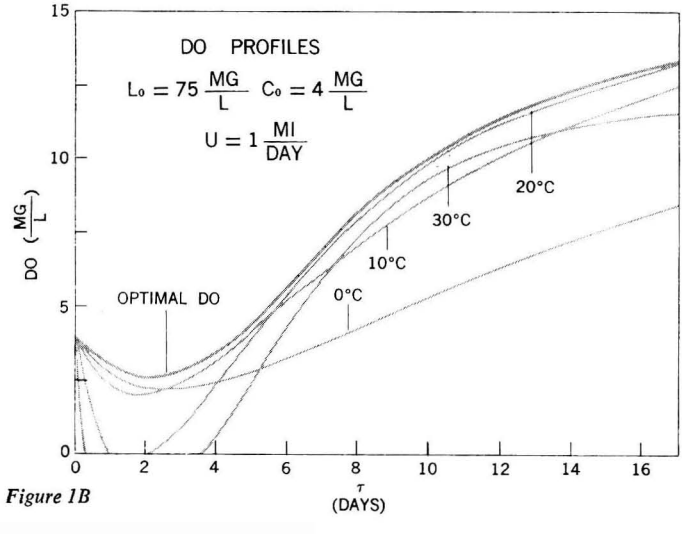


Figure 1B

$\bar{T}(\tau)$ is interior to the set of admissible decisions, $T(\tau)$, a necessary condition for $C(\tau^*)$ to be an extremum with respect to $T(\tau)$ is given by

$$\frac{\partial H}{\partial T} = 0 \qquad 12$$

The system of equations, **7** through **12**, constitutes what is termed the optimal solution to the specific thermal pollution problem under consideration.

Techniques of solution

Two different solutions result depending on whether the particular case, $L_0 = 0$, or whether the general case, $L_0 \neq 0$, applies.

For the particular case, the requirement of finding Max H in equation **10** is replaced by the necessary condition, equation **12**. Thus,

$$\frac{\partial H}{\partial T} = 0 = z_2 \frac{\partial}{\partial T}\left(\frac{dC}{d\tau}\right) \qquad 13$$

The Max H occurs at the stationary point and, therefore, the optimal temperature profile, $\bar{T}$, can be obtained from equations **8** and **13** analytically.

In the general case, a more difficult problem arises for the application of maximum principle. The performance equations (BOD and DO) and their corresponding boundary conditions are an initial value problem, whereas the adjoint vector functions, z_1 and z_2, are an end state boundary value problem. The combination of the performance equations and the adjoint vectors to formulate the Hamiltonian function, H, results in essentially a two-point boundary value problem, which requires a trial-and-error solution or some other procedure to maximize H along the DO trajectory.

For the particular case, the adjoint variables were separable, but this fortuitous condition will not occur in the case where $L_0 \neq 0$. The Max H in this instance can be found using the system of equations **7** through **10** along with their corresponding boundary values. The condition represented by equation **12** is of little use here other than to serve as a check, since it defines only a necessary condition of the algorithm.

In either situation, particular or general cases, we are confronted with computational difficulties. For the particular case, we encounter cumbersome analytical manipulations whereas in the general case, a difficult two-point boundary value problem arises.

For reasons of expediency we utilized an empirical technique for rapidly obtaining approximate optimal solutions, even for cases involving two-point boundary value problems (Burkart, 1967). The method is called *dead reckoning in function space*, and it is restricted to single decision variable problems with simple objective functions.

The method has been used (Bradshaw, 1966) on several well documented optimization problems (Fan, 1966) with considerable success; it works well so long as the reaction sequence is of the

type A $\rightleftharpoons$ B or A $\rightarrow$ B $\rightarrow$ C wherein component B is to be maximized. For a parallel reaction sequence (Horn, 1967) of the type A $\rightarrow$ B; A $\rightarrow$ C, the method fails to give reliable results.

Our reaction sequence is of the type A $\rightarrow$ B $\rightarrow$ C with B = DO and, therefore, the approximating method applies. According to the method, isothermal DO profiles are drawn by an analog computer solution of equations **1** and **2** for various realistic values of the decision variable, T. The curves are shown in Figures 1 and 2.

To obtain an indication of the direction of the optimal value, $\bar{C}$, as a function of τ, we select a value of τ, and then seek to find the intersection between the ordinate line drawn at $\tau = \tau_1$, and the isothermal temperature plot which renders DO a maximum at the intersection. In general, there will be several intersections along the ordinate line drawn at $\tau = \tau_1$, but among the set of intersections found, only one will yield a maximum DO concentration for the particular τ value chosen. Having found one optimal result, other optimal results at different τ's are found until the range of values of τ is covered. Each choice intersection of an ordinate line and an isothermal curve yields values of $\bar{C}$ and $\bar{T}$ at a particular τ.

In Figures 1 and 2, we have drawn a continuous, narrow band-line connecting the optimal points or intersections. A band-line is drawn as a reminder that the accuracy in the optimum seeking method used is not as good as an iterative Runge-Kutta routine on a digital computer (Balakrishnan, 1964; and Rosenbrock, 1967), or an iterative search technique on an analog computer (Lee, 1964). In principle, as the number of isothermal plots becomes large, the width of the band-line would decrease to differential size. Under these conditions, extremely accurate optimal profiles are obtainable under certain conditions.

In the final analysis, however, the conjectured optimal profiles for DO and temperature can be checked against the rigorously derived ones dictated by the algorithm of the maximum principle as was done on a related problem in a previous investigation (Burkart, 1967).

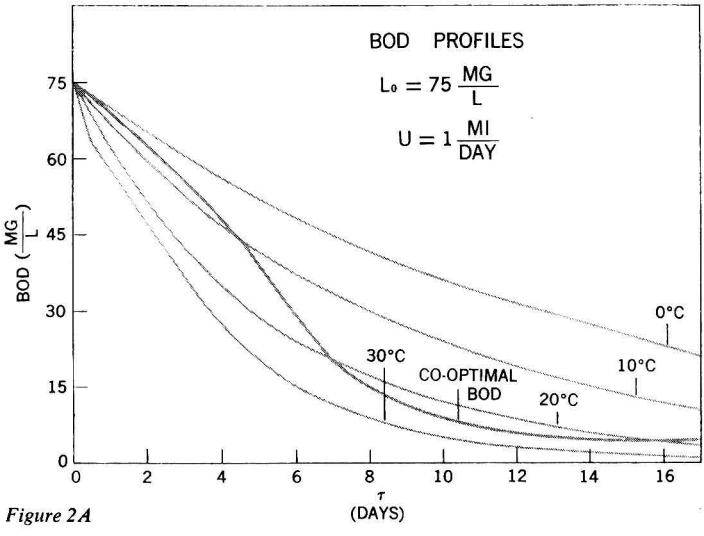


Figure 2A

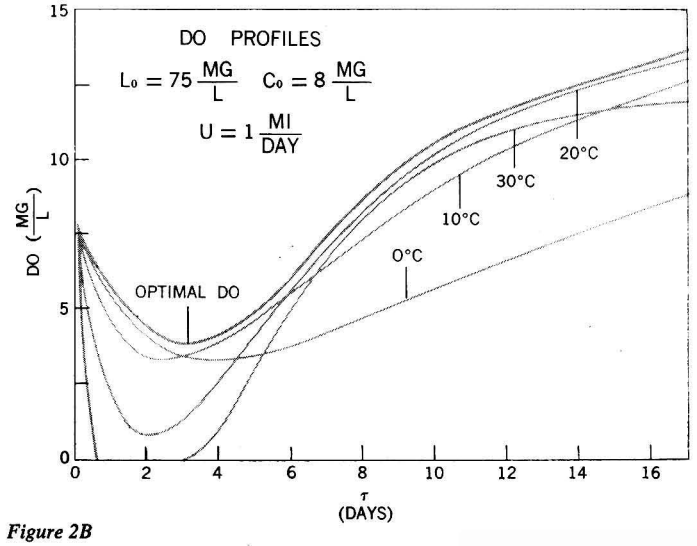


Figure 2B

Thermal energy balance

The thermal energy balance for a polluted stream may be formulated in terms of a steady-state enthalpy balance on a control volume of differential length, Δx, and constant cross-sectional area for flow. Thus,

$$\left\{\begin{matrix}\text{Rate of energy}\\ \text{in by advection}\end{matrix}\right\}_x + \left\{\begin{matrix}\text{Net rate of}\\ \text{energy transfer}\\ \text{from surroundings}\end{matrix}\right\}_{r\Delta x} = \left\{\begin{matrix}\text{Rate of energy}\\ \text{out by}\\ \text{advection}\end{matrix}\right\}_{x+\Delta x} \quad \textbf{14}$$

Transfer of energy by dispersion is neglected for nontidal streams. In differ-

ential equation form, the enthalpy balance equation is:

$$\frac{dT}{d\tau} = \frac{ru}{\rho c_p Q_R} q \qquad 15$$

where q = the net energy transfer rate.

Energy transfer from the surroundings occurs by five basic mechanisms:

- Short wave solar radiation, q_s.
- Long wave atmospheric radiation, q_{LWA}.
- Long wave back radiation from the stream, q_{LWB}.
- Convective transfer from the atmosphere, q_c.
- Evaporative enthalpy loss, q_e.

Delay and Seaders (1966) and Edinger and Geyer (1965) characterize these terms as follows:

q_s = f (season, cloud cover, time of day)
q_{LWA} = f (T_a, cloud cover, humidity)
q_{LWB} = f (T)
q_c = f (wind velocity, $T - T_a$)
q_e = f (wind velocity, $e_s - e_a$)

Conduction loss through the benthal boundary is neglected. In equation form, these functions are written as

$$q_s = q_{solar} \qquad 16$$

$$q_{LWA} = \beta\sigma(T_a + 293)^4 \qquad 17$$

$$q_{LWB} = e\sigma(T + 273)^4 \qquad 18$$

$$q_c = h_c(T - T_a) = f_c(w)[(T - T_a)] \qquad 19$$

$$q_e = h_e(e_s - e_a) = f_e(w)f(T - T_a) \qquad 20$$

where

r = stream width, 250 ft.
u = stream velocity, 1 mi./day
Q_R = stream flow, gal./day
w = wind velocity, mi./hr.
T_a = air temperature, ° C
T = stream temperature, ° C
β = cloud cover factor
σ = Stefan-Boltzmann constant
$f_c(w)$ = convective energy transfer coefficient = 6 w
$f_e(w)$ = evaporative energy transfer coefficient = 11 w
e_s = vapor pressure of water at saturation
e_a = vapor pressure of water in atmosphere
e = emissivity of surface water

Equation **15** can be rewritten in terms of equations **16** through **20** as follows

$$\frac{dT}{d\tau} = \frac{ru}{\rho c_p Q_R} \times [q_{solar} + \beta\sigma(T_a + 273)^4 - e\sigma(T + 273)^4 - h_c(e_s - e_a) - h_c(T - T_a)] \qquad 21$$

The boundary condition at $\tau = 0$ for use with equation **21** is given by

$$Q_{R_u}(T_u - T_R) + Q_E(T_E - T_R) = Q_R(T_0 - T_R) \qquad 22$$

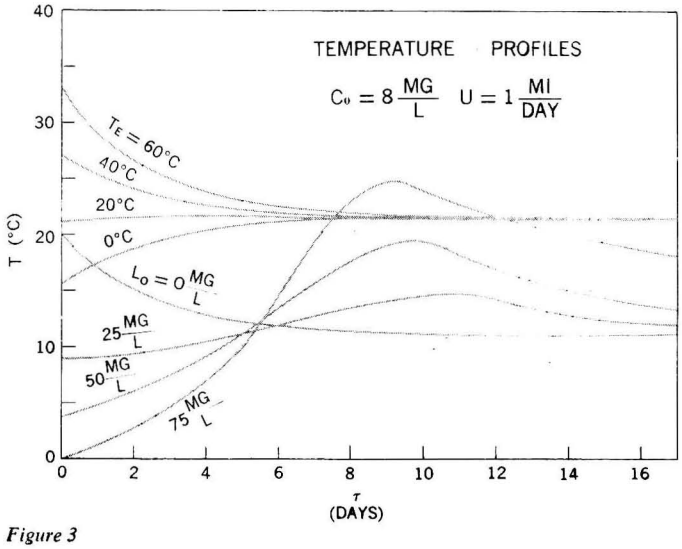


Figure 3

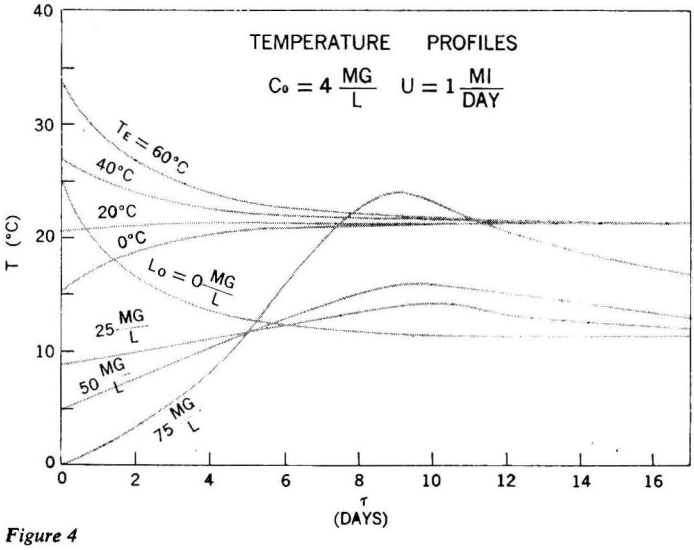


Figure 4

where

Q_{R_u} = upstream flow rate
Q_E = effluent flow rate from cooling water discharges
$Q_R = Q_{R_u} + Q_{R_E}$
T_0 = stream temperature at $\tau = 0+$
T_u = upstream temperature
T_E = effluent temperature
T_R = enthalpy reference temperature.

In order to demonstrate how the optimal temperature profile for the general case might be partially implemented, we have solved equations **1** and **2** together with equation **21**, and their respective boundary conditions, for hypothetical situations. The pertinent parameter values are:

L_0 = 0–75 p.p.m. at τ_0
C_0 = 4 or 8 p.p.m. at $\tau = 0$
α = 6
u = 1 mile/day
T_a = 32° C.
w = 10 mi./hr.
Cloud cover = 8/10
q_{solar} = 1500 B.t.u./day × ft.^{2}
β = 0.80
q_{LWA} = 2910 B.t.u./day × ft.^{2}
Relative humidity = 50%
e = 0.90
T_E = 0°, 20°, 40°, or 60° C
T_0 = 15.6°, 21.3°, 27.0°, or 32.8° C
Q_R = 70 m.g.d.
T_u = 21.9° C = equilibrium temperature, defined by T = 0
Q_{R_u} = 50 m.g.d.

Interpretation of results

The principal results are shown graphically in Figures 1 through 6. All curves were computer-drawn, with the exception of the conjectured optimal profiles, using the analog computer ensemble shown on page 622. The analog computer program is shown in Figure 7. We have limited our analyses to four initial BOD conditions and to two initial DO values at only a single injection point on the stream. Extention to multiple, pollution injection points and to different dilution ratios at these points is readily obtainable.

The optimal temperature profiles shown in Figures 3 and 4 are derivable from a series of plots of different BOD cases similar to the curves shown in Figures 1 and 2. The nonisothermal suboptimal temperature profiles are also shown for comparison with the conjectured, optimal plots. The effect of initial BOD concentration on the shape of the optimal temperature profiles is striking. As the values of L_0 decrease from 75 to 0 mg./l., the optimal profiles degenerate from skewed, bell-shaped curves into a simple monotonically decreasing temperature profile, the latter of which is very reminiscent of the type of optimality found in plug-flow, tubular reactor problems for exothermic, monomolecular reversible reaction processes.

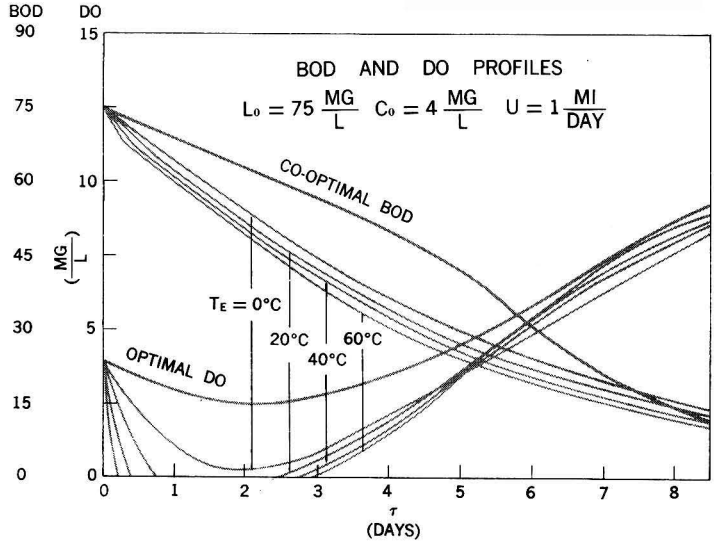


Figure 5

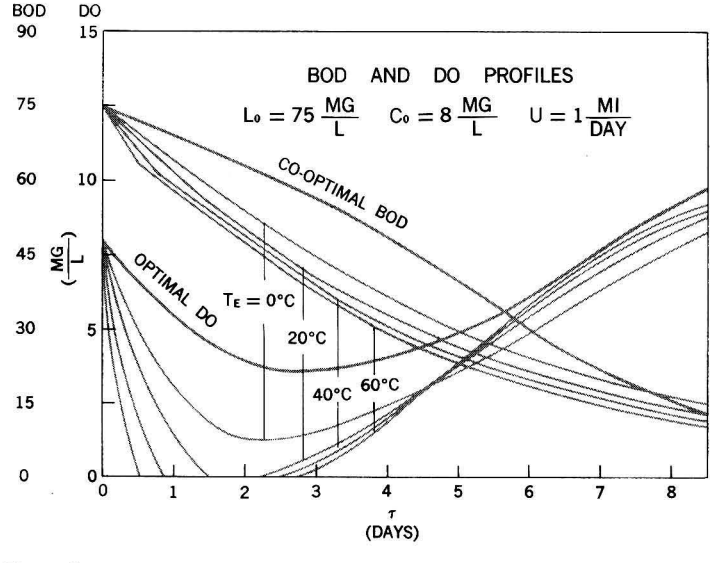


Figure 6

The accuracy of the performance equations in this study did not warrant the full numerical treatment usually associated with optimization studies of this type. It was sufficient for our purposes to merely structure the optimization problem along fundamental lines and to establish approximate trends and behavior patterns of the optimal curves for temperature and DO.

We did attempt, however, to check for the internal consistency of the conjectured, optimal curves. This check was accomplished by working the optimization problems in reverse (Bradshaw, 1966). The optimal curves for temperature, Figures 3 and 4, were fitted by simple mathematical expressions (straight lines) and inserted back into the analog programs for the BOD and DO material balances. This procedure thus eliminated consideration of temperature as an explicit variable and allowed for direct plotting of BOD and DO versus τ.

In all instances, with slight exception for the cases where $L_0 = 75$, satisfactory verification was demonstrated. Comparison of the results dictated by the reversing procedure indicated that the BOD and DO material balances were approximately satisfied.

The approximate optimal DO profiles for the cases where $L_0 = 75$ and $C_0 = 4$ and $C_0 = 8$ are compared with the suboptimal DO profiles for various values of T_E in Figures 5 and 6. The conjectured optimal DO profiles are maximum relative to the DO response curves for the different T_E conditions which were shown in Figures 3 and 4. Under approximately optimal conditions, for the case where $L_0 = 75$, anaerobic conditions are never reached, whereas under suboptimal conditions, zero DO concentrations are obtained over restricted ranges.

The results in Figures 5 and 6 show one other salient characteristic. From $\tau = 0$ to $\tau = 2.9$ days at $C_0 = 8$ or from $\tau = 0$ to $\tau = 3.4$ days at $C_0 = 4$, cold effluents are best from the viewpoint of enhancing stream DO. Moreover, if high values of DO are required downstream of $\tau = 2.9$ or $\tau = 3.4$ days, then hot effluents are best. There is an ineluctable tendency for the DO versus τ plots, whether they be isothermal or nonisothermal, to crisscross at least at one point, possibly more.

In fact, an absolutely necessary condition for temperature optimality in streams is that at least two isothermal DO response curves intersect. Otherwise, the optimal temperature profile would occur at an extreme value, either 0° C. or 100° C. In Figures 1 and 2, for example, the BOD response curves do not crisscross under the various isothermal conditions studied. The best temperature profile, which maximizes the rate of assimilation of BOD, is the highest isothermal curve. In Figures 5 and 6, the BOD response curves, under optimal temperature conditions relative to maximizing DO, are not simultaneously optimized.

Minimization of BOD and maximization of DO are disjointed in the sense that their corresponding optimal temperature policies can be determined separately. This is not a disturbing point since we did not consider BOD in the objective function at the outset.

The absence of a $\overline{P-R}$ term in the DO material balance relationship, Figure 8, shows a pronounced effect upon the feasibility of an optimal temperature profile in a polluted stream; the isothermal plots do not crisscross. The best temperature policy in this instance is 0° C. at all points downstream from the source of pollution. The worst case is the 30° C. isotherm which produces minimum DO and extensive anaerobic conditions.

The simulation and optimization analyses used in this study have uncovered the fact that BOD and $\overline{P|-R}$ are

Notation used throughout text

a, a′, a″	Parameters in temperature correction functions
b, b′, b″	Parameters in temperature correction functions
BOD	O_2 required for the stabilization of the oxidizable organic matter present after 5 days incubation at 20° C., mg./l.
c_p	Heat capacity of stream at constant pressure B.t.u./lb.m,° F
C	Dissolved oxygen concentration, mg./l.
$\bar{C}$	Optimal value of DO, mg./l.
C_0	Initial DO concentration, mg./l.
$C_s^{T°C}$	DO concentration at saturation at T° C., mg./l.
f_i	Arbitrary function
H	Hamiltonian function
K_a	Natural reaeration coefficient, day^{-1}
K_d	Reoxygenation coefficient, day^{-1}
K_r	BOD removal coefficient, day^{-1}
$\bar{L}$	BOD concentration under optimal conditions, mg./l.
L_0	Initial BOD concentration, mg./l.
P	Algal photosynthetic oxygen production, mg./l. day
p	Parameter in photosynthesis
Q	Volumetric flow rate, M gal./day
Q_{10}	Relative rates at T + 10° C. to T
R	Algal respiration, mg./l. day
r, r′	Parameters in temperature correction function
S	Benthol BOD, mg./l. day
T	Stream temperature, bulk mean, ° C.
$\bar{T}$	Optimal value, ° C.
T_a	Air temperature, ° C.
T_r	Temperature at which maximum photosynthesis occurs, ° C.
t	Time, days
u	Average stream velocity, mi./day
x	Longitudinal distance, mi.
z_i	Adjoint vector variable
α	Parameter in photosynthesis model
ρ	Stream density, lb.m./ft.^{3}
τ	Residence time, days
τ^*	Residence time at a specified, downstream point, days

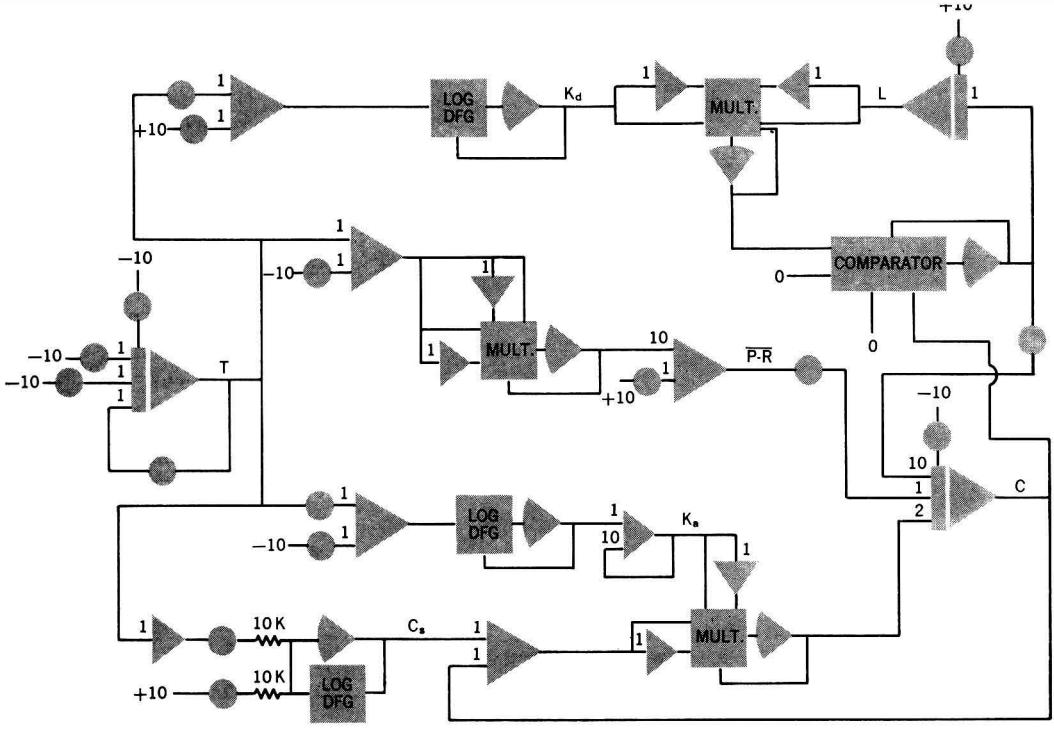


Figure 7

the major stream variables which cause the optimal temperature profile to radically change shape and degenerate into a trivial solution in the case where $\overline{P - R} = 0$.

