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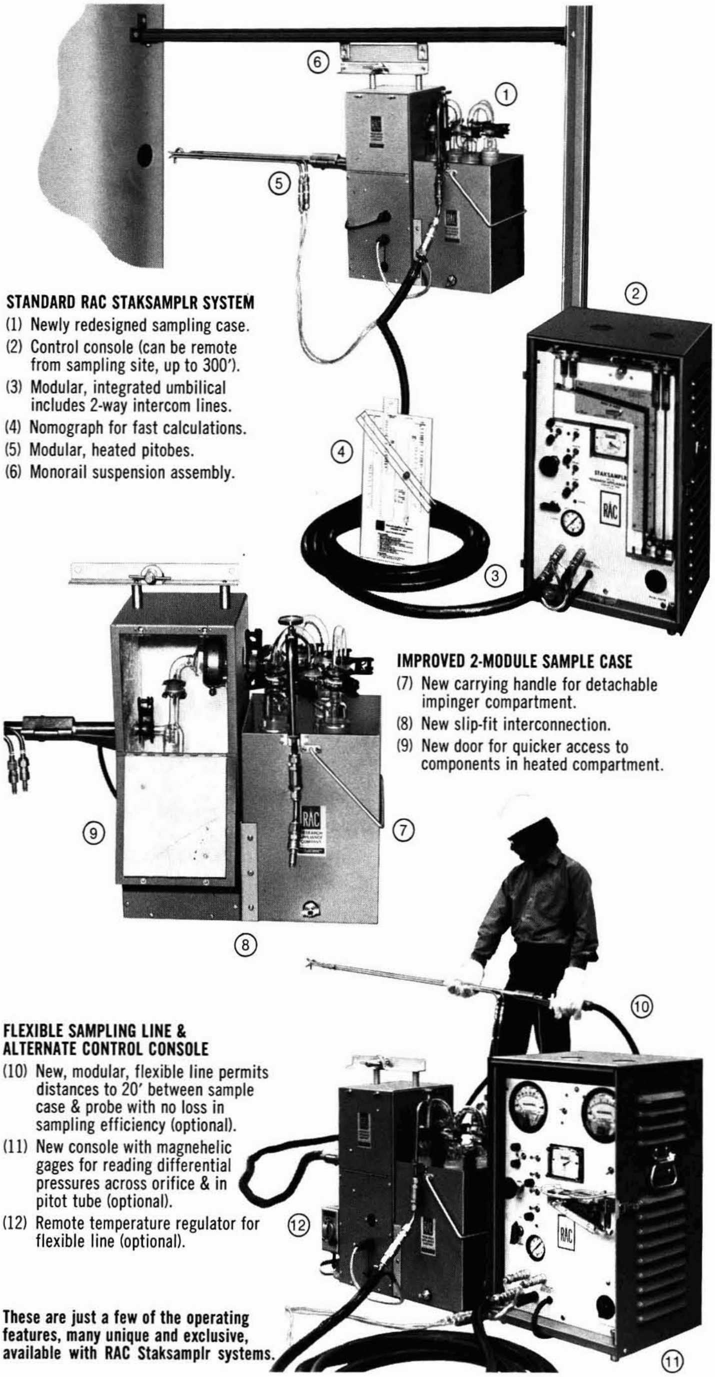

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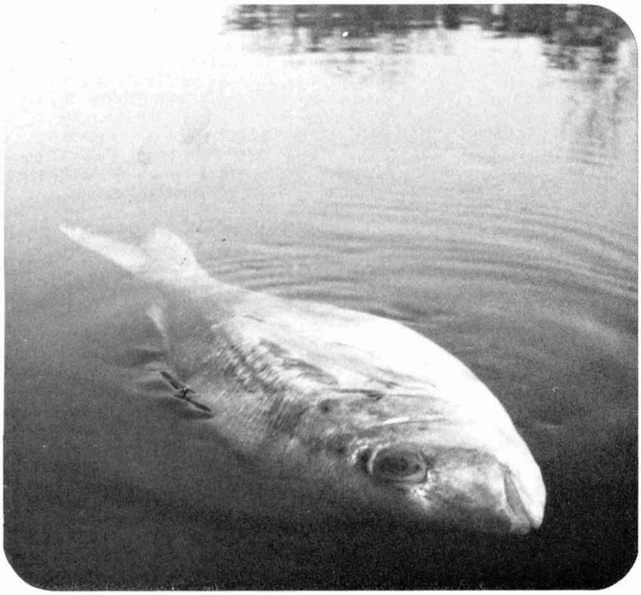

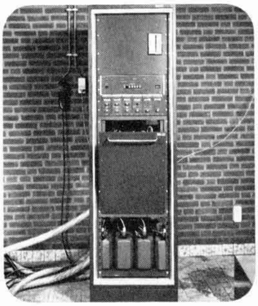

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Richard G. Zepp* and David M. Cline

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* To whom correspondence should be addressed.

This issue contains no papers for which there is supplementary material in microform.

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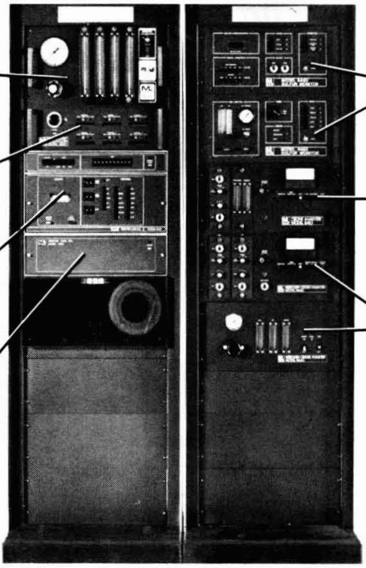

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Safe Drinking Water Act

Section 1401 of the Safe Drinking Water Act requires that the Administrator of EPA regulate contaminants that "may have any adverse effect on the health of persons." Furthermore the Act prescribes that the form of the regulation be the establishment of a maximum contaminant level (MCL) unless it is not possible to analytically monitor for that contaminant. In such cases the administrator is required to regulate anyway by prescribing a mandatory treatment process.

Among major pieces of environmental legislation P.L. 93-523 is unique in the lack of flexibility given to the regulatory agency with regard to either the selection of contaminants to be regulated or the manner in which they should be regulated. Congress intended to control drinking water quality immediately by requiring the adoption of Primary Regulations to be based upon the 1962 PHS standards and the 1973 "Blue Book" standards. The Act provides for discarding these standards, and not including among new standards those hazardous contaminants about to be designated by the National Academy of Sciences, only when the administrator can show that no adverse health effect exists. Thus, the Act places as much or more pressure on EPA to substantiate not formulating regulations as it does on formulating them.

The form of the Act, which was signed into law on December 1974, was a compromise between several different programs that were extensively debated during Congressional hearings. Plenty of arguments were presented against uniform federal standards, as Thomas Douglas has noted in his history of the development of this legislation. The 1974 National Conference of Governors opposed it on the grounds it would preempt staff responsibility; the Republican administration opposed federal enforcement and federal financial assistance to the states; the oil and gas industry opposed the provisions for underground injection control; and water works groups opposed federal prescription for plant operation and maintenance standards. Spokesman for the latter stated that ". . . innovation and flexibility have been the secret weapon of the industry . . ." Congress obviously felt that the secret was well kept.

Putting the complaints of vested interests aside, this Act is one more indication of the growing federal tendency to limit the freedom of their own agencies. This is understandable, but may be destructive of innovation in the long run, increase implementation costs, and decrease research incentive. Most importantly, this overregulation strikes at the will and integrity of an educated bureaucracy.

R F Christman

LETTERS

Opacity

Dear Sir: As one who has observed the misuse of opacity regulations over a period of years, I was interested in the EPA attitude toward such regulations as outlined by Don Goodwin in his letter to the Editor (*ES&T*, January 1977, p 10). He criticizes the findings of Weir et al. in their article "Factors Influencing Plume Opacity" (*ES&T*, June 1976, p 539), but in my opinion Weir and his colleagues have done an excellent job in pointing out some of the problems in visual evaluation of opacity.

But what bothers me most is the wide gap between "the purpose and use of opacity standards," as outlined by Goodwin, and the practice of EPA representatives in the field. Recently, a team of "enforcers" from the California Air Resources Board and EPA Region IX descended on a California steel mill and issued 1142 (yes, 1142!) opacity violations against its coke-oven facility. Each violation is subject to a $500 fine. If this were an isolated case, one could attribute it to a political battle that would eventually pass. But it is not an isolated case; it is a logical extension of practices that have gone on for years.

In many jurisdictions, any emission of an air contaminant of 20% opacity or greater (or 40% opacity or greater) is unlawful. To cite a source for a violation, an inspector need only have a certificate from a "smoke" school and declare that he has taken atmospheric and background variables into consideration in reading the specific plume, even though he did not follow the EPA Method 9 procedure.

Opacity regulations provide a cheap way to harass both large and small sources. The victim usually pays the fine without contesting the violation because he knows it is useless to argue. EPA's attempt (via Goodwin's attack on the Weir article) to legitimatize regulatory standards based on opacity by limiting their application is at considerable variance with the action of their field representatives. If Weir's article did nothing more than expose the hypocritical attitude of EPA toward opacity regulations, it was well worthwhile.

W. L. Faith
Consulting Chemical Engineer
San Marino, Calif. 91108

Environmental cancers

Dear Sir: Your special report (*ES&T*, December 1976, p 1190) pointed an accusing finger at some chemical concerns and at OSHA, but it overlooked an important part of the problem.

With a few notable exceptions, state and county public health agencies have been extremely reluctant to involve themselves in land-use planning. (Land-use planning is also called "environmental" or "urban and rural" planning.) The abundant resources available to public health agencies (expertise, staff, laboratories) are rarely utilized in guiding state and local planning bodies to select optimal locations and conditions for the various land-use activities (industrial, commercial, residential, agricultural, and other). These facts are listed in reference *1* and implied in reference *2*.

At its October 1976 Miami convention, the American Public Health Association endorsed a resolution in favor of environmental health planning. This resolution (*2*) emphasized the need for public health agencies' involvement in land-use planning.

Far too many public health agencies are encumbered with inertia, and still lack a qualified environmental health planner to interface with land-use-planning agencies and to promote environmental health concerns; but, hopefully, this inertia will not last much longer.

References

(1) Kaplan, O. B., Land Use and Health Interrelationships: A Field for Phantom Professionals. Scheduled for publication in the *Journal of Environmental Health*, February 1977.

(2) Environmental Health Planning. *The Nation's Health*, September 1976, p 8. Revised text scheduled for publication in the *American Journal of Public Health*, January 1977.

O. Benjamin Kaplan
Environmental Improvement Agency
San Bernardino, Calif. 92415

Nuclear radiation

The reply by Farwell and Fernandez (*ES&T*, December 1976, p 1185) to the *Currents* (*ES&T*, August 1976, p 730) report on their study of atmospheric tellurium-132 and iodine-132 is thoroughly confusing. The half-life of iodine-132 is 2.3 hours, so that it is generally found in equilibrium amounts with its 78-hour half-life fission product parent tellurium-132.

Unless it was present nearby an isotopes separations facility, tellurium-132–iodine-132 could only be ambient in the environment in a mixture of much greater amounts of other fission products. Since its largest relative contribution, about four days after fissioning, is about 8%, the presence of tellurium-132 in concentrations 0.20–21.20 pCi/m^3, implies total fission product concentra-

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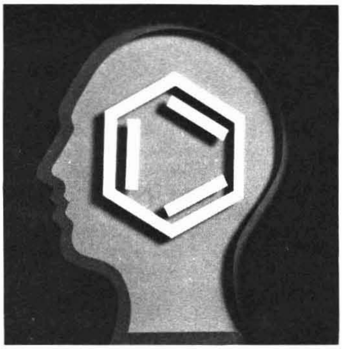

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tions of from at least 2.5 to 265 pCi/m^3 and these only if the fission event from which they originated had occurred 4–6 days previously. There is no way that the January 24, 1976 Chinese test could have produced measurable concentrations of tellurium-132 or even of 8-day iodine-131 during the sampling period April 18 to June 18, 1976.

I remain puzzled as to the choice of tellurium-132–iodine-132 for the purposes indicated in their letter.

Andrew P. Hull
Brookhaven National Laboratory
Upton, L.I., N.Y. 11973

Air pollution

Dear Sir: In his article on "Air Pollution Damage Functions" (*ES&T,* October 1976, p 992), Hershaft makes a major misinterpretation of the relation he cites between SO_2 and mortality.

While a change in the annual average SO_2 level may be reflected in a change in the annual mortality rate, there is no basis for applying a damage function derived from a regression of daily mortality changes on daily SO_2 levels to predict changes in the annual death rate from changes in the annual average SO_2 level.

Further, the inappropriately calculated predicted change in urban annual mortality rate is then multiplied by the total number of deaths in the U.S. as a whole, although there is no evidence that either the damage function or the exposure term (urban SO_2 levels) are appropriate for non-urban deaths. The number of deaths calculated in the article corresponding to changes in SO_2 levels are, therefore, completely groundless.

Samuel C. Morris
Brookhaven National Laboratory
Upton, L.I., N.Y. 11973

Smelter emissions

Dear Sir: We very much enjoyed the article on "Progress in Smelter Emission Control" (*ES&T,* August 1976, p 740). We regret that your article did not mention the use of nahcolite for SO_2 control in smelters followed by the disposal of the waste sodium sulfate by the FERSONA process (*ES&T,* July 1975, p 627) in conjunction with cement copper operations. A report of this use was presented at the 104th annual meeting of the American Institute of Metallurgical Engineers, February 1975, New York City.

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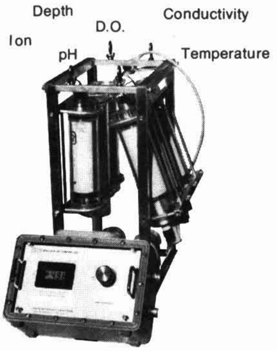

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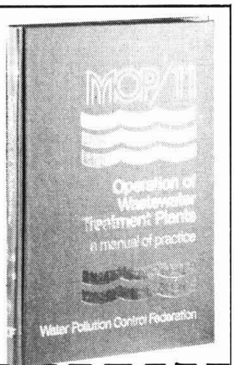

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CURRENTS

WASHINGTON

The Supreme Court ruled unanimously that the EPA can impose uniform regulations on industries to control water pollution (*ES&T*, February 1977, p 144). Eight major producers of inorganic chemicals argued that the 1972 amendments to P.L. 92-500 required that the EPA issue effluent limitation guidelines on a plant-by-plant basis. Speaking for the court, Justice John P. Stevens stated that the companies' interpretation of the law "would place an impossible burden on EPA," one that Congress did not intend. EPA will now be able to write uniform effluent limits on waste discharges for each category of industrial plant; will not be required to provide a variance procedure for new plants; but will be allowed to apply variances on existing plants.

Supreme Court Justice Stevens

Over 2 million gal of the defoliant "Herbicide Orange" will not have to be burned by the Air Force as previously planned (*ES&T*, May 1975, p 412). Herbicide Orange is contaminated with TCDD, one of the most toxic substances known to man. But two scientists with the Fish and Wildlife Service have developed a process for removing TCDD by absorbing it onto coconut charcoal filters. Once TCDD is removed, a "safe" herbicide that can be registered is formed. The Air Force plans to reprocess Herbicide Orange at the present storage sites in Gulfport, Miss., and on Johnston Island in the central Pacific Ocean. The empty steel 55-gal drums will be recycled, while the filters and contaminated carbon cartridges will be sealed in recoverable storage until safe disposal methods are developed.

The Interstate Commerce Commission ordered railroad freight rates cut for some recyclable commodities. Rate cuts in some parts of the U.S. were ordered for copper matte, zinc dross, aluminum residues, miscellaneous nonferrous metal residues, cullet and ashes. Rate reductions varying from 5–20% must be made within 60 days of February 4. Rates were not cut for scrap iron and steel, for according to the majority of the commission, the present rate structures for these commodities are "just, reasonable, and nondiscriminatory." The ICC was mandated by the Railroad Revitalization and Regulatory Reform Act of 1976 to investigate the rate structure of recyclable and recycled materials.

It is now official: Douglas M. Costle is to head the EPA and Charles Warren is to lead the CEQ. Costle's environmental credentials are impressive. He was previously commissioner of Connecticut's Environmental Protection Department, and he led the study group that recommended the creation of EPA. His most recent job was assistant director for natural resources and commerce in the Congressional budget office. Charles Warren was a California assemblyman who served as chairman of the state assembly committee on resources, land use, and energy. Warren is also highly regarded by environmentalists.

STATES

Minnesota's comprehensive packaging law was recently upheld in the U.S. District Court. Minnesota was the first state to implement packaging review legislation; this was in May 1974. After a survey showing that 35% of the waste stream is packaging material, the Minnesota Pollution Control Agency, wrote guidelines that specified the types of packages and containers that would be subject to review. If after proper review, the MCPA determines that a package constitutes a solid waste problem, the agency may prohibit sale of that package, according to the 1975 law. A group of trade associations and packaging manufacturers brought suit against the MCPA, but the court, in its recent decision, rejected the industry position.

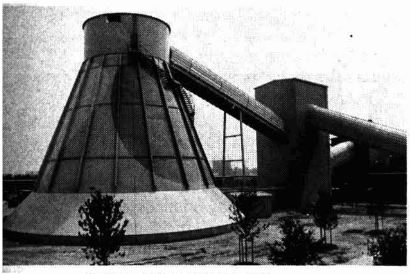
California will be the first state to test a federal program to help small businesses finance pollution control (pc) equipment. Under an amendment to the Small Business Act, the Small Business Administration can guarantee tax-free municipal bonds sold to finance pc equipment. California's program will help the SBA develop permanent regulations to enable extension of the program to other states such as Illinois, Pennsylvania, Ohio, and New York. Rules for the California program are now being drafted by the SBA and the California Pollution Control Financing Authority. In this pilot program, a public entity—probably the state—will issue tax-exempt revenue bonds. Eligible businesses will sign a contract and make payments to the public entity whose trustees will repay bondholders. The SBA has placed a limit of 25 years on guarantees; financing rates will be about 7%; and the loan will run for the life of the pc facility.

Oregon and the EPA are at odds over the size of a fine imposed under Oregon's NPDES program. A Georgia-Pacific pulp mill will not meet the July 1, 1977, effluent limitations mandated by P. L. 92-500 and its NPDES permit. Discharge does not significantly affect the water quality of the receiving body. The conflict is over EPA's supervisory role of enforcement actions taken by a state with its own NPDES permit program. Oregon wants to fine the company $50/day from July 1, 1977, until April 1, 1978; EPA says a $250/day fine is more appropriate. EPA Region X is to rule on the appropriateness of Oregon's action. This ruling will have significant ramifications for other NPDES states.

How do major urban centers affect their environment? For St. Louis, Mo., the answer is "significantly." Here, rainfall and hail storms downwind of the city are significantly increased; but while damage from hail is greater, it is offset by increases in agricultural crop yields. From the study called METROMEX, for Metropolitan Meteorological Experiment, which is funded in part by the National Science

Foundation's RANN program (*ES&T*, November 1975, p 1012), it is clear that man's activities can significantly modify the climate of urban areas. One way is by producing more particulate matter, which can serve as nuclei for raindrops and hailstones. Urban pollution also affects lung efficiency—detrimentally. Lung studies are also being conducted in Portage, Wis., Topeka, Kan., Watertown, Mass., Kingston-Harriman, Tenn., and Steubenville, Ohio.