Temperature profile optimality

We have attempted to demonstrate the manifestation of a theoretical, optimal temperature profile for a stream which renders the DO a maximum at every point downstream from a single source of pollution. Our performance equations were synthesized in a piecemeal fashion from existing literature in the field and the optimization algorithm used was borrowed from related works in the chemical engineering discipline.

The complexity of our optimization problem was studiously kept in proportion to the multidisciplinary information available for its formulation. As more information becomes available, it will be possible to improve upon the preliminary findings. Our results are of a hypothetical nature and should be used accordingly. This presentation should help clarify the thermal pollution syndrome enough to dispel any illusions that hot effluents cause uniformly adverse effects on stream DO, which is not the true situation.

Selected additional reading

Aris, R., "The Optimal Design of Chemical Reactors," Academic Press, New York, 1961.

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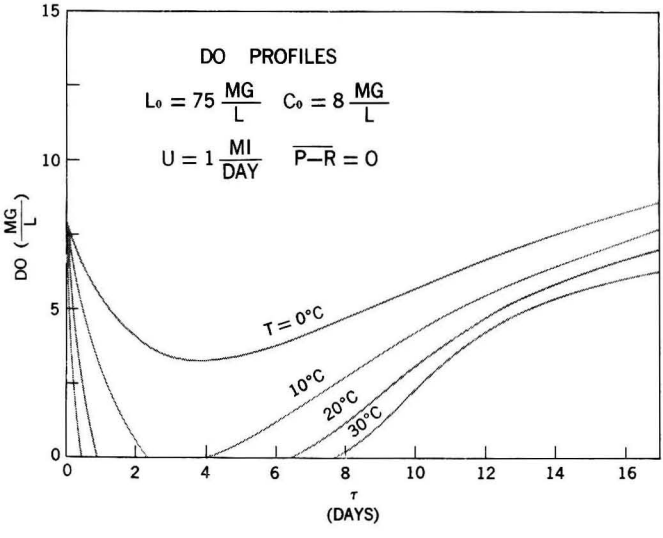
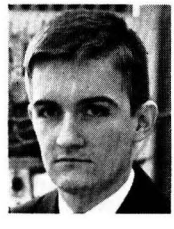


Figure 8

Dr. Burton Davidson *is an associate professor of chemical engineering at Rutgers University. Before he joined the Rutgers faculty in 1964, Dr. Davidson was an assistant professor of chemical engineering at San Jose State College (Calif.). Dr. Davidson received his B.S. (1958) and M.S. (1960) degrees in chemical engineering at Syracuse University, and his Ph.D. (1963) at Northwestern University (Evanston, Ill.). Dr. Davidson has conducted and supervised research for consecutive heterogenous petrochemical reactions, dissolved oxygen dispersion in estuaries and streams, oxygen regeneration of polluted streams, and thermal pollution analysis, and has written articles ranging from catalytic oxidation of sulfur dioxide to the mechanism of bacterial disinfection by chlorine dioxide. He is a member of AIChE and ASEE.*



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Fractionation of Organic Matter in Natural Waters on Sephadex Columns

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■ Sephadex columns have been used to fractionate organic matter in natural water into apparent molecular weight groups. Moderately colored creek water was fractionated into 10 fractions. The ratios of dichromate-oxidizable organic matter, color, and organic nitrogen were different for each fraction. Various lakes, streams, and leachable organic matter from lake sediments showed different organic carbon elution patterns. Gel permeation chromatography shows promise as a tool for fractionation of natural water organic matter and should aid in its characterization.

The study of the composition of organic matter present in natural waters may proceed via two routes: testing for a specific compound with a specific analytical technique or attempting to isolate and identify the principal compounds in a concentrate of natural water samples. Vallentyne (1957) and others (Lee, 1966) have reviewed the specific organic compounds found in natural waters. It is evident from these studies that the organic matter in natural waters is composed of many thousands of compounds, a large number of which have not been identified, since the total mass of specific compounds found does not approach the milligrams per liter of nonfilterable organic carbon found in most natural waters. Because of the large discrepancy between typical concentrations of known compounds and "dissolved" organic carbon found in natural waters, studies that attempt to isolate and identify the major components concentrated from natural waters are needed. Such a study has been initiated in this laboratory. The first phase of this project was devoted to an evaluation of Sephadex columns to fractionate concentrates of natural water organic matter into groups of compounds. This paper reports on this phase of study and is an expansion of a similar study reported by Gjessing (1965).

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Characteristics of Sephadex Chromatography

In recent years, the use of column chromatography to separate complex mixtures of compounds has received considerable attention as a result of the development of substrates that separate compounds on the basis of the molecular exclusion principle. One of the more popular substrates is Sephadex, a modified dextran obtained by crosslinking linear macromolecules, consisting of a three-dimensional network of polysaccharide chains (Flodin, 1963). Sephadex is neutral and contains few ionic sites. Its pores are determined by the degree of crosslinkage of the polymer. Seven grades of Sephadex are available, each with a different pore size (Table I).

Separation on Sephadex columns (gel filtration) is achieved by a type of molecular sieving. A small volume of the concentrate (less than 3% of the column volume) to be separated is placed on the top of the column. Small molecules move with the elutant both within and outside the Sephadex particles. Molecules larger than the pore size of the gel particles cannot penetrate the particles and, therefore, move rapidly down the column with the elutant. The smaller molecules penetrate the gel particles to a varying extent, depending on their shape and

Table I. Sephadex Types and Fractionation Range

Type	Approximate Limit for Complete Exclusion, MW	Fractionation Range, MW
G-10	700	0–700
G-15	1,500	0–1,500
G-25	5,000	100–5,000
G-50	10,000	500–10,000
G-75	50,000	1,000–50,000
G-100	100,000	5,000–100,000
G-150	150,000	5,000–150,000
G-200	200,000	5,000–200,000

size. Some compounds, such as protein, aromatics, and heterocyclics, are adsorbed by or interact with the gel particles. Therefore, separations achieved by Sephadex columns are dependent on size, shape and, to some extent, the functional groups present in the molecule.

Experimental Procedure

Concentration of Water Samples. Water was concentrated by evaporation under reduced pressure in a Precision Scientific Laboratory evaporator at 35° to 40° C. Using this apparatus, 20 liters of water were concentrated to approximately 2 liters in about 4 hours, then concentrated to 50 ml. using a Büchi Rotovapor concentrator. All water samples were filtered through glass fiber filters (Whatman GF/A) prior to concentration.

Water samples used were derived from Black Earth and Six Mile Creeks and Cranberry and Mendota Lakes. Both creeks originate in marshes and are located in Dane County near Madison, Wis. Black Earth Creek, at Water Chemistry Station 0, has moderate color in the spring runoff derived from snow melt and rains. Water Chemistry Station 0, on Six Mile Creek, is just downstream from a large marsh and the water is moderately colored throughout the year. The color in both creeks is derived from decaying vegetation in the marshes and surrounding farmlands. Lake Mendota, a hard water, eutrophic lake located at Madison, Wis., has a dissolved organic carbon of 10 mg. per liter and a color of 5 to 10 units. Cranberry Lake, located in Price County, Wis., is moderately colored. It is used as a source and disposal area for waters used in a neighboring cranberry marsh. At the time of sampling (early spring) no water had been used for this purpose for at least 6 months. Additional characteristics of these waters and the other samples used in this investigation are presented in Table II, with the results from the concentration of the different waters. All samples listed were concentrated by the evaporation procedure described, except for the mud, Lake Mendota 24/8, Lake Mendota 24/8-^{14}C, and algae.

The mud sample was a concentrated water extract of surface sediment taken from University Bay of Lake Mendota at a depth of 17 meters on May 6, 1965 (stored at +4° C. for 2 months). Three hundred grams (dry weight) of the sediments were extracted four times with 2.5 liters of distilled water. The combined extracts (10 liters) were filtered (Whatman GF/A) and evaporated to 10 ml.

Lake Mendota 24/8 was sampled Aug. 24, 1965, and stored until Nov. 20, 1965, at +4° C.

Lake Mendota 24/8-^{14}C was sampled Aug. 24, 1965. To this water were added 1 mg. per liter of PO_4 as $NaHPO_4$, 20 mg. per liter of N as $NaNO_3$, 1 mg. per liter of Fe as $FeCl_3$,

Table II. Composition of Water Samples and Concentrates

			Filtered Water				Precipitate		Filtered Concn. of Water Sample				pH		
	Date of collection 1965	Concentration Factor	COD, mg./l.	Color, mg. Pt/l.	Organic nitrogen, mg. N/l.	Conductivity, μmhos/cm. 20° C.	% COD total	Dry weight, mg./l.	% COD	% COD after storage	% Color	% Nitrogen	Water	Concentrate	% COD in Distillate
Black Earth Creek St. 0 (BEC)	Mar. 9	400	42.1	80	2.2	360	18[a]	61	74	75	...	...	7.2	9.0	2
Six Mile Creek St. 0 (SMC)	Mar. 24	400	25.8	25	...	380	...	...	87	...	...	...	...	7.4	0
Cranberry Lake (N-Wis)	Apr. 14	300	15.6	25	...	130	...	...	58	55	...	...	6.3	...	7
Lake Mendota (lake)	Feb. 24	400	15.2	5	0.5	300	16[b]	68	77	...	...	...	...	...	...
Lake Mendota (lake)	Mar. 4	400	15.5	5	0.5	300	11[c]	98	78	56	...	...	8.3	8.3	10
Lake Mendota (lake)	Aug. 24	390	16.3	8	0.3	800	...	...	77	...	48	99	...	...	9
Lake Mendota-^{14}C (lake ^{14}C)	Aug. 24	390	12.6	9	0.3	775	...	...	75	...	50	96	...	...	7
Lake Mendota (lake)	Nov. 23	400	14.3	16	0.4	370	...	...	94	...	67	86	...	...	2
Algae, *Chlorella*/ Gorham (algae)	Nov. 24	300	24.9	42[d]	0.7	825	...	...	87	...	...	...	...	...	3
Mud University Bay (mud)	May 6	1000	38.0	...	...	...	...	...	...	...	...	...	...	...	..

[a] = 48% organic matter in precipitate dissolved in 10% H_2SO_4.
[b] = 88% organic matter in precipitate dissolved in 10% H_2SO_4.
[c] = 65% organic matter in precipitate dissolved in 10% H_2SO_4.
[d] = Sample turbid, indicating poor removal of algae by filters.

and 2.5 mg. per liter of standard Na_2CO_3–^{14}C (2.58×10^6 d.p.m.). Filtered air was bubbled through 20 liters of this mixture and it was irradiated with artificial light. After 30 days under these conditions, the mixture was stoppered and stored for 2 months at room temperature in the dark.

Algae (Table II) is a concentrate of a filtered unialgal culture of *Chlorella*, grown for 10 days in Gorham's (Hughes, Gorham, *et al.*, 1958) medium.

In all cases, the concentration resulted in a solid and a liquid phase. From Table II, it may be concluded that 60 to 95% (mean 78%) of the organic matter in filtered natural waters remains in solution during the concentration process, and that a substantial part of the organic matter in the precipitates dissolves in 10% sulfuric acid. There is evidence that the color of the samples decreases when concentrated.

It is possible that the concentration and handling techniques used in this study may have changed the composition of the organics from that present initially in the sample. No attempt has been made to determine the extent of alteration.

The nonfilterable concentrate from the vacuum evaporation of the sample, usually 3 to 5 ml., was placed on top of the Sephadex column. Distilled water was passed through the column to elute the concentrate at a rate of approximately 0.5 ml. per minute. The columns consisted of a glass tube 30 mm. in diameter and 70 to 100 cm. long. Fractions (3 to 15 ml.) from the effluent of the column were collected in test tubes by a Gilson volumetric fraction collector. The chemical oxygen demand (COD), color, and, on some samples, organic nitrogen were determined on each fraction using the Technicon AutoAnalyzer (Technicon Controls, undated). The color of the fraction was determined at 420 mμ with standards based on the chloroplatinate scale (American Public Health Association, 1965). The COD is a measure of a heated dichromate-oxidizable organic matter under the conditions of the test and is merely indicative of the location of organic matter in the fractions. The Standard Methods COD (American Public Health Association, 1965) was used to determine the initial COD in the water samples and in the concentrates prior to fractionation, such as those listed in Table II. A study was conducted to determine the relationship between AutoAnalyzer COD and Standard Methods COD on selected fractions from the Sephadex column. It was found (Table VI) that 50 to 70% of Standard Methods COD was measured by the AutoAnalyzer COD procedure. The value was dependent on the particular fraction tested and showed that the AutoAnalyzer procedure used has less rigorous oxidation conditions than the Standard Methods procedure.

The specific conductivity of each fraction was determined with an Industrial Instruments conductivity bridge Model RC 16B2, using a pipet-type conductivity cell.

The Sephadex was obtained from Pharmacia Fine Chemicals, Inc., Piscataway, N. J.

Results

The results obtained for the samples listed in Table II are presented in Figures 1 to 7. In all except Figure 2, the concentration of measured parameters is plotted against a distribution coefficient, K_D (Flodin, 1963).

The areas under the different curve fractions illustrated in the figures are listed in Tables III, IV, and V, as per cent of the

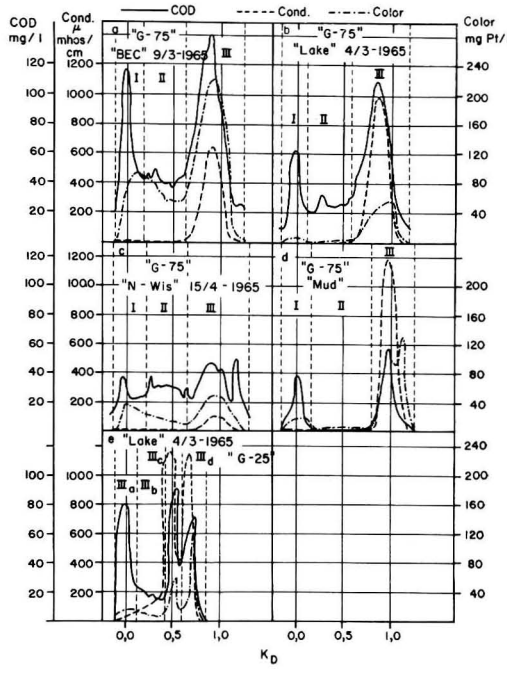

Figure 1. Separation of organic matter in water on Sephadex columns

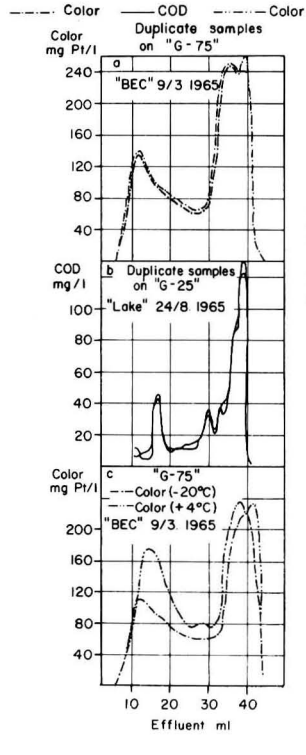

Figure 2. Reproducibility of separation of organic matter in water, from Black Earth Creek, on Sephadex columns

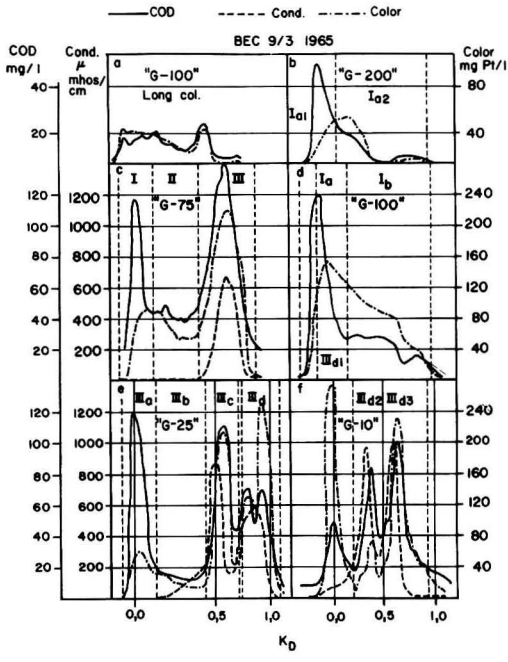

Figure 3. Separation of organic matter in water on Sephadex columns

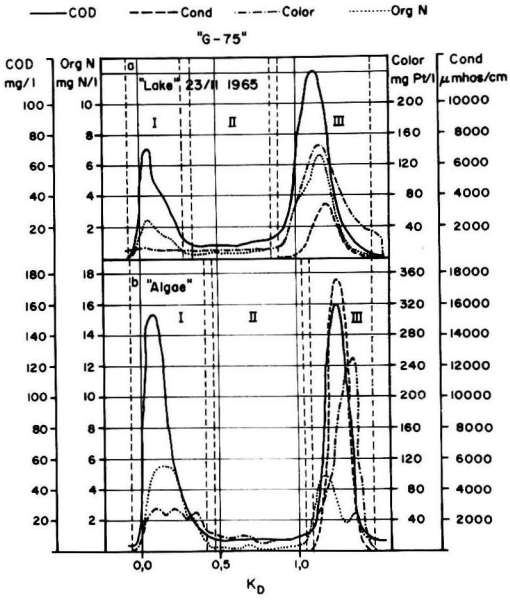

Figure 5. Separation of organic matter in water on Sephadex columns

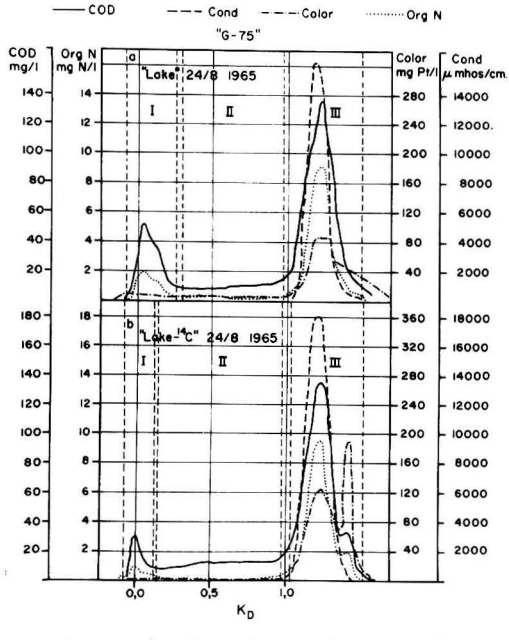

Figure 4. Separation of organic matter in water on Sephadex columns

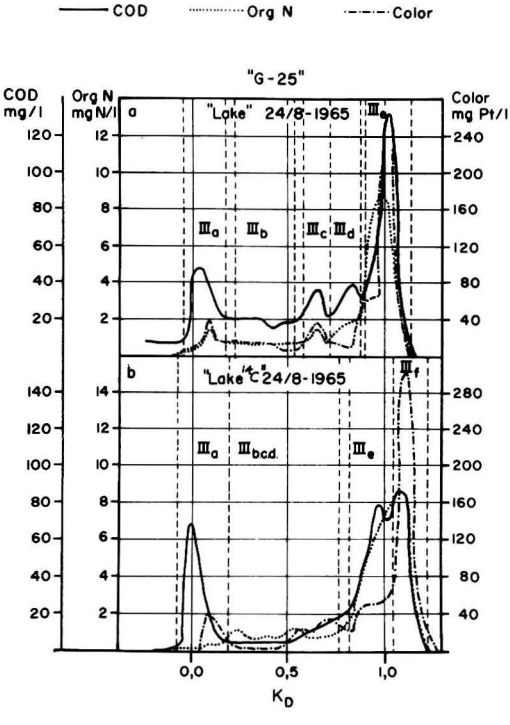

Figure 6. Separation of organic matter in water on Sephadex columns

total area. Tables III and IV also include the ratio of the areas for color and COD, and for organic nitrogen and COD. The fractions representing the peaks of the organic matter (Figures 5, 6, and 7) were divided into three fraction sets: *a* is the top fraction representing the maximum of the COD; *b* and *c* are the corresponding fractions to the left and right of the maximum.

Discussion

Reproducibility. Figure 2, *a* and *b*, illustrates the reproducibility obtained using the gel filtration technique on natural water organics in duplicate runs performed in succession on the same column. There was little difference in the results on changing from one column to another or for the first or later runs on the same column. The slight differences in replicate results can be accounted for by the analytical error.

Recovery. The degree to which the organic matter was recovered, using Sephadex columns, differed according to the grade of Sephadex used. Grade G-75 gave a recovery between 87 and 95%, with a mean of 92%. The recovery with other grades of Sephadex was 98 to 100%.

In all experiments, grade G-75 was used for the original concentrate, whereas the other grades always have been employed for concentrates of fractions obtained from previous runs on G-75.

Effect of Storage. Figure 2 *c* illustrates the results from two ways of storing the concentrated water organics for $2^1/_2$ months, one at −20° C., the other at +4° C. It is obvious that storage results in a change of composition, even though Figure 2 illustrates only the change of color.

Variation between Samples. Figure 1, *a*, *b*, and *c*, illustrates the difference between the organic matter in the samples of

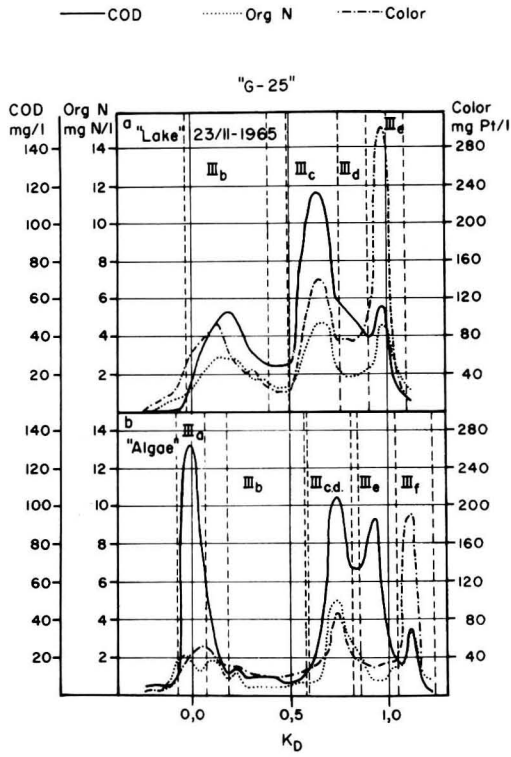

Figure 7. Separation of organic matter in water on Sephadex columns

Table III. Fractionation on Sephadex G-75

	Fraction I					Fraction II					Fraction III				
	% COD	% Color	% N	Color / COD	N / COD	% COD	% Color	% N	Color / COD	N / COD	% COD	% Color	% N	Color / COD	N / COD
BEC	25	16	...	0.7	...	16	22	...	1.5	...	59	62	...	1.0	...
N-Wis	16	24	...	0.9	...	31	22	...	0.4	...	53	54	...	0.6	...
Mud	35	11	...	0.4	...	0	0	...	...	...	65	89	...	1.6	...
Lake 4/3	17	5	...	0.0	...	14	6	...	0.1	...	69	89	...	0.6	...
Lake 24/8	18	0	15	0.0	0.4	12	0	6	0.0	0.2	70	100	79	0.5	0.6
Lake 24/8-^{14}C	6	0	6	0.0	0.4	19	0	6	0.0	0.1	75	100	88	0.7	0.6
Lake 23/11	26	0	20	0.0	0.4	11	0	8	0.0	0.4	63	100	72	0.8	0.5
Algae	51	26	53	0.3	0.5	2	12	4	0.0	0.0	47	62	43	0.9	0.5

Table IV. Fractionation on Sephadex G-25

	% COD						% Color						% N					
	IIIa	IIIb	IIIc	IIId	IIIe	IIIf	IIIa	IIIb	IIIc	IIId	IIIe	IIIf	IIIa	IIIb	IIIc	IIId	IIIe	IIIf
BEC 9/3/65	31	5	33	31	...	9	12	8	33	47	...	...	...	...	...	...	...	...
Lake 24/8/65	18	12	11	13	46	...	9	10	9	7	65	...	7	11	7	13	62	...
Lake 24/8 ^{14}C–65	22	←	16	→	32	30	6	←	19	→	18	57	2	←	22	→	37	39
Lake 23/11/65	...	32	43	15	10	...	...	39	31	1	19	...	...	38	30	13	19	...
Algae	35	4	←	31	→	25	5	19	16	←	23	→	15	27	23	12	←	34	→	15	16

	Color COD						N COD					
	IIIa	IIIb	IIIc	IIId	IIIe	IIIf	IIIa	IIIb	IIIc	IIId	IIIe	IIIf
BEC 9/3/65	0.3	1.5	0.9	1.4	...	...	...	...	...	...	...	...
Lake 24/8/65	0.4	0.6	0.4	0.4	1.0	...	0.3	0.6	0.5	0.7	1.0	...
Lake 24/8 ^{14}C–65	0.2	←	1.0	→	0.5	1.6	0.1	←	1.2	→	0.9	1.1
Lake 23/11/65	...	1.0	0.6	1.2	1.0	...	...	0.7	0.4	0.6	1.3	...
Algae	0.3	2.5	←	0.4	→	0.4	3.9	0.3	1.3	←	0.5	→	0.2	1.6

natural water studied and that the gel filtration method may be useful in classification of lakes and characterization of organic matter in water.