The city of Baltimore, Md., will continue operating the Landgard solid waste pyrolysis plant, although Monsanto, the plant's designer, has pulled out of the project. While the pilot facility worked well, the scaled-up demonstration plant (1000 tpd) has been plagued by mechanical difficulties. Monsanto has recommended that Baltimore convert the pyrolysis unit to a conventional incineration system, and this is one option open to the city if it cannot get the pyrolysis plant to operate for a continuous period of time. Monsanto has committed a total of $10.8 million, the EPA $7 million, Baltimore $5.6 million, and Maryland $4 million. Approximately $1.1 million remain for Baltimore to draw upon. The city is now attempting to run the pyrolysis unit for a continuous 30-day period.



Baltimore's pyrolysis unit

Ohio ranks as one of the major producers of industrial waste in the U.S., and a recent survey showed ineffectual control of this material from generator to ultimate disposal site. Ohio EPA currently has no legal mandate to ensure the safe transport and disposal of these wastes. The Industrial Waste Survey canvassed 12 700 of the more than 17 000 manufacturing industries in Ohio. Preliminary results show that 2.5 billion gal/y of sludges and liquids are disposed of in 128 complexes of lagoons and/or ponds; 151 million lb of wastes are spread on land; and 16 million yd^3 are landfilled. In addition to these disposal sites, some wastes from Ohio are shipped to 13 other states. The survey was taken to provide state legislators with the data base needed to support future solid waste legislation.

VIEWPOINT

"For the time being, nuclear energy offers the best, quickest, cleanest way to reduce dependence upon the whims of oil sheikhs on the Persian Gulf," 1944 Nobel Prize winner Isidor Isaac Rabi told a Scripps Institution of Oceanography (La Jolla, Calif.) press conference. He considers solar energy too expensive at present, and coal, "nastier" to the environment, despite its ability to meet U.S. energy needs. Rabi also said that fusion could be practical, and "is not against laws of physics," but is not in the cards for the lifetimes of those present at the conference. As for nuclear safeguards, Rabi asked, "How much do you want to buy? Like retirement homes with dogs and guards?" He observed that if perfect safety were required for railroads, for example, railroads would never have been built. "What is needed is common sense," he said.

MONITORING

Can one keep constant environmental tabs on everything from surface mining effects to polluters illegally discharging effluents under cover of night? According to a NASA spokesman, such complete monitoring could be done with a synchronous satellite. That type of satellite appears to stay over one point on the equator, and can "watch and listen to" what occurs in the area it observed for 24 h/d. Visual surveillance will be done by highly advanced photographic and television techniques; "listening" would involve relaying data telemetered from Earth-based Data Collection Platforms (DCP). At present DCP's and photo techniques provide such data for the Landsat at given intervals; use of the synchronous satellite would comprise the next "generation" of environmental monitoring from space.

Air Force engineers have developed a new remote-sensing pod for the EPA. This pod, called Enviro-pod, can be installed on the Cessna 172 series aircraft to photograph environmental episodes—oil spill accidents involving hazardous materials, violation of standards—and natural disasters. The Enviro-pod will provide EPA with high-resolution photographs taken from moderate altitudes; photos will cover an area 4.1 mi wide by 150 mi long. The pod is compact and lightweight, only 48 in. long and 147 lb in weight. The pod can carry a 70-mm camera capable of taking black/white, color or color ir photographs; a 35-mm camera; air sampling equipment; infrared sensors; and television cameras. The pod was certified by the FAA as accessory equipment for light aircraft.

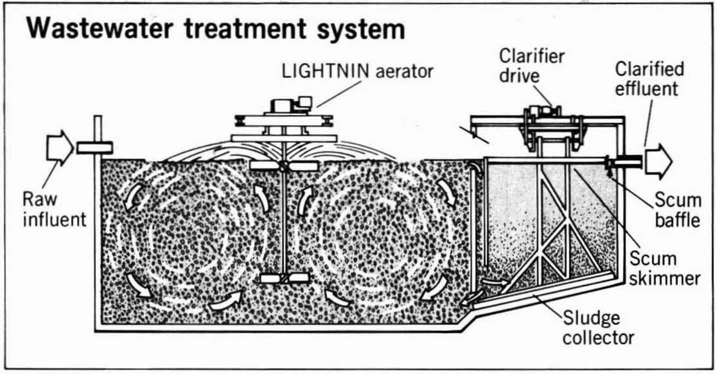
For measuring SO_2 in air, the National Bureau of Standards has issued four new Standard Reference Materials. The new SRMs and their concentrations in ppm are: SRM 1661, 480 ± 5 ppm; SRM 1662, 942 ± 10 ppm; SRM 1663, 1497 ± 15 ppm; SRM 1664, 2521 ± 25 ppm.

TECHNOLOGY

If you had to have a power plant in your back yard, would you prefer a coal or nuclear plant? Prof. Donald Barber of the University of Minnesota said that he would opt for a nuclear plant, which he considers the "safest means of power production ever devised." He explained that coal not only produces SO_x and NO_x, for example, even *with* pollution-control equipment, but also can release more radioactive isotopes to the air than would nuclear plants, in some cases. Barber also cited problems of toxic drainage from coal or ash stockpiles. He claims that some radioactive emissions alleged to be from nuclear plants may actually be blown from coal-burning plants upwind. Barber also does not worry about nuclear accidents, but only about being alerted in time, should one occur.

An answer to the problem of oily wastes in ship's bilges may be found with new demulsifiers developed by Ralph Little and Robert Patterson of the U.S. Naval Research Laboratory (NRL, Washington, D.C.). The demulsifiers can remove water from oil, or oil from water, as the case may be, effectively and economically, even at temperatures as low as 50 °F. Normally, 100 °F is needed for presently available systems. For water-in-oil emulsions, the key is a good wetting agent and high-molecular-weight polymer. For oil in water, selected quaternary ammonium chlorides can do the trick. The type of emulsion present can be determined by a simple field test. The demulsifier approach would work in fuel and storage tanks, and with oil spills, according to the NRL scientists.

A wastewater treatment system that makes solids, easily handles biological shock loads, and costs less, has been announced by Mixing Equipment Co., Inc. (Rochester, N.Y.), a unit of General Signal. Known as LIGHTNIN Treatment Systems, the equipment uses flow generated by a surface or submerged mechanical aerator to recycle settled sludge from an integral clarifier. Another feature is common wall concrete construction that enhances economy, or earthen basin construction with durable lining, where conditions permit. The system can operate at


Wastewater treatment system

2000–12 000 mg/L of solids, and higher. BOD loadings as high as 3000 mg/L, as well as suspended solids are brought down to within secondary treatment standards. The company says that all equipment can be serviced without the need to drain the system.

If you want to pyrolyze sewage sludge and cannot use natural gas as a heat source, try wood. That is what Nichols Engineering & Research Corp., a subsidiary of Neptune International Corp., did to test sewage sludge pyrolysis when gas was unavailable. The Nichols plant crew spent 9 h chopping wood, which fired the pyrolysis unit's hearth, to preheat the sludge that had been dewatered to 42% solids. The wood supplied sufficient heat to start the pyrolysis process, which became self-sustaining, and produced off-gases that burned at 1750 °F in an afterburner. Under contract to the Interstate Sanitation Commission (New York, N.Y.), Nichols was exploring the feasibility of sludge pyrolysis as an alternative to ocean dumping.

INDUSTRY

Fluidized-bed combustion (FBC) will take a leap forward when Stone & Webster Engineering Corp. (S&W, Boston, Mass.) develops the world's first designs for a commercial power plant. The plant will burn coal by atmospheric FBC (AFBC), and produce 500–600 MW of power. An S&W spokesman said that the AFBC plant, whose design contract from ERDA is worth \$1.35 million, should reduce SO_2 emissions more efficiently than would scrubber-equipped plants, and minimize NO_x. As subcontractor, **Pope, Evans and Robbins** (PER, New York, N.Y.) is to define functional characteristics, and performance and interface requirements of the proposed plant. PER has broad experience in AFBC through its engineering and management of a pilot 30-MW plant at Rivesville, W.Va. (*ES&T,* February 1976, p 120).

A three-year extension to 1980 for achieving "best practicable" (BPCTCA) secondary treatment for publicly owned treatment works (POTW's), and water quality standards should be granted by amending Section 301 of P.L. 92-500. This is the position of the **National Association of Metal Finishers** (NAMF, Montclair, N.J.), which also advocates that pretreatment should be required only when a POTW cannot meet its permit limits. The NAMF also recommends that "best available" (BATEA, 1983) requirements and the 1985 "zero-discharge" goal of P.L. 92-500 be deleted. For water quality standard achievement for certain sources, NAMF would go along with stiffer-than-BPCTCA requirements after a thorough economic, energy, and social cost-benefit determination.

Severe snags in projected coal use increases over the next 10 years may occur because of bottlenecks on congested railroads and waterways, the Electric Power Research Institute (EPRI, Palo Alto, Calif.) warned. In some cases, for example, coal would have to be shipped by roundabout rail routes, with higher shipping costs resulting. EPRI's study, prepared by **Manalytics, Inc.** (San Francisco), may have been optimistic through the assumption that railroads and rolling stock would be kept in good condition, and that conditions on waterways would be normal. The study calls for new cost models for rail, and intermodal transportation of coal.

And speaking of coal and other fossil fuels, EPRI says that concerning health effects of human SO_2 exposure, more information "is badly needed." Otherwise, it would be difficult to make rational decisions for setting sulfur emission standards, and developing control strategies. Also, technology of SO_2 control, types of control systems, and their operational costs should be tailored to the amount of emission reduction necessary, according to EPRI. These and related matters were subjects of a study report done for EPRI by **Greenfield, Attaway & Tyler, Inc.** (San Rafael, Calif). That report also recommended acquiring more knowledge concerning other airborne sulfur compounds, and called for an investigation to pinpoint what sulfur compounds pose health threats, and how they do so.

The job of building the nation's first large-scale solid waste gasification plant went to Waste Management, Inc., (WMI), under ERDA contract. The plant is to handle 100 tpd to produce about 3000 ft^3 of methane, and 3000 ft^3 of carbon dioxide per ton of processed refuse. Known as RefCOM (Refuse Conversion to Methane), such a plant could reduce solid waste and sludge volumes by 70%, H. Wayne Huizenga, WMI vice chairman, estimates. Huizenga said that the plant will be built at Pompano Beach, Fla., at a cost of \$2.8 million, and, if it were 1000 tpd, could supply gas needs for 10 000 homes. Huizenga hailed the project as "the beginning of a new era in the creative management of wastes."

An increase in the insurance commitment by \$90 million to \$390 million for each nuclear risk was announced by the Nuclear Energy Liability-Property Insurance Association (NEL-PIA, New York, N.Y.). Burt Proom, NEL-PIA general manager, said that this sum represents the total insurance available from the worldwide market, including the London syndicates. Proom ascribed the high insurance commitment to an "excellent safety record" of the industry. He noted that "over the 19-plus years of nuclear insurance, only about \$400 000 have been paid in claims resulting from nuclear accident," and called this record "superior" for an industrial activity. Proom said that no member of the public was involved, and that no claim resulted from nuclear plant operations.


NEL-PIA manager Proom

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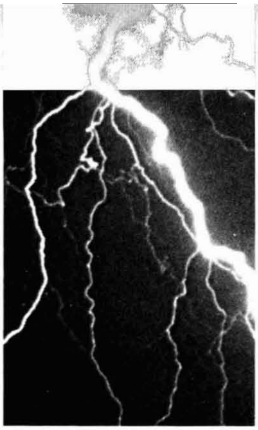

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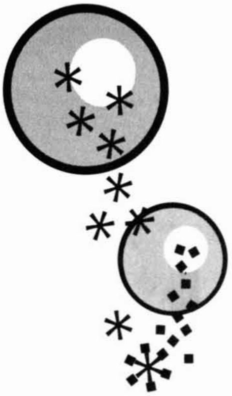

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Upgrading electrostatic precipitators

Research-Cottrell and Standard Oil (Calif.) show that imaginative engineering for meeting today's air pollution regulations can keep within refinery space limitations as well as budget

Many companies that installed air quality control equipment before the current regulations were established now face a serious problem—bringing this equipment up to standards. Having made a substantial investment in air control equipment, they now find it obsolete, unable to meet current regulations. They have a "white elephant" on their hands that must somehow be incorporated into current or future air control plans or discarded at a total loss of investment.

More than 20 years ago, Standard Oil (El Segundo, Calif.) installed a Research-Cottrell electrostatic precipitator as the final stage of a dust recovery system to capture "fines" from a fluid catalytic-cracking unit. With normal maintenance and parts replacement the unit continued to perform satisfactorily. Since that time, however, more stringent air quality control has become one of the conditions for doing business, so the original unit could no longer meet the regulations.

Faced with a seven-figure price tag for replacing the precipitator in its entirety, Standard Oil instead solved the problem by "capping" the original precipitator shell with a 4-ft extension. This allowed Research-Cottrell to design new internals that increased precipitator treatment capacity by more than 13 000 ft^2—at far below the cost of new construction. The actual cost to Standard Oil was less than 10% of the cost for new precipitators.

Capping. *This 4-ft extension cost 10% that of new units*

The choices

In most cases where precipitator efficiency must be increased, companies usually select one of two basic solutions. One is to add on the required treatment capability by building another precipitator either in series or parallel with the existing precipitator. The other is new construction, either by tearing down and replacing the old precipitator with a larger one or by building in a new location.

To Standard Oil engineers, both of the foregoing solutions were impractical because of cost and available space limitations. Also, the existing precipitator shell, though undersized, was still in good condition and they were reluctant to scrap it.

Their solution

The solution was to increase the capacity of that shell by increasing its height. In the original installation, 31 collection plates in each unit treated flue gas in three separate fields—inlet, middle, outlet—in the precipitator. Each plate measured 9 ft wide by 20 ft high for a total collection area of 66 960 ft^2. By replacing each 20-ft plate with a 24-ft plate for a new collection area total of 80 352 ft^2. Standard Oil gained 13 392 ft^2 of treatment area for roughly the construction cost of a four-foot high precipitator shell.

The steel cap itself, 4 ft high × 16 ft wide × 18 ft long, was constructed on the ground in an area near the old precipitator shell and lowered into position by a crane. The cap was then welded to the old shell and the new internals installed.

The precipitator, as designed and built by Research-Cottrell, now has a normal rated gas capacity of 150 000 acfm at 650 °F. It is two chambers wide and three fields long in the direction of the gas flow. Each field has 30 9-in. each wide ducts, formed by 31 Opzel-type collecting plates, each 24 ft high by 9 ft long.

These collection electrode plates are cleaned by magnetic impulse, gravity impact rappers. The 2160 copper Bessemer discharge electrode wires are cleaned by electric-type vibrators. Electrical energization to the precipitator is supplied by four 25 kVa, 75 kV vacuum tube rectifiers.

Six-stage collection unit

The particulate collection system is installed downstream of the fluid catalytic cracking unit to control emissions of silica alumina catalyst fines. The cracking operation generates a large quantity of these fine particles. Under current regulations Standard Oil must collection all but 30 lb/h, and they do.

To collect these highly abrasive fines, Standard Oil has three stages of cyclone separators and the three-field Research-Cottrell electrostatic precipitator. The cyclone separators filter out the larger catalyst fines, which are collected and recycled into the cracking process. Those small fines, which cannot be collected by the cyclones, pass on to the electrostatic precipitator where they are removed from the gas stream before it is released to the atmosphere. Catalyst particles collected by the precipitator that are too fine for re-use are hauled away.

Double savings by remodeling

With proven technology and some imaginative engineering design, Standard Oil has avoided a potential air pollution problem on a critical process plant. What's more, by not building a new precipitator housing shell, which would have meant an extended shutdown of the cracking unit, they saved, in addition to construction costs, literally tens of thousands of barrels of lost product.

What's going out the doors? Nitric acid?
Liquid propane? Carbon disulfide? Then there are
strict rules to follow, and HMAC is there to explain . . .

. . . How to ship hazardous materials

The dingy-looking oil lamp that Keenan Flabb bought at the antique store looked disturbingly familiar in a Middle Eastern sort of way. Also, it definitely needed a good polishing. Well, that is what Flabb started to do, and . . . you guessed it! There came an ominous hissing sound, a puff of dense smoke, and then, the lamp's genie, ready to grant his new master's wish instantly.

Previously, there was one way to describe Keenan Flabb's life—utterly uneventful. He was, to put it politely, most inconspicuous. You could meet him a dozen times in rapid succession and never remember him. You'd never see him at a party because someone forgot to invite him; no malice involved, just oversight. Same story at the office. He never got any of the important or interesting jobs to do, or any recognition for what he did do. No wonder Keenan Flabb's first and only wish was to have a real blast, for once in his life!

It was Keenan's only wish because, unfortunately, the genie was literal-minded. So it came to pass that Keenan Flabb found himself one yard away from a stalled tank car laden with liquid propane that exploded in a glorious fireball two seconds later. Back at the office, of course, nobody really noticed that Keenan was absent.

Broad authority of law

The type of accident that brought Keenan Flabb his first and only moment of excitement is, in fact, an extremely rare occurrence. It does, however, serve as a reminder that to meet the needs of a highly industrialized, technological society, the transportation and distribution of potentially hazardous materials, as well as the creation of hazardous wastes, is virtually inevitable.

For this reason, among others, Congress passed the Hazardous Materials Transportation Act of 1974, which gave the Secretary of Transportation the authority to regulate shipment of such materials. This authority has been delegated to the Materials Transportation Bureau (MTB), which has jurisdiction over just about all moving of hazardous materials in interstate commerce, whether by road, rail, air, water, or pipeline.

The Secretary's authority also covers materials deemed to pose an "unreasonable risk"; all carriers and shippers; car, container, or package makers; storage and unloading; safety aspects; and commerce *affecting* interstate commerce. He or his representatives can hold hearings, issue orders and injunctions, and move for civil or criminal penalties.

The Act, which was quite stringent, needed a response from the private sector, in order to bring about helpful changes in the law, as well as a compliance strategy. Accordingly, the Hazardous Materials Advisory Committee (HMAC) was organized in 1974. HMAC is headquartered in Washington, D.C.; as of last October, it had about 185 corporate members. This year, Don Boyd of Du Pont is the Committee's chairman.

Serves all components

As the only national organization devoted to the problems of hazardous material transportation, HMAC represents all components of the transportation community, and works toward achieving practical, efficient laws and regulations for safe movement of such materials. It brings together truckers, airlines, pipelines, waterborne carriers, insurers, and others concerned with these shipments.

HMAC is a center for information about present and proposed regulations for transportation and distribution of hazardous materials. It prepares comments for members of Congress and their staffs, and keeps close touch with government officials and agencies involved. Also, the Committee encourages research and studies to improve the safe distribution of hazardous materials. It works with all concerned at improving regulations, and means of complying with them.

Some accomplishments

One HMAC accomplishment was to point out to Congress some difficulties with existing and proposed hazardous materials legislation. The result was the Transportation Safety Act of 1975 (P.L. 93-633), which HMAC concisely summarized for its membership. The next step entailed a Hazardous Materials Seminar and Workshop, attended by more than 300 people, to outline methods by which carriers and shippers could comply with federal safe-shipment regulations. What was also discussed was how to avoid fines of up to \$25 000 for non-compliance, and how to minimize compliance costs.