The percentage of organic matter represented by Fraction-Set I on Sephadex G-75 varies between 6 and 35% in the samples studied (Figure 1 and Table III). This has, according to the literature, a molecular weight above 50,000 to 70,000. Lake Mendota 24/8–^{14}C has the low value of 6% and the mud extract the high value of 35% for the fraction.

The percentage distribution of the organic matter in Fraction-Set II (Table III) varies between samples, particularly when mud extract is compared with the sample from Lake Cranberry (N-Wis). The organics in this Fraction-Set from Lake Mendota samples were colorless.

Similarly, Table IV and Figures 6 and 7 clearly suggest that the compositions of the organic solutes in the different water samples vary. It is even difficult to point out similarities between some samples.

Molecular Distribution. Figure 3 illustrates the results obtained from five types of Sephadex; G-200, G-100, G-75, G-25, and G-10. From the curve presenting the COD values in Figure 3, it is seen that the soluble organic matter in a 400-fold concentrate from Black Earth Creek (BEC) may be separated into at least 10 fractions, according to molecular size. The measured area under the peaks is presented in Table VI. The values in the per cent COD column of Table VI are given as a percentage of the total COD in filtered water. Although the generality of the findings may be questionable, it is reasonable to conclude that the main part of the organics in natural waters are fractionable and probably do not consist of a continuous distribution of all sizes of molecules. In this table, an estimate of the molecular weights and molecular sizes of the organics is recorded, based on the distribution coefficients obtained and calculated by equations reported in the literature for the estimation of protein molecular weight (Andrews, 1964).

These values must be considered as a very rough estimate of molecular weight and molecular size, since none of the values have been confirmed through conventional methods.

Heterogeneity of Peak Values. Considering Figures 2 and 3, comparing the appropriate maxima of the COD and color curves, it is seen that the two maxima are not always in phase. The discrepancy is particularly noticeable for the lower molecular weight fractions, which again suggests that correlation is less marked between the organic matter and the color for these fractions. The maxima of the conductivity curves, in particular those from Sephadex G-25 and G-10, have different positions than in the color and COD curves.

Seasonal Variations. Figures 1, *b*, 4, *a*, and 5, *a*, and Table III present the separation of concentrated water from Lake Mendota with G-75 on March 4, October 24, and November 23, respectively. Examination of these data shows that it is impossible to point out any obvious difference in the separation patterns. On the other hand, the curves representing the separation on G-25, of the same samples (Figures 1, 3, 6*a*, and 7*a*, and Table IV) clearly illustrate the seasonal difference in the composition of the organic compounds in Lake Mendota. This is further confirmed by Table VII.

The results of the study on ^{14}C-labeled organics (Lake Mendota 24/8–^{14}C) were not completely satisfactory. However, peak I from Sephadex G-75 was found to contain significantly less organic carbon in the ^{14}C sample than is normally found in Lake Mendota water. The COD/N ratio is the same in both, but the ratios of the two COD values differ. Corresponding differences were found on the fraction of Sephadex G-25. Table II indicates that the addition of nutrient salts

Table V. Fractionation on Sephadex G-10

	% COD			% Color			Color/COD		
	IIId$_1$	IIId$_2$	IIId$_3$	IIId$_1$	IIId$_2$	IIId$_3$	IIId$_1$	IIId$_2$	IIId$_3$
BEC 9/3/65	19	30	51	41	11	48	2.9	0.5	1.3

Table VI. Fractionation of Black Earth Creek Sample

Peak	Grade	Molecular Weight Range	% COD	Molecular Size Range, Radius, Cm. × 10^{-8}
I a$_1$	G–200	>200,000	6	100
I a$_2$	G–200	100,000–200,000	4	10–50
I b	G–100	50,000–100,000	6	5–30
II	G–75	20,000–30,000	11	10–25
IIIa	G–25	3,000–5,000	12	20
IIIb	G–25	.....	2	5–15
IIIc$_1$	G–25	100–5,000	13	4
IIId$_1$	G–10	.....	2	...
IIId$_2$	G–10	.....	4	0–4
IIId$_3$	G–10	<700	6	...
Ppt. not sol. in H_2SO_4			9	
Ppt. sol. in H_2SO_4			9	
Loss on G–75			10	
Distillate			2	
Total			96	

Table VII. Composition of Fractions from the Sephadex Separation

	COD (S.M.)[a]/COD (A.A.)[b]				Color/COD (S.M.)				N/COD (S.M.)			
	24/8	24/8–^{14}C	23/11	Algae	24/8	24/8–^{14}C	23/11	Algae	24/8	24/8–^{14}C	23/11	Algae
Water	1.4	1.5	1.8	1.9	0.5	0.7	1.1	Turb.	1.8	2.4	2.8	2.9
concn. (1:250)	1.9	1.9	1.9	2.1	0.5	0.7	1.2	1.0	3.6	5.3	4.1	3.7
IB	1.2	1.4	1.1	1.3	0.1	0.5	0.3	0.2	1.9	2.6	3.4	1.7
IA	1.2	3.5	1.4	1.7	0.1	0.1	0.2	Turb.	2.1	0.7	2.5	2.0
IC	1.2	1.6	1.0	1.2	0.2	0.5	0.4	0.3	2.5	2.3	3.2	5.0
II	2.0	1.2	2.0	2.3	0.3	0.2	0.7	0.4	1.8	0.8	2.2	0.6
IIIa	0.8	1.8	...	1.0	1.6	0.9	...	0.9	5.6	3.3	...	1.7
IIIb	2.4	...	1.4	1.0	0.1	...	0.8	...	1.7	...	6.6	4.8
IIIc	1.8	...	...	...	...	...	...	...	...	...	...	...
IIId	1.7	...	...	...	0.3	...	...	...	1.7	...	...	...
IIIe	...	...	5.1	...	...	...	0.9	...	...	...	2.1	...
IIIf	...	...	...	1.1	...	1.0	...	4.2	...	3.7	...	4.7
IIIcB	...	...	1.2	...	...	...	0.2	...	...	...	...	...
IIIcA	...	...	1.2	...	...	...	1.1	...	...	...	...	...
IIIcC	...	...	0.7	...	...	...	0.9	...	...	...	...	...
IIIcdB	...	...	...	0.6	...	...	...	1.2	...	...	...	...
IIIcdA	...	...	...	0.7	...	...	...	1.4	...	...	...	...
IIIcdC	...	...	...	0.5	...	...	...	1.7	...	...	...	...
IIIeB	...	0.7	...	...	...	0.3	...	...	...	5.0	...	...
IIIeA	...	0.7	...	...	...	0.2	...	1.8	...	...	...	3.9
IIIeC	...	...	...	...	...	0.2	...	3.0	...	...	...	5.0

[a] S.M. = Standard Methods.
[b] A.A. = AutoAnalyzer

to Lake Mendota water, and bubbling air through it, result in a loss of approximately 20% of the organic matter.

Organics from a *Chlorella* Culture. Figures 5*b* and 7*b* present data for the concentrated extract of a *Chlorella* culture grown in Gorham's medium and separated on G-75 and G-25, respectively. More than 50% of the organics in this concentrate probably have a molecular weight above 50,000. The results listed in Tables II, III, IV, and VI do not give a basis for emphasizing any differences between this sample and the other water samples. However, the separation pattern of this algal concentrate on G-25, is, in many respects, different from the other samples.

Determination of Organic Carbon. Since certain compounds are known to be resistant to oxidation by the Standard Methods COD procedure, a brief study was conducted to determine the relationship between AutoAnalyzer COD and organic carbon content of certain fractions from the Sephadex columns. The organic carbon, on selected fraction, was determined by high temperature, dry combustion in a Leco low-carbon analyzer. Two milliliters of the sample were evaporated in a Vycor liner at 50° to 70° C. in the presence of a few drops of 1*N* H_2SO_4 to remove carbonates. When the sample was dry, the Vycor liner was placed in a quartz-covered crucible and carried through the normal operating procedure of the instrument (Table VIII).

Since the theoretical ratio of COD to organic carbon is 2.5, it is evident that approximately 30 to 40% of the organic carbon present in these samples is measured by the AutoAnalyzer COD procedure used.

Table VIII. Relationship of Organic Carbon to AutoAnalyzer COD for Natural Water Organics

Organic Carbon, Mg./L.	COD (A.A.), Mg./L.
40	48
41	36
60	50
128	130
265	250

Conclusions

Sephadex columns can fractionate natural water organic matter into a number of distinct fractions. Using different grades of Sephadex, it was possible to separate the Black Earth Creek sample into 10 fractions. This fractionation should greatly aid the study of the organic matter present in natural waters. One of the advantages of the technique is that the high molecular weight fractions are desalted by passage through the column. It is evident from this and previous studies (Gjessing, 1965; Povoledo, 1964) that the organic matter from different waters have different elution patterns. Based on these results, it is possible to classify lakes according to their organic matter elution patterns from different grades of Sephadex and other gels. The ratios of color, organic nitrogen, and organic carbon vary between fractions. These ranges may also aid in classification and study of composition.

One of the most significant results of the study is that the color in natural waters is composed of several groups of compounds, a significant number having molecular weight above 50,000. On the basis of separations achieved on G-75, it appears that low colored waters have most of their color in the low molecular weight fraction; in moderately or highly colored waters, more color is found in the high molecular weight fraction. Even though it is impossible to assign accurate molecular weights to each fraction because of possible sorption and other side effects, it is clear that Shapiro's (1957) average molecular weight of 456, for natural water color, is of questionable value.

Although not investigated in this study, subsequent studies in this and other laboratories have shown the pH of the eluent to affect markedly the organic carbon elution pattern on Sephadex columns.

Finally, the results obtained may, to some degree, be due to methods used in sample concentration, storage, and elution. It is possible that large, loosely bound molecules, present in the water at the time of sampling, are broken into smaller units in sample pretreatment. Hopefully, polymerization reactions were minimized by never taking the organics to dryness and by working only with aqueous systems—i.e., no organic solvents. There is a good possibility that some organic matter present in the concentrates was colloidal and not in true solution, since a 1-micron pore size filter was used. Further study will be necessary to determine the influence of methods of sample preparation on elution patterns.

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Gas-Liquid Chromatographic Separation of Some Organophosphate Pesticides, Their Hydrolysis Products, and Oxons

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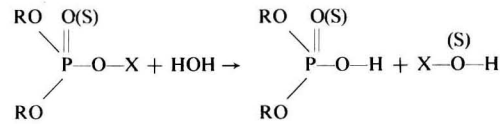
■ A gas-liquid chromatographic technique has been developed to separate and detect, simultaneously, some organophosphate pesticides, their oxons, and hydrolysis products. Reoplex-400 (polypropylene glycol adipate), a polyester liquid phase, was used to separate the organophosphate systems of Diazinon, Baytex, parathion, and malathion. Two detection systems were used—flame ionization and electron-capture. Isothermal separations at 180° C. are described for individual systems of Diazinon, Baytex, and parathion. Also chromatograms and relative retention times indicate multiple analyses of these three pesticides, their hydrolysis products, malathion, and the oxons of parathion and Diazinon. Data are given under isothermal conditions which indicate the generally greater sensitivity of the electron-capture system except for the hydrolysis products of Diazinon and Baytex. The malathion system was examined with the flame ionization detector by techniques of dual isothermal analysis or programmed temperature.

At present, there is an incomplete picture of the persistence and fate of organophosphate pesticides in natural water environments. These pesticides have the potential of causing changes in water quality which may affect human and aquatic life. Their toxicity to fish and wildlife is well known. Breidenbach (1965) has outlined other water quality problems caused by organic pesticides.

Hydrolysis products of organophosphate pesticides should not be overlooked, since their effect on drinking water quality is largely unknown. A possible effect may be provided by a hydrolysis product of parathion, *p*-nitrophenol. Baker (1963) has shown that substituted phenols affect the odor quality of drinking water. *p*-Nitrophenol may be chlorinated at a water treatment plant to produce an odorous product. Similar effects may be observed with hydrolysis products of other organophosphate pesticides.

A few studies in natural water environments have concentrated on the parent compound without consideration of the oxons or hydrolysis products (Nicholson, Webb, *et al.*, 1962; Thoman and Nicholson, 1963). The lack of sensitive and specific analytical methods for separation and identification of an organophosphate pesticide in the presence of its hydrolysis or oxidation product, may have inhibited more extensive studies. Once suitable procedures are developed, their fate and/or persistence in aqueous environments can be evaluated. This objective was fulfilled recently for one organophosphate pesticide, Dipterex (El-Rafai and Giuffrida, 1965). Gas-liquid chromatography was used to follow its disappearance and the appearance of its hydrolysis product, DDVP.

Persistence of organophosphate pesticides in natural waters may be controlled by several chemical reactions mediated in this environment of which two are hydrolysis and oxidation. The general equation of hydrolysis was expressed by Muhlman and Schrader (1957):



where R is an alkyl group, and X is an organic radical. Four general types of structures are observed, when either oxygen or sulfur is substituted in the indicated positions. Hydrolysis generally proceeds by rupture in the P(S)—O—X bond system at the P—O(S) linkage. Some dithiophosphoric acid esters, under basic hydrolysis, form a dialkyldithiophosphoric acid and an olefin, such as malathion (Gunther and Blinn, 1955). This is really a hydroxide ion–catalyzed vinylization reaction (Muhlmann and Schrader, 1957).

Oxidation of organophosphates containing the P—S group to P—O has been described by Heath (1961), to occur enzymatically in vivo or in vitro, under ultraviolet light in air, and by common oxidation systems. Oxidative processes in natural waters or at water treatment plants may convert parent compounds to oxons.

Four systems were investigated because of their extensive commercial use—Diazinon, Baytex, parathion, and malathion (Table I)—to find a liquid phase that would separate parent compounds from their hydrolysis products and oxons. This liquid phase should also be capable of separating several components of mixed systems.

Table I. Organophosphate Parent Compounds, Their Oxons, and Hydrolysis Products

Name	Purity, %	Generic Name
Diazinon	99.0	*O,O*-Diethyl-*O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate
Diazoxon	96.97	*O,O*,-Diethyl *O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphate
IMHP	Recrystallized, m.p. 174.5–5.5° C.	2-Isopropyl-4-methyl-6-hydroxypyrimidine
Baytex	99.6	*O,O*-Dimethyl-*O*-[4-(methylthio)-*m*-tolyl] phosphorothioate
Bayoxon	...	*O,O*-Dimethyl-*O*-[4-(methylthio)-*m*-tolyl] phosphate
MMTP	Recrystallized, m.p. 54–6° C.	3-Methyl-4-methylthiophenol
Parathion	99.5	*O,O*-Diethyl-*O*-*p*-nitrophenyl phosphorothioate
Paraoxon	...	*O,O*-Diethyl-*O*-*p*-nitrophenyl phosphate
p-Nitrophenol	Recrystallized, m.p. 114° C.	*p*-Nitrophenol
Malathion	99.5	*O,O*-Dimethyl-*S*-(1,2-dicarbethoxyethyl) phosphorodithioate
Malaoxon	...	*O,O*-Dimethyl-*S*-(1,2-dicarbethoxyethyl) phosphorothioate
Basic hydrolysis products of malathion	B.p. 217.9° C.[a]	*trans*-Diethyl fumarate
	B.p. 225° C.[a]	*cis*-Diethyl maleate

[a] Eastman White Label Grade, Eastman Organic Chemicals.

Table II. Operating and Chromatographic Conditions for Diazinon, Baytex, and Parathion

Liquid support–15% Reoplex-400
Solid support–Acid-washed Chromosorb W., 80 to 100 mesh
Inlet temperature–200° C.
Column temperature–180° C.
Column aging–Flame ionization–1 week at 190° C. under normal flow rate
Electron-capture–10 days at 205° C. under normal flow rate
Flow rate–Set so that the absolute retention time of Diazinon is 3 minutes

Operation	Flame Ionization Detector	Electron-Capture Detector
Column dimensions	3 feet (glass or aluminum), $^1/_{16}$-inch I.D.	4 feet (glass), $^1/_8$-inch I.D.
Flow rate	55 ml. per minute	135 ml. per minute
Detector parameters	H_2, 7.5 lb. (25 ml. per minute)	Polarizing voltage, 4.5 volts
	Air, 12 lb. (200 ml. per minute)	Detector temp., 295° C.
		Background current, 5.44×10^{-9} amp.
Recorder speed	0.3 inch per minute	0.5 inch per minute

Table III. Relative Retention Times and Sensitivity Data for Reoplex-400 Liquid Phase

		Flame Ionization		Electron-Capture	
Compound	Retention Times	Concn., μg./5 μl.	Sensitivity, coulombs $\times 10^{-9}$/μg.[a]	Concn., μg./5 μl.	Sensitivity, coulombs $\times 10^{-9}$/μg.[a]
Diazinon	1.00	1.00	3.04	0.01	205
Diazoxon	1.45	1.00	3.72	0.12	70.5
IMHP	1.77	1.00	11.60	0.50	3.50
Baytex	5.98	1.00	11.7	1.00	12.3
Bayoxon	7.66	1.00	5.80	1.00	5.75
MMTP	2.67	1.00	17.2	1.00	3.46
Parathion	7.14	5.09	6.90	0.005	3340
Paraoxon	8.25	2.00	1.53	0.055	400
p-Nitrophenol	11.7	5.00	6.98	0.005	1750
Malathion	5.09	...	...	...	...

[a] Calculated from peak areas as measured by a disk integrater using a 60-r.p.m. motor.

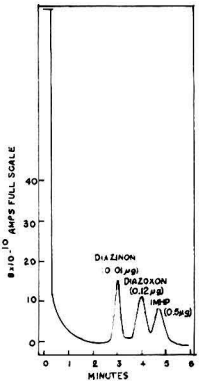


Figure 1. Chromatogram of Diazinon system

Detector–electron-capture

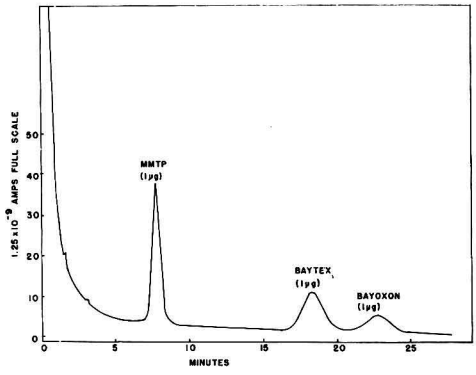


Figure 2. Chromatogram of Baytex system

Detector–flame ionization

Apparatus and Operation

A Research Specialties 600 Series gas chromatograph equipped with a flame ionization detector and programming temperature unit and a Microtek MT-200 gas chromatograph equipped with a 10-mc. Ni^{63} electron-capture detector operated at 295° C. were employed. Operating and chromatographic conditions are given in Table II for Diazinon, Baytex, and parathion. (Conditions for the malathion system are the same with exceptions noted in the legends of Figures 5 and 6.)

The liquid phase was coated on the solid phase with a method described by Burke (1965). Three different batches were used without any significant change in relative retention times. The 3-foot × $^1/_{16}$-inch I.D. columns used with the flame ionization detector contained 1.17 grams. The 4-foot × $^1/_8$-inch I.D. columns used with the electron-capture detector contained 3.80 grams.

A point of technique with Reoplex-400 must be mentioned. Insufficient aging of the column will allow bleeding that appears to coat an electron-capture foil with a polyester film. This, in turn, will inhibit the electron-capture process. The importance of preventing the column from bleeding cannot be overstressed.

Devaux and Guiochon (1967), have described the influence of bleeding of the stationary phase on the electron-capture detector response. They have shown that the maximum working temperature with an electron-capture detector is, in some cases, considerably less than with a conventional flame detector. Two precautions have been instituted in the present study to avoid the problem of bleeding. First, the columns that are used with the electron-capture detector are aged 25° C. above the working temperature at 205° C. for an extended time. Second, 3 mm. of solid phase are added to the output end of the column after aging. This additional solid support does not appear to affect resolution or sensitivity.

Results

Many liquid phases have been reported to separate organophosphate pesticides and/or organic phosphorus compounds: DC-200 (Nelson, 1965), SF-96 (Petitjean and Lantz, 1963), QF-1 (Bonelli, Hartmann, *et al.*, 1964; Kanazawa, Kubo, *et al.*, 1965), DC-200 and Tween 80 (Bosin, 1963), SE-30 and Epon 1001 (Dawson and Thain, 1964), Apiezon L and Epon 1001 (Egan, Hammond, *et al.*, 1964), SE-30 and Apiezon L, separately, (Gudzinowicz and Campbell, 1961), and Reoplex-400 (Feinland, Sass, *et al.*, 1963; Buckler, 1962; Stanley, 1966). These were reinvestigated with numerous variations in column parameters and operating conditions.

The best liquid phase for multiple analysis of an organophosphate pesticide system was the polyester, Reoplex-400. This liquid phase was used to separate many types of polar compounds and organic phosphorus compounds as noted above but apparently not organophosphate pesticides. Stanley (1966) used Reoplex-400 to separate dimethyl and diethyl phosphoric acids, hydrolysis products of organophosphate pesticides, after esterification to methyl, ethyl, or butyl esters. Esterification and separation of thio (P—S) and dithio (P—S) acid phosphates have not been reported to date.

Relative retention times and sensitivities for the isothermal separations of the Diazinon, Baytex, and parathion systems are in Table III. These data represent a search for the best resolution on a general multipurpose column, but not a search for the most sensitive conditions for each individual compound.

Figures 1 to 3 show the isothermal separations for the Diazinon, Baytex, and parathion systems. Figure 4 shows an isothermal analysis of a mixed system which includes malathion. The oxygen analog and hydrolysis products of malathion could not be resolved at 180° C., since Malaoxon appears to be unstable, and diethyl fumarate is eluted with the solvent.

Malathion and Malaoxon can be chromatographed at 160° C. on a glass column containing Reoplex-400, but the resolution is not quite complete as seen in Figure 5. The N_2 flow rate of 55 ml. per minute was used with a 2-foot column to reduce residence time. The relative retention times of malathion and Malaoxon are 6.40 and 7.61 minutes, respectively, compared with Diazinon (3 minutes). A hydrolysis product of

malathion, diethyl fumarate, can be separated from the solvent peak and its cis isomer diethyl maleate at temperatures below 90° C.

Temperature programming is one technique in which the Reoplex-400 can be utilized to separate the several constituents of the malathion system. This is limited, however, to temperatures below 160° C. since Malaoxon appears unstable above this temperature. Figure 6 shows such an analysis. After isothermal operation for 3 minutes at 85° C., the system is programmed at 20° C. per minute for 3.75 minutes to the upper temperature limit of 160° C., where it is maintained. In this way, diethyl maleate can be separated from diethyl fumarate, malathion, and Malaoxon on the same column with one injection.

Thus, the malathion system can be resolved by either of two techniques: by dual isothermal analysis at 85° C. for diethyl fumarate and diethyl maleate, and at 160° C. for malathion and Malaoxon, or by programmed temperature analysis that would quickly shift the temperature between 85° and 160° C.

Discussion

The elution order of the four parent pesticides on Reoplex-400 (Table III) was compared with other liquid phases. The authors assumed that the pesticides did not change chemically upon column injection. The order of elution of the four pesticides (Figure 4) was similar to DC-200 (Nelson, 1965): Diazinon, malathion, Baytex, and parathion. Elution order on high vacuum silicone grease and DC-11 (Kanazawa, Kubo, *et al.*, 1965), and QF-1 (Bonelli, Hartmann, *et al.*, 1964) has one change—Baytex elutes before malathion. Separation of the four pesticides can be accomplished, however, only on Reoplex-400 and QF-1. These two liquid phases can be utilized qualitatively, therefore, to confirm unknown malathion and Baytex residues. Additional confirmation may be accomplished by induced hydrolysis and analysis of the hydrolytic products on Reoplex-400.

Table III shows that the oxon retention times are longer than their respective parent organophosphate pesticides on Reoplex-400. Retention times on DC-200 (a polymethyl siloxane) for parathion and Paraoxon show the reverse phenomena where the retention time of Paraoxon is less than parathion (Giuffrida, 1964).

The primary factors governing retention time on a liquid phase are the solute's vapor pressure and the amount of electron donor–acceptor interaction occurring between the solute and the liquid phase. Structures of the oxons are such that the more electronegative oxygen atom causes a larger electrophilic inductive effect on the central phosphorus atom than the sulfur atom of the parent compound. This effect, therefore, causes a larger positive formal charge on the central phosphorus atom of the oxon. Thus, there will be a stronger interaction of the oxon with an "elector donor" liquid phase than will occur with the parent compound.

DC-200 is classified as a nonpolar liquid phase (Brown, 1963), whereas Reoplex-400 is characterized as an "electron donor" liquid phase (Brown, 1960, 1963; Chovin, 1964). The latter has electrons available to interact with a solute

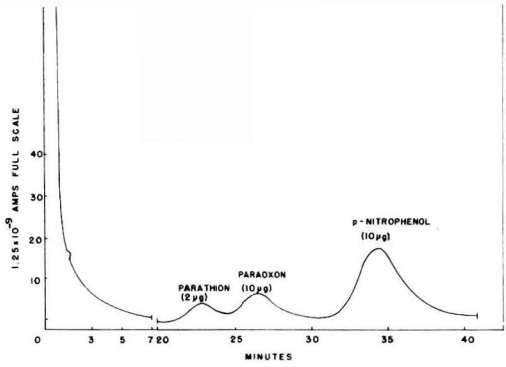


Figure 3. Chromatogram of parathion system

Detector–flame ionization

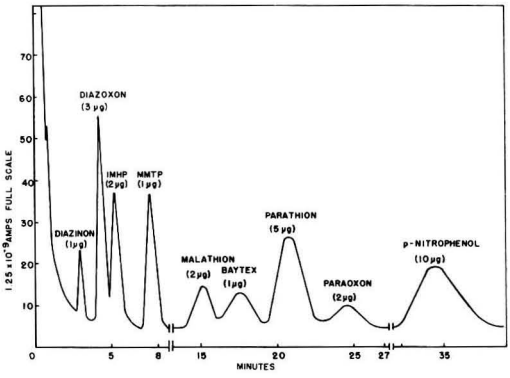


Figure 4. Chromatogram of a mixed system

Detector–flame ionization

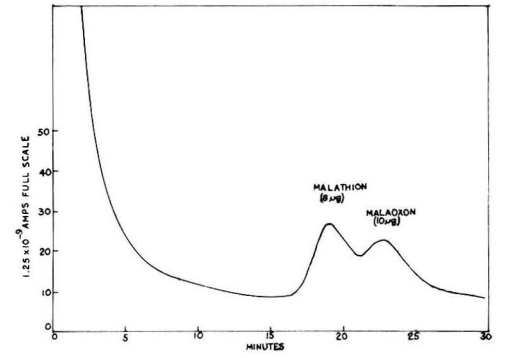


Figure 5. Chromatogram of malathion and Malaoxon

Detector–flame ionization
Column–2-foot, 1/16-inch I. D.
Temperature–160° C.

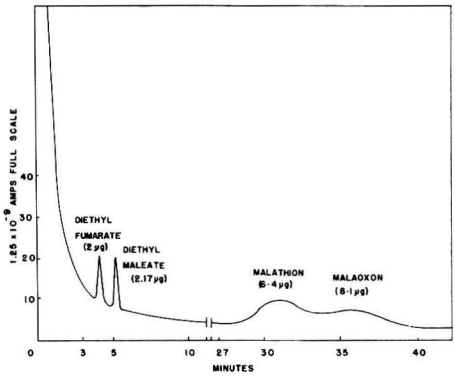


Figure 6. Programmed temperature chromatogram of the malathion system

Detector–flame ionization
Column–2 feet, $^1/_{16}$-inch I. D.
Flow rate–48 ml. per minute

that is a better "electron acceptor." The oxons of the organophosphate pesticide on this phase, therefore, have a longer retention time than the parents.

Sensitivities are reported in Table III in terms of the fundamental measure of peak area coulombs per microgram (Cook, Stanley, *et al.*, 1964; Gudzinowicz and Clark, 1964). A disc integrator accurately measured the coulombs. The sensitivity values represent the pesticide detectability for these chromatographic systems and are not necessarily optimum for each compound. The sensitivity data indicate the detection system of choice for a particular analysis after consideration of the type of sample, necessary concentration range, extraction method, and cleanup procedure.

Sensitivity data for the electron-capture detector show that the parent compounds ($\diagup$ S ‖ P—O) are more sensitive to the electron-capture process than the oxons ($\diagup$ O ‖ P—O). This observation agrees with Cook, Stanley, *et al.* (1964), for the parathion and Systox systems and for the Dimethoate system (Gudzinowicz and Campbell, 1961). Hydrolysis products are all less sensitive to the electron-capture process than their respective parents. For flame ionization detectors, however, hydrolysis products are the most sensitive compound of a family.

Sensitivity data of the two detection systems (Table III) should be compared on a semiquantitative basis, since different column dimensions, flow rates, and instruments were used. The parathion and Diazinon systems are much more sensitive to the electron-capture process, except for IMHP. Very little difference of preferential detector sensitivity is observed for Baytex and Bayoxon, but MMTP is more sensitive to the flame ionization process. Baytex was reported 1.53 times more sensitive to the flame ionization process with a 5% QF-1 column than to the electron-capture process with a 5% SE-30 column (Gudzinowicz and Clark, 1964). The incongruities between the present work and the work of these authors are small and can probably be explained by differences in liquid and solid phase, flow rate, column dimensions, and retention times of the molecules.

Relative retention times reported in this paper represent primarily a search for the best resolution on a general multipurpose column. They do not represent a search for the most sensitive conditions for each individual compound. The choice of the absolute retention time of Diazinon of approximately 3 minutes assures resolution of early peaks and minimizes the broadening of later ones.

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Effects of Air Pollutants on Apparent Photosynthesis and Water Use by Citrus Trees

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■ Commercially producing lemon and navel orange trees were tested to determine the effects of ambient air pollutants which occur in the Los Angeles basin on water use (transpiration) and apparent photosynthesis. The entire trees were enclosed in plastic covered greenhouses and were supplied various fractions of the atmosphere to find out whether ozone, peroxyacyl nitrates, or fluorides were causing deleterious effects. Nitric oxide was added to the air in one treatment to reduce ozone selectively but in so doing, nitrogen dioxide in amounts equal to the ozone was formed. The results showed that the total photochemical smog complex reduced the rate of water use by lemon trees and also reduced the rate of apparent photosynthesis. Fluoride levels occurring in the atmosphere caused no detectable effects. Attempts to evaluate the separate effects of ozone and peroxyacyl nitrates were unsuccessful. Reduction of the ozone in the tree atmospheres by addition of nitric oxide failed to overcome the reduced water use and lowered apparent photosynthesis.

Air pollutants, especially photochemical smog and fluorides, cause major damage to agricultural crops when certain levels are exceeded (Darley and Middleton, 1966; Middleton, 1961; Thomas, 1961; Middleton *et al.*, 1965). Commercial production of some leafy vegetables has virtually ceased in the Los Angeles Basin because of oxidant lesions which reduce quality or render the crop totally unsalable. Fluorides can cause visible damage to crops if levels are high enough, but where no outward symptoms occur, environmentally controlled studies are required to determine the extent of injury. The present studies were initiated in 1960 under a unique cooperative effort (Richards and Taylor, 1960) supported financially by agriculture, industry, local and national governments, various private organizations, and the University of California with an avowed purpose to "measure under field conditions the effect of the various atmospheric phytotoxicants on agricultural crops growing in the Upper Santa Ana Drainage Basin."

There was a serious question as to whether photochemical smog and/or fluorides were responsible for major economic losses by the citrus industry and, if so, how much. Thus, the present study reports the effects of ambient pollutants on apparent photosynthesis and water use of citrus trees because they show definitive results. Design and performance of the greenhouses were reported earlier (Thompson and Taylor, 1966). Details of the systems for supplying controlled levels of nitric oxide and hydrogen fluoride to the trees also have been published (Thompson and Ivie, 1965). Data showing effects on leaf drop, fruit drop, and fruit yield are still being recorded, but preliminary indications are that all three responses are being adversely affected by photochemical smog. Fluorides seem to have no measurable effect. Details will be reported in a subsequent manuscript.

Methods

The work was begun on lemons because these trees grow rapidly and set several flushes of leaves during the year, and experimental effects would probably appear sooner than with other, slower growing citrus species. Two groves were leased where both photochemical smog and atmospheric fluoride occur. These groves had uniform trees and were six and nine years of age, respectively. Later a navel orange grove nine years of age was added to the study. At each location, 24 experimental trees were selected and divided according to a randomized block design into six treatments with four replications each (Table I). All trees were enclosed in individual aluminum-framed plastic covered greenhouses (Thompson and Taylor, 1966) equipped with squirrel-cage blowers (Figure 1). Total volume of the houses was 41.5 cu. meters. Air was supplied

Figure 1. Plastic covered greenhouses installed over bearing lemon trees near Upland, Calif.

Table I. Experimental Field Installations on Citrus Upland and Cucamonga, Calif.

Tree Atmosphere	Treatment of Atmospheres	Toxicant Remaining
Filtered air	Activated carbon, limestone	....
Ambient air	....	Fluoride, ozone, PAN[a]
Low fluoride air	Limestone	Ozone, PAN
Low ozone air	Nitric oxide	Fluoride, NO, NO_2, PAN
Filtered air + fluoride	Limestone, activated carbon, hydrogen fluoride	Fluoride
Low ozone, low F^- air	Limestone, nitric oxide	PAN, NO, NO_2

[a] Peroxyacyl nitrates.

Table II. Total Oxidant Levels in Greenhouses after Activated Carbon Filtration or NO Treatment[a]

July 5, 1965 Orange 1 Begun 1350 o'clock		July 6, 1965 Lemon 1 Begun 1605 o'clock	
Outside air	0.16	Outside air	0.25
Filtered air + F^-	0.05	Filtered air	0.05
Filtered air	0.05	Filtered air + F^-	0.05
Low ozone air	0.05	Low ozone air	0.03
Low ozone, low F^- air	0.05	Outside air	0.25
Low fluoride air	0.13	Ended 1525 o'clock	
Outside air	0.16		
Ended 1410 o'clock			

[a] All data are in parts per million by volume.

continuously to the top of the houses at about 80 cu. meters per minute in an effort to change the air twice per minute. Temperatures rose 4° to 6° C. inside the houses over outside readings on hot days. The blowers were enclosed in steel cabinets. In treatments requiring filters, three Filterfold cannisters (Barneby-Cheney Co., Los Angeles, Calif. 90063) were filled with activated coconut charcoal and/or six-mesh limestone and were interposed in the cabinets ahead of the blower which was rated for 85 cu. meters per minute but inside fiberglass dust filters. Dust filters were changed on a 4-week schedule or more often if accumulations became too heavy.

Commercial furrow-type irrigation practices were followed by the grove owner but when trees approached a soil suction of 0.5 atm., supplemental water was applied. Pruning was done as required to keep the trees from abrading the plastic sides and allow circulation of air.

The "filtered" treatment (Table I) consisted of both activated carbon and limestone filtration. The carbon was used to remove ozone, and peroxyacyl nitrates plus some of the hydrocarbons. Limestone removed acid gaseous fluorides. Typical data showing total oxidant reduction are given in Table II. Oxidant was measured with a Mast ozone meter (Mast Development Co., Davenport, Iowa). This instrument gives a partial response to nitrogen dioxide which could account for a small part of the residual oxidant, but small filter voids and leaks also allow some of these compounds to get into the houses.

Several dozen determinations of residual oxidants in "filtered" greenhouses showed a mean reduction of 80%. "Ambient air" as it occurred in the area was drawn into the houses through wirecloth screens. If dusty tillage operations occurred, fiberglass dust filters were used. "Low fluoride air" consisted of ambient air which was passed through dust and limestone filters. "Low ozone air" consisted of ambient air to which nitric oxide was added to react with the ozone. This addition was begun when the total oxidant level of the ambient atmosphere of the grove reached 0.10 p.p.m. (Thompson and Ivie, 1965). At that time, 0.20 p.p.m. of NO on a volume basis was added to the intake of the blowers. The NO was diluted with 50 volumes of cylinder nitrogen before injection into the blowers to prevent premature oxidation by oxygen of the air. This 2-to-1 ratio of NO to the total oxidant was maintained as the photochemical smog increased, often necessitating the addition of 0.8 to 1.0 p.p.m. of NO.

To find out what was happening to the oxides of nitrogen both NO and NO_2 were measured at the outlet of greenhouses to which NO was added. Nitric oxide and nitrogen dioxide were determined by aspirating two air samples, one through dichromate coated paper which oxidized the NO to NO_2 and a second untreated sample through Saltzman reagent and measuring color development at 550 mμ (Saltzman, 1960). NO values were obtained by difference. Total oxidant outside and that in air issuing from the houses was correlated with the NO to NO_2, Table III. Because of the large volumes of air processed, it was questionable as to whether addition of NO was 100% effective in removing ozone. Also, even if ozone removal was quantitative, both NO_2 and PAN react to give some response with the total oxidant analyzer, thus leaving a question as to the actual amounts of residual ozone. Despite these interferences, 0.02 to 0.07 p.p.m. of the total oxidant as measured by the Mast ozone meter was all that remained.

Comparison of the NO_2 produced from the ozone plus NO showed a reasonably quantitative conversion of NO to NO_2. The sum of the two values, NO + NO_2, was also well correlated with the NO added showing that the stoichiometry of the reaction was being measured by the analytical determinations.

"Low ozone, low fluoride air" combined the use of nitric oxide addition and limestone filtration as described previously. "Filtered air plus fluoride" presented a special case because extended studies were unsuccessful in removing oxidants while still allowing all of the atmospheric fluoride to enter the houses. All adsorbents, catalysts, etc., which were tried for taking up or destroying oxidants, removed substantial amounts of fluoride. Accordingly both activated carbon and limestone filters were used as in "filtered air" and hydrogen fluoride was added back to the airstream at ambient levels but on a 24-hour delayed basis. Details are published elsewhere (Thompson and Ivie, 1965).

Tensiometers were installed in all houses about $1\frac{1}{2}$ meters from the tree at a depth of $\frac{1}{2}$ meter to monitor soil moisture. One tree in each block had a tensiometer at $\frac{3}{4}$ meter to determine moisture at the greater depth. Tabulations of soil suction were made daily. Total oxidant levels in air were monitored continuously by a Mast ozone meter. Typical results showing

Table III. Total Oxidant Reduction, Nitric Oxide, and Nitrogen Dioxide Content of "Low Ozone Air" in Greenhouses Treated with NO[a]

Date	Outside Total Oxidant	NO Added	At Greenhouse Outlet			
			Total Oxidant	NO_2	NO	NO plus NO_2
July 20	0.26	0.50	...	0.26	...	...
July 27	0.18	0.30	0.07	0.11	...	...
July 29	0.12	0.20	0.05	0.20	0.11	0.31
August 2	0.20	0.40	0.05	0.28	0.10	0.38
August 16	0.28	0.60	0.02	0.32	0.26	0.58
August 17	0.25	0.50	...	0.31	0.25	0.56
August 25	0.28	0.50	...	0.41	0.12	0.53

[a] All data in parts per million by volume.

the number of hours during which the levels were above 0.10 p.p.m. at Lemon Division 1 are given in Figure 2. Atmospheric hydrogen fluoride was measured continuously by a fluorometric analyzer (Ivie *et al.*, 1965), and total fluorides were determined daily by titration or colorimetrically from impinger samples (Bellack and Schouboe, 1958; Willard and Winter, 1933). Typical data for total daily fluoride levels are given in Table IV. Checks on the amount of total fluoride inside of the greenhouses were made periodically and leaf accumulations were determined at 3- to 4-month intervals.

The degree of removal of gaseous fluoride, principally hydrogen fluoride, by the limestone filters was difficult to determine precisely because the fluorometric analyzer available (Ivie *et al.*, 1965) had a lower limit of about 0.10 μg. per cu. meter of hydrogen fluoride. With ambient levels of only 0.1 to 0.5 μg. per cu. meter of hydrogen fluoride and with laboratory trials showing 90 to 97% removal by the limestone filters, the lower limit of the analyzer was exceeded. Several simultaneous checks of total fluorides from outside and within houses by the impinger method having limestone filters showed a reduction in total fluoride of about 75%. Average leaf accumulations in trees receiving limestone filtered air after 8 months of exposure was 10 p.p.m. on a dry weight basis, while trees receiving ambient air had 27 p.p.m. Some of this amount is considered "background" possibly accumulated by absorption and translocation from soil through the tree.

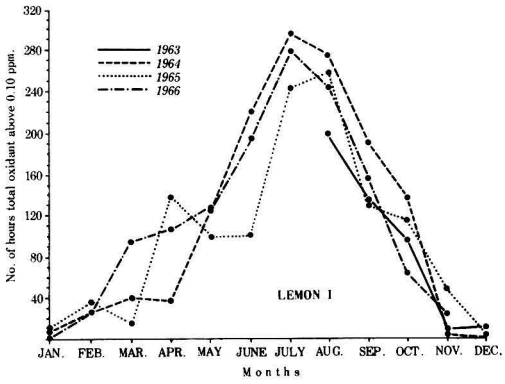

Figure 2. Total number of hours per month during which total oxidant levels were above 0.10 p.p.m. at Upland, Calif.

Experimental Results

Effect of Air Pollutants on Water Use of Trees. Within a few weeks after the experimental treatments began in 1962, water use by trees in the various groups in Lemon Division 1

Table IV. Average Total Fluoride Levels for 24 Hours at Experimental Locations

(Micrograms per cubic meter)

	Lemon 1 (21st-Euclid, Upland)	Lemon 2 (Ramona-Church Sts.) (Cucamonga)	Orange 1 (23rd-Euclid, Upland)
	JULY 1964		
High	0.80	0.91	0.63
Low	0.30	0.30	0.13
Mean	0.41	0.55	0.32
	AUGUST 1964		
High	0.85	0.93	0.62
Low	0.19	0.34	0.23
Mean	0.55	0.70	0.54
	SEPTEMBER 1964		
High	0.92	1.80	0.56
Low	0.21	0.27	0.25
Mean	0.46	0.77	0.39

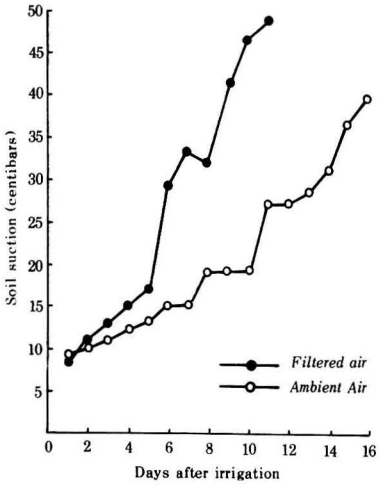

Figure 3. Typical record of soil suction increase in tree root zone following irrigation at Lemon Division 1

differed appreciably. The owner irrigated on a 15-day schedule, but some trees required "extra" irrigations more frequently than others. "Extra" irrigations were those required when tensiometers buried at 50-cm. depth in soil under the skirts of the trees reached soil suction of 45 centibars. This extra water was applied so that the suction never went above 50 centibars. The tentative conclusions of 1962 were confirmed during the succeeding years (Table V) and showed that trees receiving "filtered air" required more extra irrigations than those with "ambient air" during 1963, 1964, and 1965. In 1963 and 1964, this was statistically greater at the 1% level; in 1965, at the 5% level. "Ozone low air" trees and "ozone, fluoride low air" trees lost less water than "filtered air" in 1964 and 1965 (5% level). All other treatments were not different from "filtered air" statistically but all average values were numerically less.

Typical rates of increase in soil suction are shown in Figure 3 for "filtered air" and "ambient air." Lemon 2 did not show the differences in water use because the grove operator irrigated the trees weekly. The orange grove showed a greater numerical frequency of extra irrigations for trees in "filtered air," but these were not statistically different.

Effect of Air Pollutants on Apparent Photosynthesis of Entire Trees. To measure another effect of pollutants on the metabolism of the lemon trees, apparent photosynthesis was measured on the entire trees of Lemon 1 during 1961 and 1962 (Ivie *et al.*, 1963). In this method, doors were installed on the intake blowers which when closed reduced airflow. This was necessary to allow enough CO_2 reduction so that it could be measured accurately. Speed of the blower motors was also reduced from 1750 to 1140 r.p.m., resulting in a decreased air movement from 80 to 20 cu. meters per minute during the first period of measurement of apparent photosynthesis. Air samples from the intake and outlet of each house were drawn through aluminum tubes to a central control room where they were stored in vinyl plastic bags until analyzed sequentially by an infrared analyzer. Carbon dioxide changes in one set of 12 houses comprising two enclosed trees from each treatment were measured for one week after which the remaining 12 trees were monitored.

Before the actual air treatments were started at Lemon 1 but after erection of the houses, the rate of apparent photosynthesis of all trees was determined as a base line (Table VI). These measurements were made from September to November 1961. Treatments were then begun in January 1962. The results shown as 1962 treatment were taken from April–June 1962 and represent the average amounts of carbon dioxide absorbed by each tree as compared with trees receiving "filtered air." Because the trees varied in size the pretreatment values varied from the "filtered air" base, but after the treatments of 3 months, the "filtered air" and "filtered air plus fluoride" had the highest average rate of apparent photosynthesis.

A more precise evaluation was made by taking six successive periods in January, June, and November of 1962 during which

Table V. Total Number of "Extra" Irrigations Required by Trees in Different Treatments during the Year

	Lemon 1				
Treatment	1962[a]	1963	1964	1965	1966
Filtered air	23	43	36	24	20
Ambient air	3	7[b]	5[b]	4[c]	6
Low fluoride air	16	37	26	14	18
Low ozone air	7	19	12[c]	10	7
Filtered air plus fluoride	14	39	28	15	16
Low ozone, low fluoride	12	37	22	5[c]	9

[a] Three months of the year.
[b] Significantly less than filtered air at 1%.
[c] Significantly less than filtered air at 5%.

Table VI. Apparent Photosynthesis of Entire Trees as Per Cent of Trees with Filtered Air

	Initial Period before Treatment, 1961		Treatment Period, 1962	
Atmosphere	AM[a]	PM[b]	AM[a]	PM[b]
Filtered air	100	100	100	100
Ambient air	95	118	61	78
Low fluoride air	127	105	81	97
Low ozone air	125	111	68	93
Low ozone, low fluoride air	104	106	94	95
Filtered air + HF	88	107	120	96

[a] 0700–1000 with reduced airflow (20 cu. meters/min.) through houses.
[b] 1100–1500 with full airflow (80 cu. meters/min.) through houses.