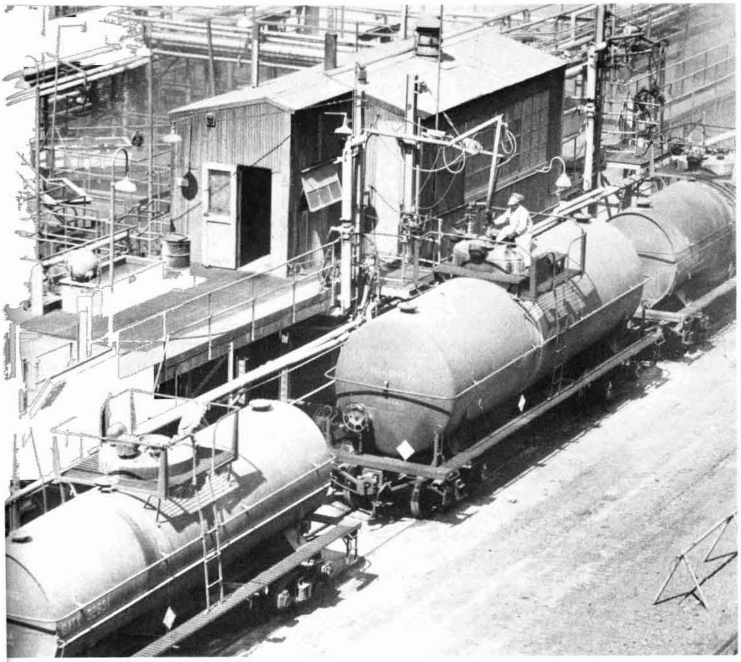
Then, HMAC arranged seminars at which attendees learned about various companies' in-house systems for safety and compliance, as well as new industry practices, legislation, regulation, and training needs. Speakers were from companies, and from the MTB, EPA, OSHA, Coast Guard, Office of Hazardous Materials, and other cognizant federal agencies.

Sign of the Red Diamond

No, the Red Diamond is not a British pub. It is the sign that is supposed to be seen on any car, trailer, package, or the like, containing hazardous materials. There is an international code of Red Diamond signs for flammables, oxidizers, poisons, or other substances that could present a danger.

Therefore, the name "Red Diamond" for HMAC's training program in new hazardous materials regulations was adopted. The program was developed under the direction of the Committee's Education and Training Task Force by Paul Numerof

Du Pont's Don Boyd
This year's HMAC chairman



Loading. *These tank cars must carry the proper labels and warnings*

Associates (Edison, N.J.). It is meant for all companies and personnel in the field. Those who successfully complete the program are awarded a certificate.

For example, the program was conducted last November in many parts of the U.S., and, as this goes to press, HMAC is finalizing plans for more nationwide sessions. A typical session lasts one day. It begins at 8:30 a.m., and concludes with an open-ended problem-solving forum that starts at 5:00 p.m. The intensive program:

- tells how to comply with federal hazardous materials regulations
- focuses on latest rules, and teaches what is required of shippers and carriers
- provides workshop and problem-solving sessions
- trains program registrants to train others, pursuant to requirements of P.L. 93-633.

Among topics covered are training requirements, labeling, priority order of hazards for multiple hazards, radioactive materials handling, proper shipping papers, and other pertinent subjects. In addition, HMAC holds frequent workshops and seminars, lasting 2–3 days, that cover selected topics in depth. A typical meeting of that sort, held at Arlington, Va., in October 1975, dealt with hazard information systems. Also, a seminar on safe packaging took place at Chicago, Ill., late last month.

The EPA connection

Last December, the MTB advised that it proposed to make rules concerning certain materials deemed potentially hazardous to humans or the environment, and not covered by existing hazardous materials regulations (*Federal Register*, 41 FR 53824, December 9, 1976). Of particular concern were those materials whose potential release during transportation could cause "unreasonable risk" to people, property, or the environment. The EPA listed some 200 materials not so regulated as this goes to press, which the agency would like the MTB to regulate.

In any such rulemaking procedure, the MTB looks for input from the public as to whether such rules are needed; which human health and environmental effects should be considered; and what criteria are applicable to determining these effects and identifying materials of concern. Also, the Bureau wants to know whether modifications to existing hazard classes, or the creation of new classes are in order, to "accommodate identified environmental and health effects of materials." Finally, public input on what transportation controls are needed is invited.

Meanwhile, out west . . .

Since August 1973, a concerted attack on the problem of hazardous materials and wastes has been conducted by the Federal Task Force for Hazardous Materials Management. This task force is part of the Western Federal Regional Council, and works in coordination with EPA Region IX (San Francisco, Calif.). Its objectives, while tailored to the region, could apply to the nation as a whole. Among them are:

- compilation of a list of personnel contacts for hazardous materials as related to environment
- information and technology transfer relating to the environmentally safe measurement of hazardous materials
- development of an inventory of excess hazardous materials and wastes under federal agency purview
- development of action plans for environmentally safe hazardous material/wastes management
- coordination of final disposition actions with appropriate state agencies.

Among recent activities of the task force was holding the National Conference about Hazardous Waste Management, which took place in San Francisco in early February. One of the conference's principal organizers was Harvey Collins of the Vector and Waste Management Section, California State Department of Health (Sacramento). Among the aims of the conference was bringing attendees up to date on the latest hazardous waste management technology and operating methods, and explaining a plan of work with timetables for accomplishment. The task force's work was to be emphasized.

The task force's activities are due to be completed on September 30 after publication of a final report presently in draft and review stages. That report will include criteria for location and organization of hazardous waste disposal sites, as well as many other appropriate subjects. For more details, contact Charles T. Bourns, Chief, Solid and Hazardous Waste Management Program, EPA Region IX, 100 California St., San Francisco, Calif. 94111. Ask about the Final Report of the Western Federal Regional Council Task Force for Hazardous Waste Management, due to appear about June 1.

One final thought about the late Keenan Flabb who went out literally in a blaze of glory after the propane explosion. When those who manage hazardous materials achieve their objectives, people like Flabb, who feel they are in a rut, will have to wish for other ways to bring a moment of excitement into their otherwise humdrum lives. JJ

Out west, they talked about cadmium

That metal has, and will have, many uses. The First International Cadmium Conference discussed these uses, as well as environmental problems and safeguards

Funny thing about cadmium—while it has many uses, it is not a primary product, but rather, a by-product metal. By contrast, lead and zinc are primary products, but these cannot be extracted and refined without the concurrent production of cadmium. This is especially true in the case of zinc metallurgy, for, as the Mendeleyev periodic table shows, zinc and cadmium belong to the same metal "family."

However, by-product or not, cadmium has many applications. Free-world production of cadmium over the past several years has ranged about 10 000–14 300 metric tons (mt)/y. But whatever its uses, cadmium is a toxic material that has certain environmental and occupational health implications. To consider these implications and what can be done about them, the Cadmium Council was formed at New York City last year by the Zinc Institute, Inc. Also last year, the Cadmium Association was organized at London, England, as an affiliate of the Zinc Development Association. They all work closely with the International Lead/Zinc Research Organization (ILZRO), which has intensified its environmental research concerning cadmium. The Council comprises North American producers and the Association covers Europe, but they cooperate.

Because of the environment/workplace problems that cadmium presents, the Association, the Council, and ILZRO held the First International Cadmium Conference at San Francisco, Calif., in early February. About 250 people from the U.S., Australia, Belgium, Britain, Canada, France, W. Germany, Japan, New Zealand, Sweden, and other nations, attended. Japanese attendance was sufficiently heavy to warrant the installation of an English-Japanese simultaneous translation system. The Conference heard keynoter Keith Hendrick, president of Noranda Sales Corp. (Toronto, Canada), and vice chairman of ILZRO, advocate environmentally safe use of cadmium. Hendrick noted, however, that much more knowledge of cadmium's properties, and environmental and health effects is needed, as are meaningful bio-assays for cadmium, such as have been done for lead.

How it is used

Perhaps a cogent reason for the conference was to reconcile the many technical needs for cadmium with the necessity for improved environmental safeguards, as well as a better definition of what those safeguards should be. But what are the technological uses of cadmium that make it widespread enough to be a matter for concern?

The four major cadmium-consuming nations are the U.S., W. Germany, Britain, and Japan, in that order. The principal use of cadmium in these countries, comprising about 35%, is electroplating, followed by pigments (23%), such as the yellow of cadmium sulfide (CdS), for example. Other uses include stabilizers for polyvinyl chloride or PVC (about 16%), and nickel-cadmium batteries (13%). These percentages may change, however, because improved batteries, for example, are a fast-growing application, among others. Yet another use entails light-sensitive systems containing CdS.

One newer use of cadmium might be found in solar energy collectors. It is quite possible that these collectors may account for more than 50% of the future consumption of the metal. A substantial portion of the necessary cadmium may have to be imported, since U.S. production peaked out at 5736 mt in 1969, and was as low as 2000 mt in 1975, principally because of depletion of some older mines.


ILZRO vice chairman Hendrick
"More bio-assays needed"

"Ouch-ouch"

Cadmium has been blamed for a number of human health problems, the most drastic of which was the painful itái-itái ("ouch-ouch") disease suffered mainly by post-menopausal women in the Jinzu River area of Toyama Prefecture, Japan. One alleged source of cadmium was drinking water taken from the river flowing downstream from rich zinc mines in the prefecture; another was rice grown in river water, which took up cadmium. Itái-itái gives rise to symptoms of severe pain stemming from bone lesions, which, in turn, are manifestations of bone softening, porosity, and embrittlement.

One hypothesis of itái-itái etiology is that the bone lesions arise from lesions in the kidney tubules, in which cadmium accumulation causes undue loss of bone-strengthening phosphorus. This hypothesis was given support by findings of higher cadmium concentration in itái-itái patients' urine, and in that of nonpatients in the Jinzu River area, than in that of people in a control area.