Table VII. Apparent Photosynthesis of Lemon Trees during January, June, and November 1962

Date of Treatment	Adjusted Grams Dry Matter per Hour[a]					
	Filtered	Ambient	Filtered + F	Low O_3	Low O_3, F	Low F
1-15-62 to 1-21-62	5.9	2.2	5.3	2.6	4.2	3.8
	2.4	1.3	4.4	2.8	3.2	2.9
1-21-62 to 1-31-62	6.1	3.0	5.1	2.9	3.2	4.1
	3.4	0.9	6.9	2.2	2.5	3.6
Av.	4.5	1.9	5.4	2.6	3.3	3.6
Treatments greater than ambient	[b]		[b]			[c]
6-6-62 to 6-11-62	5.1	3.5	5.0	4.3	5.3	2.8
	5.0	4.3	5.1	3.8	5.2	5.5
6-13-62 to 6-18-62	2.4	2.4	3.6	2.6	2.7	3.9
	3.8	2.8	4.7	2.5	4.5	3.1
Av.	4.1	3.2	4.6	3.3	4.4	3.8
Treatments greater than ambient			[c]			
11-1-62 to 11-13-62	8.6	8.3	11.5	8.8	10.9	6.7
	12.5	9.2	13.4	9.1	10.0	10.3
11-14-62 to 11-26-62	8.7	6.0	9.8	5.9	5.4	7.1
	10.3	7.0	10.8	5.4	9.3	8.3
Av.	10.0	7.6	11.4	7.3	8.9	8.1
Treatments greater than ambient	[c]		[b]			

[a] Adjusted for pretreatment grams dry matter/hour.
[b] Greater than ambient at 1% level of significance.
[c] Greater than ambient at 5% level of significance.

apparent photosynthesis was measured. The amount of CO_2 absorbed was determined, and the grams of dry matter assimilated per tree per hour were calculated. This assumes 44% carbon in vegetation and requires 1.63 grams of CO_2 to produce 1 gram of dry matter (Franck and Loomis, 1949). The results (Table VII) show how much CO_2 was absorbed during the morning hours with the blower door closed and reduced air flow through the houses. The individual values were adjusted by the pretreatment CO_2 absorption values. The "ambient air" treatment is compared statistically with all other treatments by the procedure of Dunnett (1955) and shows that in January "filtered air" and "filtered air plus fluoride" are significantly greater than "ambient air" at the 1% level. "Low fluoride air" is greater at the 5% level. In June, "filtered air plus fluoride" was greater than "ambient air" at the 5% level. In November, the results showed that "filtered air" and "filtered air plus fluoride" are greater than "ambient air" at the 5% level, and in the latter treatment, are greater at the 1% level.

Effect of Air Pollutants on Apparent Photosynthesis of an Isolated Branch. In an attempt to obtain a measurement of apparent photosynthesis which could be related directly to leaf area, six leaf chambers were constructed, and the measurement procedure of Taylor *et al.* (1965) was used. In this method five to six leaves on one branch are enclosed in a plastic chamber fitted with an artificial light source. The chambers have inlet and outlet connections for obtaining simultaneous CO_2 samples. These chambers were installed in six greenhouses, one in each of the six treatments, and the amount of CO_2 in the particular greenhouse *vs.* that coming from each leaf chamber was measured for one week; a second set of leaves was measured on the same tree for a second week. The chambers were then moved to a second replicate of six houses for two weeks and successively on to the third and fourth replicates, making an 8-week measurement period in all. Leaf area in each chamber was measured by tracing and planimetry. Carbon dioxide chart readings were converted to parts per million and then to milligrams of CO_2 per sq. decimeter per hour. Data from four 8-week periods of measurement are shown in Table VIII. For the two periods in 1963, three covariates, temperature, total leaf area, and average area per leaf, were tested for significance. As temperature was the only significant covariate (Figure 4), a mean temperature value was calculated, and the CO_2 values were adjusted for this covariate. These results showed that during August and September "filtered air" had greater CO_2 absorption than "ambient air" at the 1% level (Table VIII). Also "low ozone air" and "low fluoride air" were greater than "ambient air" at the 5% level. In October and November, "filtered air" and "filtered air plus fluoride" exceeded "ambient air" at the 5% level. The grand averages of all treatments compared were numerically greater than those of "ambient air."

In June-October 1964, a similar measurement was made. Evaluation of the data adjusted by the covariates of branch

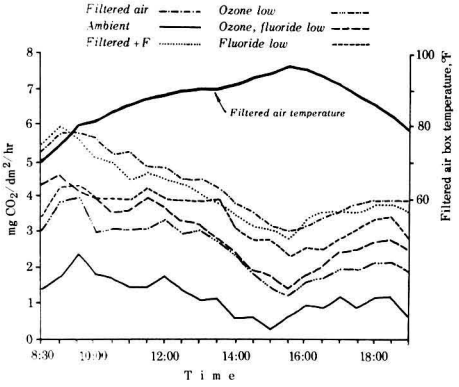

Figure 4. Correlation of air temperatures and rates of apparent photosynthesis of lemon branches exposed to the various experimental atmospheres

diameter and leaf area showed no treatments were statistically greater than ambient. All grand averages except "low fluoride air" in the last period were numerically greater than "ambient air."

Because the trees which received "filtered air" required more frequent irrigations and were thus assumed to be transpiring more moisture than the other plants, an attempt was made to measure the amount of moisture given off directly. The same air samples used for the apparent photosynthesis measurement in 1964 were exhausted from the infrared CO_2 analyzer over wet bulb thermocouples in an apparatus similar to the equipment designed originally by Slatyer and Bierhuizen (1964). Thus a measure of the water content of the intake and outlet air of the leaf chamber was obtained, and the milligrams of water transpired per square decimeter of lea surface per hour were determined (Table IX). The values were adjusted for covariates of temperature and branch diameter. Statistical evaluation showed no differences between the different treatments. Variations were very large, and some un-

Table VIII. Apparent Photosynthesis of Selected Lemon Branches Adjusted[a] Av. Mg. CO_2/Dm.²/Hr.

		Treatment					
Group	Date	Filtered	Ambient	Filtered +F^-	Low O_3	Low O_3 F^-	Low F^-
I	8-5-63 to 8-16-63	6.2	3.3	4.6	4.6	5.9	6.1
II	8-19-63 to 8-30-63	5.6	3.0	4.3	5.1	4.9	4.7
III	9-9-63 to 9-20-63	6.7	3.5	4.4	5.8	4.5	4.6
IV	9-23-63 to 10-4-63	7.3	4.9	5.8	5.5	3.7	5.4
Grand av.		6.4	3.7	4.8	5.3	4.7	5.2
Treatments greater than ambient		[b]			[c]		[c]
I	10-7-63 to 10-18-63	6.9	5.1	7.9	3.8	6.7	5.2
II	10-21-63 to 11-1-63	6.4	4.9	7.4	7.0	8.2	4.6
III	11-4-63 to 11-15-63	5.4	3.2	5.6	6.0	4.0	3.1
IV	11-18-63 to 1-31-64	3.7	1.8	2.2	2.5	2.0	3.3
Grand av.		5.6	3.8	5.8	4.8	5.2	4.1
Treatments greater than ambient		[c]		[c]			
IV	6-24-64 to 7-7-64	2.6	1.4	0.9	1.5	2.3	0.6
III	7-8-64 to 8-4-64	2.0	1.1	3.1	1.1	2.5	1.6
I	8-5-64 to 8-19-64	4.8	1.8	2.0	2.4	2.2	4.7
II	8-20-64 to 8-31-64	2.4	1.7	4.0	2.7	2.0	1.3
Grand av.		2.9	1.5	2.5	1.9	2.3	2.1
No treatments greater than ambient							
IV	9-14-64 to 9-26 64	4.0	4.9	4.1	4.8	5.0	3.9
III	9-28-64 to 10-11-64	4.1	1.2	3.8	3.0	4.3	2.2
I	10-12-64 to 10-25-64	6.5	4.4	3.5	2.8	5.0	2.0
II	10-26-64 to 11-8-64	5.4	3.5	2.9	4.8	3.5	2.4
Grand av.		5.0	3.5	3.6	3.9	4.4	2.6
No treatments greater than ambient							

[a] Adjusted for covariates.
[b] Greater than ambient at 1% level of significance.
[c] Greater than ambient at 5% level of significance.

Table IX. Rate of Transpiration of Selected Lemon Branches Adjusted Average Mg. H_2O/Dm.^{2}/Hr.[a]

Treatment	Filtered	Ambient	Filtered $+F^-$	Low O_3	Low O_3 F^-	Low F^-
Grand av. 6-24-64 to 8-31-64	494	302	389	312	316	399
Grand av. 9-14-64 to 11-8-64	488	492	366	439	383	362

No significant treatment differences

[a] Adjusted for covariates.

known or extraneous factors may have affected these measurements to cause such large differences between individual values and thus invalidate the results.

The increased water use by the lemon trees receiving filtered air as compared with ambient air is indicative of an increased transpirational rate. Attempts to examine stomatal openings directly with the microscope or by silicone impressions to make visual comparisons were unsuccessful because the stomates in citrus are deeply recessed. Attempts to confirm the increased rate of transpiration by determining the water content of air samples coming from the leaf chambers could have encountered interference by condensation of water in the aluminum sampling lines which were as much as 40 meters in length. If this occurred during the night and a slow evaporation of liquid droplets occurred during the measuring period, the results could be meaningless. Also transpirational rate of some proceeds by regular cycles (Ehrler *et al.*, 1965), and because the air samples were only drawn from a given sampling chamber for 2 minutes during each 30-minute period, the rates could have varied rather widely depending upon which part of the cycle the leaves were in at the time of sampling.

Discussion

The higher rate of apparent photosynthesis of the entire trees receiving filtered air as compared with ambient air could be caused by several factors. Increased senescence and early abscission of leaves reported with other plants (Darley, 1959) could reduce effective photosynthetic capacity. Probably other metabolic changes such as those described by Dugger *et al.* (1966) are more important. They observed that lemon seedlings, fumigated with ozone, had less starch and more reducing sugars than controls, increased permeability to exogenous sugars and an increased rate of respiration.

Why the apparent photosynthesis of isolated leaves receiving "filtered air" and "filtered air plus fluoride" was not statistically greater than ambient air during 1964 as it was in 1963 is unexplained. Individual variation in photosynthesis between leaves is great, and the cycling in rates of CO_2 absorption observed with cotton by Pallas *et al.* (1967) also occurs with lemons. This phenomenon coupled with the short sampling periods could give such great variability as to invalidate the results during this period even though the average value of the filtered air was highest.

Another possible explanation of the reduced water use and lower apparent photosynthesis of trees in the four groups which did not have carbon filtered air—i.e., ambient, low ozone, low ozone-low fluoride, and low fluoride air—is that peroxyacyl nitrates were causing the effect. These compounds occur in concentrations from 3 to 12% of that of the ozone in this area.

In planning the study, the authors assumed that the addition of nitric oxide to react with ozone when total oxidant reached 0.10 p.p.m. would give a beneficial effect. Nitrogen dioxide was thought to be less phytotoxic than ozone. However, the results show little improvement and suggest that either the nitrogen dioxide is as deleterious as ozone or that the treatment with NO should have been started at lower levels of total oxidant—i.e., enough damage was caused by oxidant at 0.10 p.p.m. that additional oxidant had a relatively minor effect. Additional information on the effects of NO_2 on citrus is needed badly to aid in interpreting these results.

Atmospheric fluoride levels in the experimental areas seemed to have little deleterious effect on the trees. Average accumulations in 8-month-old leaves were 50 p.p.m. on a dry weight basis in 1961. Accumulations declined in similar aged leaves to 40 p.p.m. by the close of 1964.

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A Comparison of Natural and Urban Aerosol Distribution Measured with the Aerosol Spectrometer

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■ Air samples were collected with the Goetz aerosol spectrometer both in town and in the mountains. By counting the deposited particles in the microscope, the size frequency of the aerosol was determined. Owing to the resolution power of the microscope, the size range measured was limited to particles larger than 0.27 micron in diameter. The size frequency curve has in general the same shape both in town and in the mountains, whereas the total particle number varies widely—i.e., 5000 particles per cc. downtown, fewer than 800 particles per cc. in the residential area, and fewer than 300 particles per cc. in natural aerosols. Normally, the particle number decreases during rainfall and increases in fair weather, whereas the mode of particle size increases slightly during rainfall and decreases during fair weather, especially in haze. The smallest particles occur in combustion aerosols. Investigations on the metastability of the aerosol particles showed that the urban aerosol is less stable than the natural aerosol.

The atmospheric aerosol consists of particles which come from various sources. Generally, aerosol particles which remain suspended in a gas for long periods of time have a diameter on the order of 2 microns or smaller. Particles in the 0.2- to 2-micron range are important for the visual quality of air, and their concentration varies widely both in space and in time. These variations can be verified easily by studies of the visual range; but to obtain more detailed information, it is desirable to know the size frequency curve $c(d)$ of the aerosol [from $c(d)$, the number of particles per unit volume air within the diameter range $(d,d + \Delta d)$ is given by $c(d) \times \Delta d$].

Apparatus

Aerosol Spectrometer. This centrifugal instrument can be used to measure size frequencies in the range from 2 to 0.05 microns in diameter, (Goetz, Preining, *et al.*, 1961). (The Stokes diameter of an unknown particle is defined as the diameter of a sphere with unit density, which, under influence of gravity, has the same falling speed as the unknown particle.) The main part of the aerosol spectrometer is a cone, rotating at high speed (up to 20,000 r.p.m.), in which there are two channels formed by helical grooves which are covered with a tight-fitting detachable cap. The deposit is formed on a polished chrome foil, which is placed in this cap.

Because of the conical form of the instrument, an airflow through the two channels takes place and gradual precipitation occurs while the air moves through the channels, owing to high centrifugal acceleration (20,000 × G). By varying the rotation speed and the flow rate through the channels (with the aid of interchangeable restricting orifices at the end of the channel), the size range of the particles to be precipitated can be varied widely. Monodispersed particles are deposited from the upper end of the channel with a nearly constant surface concentration until the particles which entered the channel at the inside are all deposited. At this point, the concentration goes down to zero suddenly. The length of the deposit is longer for smaller particle sizes. In this way, the different particle sizes can be deduced by a simple calculation, based on a calibration. The standard method used for evaluation was described by Goetz and Preining (1960). The size frequencies in this paper are given in particles per cubic centimeter and 0.1-micron diameter interval. (The total particle number can be roughly determined by taking the ordinates of the size frequency curve at 0.1-micron intervals and adding them.)

Microscope. The foils with the precipitated particles were photographed in a microscope on a special stage (Preining, 1962) with dark field illumination. The objective used was a Reichert 26× (NA 0.4). The total magnification was 109. The particle number on the film was counted and used for the determination of the size frequency. In the dark field microscope, every particle appears as a small luminous point; the intensity of light decreases with the size of the particle. When the contrast between the background of the film and the point is smaller than a certain amount, the particle is not seen. To see this particular particle, the photographic exposure time can be increased and thus the contrast is improved. It was not possible to use exposure times longer than 10 seconds, because at the beginning of the channel, the image of the large particle would make it impossible to recognize the small and medium particles. The variation of the photographic exposure time provides a means for determining a lower limit for recognition of particles. Smaller particles can be seen with a longer photographic exposure time. Since the concentration of a deposit of uniformly sized particles is constant along the channel, the curve of particle size *vs.* length of the channel for the short exposure time should be translated a certain distance from the curve for the long exposure time. As with the shorter exposure time, some particles are not seen; however, the distance between the two curves becomes smaller.

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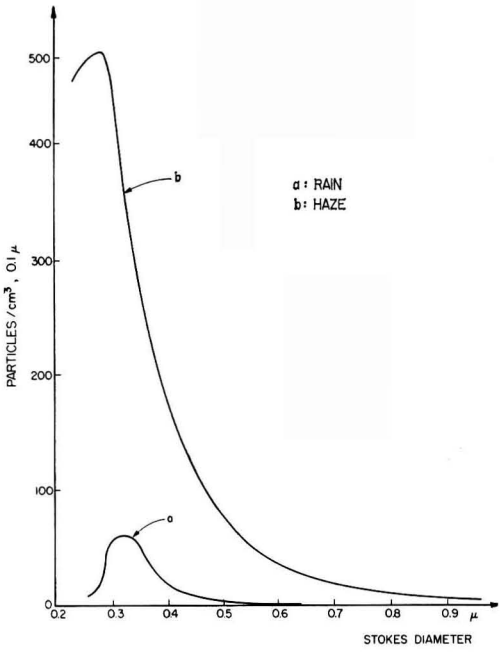

Figure 1. Typical particle size frequency

Both samples were taken on top of a mountain (1600 meters) under different weather conditions

With the calibration curve of the Aerosol spectrometer, the size range where all the particles are recognized can be calculated. The microscope used had a lower limit of about 0.27 micron. If particles smaller than this size are seen, certainly they exist; however, more particles than are seen could exist. Thus, for the present purpose, the measuring range was from 0.2- to 1-micron Stokes diameter. The upper limit was given by the aerosol itself, the lower limit by the microscope.

Atmospheric Aerosol in the Mountains

On top of a mountain in the Steirisch-Niederösterreichische Kalkalpen near Mariazell (about 90 km. west southwest of Vienna, Austria), during a period of 20 days, continuous samples were taken. Since there was no industry for a distance of 60 km., the aerosol should represent a background (or natural) quantity. A few measurements were disturbed by the use of a small gasoline engine near the inlet of the aerosol spectrometer. The shape of the size frequency curve was always approximately the same. Two typical size frequency curves are shown in Figure 1. In nearly all of these cases, the curve had a maximum around 0.35-micron diameter. For correlation between size frequency and meteorological conditions, the following characteristics of the size frequency curve were taken: the diameter at which the maximum number occurs, the total particle number between 0.3- and 1.2-micron Stokes diameter, and the height of the maximum.

These quantities as functions of the time and the meterorological conditions are shown in Figure 2. The total number of the particles is larger in fair weather than in rainy weather. Especially high concentrations are measured in haze, but these measurements cannot give general information, because the concentration in haze varies strongly with the altitude. The particle numbers in foggy weather (or especially during snowfall) were smaller than in rainy weather.

The position of the maximum shows that, in general, the diameter is larger during rainy weather and smaller in fair weather, especially in haze. The size minimum on September 11, 1964, and the two minima on September 14, 1964, are due to a gasoline motor and a fire. The very large diameter on September 10–11, 1964, is probably due to 97% relative humidity. In this case, the mixed nuclei grow because water condenses on them.

Several foils with sampled aerosol particles were rephotographed after three days of storage and in all cases the particle number decreased. Two foils were exposed several hours to sunlight with similar particle number decrease. This leads to the conclusion that the particles are unstable and disintegrate with time. The sunlight seems to accelerate this. If we also accept this to be true in the airborne state, the decrease of diameter during fair weather can be explained. Also the lower humidity favors this decrease.

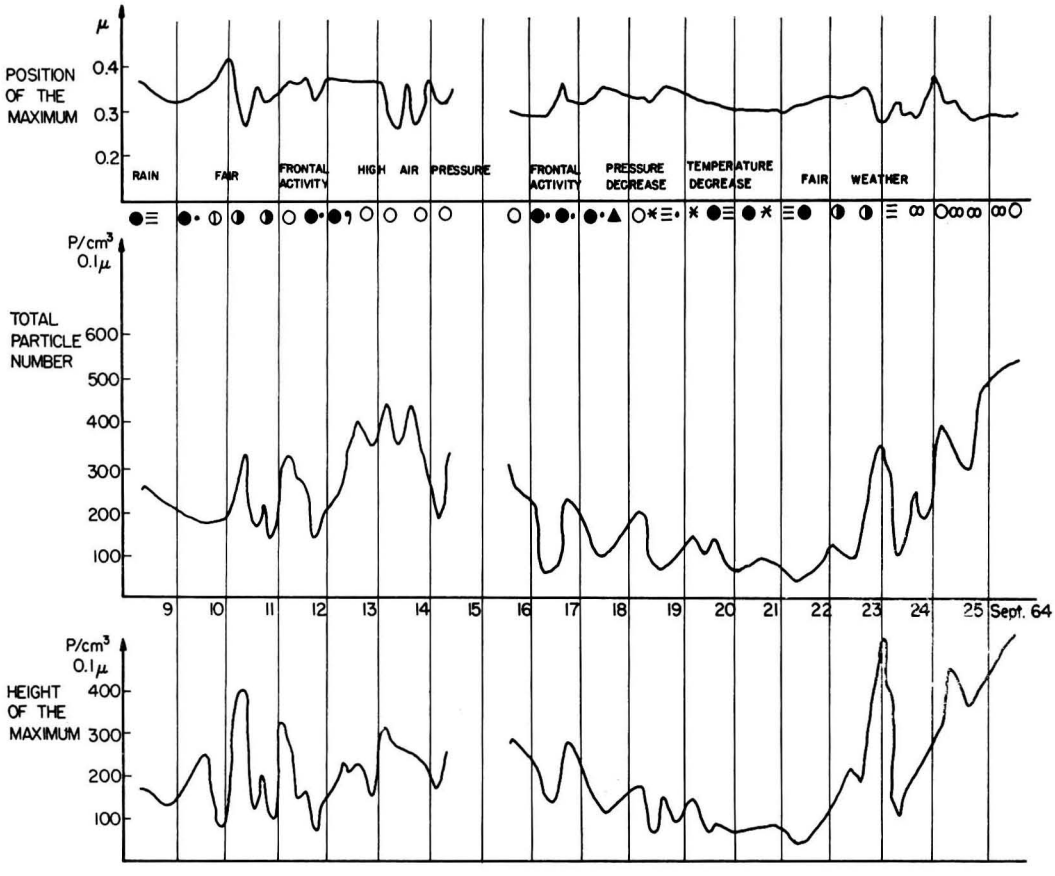

Figure 2. Variation of the characteristics of the size frequency curve with the meteorologic conditions

To compare the measured size frequencies, each curve was normalized by dividing the size frequency number by the total particle number between 0.3 and 1.2 microns and all of these curves are plotted on one graph (Figure 3). The average between 0.35 and 1.2 microns diameter is a curve which has the equation $c(d) = K \cdot d^{-4.56}$ in agreement to Junge's law (Junge, 1952) where the exponent should be approximately -4. Assuming an equilibrium between the effects of coagulation and sedimentation (Friedlander, 1960), the exponent should be -4.75 which is in very good agreement to the measured size frequency.

From some of these measured size distributions, the light absorption coefficient was calculated with the Mie theory. The calculated and observed visual ranges are:

V Calculated

45 43 75 65 48 46 33 29 44 55 100 119 41 45 38 40

V Observed

52 43 80 80 52 52 52 28 52 52 60 100 40 40 40 52

There is good agreement between theory and observation, with only statistical fluctuations. A more detailed description of the Mie Theory and the Koschmieder Formula is given by Middleton (1963).

Atmospheric Aerosol in Town

It is not so easy to obtain general information on the urban aerosol because it depends strongly on the location where the sample is taken. One measurement was made in the court of the Department of Physics at the University of Vienna. Since there were no aerosol sources in the near surroundings, this is probably a well-aged aerosol. Figure 4 shows five size frequency curves from samples at this location. The particle concentration is much higher than in the corresponding meteorological conditions in the mountains. These size frequency curves were obtained during the change from a period of fair weather to a period of rainy weather. The first sample was taken during sunshine, the next one during the beginning of a thunderstorm, and the other three during rain in the next three days. The shape of the curve is the same as that for samples in the mountains. In wintertime when all homes are

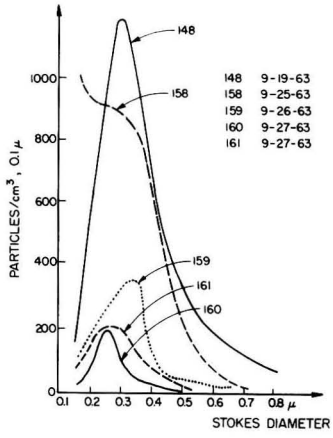

Figure 4. Decrease of particle numbers during a change from fair weather to rainy weather

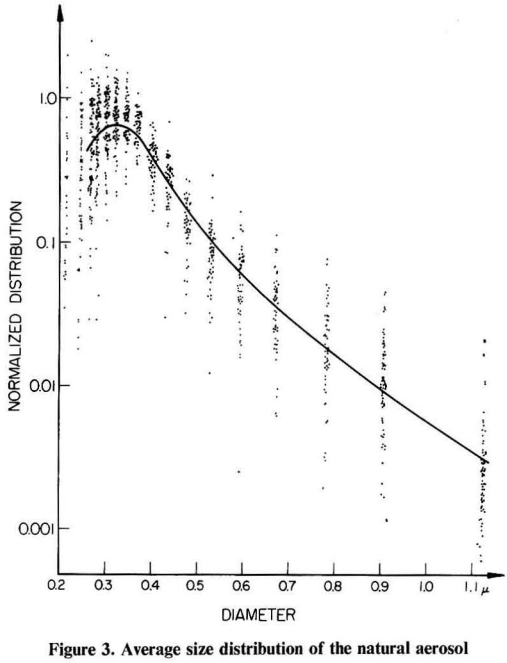

Figure 3. Average size distribution of the natural aerosol

Every individual size frequency curve was normalized, so that its area between 0.3 and 1.2 is unity

heated, the maximum moves to smaller particles and the concentration is higher.

The shape of the size distribution curve is different when the samples are taken at busy intersections (Figure 5). The size frequency maximum in this case is at about 0.2 micron instead of the normal 0.3-micron diameter. The small particles seem to be typical for a combustion aerosol (young aerosol, see also measurements in the mountains, Figure 2). Because of the turbulence and the location near the ground level, there are more large particles observed than normally. The total particle number is about five times higher than in measurements in the court of the Physics Department.

To obtain some average particle size frequency, measurements on top of a 150-meter-high tower were made in the eastern part of Vienna. In this way, the author hoped to get an average of the particle production of the town. One sample was taken on a very windy day (Figure 6), and its size frequency was very similar to the frequencies measured in the mountains, both in shape and in total number. In this case, little urban aerosol was mixed to the natural aerosol; also the particles are very stable. After the foil was stored for two months and rephotographed, the particle number decreased only a small amount. The size frequency is very different when in calm weather. Figure 7 shows the change of size frequency during a sunny day. The concentration was the highest in the morning and decreased during the day, but the shape of the curve did not change very much. This was observed on several days; in the evening the concentration usually increased again. The opposite kind of change in size frequency occurs when there is no sunshine; then, the particle number increases during the day as more particles are produced by industry, traffic, and burning of fuels.

Investigations on the stability of the aerosol showed again that a large fraction of these particles is unstable. Figure 8

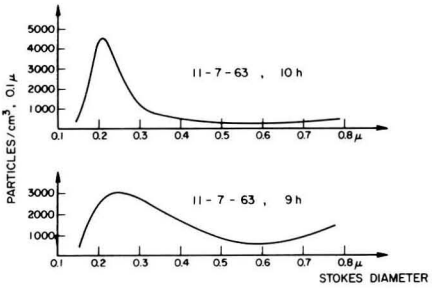

Figure 5. Traffic aerosol size distribution

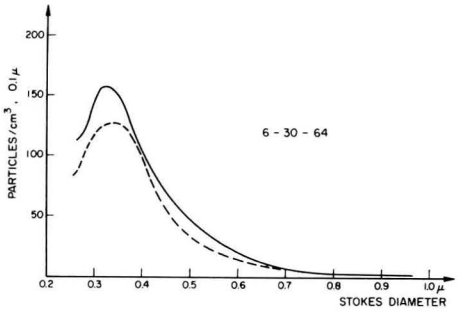

Figure 6. Natural aerosol measured during strong winds in Vienna

------ Size distribution obtained after 2-months storage

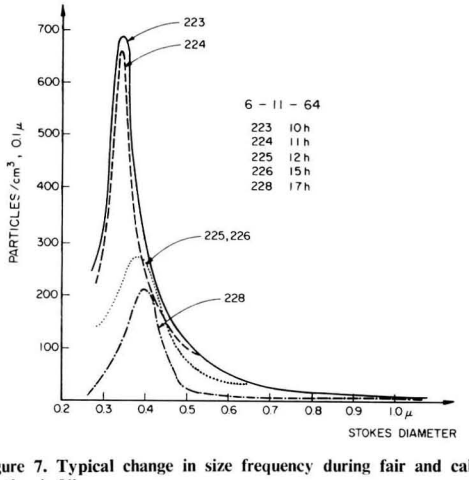

Figure 7. Typical change in size frequency during fair and calm weather in Vienna

The maximum probably shifts to bigger particles owing to coagulation

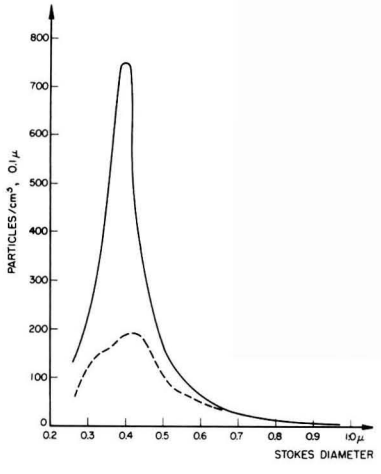

Figure 8. Typical decrease of particle number of urban aerosol during storage

shows the decrease in particle number after three days' storage of the foil. This leads to the assumption that besides convection, the disintegration of particles might be important to the decrease of particle concentration during sunshine.

Conclusions

In the size range that can be covered with the aerosol spectrometer, the size distribution of the atmospheric aerosol has in general the same shape both for natural and urban aerosols. The highest concentrations, about 5000 particles per cc., were measured at intersections with heavy traffic. In less busy areas of the town, the total particle number amounts to 800 particles per cc. or fewer. In the mountains, concentrations less than 300 particles per cc. were measured. In general, the particle number decreases during rainfall and increases in fair weather, whereas the mode of particle size increases slightly during rainfall and decreases during fair weather. Urban aerosols are in general less stable than natural aerosols.

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Singlet Oxygen in the Environmental Sciences

The Role of Singlet Molecular Oxygen in the Production of Photochemical Air Pollution

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■ A new mechanism is proposed to explain the rapid conversion of NO into NO_2 with a concurrent disappearance of hydrocarbons and appearance of oxidants in photochemical air pollution. Singlet oxygen generated by triplet energy transfer from strongly absorbing polynuclear aromatic hydrocarbons to normal oxygen produces excited singlet molecular oxygen which attacks olefins to give unstable peroxides. A mechanistic chain is set up involving free radicals generated by decomposition of these peroxides. A solution of the differential equations relating to the proposed mechanism yields a set of rate-time curves for NO–NO_2–O_3 which have the same general characteristics as those observed in actual smoggy atmospheres. The presence of singlet oxygen in urban atmospheres has potentially great implications in the environmental sciences.

Over the last decade, considerable understanding of photochemical smog has been obtained (Altshuller and Bufalini, 1965; Leighton, 1961). The intensity of smog is known to depend, in an approximately linear manner, on the concentration of hydrocarbon pollutants in the atmosphere and in a more complex manner on the concentrations of oxides of nitrogen. In the absence of either of these contaminants, photochemical smog does not occur in the atmosphere nor can it be generated in test chambers. The initial process in the formation of smog is the conversion of nitric oxide, released in automobile exhaust gases, into NO_2 and the buildup of oxidants, principally ozone and peroxyacylnitrate (PAN). This paper is a brief review of the significant aspects of the currently "accepted" explanation of this complex phenomenon and a proposal for an alternate, but not exclusive, hypothesis. The authors propose that electronically excited singlet molecular oxygen plays a significant role in the formation of photochemical smog including involvement in the rapid photoconversion of NO to NO_2 in the atmosphere or in chamber studies.

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In photochemical smog, either in the atmosphere or in chambers, with the system NO_x–O_2–hydrocarbon irradiated at wavelengths shorter than 4200 A. (Altshuller and Bufalini, 1965), the equilibrium

$$NO_2 + O_2 \overset{h\nu}{\rightleftarrows} NO + O_3 \qquad (1)$$

is attained and the ozone or atomic oxygen produced attacks olefinic hydrocarbons in a manner which, although not yet fully elucidated, appears to raise no fundamentally chemical problems.

Perhaps the most perplexing aspect of smog production is the rapid conversion of NO to NO_2 in these systems. The ozonosphere restricts radiation at the surface of the earth to wavelengths greater than 3000 A., so direct photochemical decomposition is prohibited. The thermal reaction

$$2NO + O_2 \rightarrow 2NO_2 \qquad (2)$$

is much too slow under atmospheric conditions to be significant. Obviously, a very efficient photochemical process exists.

The possibility that singlet molecular oxygen is involved in this system was first discussed by Leighton (1961). Normal oxygen in its triplet ground state, $O_2(^3\Sigma_g^-)$ absorbs very faintly in the red end of the visible spectrum, as well as in the near infrared. These absorptions correspond to the very weak forbidden electronic transitions:

$$O_2(^3\Sigma_g^-) + h\nu(7578\text{ A.}) \rightarrow O_2(^1\Sigma_g^+) \qquad (3)$$

$$O_2(^3\Sigma_g^-) + h\nu(12{,}629\text{ A.}) \rightarrow O_2(^1\Delta_g) \qquad (4)$$

The wavelengths cited are for the O,O bands and correspond to 22.63 and 37.70 kcal. per mole for the $^1\Delta_g$ and $^1\Sigma_g^+$ states, respectively [for a discussion of spectroscopic and photochemical properties of molecular and atomic oxygen, see Calvert and Pitts (1966)].

On the basis of the very low absorption probabilities, the calculated short lifetime of the $^1\Sigma_g^+$ state at atmospheric pressure and the fact that in 1961 there was no direct evidence that either state of singlet oxygen reacted with hydrocarbons at room temperature, Leighton concluded that the role of singlet oxygen in the photochemistry of urban atmospheres was unimportant.

Subsequent developments in the spectroscopy (Khan and Kasha, 1963; Arnold, Ogryzlo, *et al.*, 1964) and the photochemical reactivity of singlet oxygen (Corey and Taylor, 1964; Foote and Wexler, 1964) now appear to invalidate the objections of Leighton (Gollnick, 1967; Gollnick and Schenck, 1967).

In 1964, Bayes demonstrated that singlet oxygen reacted with tetramethylethylene in the gas phase to give the same hydroperoxide as was produced in solution oxidation (Bayes, 1964; Winer and Bayes, 1966). On the basis of this experiment and calculations, Bayes concluded that singlet oxygen formed by direct absorption of solar energy, may "contribute significantly to the reactions of photochemical smog."

The present authors' hypothesis that singlet oxygen is important in photochemical smog accepts the view of Bayes that, once formed, singlet oxygen has a long lifetime even at atmospheric pressure, and that it exhibits a high degree of reactivity with olefins in the gas phase (or in heterogeneous systems). However, the authors avoid the problem of the small concentrations of singlet oxygen produced by direct absorption of radiation by proposing that a high yield of singlet oxygen can be obtained in a system in which solar radiation is absorbed, first by an organic molecule and then, on collision, the energy is transferred from this donor to normal oxygen to produce singlet excited oxygen. The over-all mechanism may be represented as

$$D(S_0) + h\nu \rightarrow D^*(S_1) \quad (5)$$

$$D^*(S_1) \xrightarrow[\text{crossing}]{\text{intersystem}} D^{**}(T_1) \quad (6)$$

$$D^{**}(T_1) + O_2(^3\Sigma_g^-) \rightarrow D(S_0) + O_2(^1\Delta_g \text{ or } ^1\Sigma_g^+) \quad (7)$$

$$O_2(^1\Delta_g \text{ or } ^1\Sigma_g^+) + \underset{\displaystyle H \quad H}{\overset{\displaystyle | \quad | \quad | \quad |}{-C=C-C-}} \rightarrow \underset{\displaystyle OOH}{\overset{\displaystyle | \quad | \quad |}{-C-C=C-}} \quad (8)$$

where D represents the donor organic molecule which absorbs the sunlight, and the symbols S_0 S_1, and T_1 represent the ground state and first excited singlet and triplet states, respectively.

The mechanism for producing singlet oxygen by transfer of electronic energy from the excited states of organic molecules was first proposed by Kautsky (1939) but went generally unnoticed. Recently, the discovery of singlet oxygen in the reaction of H_2O_2 and NaOCl (Khan and Kasha, 1963) revived the Kautsky proposal, and it now has general acceptance (Gollnick, 1967). Thus, for example, Kawaoka, Khan *et al.* (1967) calculated a high probability for the transfer of electronic energy from the donor triplet states to $O_2(^1\Sigma_g^+, ^1\Delta_g)$.

Examination of our mechanism shows that Reactions 5, 6, and 7, which produce $^1O_2$, replace the direct absorption processes suggested by Bayes (1964) and Winer and Bayes (1966). Actually, of course, the two mechanisms are not exclusive, but the authors feel that, particularly because of the low efficiency of the direct absorption of oxygen, the energy transfer mechanism is more important in urban air.

The donor molecule in the mechanism above could be any one of a variety of organic compounds that absorb radiation at wavelengths greater than the atmospheric cutoff of 3000 A. For example, if one makes a reasonable estimate of the concentration of polynuclear aromatic hydrocarbons in urban atmospheres, one can calculate that of the order of 25% of the photon flux in the region 3000 to 3200 A. is absorbed by such hydrocarbons (Begeman, 1964) (these calculations will be given in the full paper to be forthcoming shortly). This leads to a calculated rate of formation of singlet oxygen of the same order as the rate of formation of oxygen atoms from the photolysis of NO_2 in the atmosphere.

Acknowledgment

The authors thank Ed Schuck, Klaus Gollnick, and William Gleason for helpful discussions, and C. Bennett for skilled technical assistance.

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Gas Analysis by Polymer Chain Scission

Ozonolysis of Polystyrene

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■ The feasibility of gas analysis by random chain scission of linear polymers has been shown in principle. Polystyrene in carbon tetrachloride has been ozonolyzed. Random chain scission with an energy of activation of 28.5 kcal. per mole takes place. Under conditions used in the present work, 20 p.p.m. can be easily ascertained quantitatively. The sensitivity of this method can most likely be increased to 0.02 p.p.m. and experiments to this effect are in progress, in addition to experiments of shortening the reaction time and making the apparatus more convenient to handle.

Chemical reactions which lead to a few chain scissions in a polymer molecule are of negligible magnitude but are easily detectable owing to changes in the length of the threadlike polymer molecule (molecular weight). In principle, chain rupture should lend itself to analysis of minute amounts of gases which react with polymer molecules leading to chain scission.

The feasibility of using chain rupture for analytical purposes has been investigated in the case of ozone and polystyrene and is reported below. The only method for ozone determination, which has some similarity to the one proposed here, is one based on the effect of ozone on rubber held under tension. The time for the onset of surface cracking was taken as a measure of ozone concentration (Crabtree and Erickson, 1952).

In the present work, polystyrene in carbon tetrachloride is used as the polymer to be fragmented by ozone. This polymer is a sample polymerized thermally in the presence of a catalyst and is assumed to have a random molecular size distribution. All other reagents used in this work were of reagent grade.

Dry air containing small amounts of ozone was produced in an ozonator (03VI Ozonator, Ozone Research and Equipment Co.) with a flowmeter attachment. Ozone concentrations were determined by the KI method (Boelter, 1950).

Optimum conditions of sensitivity were not attempted in the present work, but the purpose was to determine if such a method is feasible. The apparatus is shown in Figure 1. Dry, ozonized air was passed from the ozonator to the evacuated reaction vessel, *F* (volume 4.785 liters corrected for the volume of the polymer solution), until the gas pressure was about 1 atm. The gas was then swept out of the flask with dry

A. Cooling coil
B. Stirrer
C. Temperature control
D. Thermometer
E Heater
F. Reaction vessel
G. Magnetic stirrer
H. Water bath
I. Dilution flask
J. Vacuum pump
K. Ozonator
L. Pressure reservoir
M. Air filter
N. Air pump

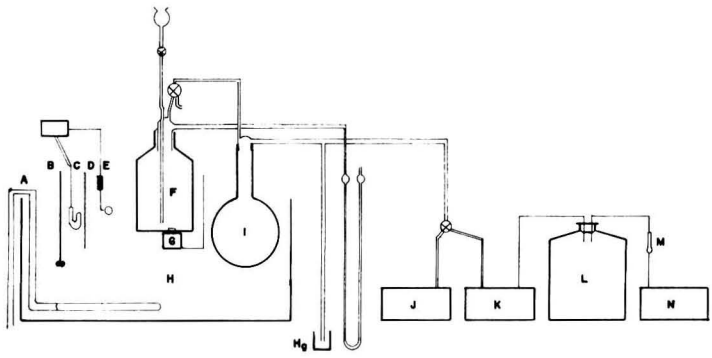

Figure 1. Ozonolysis apparatus

air and passed through an analytical KI solution. In this way, the total amount of O_3 in the vessel was ascertained. The reaction flask was then filled up again with ozonized air under the same flow and generating conditions. Four hundred milliliters of a 2% w./v. polystyrene solution in CCl_4 were then added and continuously stirred by a magnetic stirrer. Aliquots of 1 ml. each were withdrawn at definite time intervals. The intrinsic viscosity $[\eta]$ in (grams per dl.)$^{-1}$ was determined and plotted against reaction time for 25°, 35°, and 45° C. (Figure 2).

For a polymer sample of random distribution (M_w/M_n = 2), the following Mark-Houwink relationship is valid:

$$[\eta] = KM_n^{\gamma}$$

where M_n is the number average molecular weight; K, a constant; and γ, another constant, has been taken as 0.73, which is a reasonable average value of published data. Even if this constant is not quite correct, it will give values not too far out of line for the present purpose. The same is true for the constant K. Equation 1 leads to:

$$\frac{1}{[\eta]_t^{1/\gamma}} - \frac{1}{[\eta]_{t=0}^{1/\gamma}} = k_{tr} K^{-1/\gamma} = k_1 t \qquad (2)$$

or

$$\frac{1}{\overline{DP}_{n,t}} - \frac{1}{\overline{DP}_{n,0}} = k_{tr} M_1 K^{-1/\gamma} t = k_2 t \qquad (3)$$

where M_1 is the molecular weight of the monomer and k_{tr} the random degradation rate constant. The rate constant, k_1, was derived from the initial parts of the $\frac{1}{[\eta]_t^{1/\gamma}} - \frac{1}{[\eta]_{t=0}^{1/\gamma}}$ time plots, and its values are given below:

° C.	25°	35°	45°
k_1(hour^{-1})	8.00×10^{-2}	2.86×10^{-1}	1.60

An Arrhenius plot gave a very good straight line, yielding an energy of activation of 28.5 kcal. per mole. The energy of activation for the initial stages of oxidation of polystyrene is 25.2 kcal. per mole (Jellinek, 1949). Lacau and Magat (1947) found for the initial stages of oxidation of GR-S (oxidative scission) in toluene 20 to 25 kcal. per mole. Experiment, using KI solution, showed that ozone was completely used up after reacting for 48 hours with the polymer at 25° C.

One experiment was carried out to obtain an estimate of the sensitivity of the method under the prevailing conditions. For this purpose, flask *I* (Figure 1) was filled with ozonized air to a pressure of 0.66 atm. The flask plus dead space had a

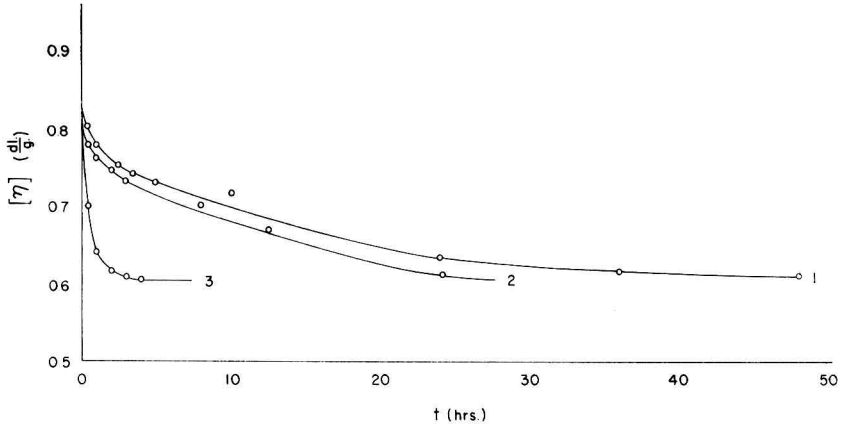

Figure 2. Intrinsic viscosity as function of reaction time and temperature: 1, 25°; 2, 35°; 3, 45° C.

volume of 5.95 liters. This mixture was then flushed with dry air through analytical KI solution. The amount of ozone obtained in this way was 7.50×10^{-5} mole. Flask *I* was then filled up again to 0.66 atm. under the same flow and generating conditions. A certain amount of ozonized air was introduced from flask *I* to the reaction flask *F*, and the latter was filled up with dry air to 1 atm. The amount introduced from flask *I* to flask *F* could be ascertained from the pressure decrease in flask *I*. Four hundred milliliters of 2% w./v. of polystyrene in CCl_4 were then introduced into flask *F* and exposed to the ozonized air for 48 hours under stirring at constant temperature (25° C.), and the intrinsic viscosity was determined. The reason for the determination of the ozone concentration before dilution is the decrease in accuracy of the KI titration method at low ozone concentration. The average number of chain scissions each original chain molecule has suffered is given by,

$$s = \left(\frac{[\eta]_{t=0}}{[\eta]_t}\right)^{1/\gamma} - 1 \tag{4}$$

The over-all number $\bar{\phi}$ of O_3 molecules needed for each break, calculated for the end of the reaction (48 hours at 25°) is given by:

$$\bar{\phi} = \frac{N_{O_3}}{N_O s} = \frac{N_{O_3}\,\overline{DP}_{n,0}}{s n_0} \tag{5}$$

where N_{O_3} and N_O are the total moles of O_3 and chain molecules, respectively, in the reaction flask *F*. N_O is given by $N_O = \frac{n_0}{\overline{DP}_{n,0}}$, where n_0 is the total number of monomeric unit moles of polystyrene available and $\overline{DP}_{n,0}$ the initial number average chain length; the latter can be obtained from the following relationship:

$$[\eta] = K'(\overline{DP}_{v,0}M_1)\,\frac{dl}{g} \tag{6}$$

where $\overline{DP}_{v,0}$ is the initial viscosity average chain length, the γ value is the same as in Equation 1. The K' value has been chosen as $K' = 1.06 \times 10^{-4}$. For a random distribution

$$DP_{v,0} = \overline{DP}_{n,0}\{(\gamma + 1)\Gamma(\gamma + 1)^{1/\gamma}\} \tag{7}$$

In this case, $\overline{DP}_{v,0} = 2.34 \times 10^3$ and $\overline{DP}_{n,0} = 1.26 \times 10^3$. The experimental results are given below: $[\eta]_{t=0} = 0.826$

Molar Ratio, O_3/Air	O_3, P.P.M.	$[\eta]_{t=48\ hr.}$	$s_{t=48\ hr.}$	$\bar{\phi}_{t=48\ hr.}$ O_3 Molecules/Break
7.2×10^{-4}	1195	0.610	0.50	4.60
2.55×10^{-5}	40.2	0.785	0.07	1.18

Apparently, $\bar{\phi}$ approaches the value of one with increasing dilution. The sensitivity of the method under prevailing conditions is about 20 p.p.m.

That certain fractions of links are re-formed at higher concentrations of ozone is not unlikely; this would account for the increase in $\bar{\phi}$ with concentration. If recombining is assumed, then the number of links broken in the total system at the end of the reaction, when all ozone is used up, is given by

$$N_O s = N_{O_3}(1 - \bar{f}) \tag{8}$$

where N_{O_3} is the total number of moles of ozone in the system and $\bar{f}$ is the over-all fraction of O_3 molecules not breaking links. Further, the over-all number of O_3 molecules—in contrast to the instantaneous number at time, *t*—needed for each break is given by $\bar{\phi}$. The number of O_3 molecules not breaking links is then $\bar{\phi} - 1$ and the fraction of O_3 molecules not leading to scission is $(\bar{\phi} - 1)/\bar{\phi} = \bar{f}$. Hence, Equation 8 becomes

$$N_O s = \frac{1}{\bar{\phi}}\,N_{O_3} \tag{9}$$

Further, since $N_O s = \frac{n_0}{DP_{n,0}}$, the average number of breaks in each original chain is

$$s = \frac{N_{O_3} DP_{n,0}}{n_0\,\bar{\phi}}$$

or

$$s = \frac{[N_{O_3}]\,\overline{DP}_{n,0}\,V_{\text{flask }F}}{[n_0]\bar{\phi}V_{\text{polymer solution}}} \tag{10}$$

The terms in brackets represent molar concentrations.

Equation 10 shows clearly that in order to obtain, on the average, more chain scissions per original chain molecule for a given O_3 concentration, the concentration of the polymer has to be decreased, the chain length has to be increased, the volume of the polymer solution has to be decreased, and the volume of the reaction flask has to be increased. A 10-fold increase in chain length (a polymer fraction is preferable) combined with a 10-fold decrease of the volume of the polymer solution with a tenth of the concentration used here would increase the sensitivity of the method by a factor of 1000. This would increase the sensitivity to 0.02 p.p.m. of O_3. The safe limit for humans is about 0.15 to 1 p.p.m. From previous knowledge of random degradation reactions (Jellinek, 1955) there is no doubt that the sensitivity can be suitably increased and experiments to this effect are in progress.