Lately, however, Jugoro Takeuchi of the Tokyo Medical and Dental University (Japan) questioned this itái-itái etiology hypothesis. He told the conference that the disease was found in some cadmium-free areas, and was not found in certain cadmium-contaminated areas. He also said that if cadmium suppresses renal vitamin D activation, itái-itái symptoms should have appeared in other cadmium-polluted areas, such as Ikuno and Tsushima.

Takeuchi pointed out that itái-itái patients responded well to large doses—100 000 international units/d minimum—of vitamin D. He also observed that incidence of the disease fell rapidly since 1960, after housing and dietary conditions were markedly improved.

Thus, Takeuchi believes—with far from universal agreement—that itái-itái is a disease more of vitamin D deficiency than anything else. He does acknowledge, however, that cadmium ions do have deteriorative effects on certain renal tubular functions, and that "the possibility that cadmium had modified itái-itái symptoms induced by vitamin D deficiency caused by environmental conditions cannot be ruled out." In any case, the etiology of the disease has certainly become a subject of spirited debate!

Other health indications

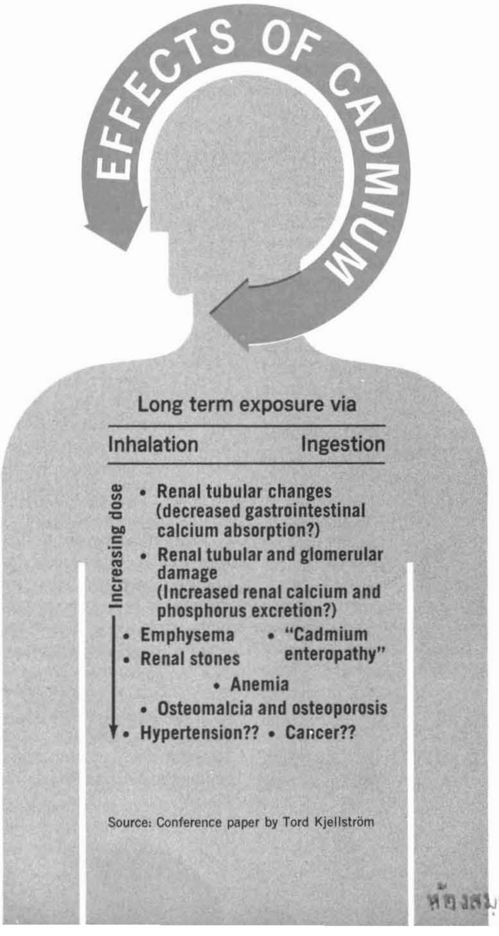
The controversy over itái-itái disease origins, and the fact that the illness is a largely local phenomenon, do nothing, of course, to lessen its victim's misery. But whether or not cadmium is the itái-itái culprit, it is toxic. For example, the World Health Organization estimates that an 8-h exposure to 5 mg/m^3 of cadmium oxide (CdO) fumes can be fatal to humans. Indeed, animal experiments indicate that exposure to a five-times-lower CdO fume concentration could be very dangerous. However, at present, typical factory exposures rarely exceed 0.05 mg/m^3.

Typical inhalation symptoms are nasopharyngeal irritation, headache, and dizziness, followed by nausea, vomiting, and fever. In extreme cases, respiratory effects follow, with death caused by cardiopulmonary insufficiency arising from pulmonary edema. However, if the patient does not die, he usually recovers from pneumonitis within 7–10 d, but there may be decreased lung function for some years.

Such effects, however, are not common; the main cadmium repositories in the body are the liver, and, especially, the kidneys. Animal experiments indicate that at first a cadmium tolerance builds up in the kidneys, but later, dysfunction of the renal tubules manifests itself. For the case of humans, perhaps some light was shed on kidney impairment by George Kazantzis of the Middlesex Hospital (London).

Kazantzis studied men who were exposed to CdS and CdO fumes and dust, and was able to do follow-up studies on six men who were exposed to CdS for 28–45 y, and to CdO for less time. He also studied other cadmium workers.

Kazantzis found tubular proteinuria (protein loss to urine) even for many years after cadmium exposure had stopped. Of the six men in the long-term study, one died of bronchial carcinoma in 1964, but the surviving five continued to be observed. All had tubular proteinuria, and were also excreting excessive calcium in the urine to 300 mg/24 h (600 mg/24 h in one case). Two men became recurrent kidney stone formers; another developed vitamin D-resistant osteomalacia (bone softening). Other renal biochemical symptoms were noted; however, Kazantzis cautioned that many more carefully controlled studies must be pursued before any pronouncement can be made on morbidity and mortality effects of kidney toxicity of cadmium.



Source: Conference paper by Tord Kjellström

Perhaps Tord Kjellström of the University of Auckland (New Zealand) most succinctly defined the most significant pathways of cadmium toxicity in humans. He showed what could happen after excessive cadmium is ingested or inhaled. And Robert James of Stanford University (Calif.) discussed cadmium's effects on aquatic—especially marine—life. He suggested that one vehicle for bioaccumulation of cadmium in polluted waters might exist because of the metal's strong propensity to form chloride ion complexes. These complexes would make cadmium more available to marine organisms, because it is less removable than, say, lead and zinc, through oxide and carbonate sedimentation.

No phase out

Still, cadmium is and will be important to the world technological economy. It will not be phased out, so the search is on for ways to make its use safer. For the workplace, for example, Kenzaburo Tsuchiya of Keio University (Tokyo), and Robert Lauwerys of the Catholic University (Louvain, Belgium) recommended maximum exposure of 50 μg/shift. NIOSH recommends 40, but Finland's limits are 10–20 μg/shift, and that low limit was advocated by Lars Friberg of the Karolinska Institute (Sweden). The NIOSH/OSHA position on cadmium is to be found in the *Federal Register,* Vol. **42,** No. 19, January 28, 1977.

Some other straws in the wind have shown up. For instance, Rufus Chaney of the U.S. Department of Agriculture warned the conference that cadmium, if present in land-disposed sewage sludge, could concentrate in leafy vegetables. Also, near Philadelphia's ocean dump site for sewage sludge, scallops were found to have 59 ppm of cadmium (the drinking water limit is 0.01 ppm). And the American Chemical Society learned from Lawrence Loeb and Michael Seriover of the Institute for Cancer Research (Philadelphia, Pa.) that cadmium increases errors in cellular deoxyribonucleic acid (DNA) replications in genes and chromosomes.

For these and other reasons, and to assure safe cadmium supply for existing and future technology, the Cadmium Council, the Cadmium Association, and, especially, ILZRO, are setting up a nationwide study to monitor health effects on all workers exposed to the metal for more than one year from 1946 through 1976. These groups are also working to develop the necessary pool of knowledge and technology so that the use of cadmium—a by-product metal, perhaps, but so critically important in many fields—will not be discontinued. JJ

Prizes for cleanup achievements

Are environmental quality and economic growth compatible? EIC says "yes," and is giving out coveted awards to companies that prove it

Prizewinner. *Wheelabrator-Frye president Michael Dingman accepts EIC Premier Award for RESCO facility*

Many industrial companies endeavor to be "good citizens" of their respective communities these days. Some do so because of the force of the law, but others do so quite voluntarily, and some have even profited (*ES&T*, March 1977, p 234). Indeed, certain companies have become outstanding as "good citizens" from the environmental standpoint, and these have been recognized through the presentation of awards by the Environmental Industry Council (EIC) headquartered at Washington, D.C. (*ES&T*, February 1977, p 132). These awards were given for excellence in air, water/wastewater, and noise pollution control, solid waste management, and land reclamation.

Easing burdens

The actual presentation of awards was preceded by the environmental industry conference, "Economic Growth With Environmental Quality," held in Washington in late February, and attended by over 200 people. They heard EIC chairman John Autry, of Johns-Manville Corp., keynote the conference by explaining that the Council represents industry as a whole, and tries to help customers of the environmental equipment, consulting, and supply sectors ease the burden of compliance so that these customers may stay profitable. Autry also said that the EIC stands ready to explain the nature of the environmental industry; undertake projects; offer counsel concerning regulations; act as an information clearinghouse; and provide its membership with a voice in Washington.

The conference chairman, Frank Sebastian of Envirotech Corp., noted that it was a sequel to a meeting called in December 1975 by the Council on Environmental Quality (CEQ). At that conference, CEQ had estimated that pollution created 1 million jobs; at the February conference, Sebastian quoted a CEQ estimate that pollution control made 2 million jobs in 1976.

The conference heard from a panoply of speakers that could read like pages from "*Who's Who*." In addition to Autry and Sebastian, there were Harvard economist Otto Eckstein, Arthur D. Little consultant Craig Lentz, and former EPA administrator William Ruckelshaus. Futurist and Hudson Institute director Herman Kahn, Rep. Paul Rogers (D, Fla.), chairman of the House Health and Environmental Subcommittee, and other very highly distinguished speakers were also heard. Indeed, every speaker or panelist, whether from academia, industry, or federal or state government, was someone most notable in his field. If there was one thing they all agreed upon, it was that environmental compliance costs must henceforth be considered as part of the costs of doing business.

Air and water

For water, the first National Environmental Award went to Great Lakes Paper Co. (Thunder Bay, Ont., Canada). Great Lakes had to treat wastewater from its 250 000-tpy kraft pulp mill without aeration tanks or standard external treatment technology, because of the plant's small area. The answer was to install a Rapson-Reeve closed-cycle mill that discharges virtually clean water, and recycles heat, chemicals, fibers, and organics that are normally lost.

The clean air prize went to Volvo of America Corp., for its "240" series cars that meet Clean Air Act hydrocarbon, CO, *and* NO_x standards for 1978. The trick is a catalytic converter and exhaust gas sensor that controls all three pollutants, and helps to keep air/fuel mixtures at optimum levels, thereby enhancing fuel economy. The converter was developed jointly by Volvo and Engelhard Industries; and the sensor by Volvo and Robert Bosch GmbH of W. Germany. Perhaps this award will inspire other car makers to "try harder."