The apparatus could eventually be made of more convenient dimensions. The only unfavorable point in the analysis is the length of time at 25° C. needed for the reaction; however, one could work at 85° C., which would cut the reaction time to about a couple of hours. Another possibility would be to select a polymer more susceptible to ozonolysis; however, at the same time, the polymer would also become more sensitive towards oxygen.

Therefore, the proposed method appears sensitive and accurate enough for analysis of ozone in the atmosphere.

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Nucleation of Crystalline Phases from Sea Water and Sea Water Concentrates

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■ When sea water is heated rapidly in a pressure vessel, a whisker-like crystalline phase forms at 180° C. These whiskers redissolve rapidly at high temperatures if the reaction vessel is cooled immediately; but, if the temperature is held at 140° to 180° C., they break up into short fat needles, which redissolve slowly at room temperature. X-ray analysis showed that the needles recovered from a typical experiment were anhydrite ($CaSO_4$).

To make exploratory observations on the nucleation of crystalline phases in sea water and sea water concentrates, a small pressure vessel (~0.2 cc.) equipped with a viewing window was constructed (Figure 1). The vessel was heated on a microscope hot stage equipped with a temperature controller. The optical setup shown in Figure 2 was used to observe and photograph the interior of the vessel.

Observations were made on sea water and on mixtures of sea water with a brine obtained by concentrating sea water about six times (nominal 6× brine, Shaffer, 1967). When sea water was heated rapidly (1° to 4° per minute), very long thin needles would form in the liquid at ~185° C. (Figure 3, *A* and *B*). When brine samples were heated, these needles were not always seen, but often a shorter fatter type of crystal appeared. If samples containing the very long thin needles were cooled immediately, these needles redissolved rapidly at temperatures ranging from 131° C. (sea water) to 149° C. (3× brine).

If the samples were repeatedly reheated, or if they were held at 185° to 190° C. for an appreciable length of time, a different kind of crystal formed (Figure 3, *C* through *F*). The new material was also needle-like, but the needles were relatively short and fat and did not redissolve rapidly when the sample was cooled. By taking advantage of this in a separate experiment, a small quantity of the more stable crystals could be recovered. X-ray examination showed that they were an-

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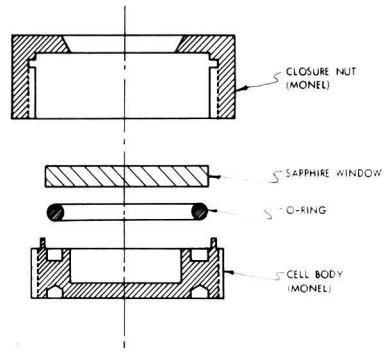


Figure 1. Nucleation test cell

To scale: cell diameter = 1.10 cm., viewing window = 1.03 cm.

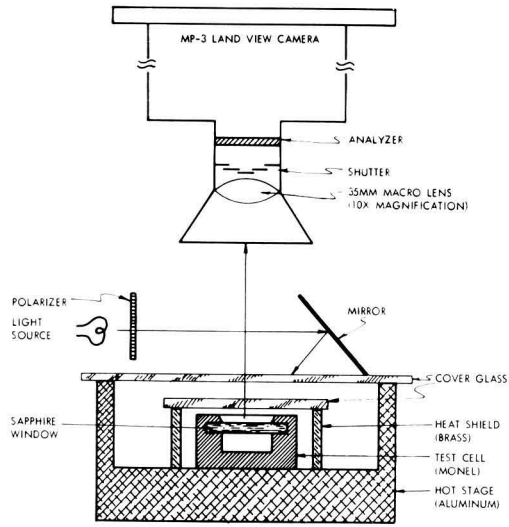
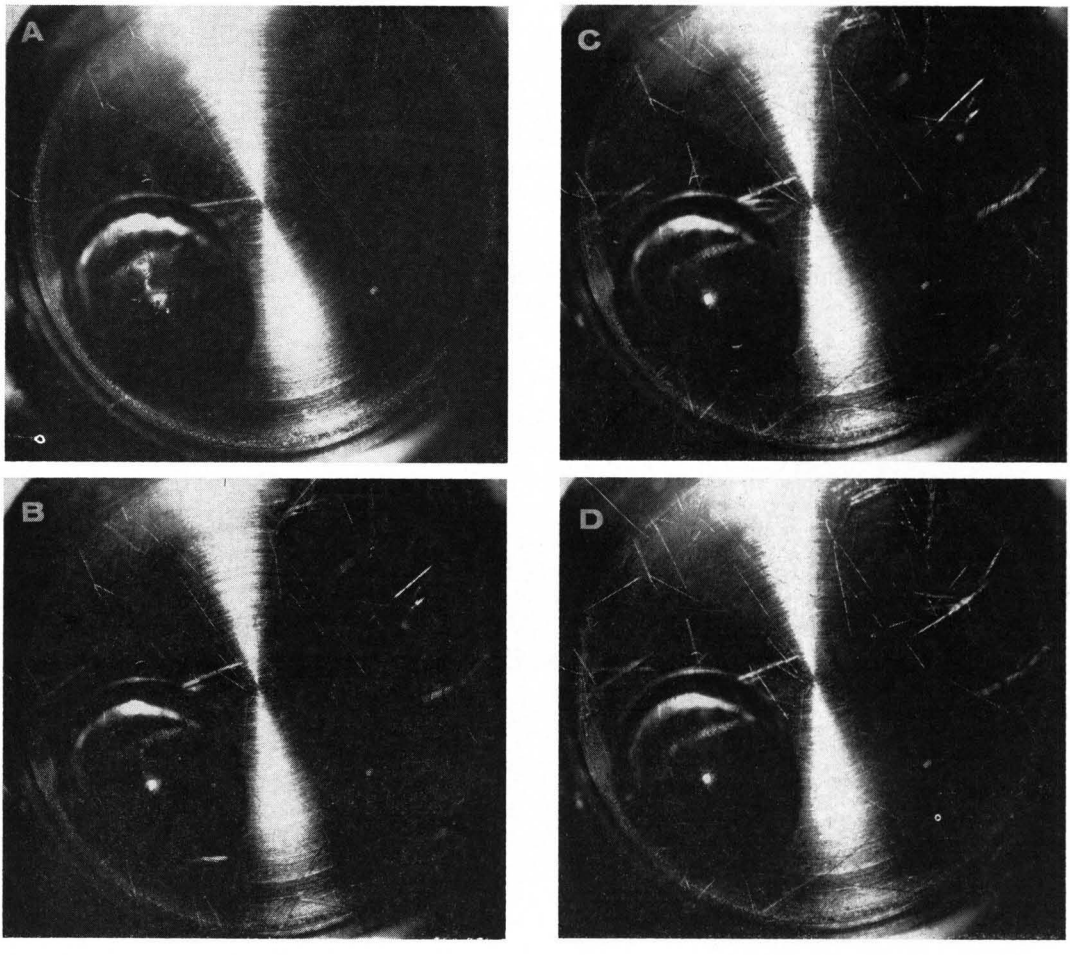


Figure 2. Optical system for nucleation experiments



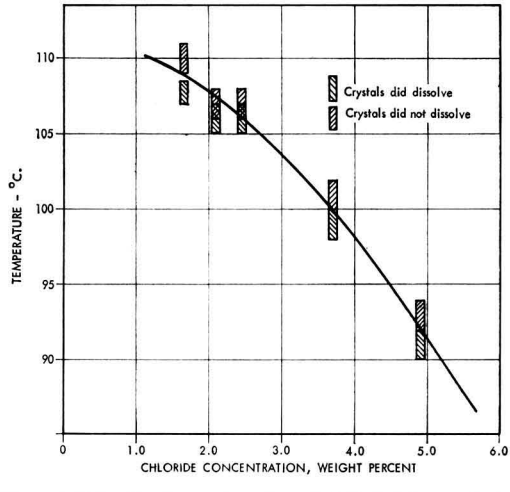


Figure 4. Saturation temperatures for anhydrite in brines made by mixing sea water with a 6× concentrate

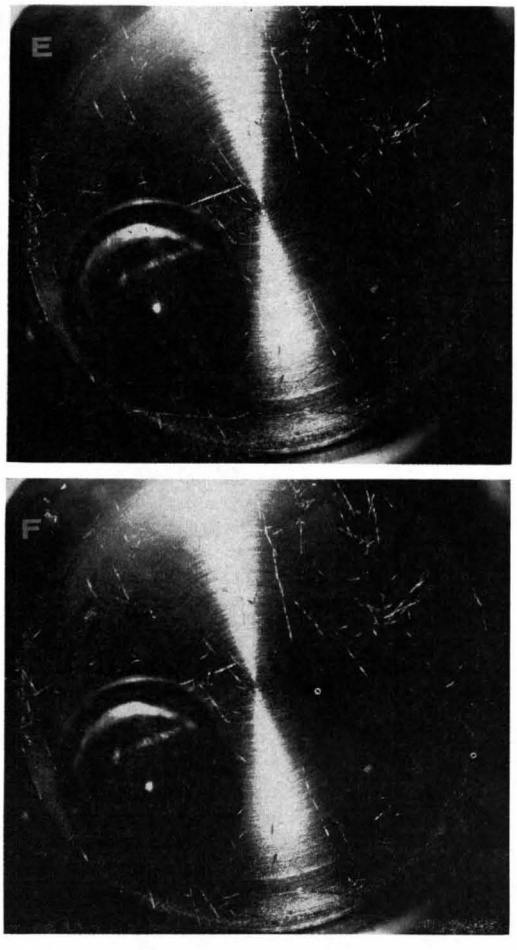


Figure 3. Nucleation experiment

Sea water at 190° C.

These photographs are time exposures of about 1-min. duration

- ***A.*** **Interior of vessel after 1 to 2 min. Note extremely long whiskers**
- ***B.*** **After 5 min. Note extremely long whiskers; the blurs are crystals which are moving or falling to the bottom of the vessel**
- ***C.*** **After 15 min.**
- ***D.*** **After 20 min. Crystals are beginning to convert to a second form**
- ***E.*** **After 30 min. Partial conversion to second form**
- ***F.*** **After 50 min. Conversion appears to be completed**

hydrite. The authors found no way to recover the extremely long thin needles which formed at first, and therefore no definitive identification was possible.

In a series of experiments in which the fat needles were induced to form in various brines having chloride contents ranging from 1.66 to 4.90%, the temperature at which the crystals would just dissolve in approximately 16 hours was observed. The saturation temperatures thus determined are plotted as a function of the chlorinity of the brine in Figure 4. The points at 1.66 and 4.9% Cl correspond to compositions that also were studied by Hara *et al.* (1932, 1934). For comparison, the solubility products were calculated from the known composition of the authors' brines, and the results are compared with the data reported by Hara *et al.* in Table I. The authors' solubility product values are somewhat lower than the values reported by Hara *et al.* It appears desirable, therefore, to remeasure the actual solubilities of anhydrite in sea water and sea water concentrates.

Table I. Solubility Products for Anhydrite in Sea Water

Brine, %Cl^-	Calcium Molality	Sulfate Molality	Saturation Temperature	Molal Solubility Product
1.66	0.913×10^{-2}	2.54×10^{-2}	106.5	2.32×10^{-4a}
1.63	1.17×10^{-2}	2.72×10^{-2}	106.5	3.18×10^{-4b}
4.90	$1.32_5 \times 10^{-2}$	6.51×10^{-2}	92	8.63×10^{-4a}
4.96	1.72×10^{-2}	6.84×10^{-2}	92	11.7×10^{-4b}

[a] Deduced from compositions of test brines (Shaffer, 1967).
[b] Calculated from cross plot of data reported by Hara *et al.* (1932, 1934).

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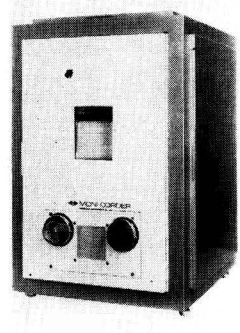

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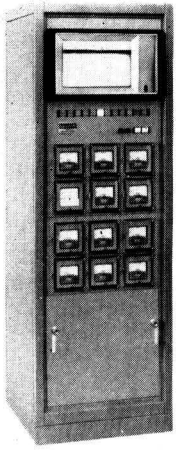

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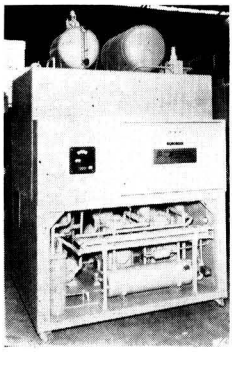

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Model 80TS automatic tape sampler for measurement of particulates in air has been added to the Unico line of automatic air samplers, reagents, and color standards. Also available: gas detector tubes, pumps, filter holders, microimpingers, and other equipment. Union Industrial Equipment Corp. **73**

Test Specific for NO_2

A stable formula sensitive only to NO_2 is the basis for a test providing quantitative measurement of nitrogen dioxide. Measurements are accurate from 0.5 p.p.m. up and are determined by attached colorimetric scales on a concentration/exposure time basis. Resource Control, Inc. **74**

Two-Thermistor Indicator

A battery-powered, panel-mounted psychrometer (wet and dry bulb measurements) features remote-reading thermistor sensors with a built-in aspirator and water supply system. The two readings can be made in less than 60 seconds within 0.5% accuracy of actual relative humidity over most of range (70° to 170° F.). Atkins Technical, Inc. **75**

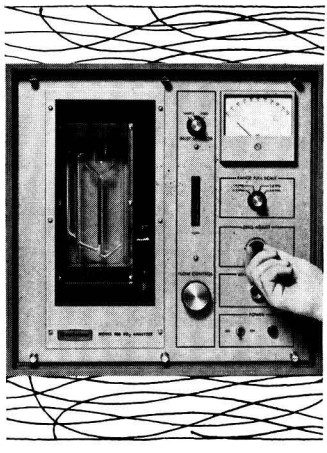
Clean Benches

A line of lab benches which remove airborne contaminants down to 0.03 micron size includes seven floor and table-top models of crossflow, downflow, recirculating, and suction-exhaust types. Each unit provides 14 cu. ft. of unobstructed clean work area, 200 foot-candle glareproof illumination, and an electrical outlet. Envirco, Inc. **76**

Gas Chromatograph-Trace Gas Analyzer

Ultrasensitive dual helium detectors provide precise separation and detection of most gases and vapors in the p.p.b. range, without preconcentration. A regulated dual 400-volt power supply, dual columns, a gas purification system, and a special gas sample introduction device are all standard with the instrument, and provide increased sensitivity. Varian Aerograph. **77**

Specific, simple SO_2 monitoring from Beckman.



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NEW LITERATURE DIGEST

Total organic carbon analyzer. A 4-page folder describes Model 634-900 total organic carbon analyzer for liquid samples. According to the company the unit features direct readout, automatic operation, solid state design, 3-minute analysis time, and strip chart recording outlet for attachment of a recorder, if desired. Laboratory Equipment Corp. **78**

Solids-liquid separation. *Filter Facts,* a factsheet issued periodically, highlights recovery of copper, a filter plate, and a filter for centrifugation in its June issue. T. Shriver & Co., Inc. **79**

Instruments. An illustrated 20-page catalog lists a variety of instruments for the detection of gaseous and liquid pollutants, as well as valves, pumps, alarms, impingers, regulators, and other laboratory equipment valuable in environmental quality control. Union Industrial Equipment Corp. **80**

Corrosion resistant equipment. Catalog C advertises chemical resistant equipment such as exhaust hoods, fans, tank heaters, tanks and liners, ducts and stacks, fume scrubbers, plastic pipes and fittings, and special flooring materials. Heil Process Equipment Corp. **81**

Dust/fume collectors. Catalog No. 2.1 on swirl-orifice dust and fume collectors and catalog No. 3.1 on vertical rotor dust and fume collectors are available. United Sheet Metal Co., Inc. **82**

New quarterly index. *ISA Instrumentation Index,* the first issue of which appeared in May 1967, is available by subscription. Instrument Society of America. **83**

Air pollution. *Air Pollution: The Facts* is an 8-page folder setting forth some thoughts on the sources, harmful effects, and methods of controlling air pollution. National Tuberculosis Association. **84**

Activated carbon filters. Catalog SD-1000 is an illustrated 4-page folder describing an activated carbon filter with 12 removable carbon cartridges. Steffey Metal Products, Inc. **85**

Sulfur recovery. *Clean Air-Pure Sulfur* is a full-color, 8-page brochure that gives the design and operating details of sulfur recovery units designed to control air pollution from hydrogen sulfide gas. Petrochemical plants, oil refining and processing plants, and other process industry installations are described in the publication, too. Ford, Bacon & Davis Texas, Inc. **86**

Thermogravimetric analysis. Bulletin 10-560-100 describes a modular system for micro-thermogravimetric analysis, which the makers claim is easily adapted for differential thermal analysis and derivative thermogravimetric analysis. Fisher Scientific Co. **87**

Gas chromatography: integration methods. The July issue of *Previews and Reviews* highlights analog to digital conversion (integration) for quantitative gas chromatography. A simple ball and disc integrator, manual methods, and an electronic digital integrator are discussed. Varian Aerograph. **88**

pH electrodes. A 12-page, illustrated product bulletin presents a line of pH electrodes and buffer solutions. Fisher Scientific Co. **89**

Specific ion meter. Model 401 portable specific ion meter is described in a 4-page folder. The meter has zero drift, photomodulator circuitry, and a tautband mirror scale to eliminate parallax. The instrument provides direct readout of ion activities as well as conventional pH and millivolt measurements. Orion Research, Inc. **90**

Vortex burners. Bulletin 129 illustrates and describes short flame, high-heat-release burners for use in air heaters, furnaces, dryers, kilns, incinerators, and submerged combustion equipment. Heat release rates range from 1.3 to 60 million B.t.u./hr. Thermal Research & Engineering Corp. **91**

Liquid filters and separator/filters. Bulletin 290.1 lists with specifications a complete line of filters used to remove solid matter suspended in liquids. Bulletin 390.1 details the complete line of filters for liquid/liquid separations. Each includes applications, and sizing and selection procedures. Fram Corp. **92**

Flow finder. A 2-page bulletin (D-100) describes a low-flow indicator for determining whether small amounts of water are leaking through a plumbing system. The Flow Finder enables water utilities to show their customers that undetected leaks may be contributing to high water bills. Badger Meter Mfg. Co. **93**

Recovery systems. A comprehensive program for the purchase or leasing of complete vapor or liquid chemical waste recovery systems is presented in bulletin 767. Mercury Chemical Corp. **94**

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Balancing environmental quality against cost

Environmental Quality in a Growing Economy. Edited by Henry Jarrett. xv + 173 pages. The Johns Hopkins Press, Baltimore, Md. 21218. 1966. $5.00, hard cover. *Lloyd M. Cooke is assistant director of Union Carbide Corp.'s Food Products division, Chicago, Ill. Dr. Cooke also serves as Chairman of the Subcommittee on Environmental Improvement of the ACS Committee on Chemistry and Public Affairs.*

By Lloyd M. Cooke

Many chemists and engineers concerned with problems related to pollution and its abatement are either so deeply committed to highly specialized problems or so polarized by defensive bias or by zealous conservationism that they seldom delve into other vitally important aspects of environmental quality. Consequently, they should welcome this series of 12 essays by economists, geographers, lawyers, and medical scientists who probe the fundamental question, "What quality of environment do Americans want and how much are they willing to pay for higher quality in dollars and effort."

The essays evolved from the 1966 Annual Forum sponsored by Resources for the Future (RFF), a nonprofit corporation for research and education in the development, conservation, and use of natural resources. The authors, all of whom bear excellent credentials, are used in an interesting manner. They are paired so that one expert presents a thesis and a second expert speaks to, about, or in addition to the first expert's thesis. The technique provides a built-in critique that engenders a reassuring feeling for comprehensiveness.

Henry Jarrett, editor of the compilation of essays and Director of Publications for RFF, provides broad-stroke summaries of each of the essays in the introduction. His summaries capture the spirit and the sense of each of the essays so realistically that they are excerpted freely in the following description of the contents.

Resources Development and the Environment is the heading for essays by Kenneth E. Boulding, economist (University of Michigan, Ann Arbor) and Harold J. Barnett, economist (Washington University, St. Louis) entitled *The Economics of the Coming Spaceship Earth* and *Pressures of Growth upon Environment,* respectively. These two essays open the inquiry with a broad look at how development of natural resources has affected the environment and may be expected to affect it in the future. Mr. Boulding sees the advance of technology and the growth of population as forces that are making it increasingly plain that the planet Earth is a self-contained spaceship with diminishing new sources of materials and less and less room for disposal of wastes. And he questions the familiar idea that continuingly increasing production and consumption of goods are in themselves desirable.

Dr. Barnett explores the effects of economic growth upon the natural environment, and asks whether the ideal of a competitive self-regulating market will be as useful in the decades ahead as it was in the nineteenth century and the first part of the twentieth.

Health and adaptability

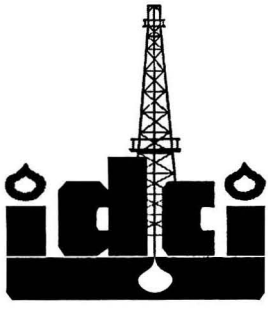
Under the heading *Environment and Human Health,* René Dubos, microbiologist (Rockefeller Institute) discusses *Promises and Hazards of Man's Adaptability* and Leonard Duhl, psychiatrist (consultant to Department of Housing and Urban Development), *Mental Health in an Urban Society.* René Dubos sees a crucial problem in the contrast between man's biological stability and his formidable capacity to form new social and cultural patterns and to survive, at least for many years, under new conditions. Because of man's adaptability some apparently harmless effects of urban living may begin to take their toll decades later and in indirect ways. Furthermore, who can say whether man's remarkable capacity to adapt will always carry him in what by present values appear to be desirable directions?

Leonard J. Duhl, interested mainly in mental health, sees, along with Dr. Dubos, the spread of urbanization as the central issue. Fragmentation, he believes, causes much of the difficulty—a tendency to take a piecemeal approach instead of viewing the complex problem of city living as a whole. As things stand, municipal agencies are intent on only their particular programs and individuals are subject to conflicting pressures from many quarters. He sees need for new institutions to put the bewildering pieces of the picture together.

Economic problems

The fact that many of the economic problems of environmental quality are caused or aggravated by lying outside the market economy raises many problems and possibilities that have not been well explored, according to Ralph Turvey, economist (Britain's Electricity Council) and Roland N. McKean, economist (U.C.L.A.) in essays entitled *Side Effects of Resource Use* and *Some Problems of Criteria and Acquiring Information* under the main heading *Beyond the Market Mechanism.* Mr. Turvey employs a series of examples wherein realistic measurements of gains and losses are insufficient (even when measurable) to pinpoint the right course of action. He concludes that each case must be considered on its merits and that these should be set out in economic terms as far as possible. Administrators should consider alternatives to direct regulation, economists should not exaggerate the applicability of tax devices, and both should remember that

if you have an industrial waste pollution problem . . .



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questions of fairness require legal or political decision. Dr. McKean probes more deeply into external costs, especially with regard to acquiring data needed to resolve problems created by the side effects of resource use.

Economic Research in Problems of Environment is discussed by Allen V. Kneese, economist (director of research on environmental quality for RFF) and M. Mason Gaffney, economist (Wisconsin). Dr. Kneese in *Research Goals and Progress Toward Them* cites a number of examples of economic research projects now under way by public and private agencies. This essay provides valuable perspective to the noneconomist on evaluation studies concerned with the following:

- The willingness of individual decision units (municipalities, industries, and individuals) to pay for the avoidance of damages.
- What the cost would be to those decision units that found it necessary to take mitigating action to reduce external costs.

Dr. Gaffney's essay both reinforces and extends Dr. Kneese's thesis. He explores some of the general problems of environmental research in the light of welfare economics and supplements Dr. Kneese's findings in research gaps with further suggestions of urgently needed lines of inquiry.