The Premier Award

A novel steam power station design providing for special low transmission walls and other features cut noise so much that Long Island Lighting Co. (LILCO, N.Y.) was able to install such stations near residential areas. This type of installation can reduce distances needed to transmit power to consumers, and earned for LILCO an award for noise abatement. And Erie Mining Co. (Hoyt Lakes, Minn.) was honored for its successful program leading to revegetation of infertile taconite mining wastes—a task previously considered impossible.

The Premier Award, however, came straight from the waste can. That top prize went to the Refuse Energy Systems Co. (RESCO, Saugus, Mass., *ES&T*, August 1974, p 692), owned by Wheelabrator-Frye, Inc., now of Hampton, N.H. in the first year of operation, the RESCO facility disposed of more than 250 000 t of solid waste, and made over 1 billion lbs of steam for the nearby General Electric Lynn River Works. Also, cost of garbage collection is reduced, and resources are recovered. Incidentally, the conference heard an estimate that energy from solid waste, extracted at the RESCO plant, is equivalent to that from 16–18 million gal/y of fuel oil, and, when the plant is fully on steam, will ultimately supplant that now derived from about 30 million gal/y of fuel oil.

All of these awards also do something else that is noteworthy. They serve as concrete evidence that environmental protection and economic growth can be quite compatible. This compatibility will be enhanced by the ingenuity, knowhow, and increasing corporate good citizenship of U.S. industry. It will act as a tangible expression of the "can-do" attitude that forms the backbone of the nation's strength, and is being fostered in environmental efforts through the activities of the EIC. JJ

Environmental health research update

"Human decisions . . . that influence our environment shape to a considerable degree the quality of our lives and the time and manner of our deaths." Then, with this premise in mind, what directions should environmental health research programs take in the next 5–8 years to ameliorate the adverse health effects of past decisions and prevent them from reoccurring? A task force composed of the nation's 80 leading health scientists was charged with answering that question.

The task force was formed in 1975 under the auspices of the National Institute of Environmental Health Sciences at the request of the House Committee on Appropriations. The House committee wanted an update of a 1970 report. The statement quoted above is from that update entitled "Human Health and the Environment—Some Research Needs," which was prepared under the direction of Norton Nelson (New York University) and James L. Whittenberger (Harvard School of Public Health).

Selective recommendations

This second report was produced against the backdrop of rising medical-care costs and the certainty that many environmentally caused diseases can be prevented or controlled. But the shibboleth in prevention is knowledge; that is, a better understanding of how environmental factors cause disease.

Eschewing sweeping recommendations, the scientists chose to identify only what they considered to be major and urgent issues demanding research. The report was written to serve as a "useful guide" for ordering priorities for research. All recommendations stressed disease prevention.

The report's drafters called for a better understanding of how toxic agents perform their dire deeds within cells. But they also recognized the need for more precise information on the transportation and transformation of pollutants at the global scale.

Air pollution

The task force considered four major groups of air pollutants—sulfur oxides, carbon monoxide (CO), photochemical oxidants and nitrogen oxides—and recommended that in the study of these pollutants, researchers consider pollutant concentrations as well as the temperature and humidity of the environments in which the pollutants are found. The report called for an examination of the synergistic actions of pollutants and for a greater consideration of the variations within and among species.

Citing the lack of specific information—in part because of current monitoring techniques—on the variety of molecular species and physical forms of sulfur oxides, the task force suggested that changes in the present ambient air standards for SO_2 and total suspended particulates not be made until such information is acquired.

Water pollution

Since organic chemicals in drinking water have been implicated in both heart disease and cancer, further research is needed to validate and then better define the relationship between these chemicals and the diseases. More refined analytical techniques are also needed to detect those nonvolatile organic compounds now going undetected.

Acknowledging that current disinfection methods produce potentially harmful organic compounds, the task force cited the need for studies to clarify the conditions that enhance the formation and/or retention of these compounds.

Inorganic elements such as sodium and cadmium as well as water hardness also influence heart disease. Elucidating their causative or protective roles is clearly an area for further research.

Occupational, other exposures

Occupational diseases is an area ripe for preventive strategies and for gathering valuable information on environmental hazards in general. Yet, the task force cited "an abysmal lack of information about many occupational exposures and their relation to disease." To remedy this, the task force called for the establishment of a National Death Index, and for better epidemiologic studies.

Beyond the workplace, studies are needed to better define indoor air pollution hazards in non-industrial buildings. And, with the adoption of a conservation program in the U.S., studies will be needed to elucidate the health effects of recycling and reusing waste materials.

The task force recommended . . .

- ***Better sampling, especially personal samplers, and analyzing techniques; more adequate quality control and calibration procedures***
- ***Better predictive tests; forecasting and assessment capabilities***
- ***Better correlation between epidemiologic and laboratory studies***
- ***Better understanding of how physical, chemical and biologic agents interact; more interdisciplinary research***
- ***Better understanding of the transport and transformation of synthetic chemicals***
- ***Improved capacity to extrapolate data from experimental test systems to man***
- ***Increased resources for the training of environmental health scientists and for basic research***

With the development of rapid-screening tests came the recognition of the plethora of compounds that can potentially cause birth defects, genetic diseases and cancers. The development of additional tests should only serve to indict more substances. Accepting this premise, the task force recommended that increased resources be made available for programs:

- to screen more compounds
- to monitor the population
- to study basic mechanisms
- to extrapolate data from experimental models to man
- to assess risk
- to train research scientists.

Early-warning signals

Behavioral toxicology as a new subspecialty evolved from the recognition of the sometimes subtle behavioral consequences of exposure to environmental contaminants. Here the task force recommended that procedures be developed for monitoring human populations to detect behavioral signs of intoxication early enough to ward off irreversible damage.

Other tests need to be developed to detect early toxic effects of pollutants on individual organ systems. Basic information, however, is now lacking on the reserve capacity of major organ systems and on the ability of these organs to adapt to environmental stresses. What information now exists clearly implicates some environmental toxicants in the induction or exacerbation, either directly or indirectly, of diseases of the heart, lungs, kidneys, blood vessels, blood-forming elements, and the nervous system.

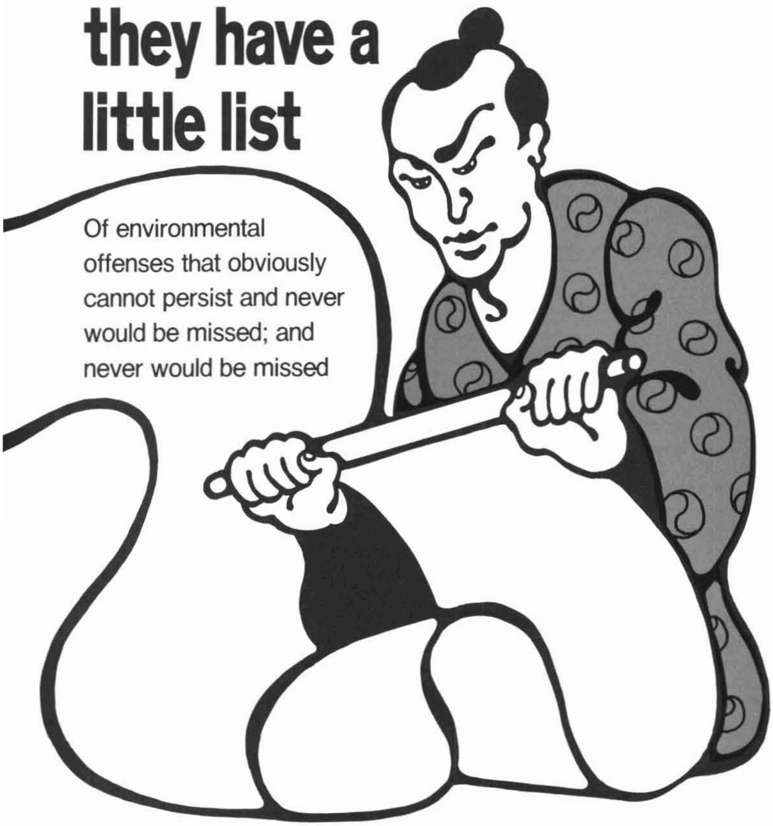
To standardize procedures

Noting that data insufficiency exists because of inadequate measurement methods or poor quality control and calibration of collected data, the task force called for the establishment of still another data bank—a National Environmental Data Registry. The task force felt that such a registry, properly designed and periodically updated, would ensure the collection, storage and retrieval of reliable data.

The reoccurring theme in the report was a more precise understanding of the relationship between environmental factors and disease so that points of intervention for control can be delineated and preventive measures taken. Clearly, the spiraling costs of therapeutic approaches dictate that preventive approaches be attempted. LRE

Environmentalists, they have a little list

Of environmental offenses that obviously cannot persist and never would be missed; and never would be missed



An unprecedented event occurred recently. Twelve of the nation's leading environmental groups, working as a task force under the sponsorship of the Rockefeller Brothers Fund, agreed to agree—at least on the major environmental goals that still need to be addressed by the U.S. in the next several decades.

The task force's deliberations were published as a consensus report entitled **The Unfinished Agenda.** To herald this "blueprint for action," a meeting was held last February in Washington, D.C., to which 250 of the faithful flocked. The well-timed release of the report, coming as it did at the beginning of the new Carter administration and before EPA and CEQ administrators were named, will no doubt influence the direction environmental matters take in the years to come.

In the report, the task force identifies nine problem areas—from energy, natural resources and pollution abatement to population control and genetic engineering—and proposes 75 specific actions to ameliorate, if not solve, present and foreseeable problems.