Public attitude

An essay by Gilbert F. White, geographer (Chicago) on *Formation and Role of Public Attitudes* is paired with one by David Lowenthal, geographer and historian (American Geographical Society), on *Assumptions Behind the Public Attitudes.* These essays speak to the point that modern man has a wide range of choices which must be made without the aid of the semi-automatic functioning of a market and this heightens the importance of public attitudes that affect political and private action. How such attitudes are formed, how they may be measured, and how they convert into action are discussed in interesting detail by Dr. White. Here a geographer draws upon the counsel of social psychologists to describe a broad field which is in the process of changing from an art to a science, noting the progress made and defining the large amount of work to be done. Dr. Lowenthal, as might be expected from a historian, comments mainly on the nature and significance of assumptions that underlie attitudes toward the environment and thereby focuses on an aspect of the problem antecedent to those discussed by Dr. White.

Strategy proposed

The collection of essays ends logically with *Some New Machinery to Help Do the Job* by Jacob H. Beuscher, lawyer (Wisconsin), following a paper by Norton E. Long, professor of government (Brandeis) entitled *New Tasks for All Levels of Government.* The two writers refer to the fact that many of the nation's current policies and institutions date from times of simple technology and a small rural population. Thus many new tasks confront national, state, and local governments that are unprepared to handle them apart from their interaction under a federal system.

The leadership of the Federal Government in improvement in the quality of environment is documented, and, in a sense, justified by Dr. Long. Dr. Beuscher concurs that the dominant role must be played by the Federal Government, but also assigns important secondary roles to the states. To achieve this objective he suggests some new kinds of government machinery that might be used, including joint boards and compacts for interstate action, methods of operation in metropolitan regions, and the role of the state courts.

Scientists will doubtlessly be best served, and perhaps most impressed, by the information provided by the Kneese-Gaffney essays on economic research and the White-Lowenthal essays on public attitudes. All four essays refer to numerous excellent primary sources (as evidenced by a few randomly selected by the reviewer).

The editor concludes his introduction by remarking at one point that "this book leaves out more than it puts in." However, for the chemist and sanitary engineer directly or indirectly concerned with problems of environmental quality, this book fortuitously omits most of that with which they are familiar and provides a broad collection of analysis and research findings on other salient pieces of the problem by scholars who speak from many years of experience.

MEETING GUIDE

September 6–9
Society of Mining Engineers of AIME, and Rocky Mountain Minerals Conference

SME Fall Meeting

Las Vegas, Nev.

Technical papers will be presented on solid fuel in pelletizing shaft furnaces, sulfur recovery from coal and flue gases, methane monitoring in coal mines, and acid mine drainage, among other topics.

September 10–15
American Chemical Society

154th National Meeting

Chicago, Ill.

The Division of Water, Air, and Waste Chemistry will present, in joint efforts with other Divisions, discussions of scientific information resources for the water researcher; water resources; and adsorption from aqueous solutions. For detailed program, please see ES&T, July, pages 591–2. A symposium on experience with pollution control equipment (joint with the Division of Petroleum Chemistry) and the Division's general papers are detailed on pages 673–4 of this issue. Other programs of interest planned are **Foam Fractionation** by the Division of Industrial and Engineering Chemistry and **Microbial Waste Treatment** by the Division of Microbial Chemistry and Technology.

September 11–14
Instrument Society of America

22nd Annual International Instrument-Automation Conference

Chicago, Ill.

Concurrent with the conference are symposia on data handling and computation, measurement standards, and physical and mechanical measurement instrumentation. The conference will highlight the areas of automation, biomedicine, and food.

September 12–14
Polytechnic Institute of Brooklyn and Naval Applied Science Laboratory

Materials-Key to Effective Use of the Sea

Statler Hilton Hotel, New York, N.Y.

Current research and development programs and materials problems will be emphasized the first day; the behavior of materials in ocean environments will be summarized the second day; and materials technology in the ocean engineering field will be discussed on the third day.

September 18–22; 25–27; October 2–December 11
Cleveland State University

Water Pollution Control

Stilwell Hall, Cleveland State University, Cleveland, Ohio

Designed to assist people who have had some technical training in better understanding the problems and developments in water pollution control, three separate programs have been set up at Cleveland State University. The Sept. 18–22 session will feature biological and chemical laboratory procedures in water pollution control. Fee: $75. The Sept. 25–27 session will feature an institute on technical aspects of water pollution control (lectures only). Fee: $50. The session beginning on Oct. 2 and continuing on Monday afternoons through Dec. 11 is a seminar series on selected topics in water pollution control. Seminar fee: $50. For further information contact Dr. Paul Olynyk, Chemistry Dept., Cleveland State University, Cleveland, Ohio 44115.

September 21–22
Illinois Basin Section of the Society of Petroleum Engineers of AIME

Midwest Regional Meeting

McCurdy Motor Hotel, Evansville, Ind.

Technical papers will be presented on new logging techniques, new tools to be used in gas storage, automation in oil field operations, and the application of oil field technology to industrial fluid disposal problems, among others.

September 24–27
American Institute of Chemical Engineers and Instituto Mexicano de Ingenieros Quimicos

2nd Joint Meeting

Hotel Maria Isabel, Mexico City, Mex.

There will be symposiums on air and water pollution as well as on the prediction of thermodynamic and transport properties, separation and purification by crystallization from the melt, on-line computer control, and others.

October 1–4
Society of Petroleum Engineers of AIME

42nd Annual Fall Meeting

Sam Houston Coliseum and Music Hall, Houston, Tex.

There will be sessions on water treatment, gas well testing and nuclear stimulation, reservoir analysis, and thermal recovery, among others.

October 1–6
American Institute of Planners

50th Year Conference: The Future Environment of a Democracy

Shoreham Hotel, Washington, D.C.

This multidisciplinary leadership conference is Part II of the Institute's two-year national consultation to try to create a better awareness of what might happen in the future and, therefore, to consider the impact that current decisions might have upon it. The role of the individual and the community in problems related to housing, transportation, urban form, resources, manpower, and population are a few of the topics to be discussed.

October 2–6
National Institutes of Health

17th Annual Instrument Symposium and Research Equipment Exhibit

National Institutes of Health, Bethesda, Md.

The instrument symposium will include discussions of holography, laboratory computer usage, ultramicroanalytical techniques, new frontiers in spectroscopy, thermoanalytical methods, low-temperature luminescence, and molecular separation by size and charge. The exhibit (which ends Oct. 5) will include examples of the latest types of research equipment available from instrument manufacturers.

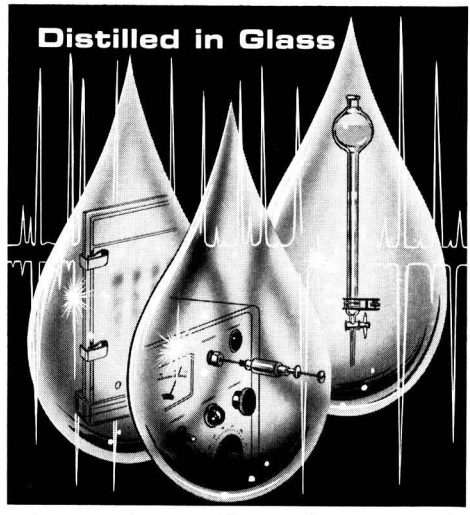
October 8–13 and 15–18
Water Pollution Control Federation

40th Annual Conference

Hotel Americana, New York, N.Y. (Oct. 8–13)

Puerto Rico Sheraton Hotel, San Juan, Puerto Rico (Oct. 15–18)

The meeting will take place in two sessions. The first will take place in New York City from October 8–13; the meeting will reconvene in San Juan, Puerto Rico, from October 15–18. The New York sessions will include a special symposium on water quality analysis as well as sessions on water quality standards, industrial wastewater research, estuary problems, nutrient removal, and like topics. The Puerto Rico sessions will be concerned with refinery waste treatment, refinery wastes effect on marine biology, open-pit mines, rum distillery wastes, and other problems.



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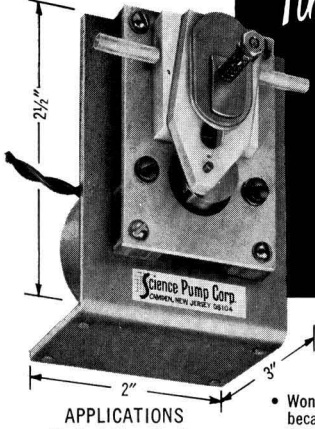

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MEETING GUIDE continued

October 9–12
Association of Official Analytical Chemists
81st Annual Meeting

Marriott Motor Hotel, Washington, D.C.

Methods, instrumentation, and techniques for analysis of feeds, fertilizers, pesticides, food additives, hazardous substances, and other materials, will be discussed. There will be a special symposium on drugs.

October 16–20
American Society of Civil Engineers
Water Resources Engineering

Statler Hilton Hotel, New York, N.Y.

Water resources planning, urban planning, water power and service continuity, flood damage reduction, pipeline design, tidal hydraulics, water regulation and rights, river and lake control, and weather modification will be discussed during the first three days of the meeting. Low flow hydrology, dams, drought, ground water, eutrophication, and watershed management are among the topics to be presented during the final two days.

October 23–24
Metropolitan Engineers Council on Air Resources (MECAR)
New Developments in Air Pollution Control

Commodore Hotel, New York, N.Y.

The two-day technical symposium will emphasize major developments in the areas of recovery of sulfur oxides from stack gases, control of noxious gaseous emissions, control of particulate emissions, and control of solvent emissions. Attendance is limited and will be by preregistration only, $15.00 per person. Contact Robert A. Fox, P.O. Box 607, Grand Central Post Office, New York, N.Y. 10017.

October 23–24
1967 Cleaner Air Exposition

Commodore Hotel, New York, N.Y.

The exposition is held in conjunction with the nationwide observance of Cleaner Air Week, October 22–28. It will feature exhibits by manufacturers of air pollution control equipment, publishers of air pollution control literature, consulting and engineering services, and air pollution control agencies.

October 23–27
American Public Health Association
95th Annual Meeting

Fontainebleau Hotel, Miami Beach, Fla.

A special session on environmental health will cover man-made environmental hazards and what can be done to restore the environment. Another featured session will be on the maximum social use of land, air, and water resources. Other topics include respiratory diseases in industry, use and control of radiation in clinical medicine, health problems in the aerospace industry, noise and its impact on health, laboratory analytical methods in environmental surveillance, environmental epidemiology, and comprehensive environmental health planning.

Symposiums on Air Quality Set for September

The 154th National ACS Meeting in Chicago will feature (Monday, Sept. 11) a joint symposium of the Divisions of Petroleum Chemistry and Air, Water, and Waste Chemistry on the subject of Experience with Pollution Control Equipment. General papers of the Division of Air, Water, and Waste Chemistry will be presented during the remainder of the week. See pages 591–2 (ES&T, July) for other meetings of interest

SYMPOSIUM

Experience with Pollution Control Equipment

J. K. Patterson, Presiding

MONDAY MORNING (SEPT. 11)

9:30–9:40 **J. K. Patterson.** Introductory Remarks.

9:40–10:10 **P. W. Spaite.** Development of Limestone Based Processes for Sulfur Oxide Control.

10:10–10:40 **J. H. Field, J. G. Myers, J. W. Mulvihill, and H. W. Wainwright.** New Potential Absorbents for Sulfur Oxides Removal from Flue Gas.

10:40–11:10 **P. R. Ryason and J. Harkins.** A Method of Removing Potentially Harmful Oxides from Combustion Gases.

11:10–11:35 **W. F. Arey, Jr., and F. X. Mayer.** Desulfurization of Residual Fuel Oils.

11:35 **S. W. Dickey and C. W. Phillips.** Refinery Air Pollution Practice Problems.

MONDAY AFTERNOON (SEPT. 11)

F. N. Kemmer, Presiding

2:30–2:40 **F. N. Kemmer.** Introductory Remarks.

2:40–3:00 **R. J. Leak, J. T. Brandenburg, and M. D. Behrens.** Use of Alumina-Coated Filaments in Catalytic Mufflers. Part I: Testing with Single Cylinder Engine.

3:00–3:30 **R. J. Leak, J. T. Brandenburg, and M. D. Behrens.** Use of Alumina-Coated Filaments in Catalytic Mufflers. Part II: Testing with Multi-Cylinder Engine and Vehicles.

3:30–4:00 **R. G. Larsen.** Biological Treatment in Water Conservation.

4:00–4:30 **J. F. Marten and E. W. Catanzaro.** The Design and Operation of a Continuous Multiple Simultaneous Analyzer for Water Quality Control.

4:30 **J. J. Hickey.** Analytical Techniques for Water Pollution Control in the Petroleum Industry.

GENERAL PAPERS

TUESDAY MORNING (SEPT. 12)

Chairman: **A. P. Altshuller**

9:30–9:45 **L. A. Elfers and C. E. Decker.** Analysis of Fluoride in Air and Stack Gas Samples by Use of a Specific Ion Electrode.

9:45–9:50 **Discussion**

9:50–10:05 **J. E. Sigsby, Jr.** Evaluation of Evaporative Emissions from Automotive Fuel Tanks.

10:05–10:10 **Discussion**

10:10–10:30 **J. E. Sigsby, Jr., J. Miller, M. L. Bellar, M. Morgan.** Evaluation of Automotive Control Devices.

10:30–10:35 **Discussion**

10:35–10:55 **W. A. Lonneman, T. A. Bellar, and A. P. Altshuller.** Aromatic Hydrocarbons in the Atmosphere of the Los Angeles Basin.

10:55–11:00 **Discussion**

11:00–11:20 **G. C. Ortman and A. E. O'Keeffe.** Micrometering Pure Gases.

11:20 **Discussion**

TUESDAY AFTERNOON (SEPT. 12)

Chairman: **A. P. Altshuller**

2:00–2:15 **A. E. O'Keeffe and P. A. Wilks.** A New Family of Air-Monitoring Instruments.

2:15–2:20 **Discussion**

2:20–2:40 **E. Sawicki, C. R. Engel, and W. C. Elbert.** Chromatographic Location and Colorimetric Determination of Mercaptans, Prolines, and Free Radical Precursors.

2:40–2:45 **Discussion**

2:45–3:05 **C. R. Engel, E. Sawicki, and M. Guyer.** Superior Electrophoretic and Thin-layer Chromatographic Procedures for the Separation of Aza Arenes and Their Application to Air Pollution Analysis.

3:05–3:10 **Discussion**

3:10–3:25 **S. W. Horstman, C. H. Norris, and J. Wagman.** Size Distribution of Acid Aerosols in Urban Air Samples Using a Metal Film Technique.

3:25 **Discussion**

WEDNESDAY MORNING (SEPT. 13)

SYMPOSIUM ON CHEMISTRY OF THE NATURAL ATMOSPHERE

Chairman: **R. D. Cadle**

9:00–9:05 Introductory Remarks. **R. D. Cadle.**

9:05–9:25 **C. A. Knight.** Further Work on the "Contact Angle" of Water on Ice and Its Importance.

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9:25–9:35 **Discussion**

9:35–10:05 **C. E. Junge.** Recent Studies on the Physics and Chemistry of Atmospheric Aerosols.

10:05–10:15 **Discussion**

10:15–10:30 **J. P. Shedlovsky.** Composition and Distribution of Aerosols.

10:30–10:35 **Discussion**

10:35–10:45 Intermission

10:45–11:00 **E. R. Allen and J. G. Mehollin.** Concerning the Origin of Sodium in the Chemosphere.

11:00–11:05 **Discussion**

11:05–11:35 **A. Foutijn.** The Study of Atmospheric Properties by Chemical Release Methods. Results of Recent Laboratory and Field Investigations.

11:35 **Discussion**

WEDNESDAY AFTERNOON (SEPT. 13)
SYMPOSIUM ON CHEMISTRY OF THE NATURAL ATMOSPHERE

Chairman: **R. D. Cadle**

2:00–2:20 **P. Harteck and R. R. Reeves, Jr.** Some Specific Photochemical Reactions in the Atmosphere.

2:20–2:30 **Discussion**

2:30–2:50 **A. Goetz and O. J. Klejnot.** Transformations of Gaseous Reactive Hydrocarbons into Aerocolloids by Ultraviolet Irradiation.

2:50–3:00 **Discussion**

3:00–3:15 **L. A. Ripperton, O. White, and H. E. Jeffries.** Gas-Phase Ozone-Pinene Reactions.

3:15–3:20 **Discussion**

3:20–3:40 **W. H. Fischer, E. R. Frank, and J. P. Lodge, Jr.** Some Preliminary Atmospheric Chemistry Measurements in Antarctica.

3:40 **Discussion**

THURSDAY MORNING (SEPT. 14)
SYMPOSIUM ON CHEMISTRY OF THE NATURAL ATMOSPHERE

Chairman: **R. D. Cadle**

9:00–9:30 **H. E. Suess.** On the Carbon Dioxide Content of the Atmosphere.

9:30–9:40 **Discussion**

9:40–9:55 **J. W. Winchester.** Selective Oxidation of Bromide in Aerosols.

9:55–10:00 **Discussion**

10:00–10:15 **R. A. Duce.** Iodine in the Atmosphere.

10:15–10:20 **Discussion**

10:20–10:30 Intermission

10:30–10:50 **E. A. Martell.** Some Aspects of the Atmospheric Geochemistry of Sulfur.

10:50–11:00 **Discussion**

11:00–11:15 **J. B. Pate, E. R. Frank, and J. P. Longe, Jr.** Maritime-Continental Relationship of Ammonia, Sulfuric Acid, and Ammonium Sulfate in the Humid Tropics.

11:15–11:20 **Discussion**

11:20–11:40 **W. D. Green.** Identification of Chemical Constituents in Single Aerosol Particles.

11:40–11:50 **Discussion**

11:50 Concluding Remarks: **R. D. Cadle**

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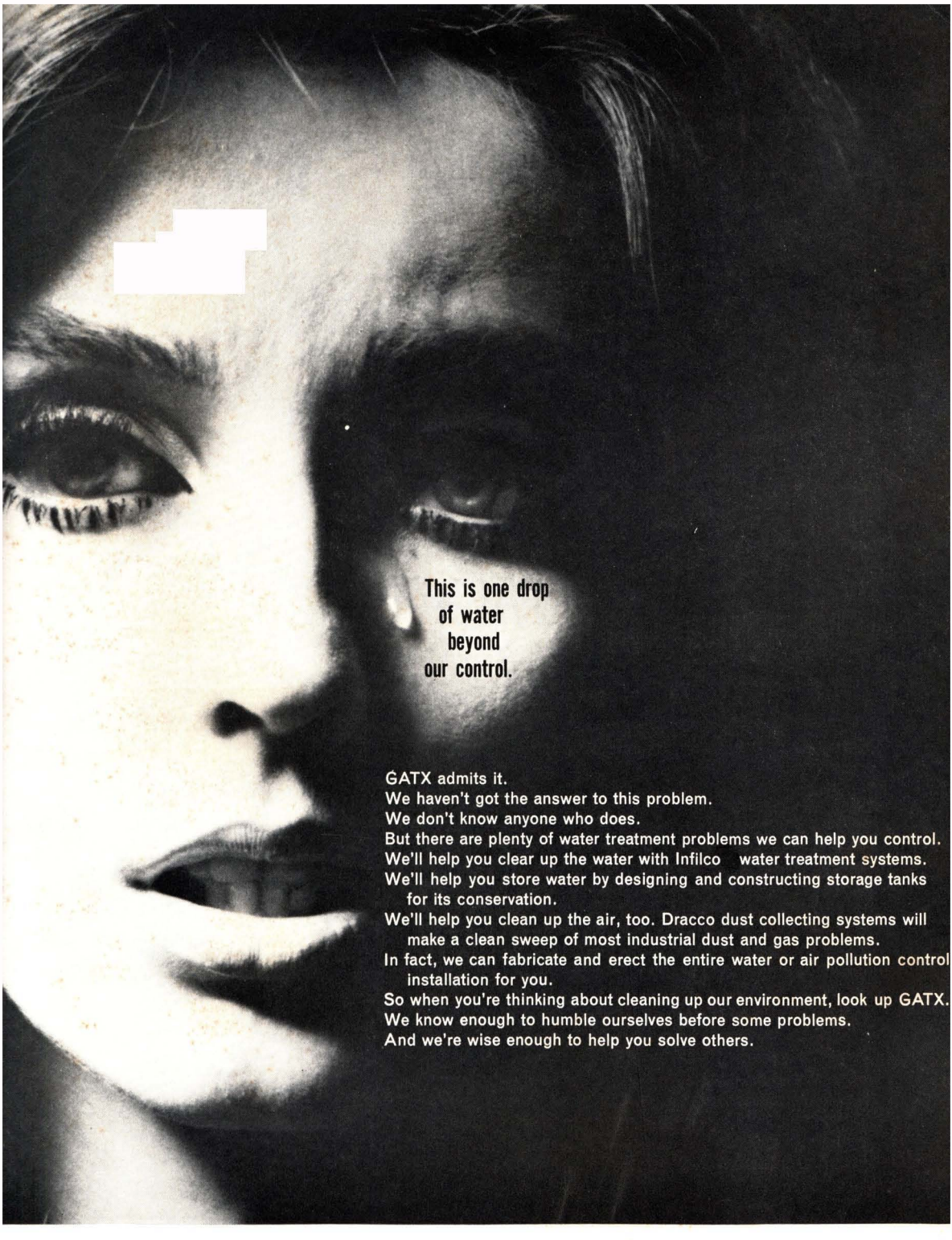

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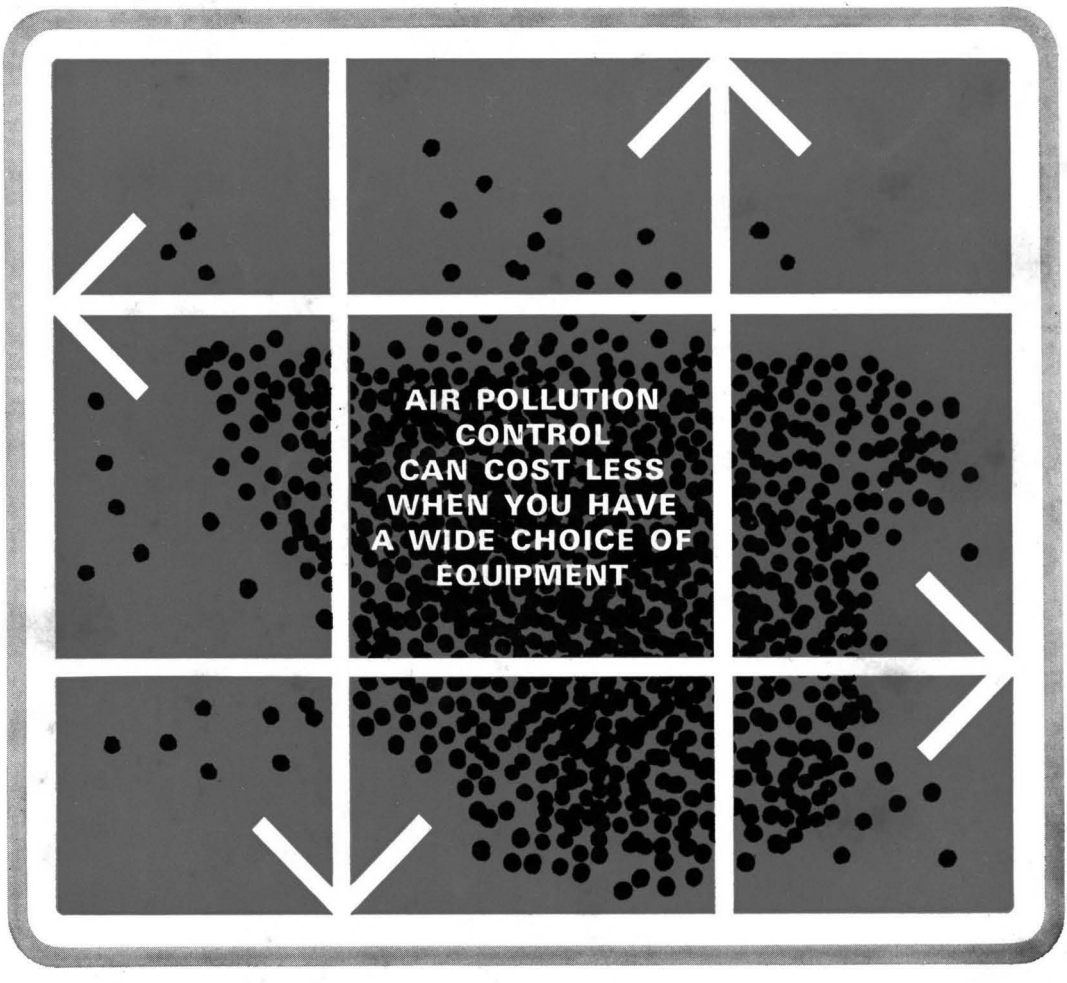

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