In constructive, thoughtful and, at times, lyrical prose, the environmentalists advocate that America shift from a "Consumer Society" to a "Conserver Society." Their agenda, which stresses conservation, reuse and recycling of materials, offers a society in transition the means of supporting itself as it moves from an era of natural resource abundance into an era of scarcity.

Energy: shift to low technology

Nuclear fission and synthetic fuels made from coal are wasteful of capital and energy, and are also environmentally and socially costly. Massive strip mining in the semi-arid West will probably never be acceptable, according to the report's drafters. Further, the task force proclaims, the electric utility industry is suffering from outdated utility laws that force the industry into practices wasteful of both capital and energy.

So what does a nation turn to when these high-technology options become infeasible? The task force's answer: soft technologies—solar and wind energy whose generating systems are small, numerous and near the point of use. And in this shift from depletable to renewable energy sources, the task force calls for end-use conservation through a better matching of energy supply to end-use needs.

Obviously, there will be energy gaps during this transition period. But, with the use of solar energy for space heating and cooling and the conversion of organic wastes to fuel alcohols, the sparing but more efficient use of fossil fuels can bridge the gaps.

On the matter of a nuclear future, the report calls for a phasing out of fission power generation. To keep the fusion option alive, the task force recommends the continuation of fusion research, but funded at a vastly reduced level.

While the report recommends a better integration of solid and animal waste management systems with energy and materials-recycling systems, future prospects are not so promising as they once appeared. Recently, Union Electric Co. of St. Louis, Mo. (*ES&T*, May 1975, p 418), abandoned plans for a solid-waste utilization system, and Monsanto pulled out of the Landgard solid waste pyrolysis plant that it designed for Baltimore, Md., although the city will continue operating the unit in hopes of correcting the bugs that have plagued the project.

From abundance to scarcity

In the face of an energy and minerals glut, the U.S. and other industrialized nations have prospered. Now, in the face of scarcity, comes the need for resource conservation, recycling and reuse of natural resources. As incentives, the task force recommends that product durability, especially for automobiles, be increased; that the sales price of manufactured goods reflect disposal costs; and that all interstate goods be labeled with disposal instructions.

A concomitant of increased durability would be the enhanced potential for reuse. And reuse would eliminate some of the problems attendant to recycling, namely, increased energy consumption and, occasionally, severe pollution problems.

A rather pedestrian but absolutely essential resource is becoming limited. This resource is water. To counteract present wasteful practices, the task force proposes that whenever economically plausible, water be recycled and reused. And, at the very least, a general principle should be adopted under which the users of water pay the total costs of providing that water.

Conceptually, a national water policy would consider industrial and agricultural development and environmental impacts. Since the U.S. presently has no water policy, the task force recommends that a commission be established to develop one.

Progress in air, water cleanup?

For lack of good monitoring systems, progress in air and water cleanup is difficult to judge. While emissions of the six criteria air pollutants have decreased since 1970, the data on water pollutants are too inconclusive to determine whether improvement has occurred nationwide.

However, it is becoming evident that current regulatory practices encourage non-compliance or unconscionable delays in abating air and water pollution. To rectify this, the task force recommends that a hybrid system be instituted whereby effluent (emission) fees or charges be tried on a nationwide basis for one pollutant or one industry while present regulatory limits also remain in effect.

On the water front, the task force comes down heavily on the recommendations of the National Commission on Water Quality. In contrast, the task force proposes that the principle supporting the goal of zero discharge by 1985 be reaffirmed; that timetables for compliance not be delayed; and that the provisions of P.L. 92-500 regulating toxic wastes, and state and areawide agency 208 plans for point and nonpoint sources be strengthened.

To combat air pollution, the task force proposes that EPA once again begin to establish national air quality goals for toxic pollutants such as fine particulate matter, especially lead, sulfates, organics and asbestos. More specifically, the task force recommends that EPA's research funds be significantly increased for programs to study the health effects of air pollution and to devise adequate monitoring networks.

Task force members

Gerald O. Barney
Rockefeller Brothers Fund

John H. Adams
Natural Resources Defense Council

David R. Brower
Friends of the Earth

George D. Davis
The Wilderness Society

Robert T. Dennis
Zero Population Growth

Thomas L. Kimball
National Wildlife Federation

Ian C. T. Nisbet
Massachusetts Audubon Society

G. Jon Roush
The Nature Conservancy

Arlie Schardt
Environmental Defense Fund

Maitland S. Sharpe
Izaak Walton League of America

Anthony Wayne Smith
National Parks and Conservation Association

Elvis J. Stahr
National Audubon Society

Paul Swatek
Sierra Club

The task force cites the need for revision of air quality criteria to include combinations of pollutants, and for research into their adverse effects.

Adding to the more frequent recommendations made for the regulation of toxic substances, namely better federal interagency coordination and full implementation of the new Toxic Substances Control Act, the task force calls for an "all-out effort to eliminate the single most significant cause of human cancer—tobacco smoke." Another less controversial recommendation is the establishment of a national registry of birth defects that would permit the identification of environmental teratogens in the course of epidemiological studies.

Threats from the engineered cell

A biological turning point, the ability to create new life forms, was reached when scientists learned how to manipulate the genetic material, DNA, through cutting and splicing techniques. The ability to insert gene-length segments of DNA from one organism into another, while it offers the opportunity for some startling medical and agricultural breakthroughs, presents grave threats to the environment because the results of these sophisticated manipulations are essentially irreversible.

The possibility of creating a life form that would be deadly to man or his domesticated animals is perhaps the worst consequence. But equally disastrous to man would be an outbreak of disease in an important agricultural crop or a significant disturbance to the ecology of a region. The major recommendation here is that recombinant DNA research be specifically restricted to laboratories of high competence and reputations, and that these laboratories be covered by complete and comprehensive guidelines.

Abolish "ad hocracy"

Citing both high inflation and unemployment rates as well as the increasing need to import more of our energy supply, the task force submits that something is awry in our national socio-economic system. In addition to the need to pay more attention to the preservation and enhancement of the environment, the task force calls for a restructuring of the decision-making process.

"Decision-making must be approached with more and better information, broader and more holistic analysis, and a longer-term perspective that corresponds with the fundamental problems now troubling the nation." Rather than more mindless growth, the task force asks for a rethinking of economic growth and serious consideration of a steady-state economy in which population and the stock of goods (including capital) are held constant, but technology, wealth and income, product mix, and such intangibles as wisdom and goodness, are in a state of flux. LRE

FEATURE

How to protect drinking water sources

Providing greater quantities, with improved quality, and without increasing costs was a topic that got top billing at the recent New Orleans National ACS Meeting

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It has been estimated by the U.S. Environmental Protection Agency (EPA) that there are between 30 000 and 40 000 municipal water supply systems in the U.S. having at least 15 service connections or regularly serving at least 25 people. In addition, there are more than 200 000 water supply systems serving non-residential locations. Many of these systems are simply not equipped to treat water from contaminated sources. Instead, they are designed primarily to disinfect relatively pure water from a carefully selected source.

As the demand for water continues to rise steadily, alternate systems may be pressed into service. This situation, coupled with the increasing volume, variety, and complexity of contaminants that have been allowed to enter these drinking water sources, have posed some serious questions concerning the potability of the water.

The National Community Water Supply Study of 1970 and the National Organics Reconnaissance Survey of 1975 have each focused upon the often-serious recorded instances of drinking water contamination in the U.S. During the period 1961–1973, there were more than 200 outbreaks of disease or poisoning conclusively attributed to drinking water. These outbreaks resulted in 54 537 recorded illnesses, many of which were serious; twenty-two people died as a result of these illnesses.

Many water supply experts believe that perhaps ten times as many such outbreaks occur, but go unreported for a variety of reasons. Countless individual sufferers and even their doctors often fail to associate ailments with contaminated water. Furthermore, these statistics represent only the acute effects and not the hard-to-measure chronic effects that may take many years to aggregate their impact. A case in point is the chemicals identified in drinking water that are known carcinogenic or mutagenic agents.

In many countries of Asia, Africa, and Latin America, the situation is beset with even more serious problems. Water-borne diseases exact a heavy toll on their population, especially the young. Deaths in these countries from enteric diseases are often more than one hundred times greater than the statistics quoted above.

A national program designed to resolve these problems was initiated with the enactment of the Safe Drinking Water Act on December 16, 1974 (*ES&T*, March 1975, p 194). The Act marks the first time a national commitment has been made to safeguard public drinking water. One of the more obvious effects of the passage of this legislation has been a growing realization that the national water supply requires better management and control. Safe drinking water can be considered neither unlimited in supply nor virtually a free commodity.

In its implementation of the Act, the EPA has expressed the need for well-designed water treatment facilities operated by competent personnel to assure the production of water that poses no threat to the consumer's health and is aesthetically acceptable. Because many systems do not currently provide the level of treatment necessary to remove many of the contaminants listed in the EPA-promulgated Primary Drinking Water Regulations, there will be a substantial need to upgrade facilities. Many systems will need to invest significant sums of capital because of the high cost of advanced treatment techniques.

A significant number of local water suppliers may in fact face serious financial problems meeting these regulations. There is no question that water treatment facilities can ultimately be designed to provide safe water to the consumers. However, it is doubtful whether the resources or the specially trained manpower to operate the plants are available. The abatement and control of contamination at the drinking water source may become increasingly important to assist in the production of potable water that will be in full compliance with the provisions of these regulations.

The symposium

Because of the potential that water quality enhancement through source protection offers in helping to hold down the rising cost of drinking water treatment, the Environmental Chemistry Division of the American Chemical Society sponsored a symposium on this topic at the national meeting in New Orleans, La., featuring a program of 26 speakers. A wide variety of source protection alternatives were presented for both surface and groundwater potable supplies. Emphasis was placed on the objective of addressing the effectiveness of these resource management techniques and the potential savings they may offer by lowering the operating costs of existing water facilities or by allowing a supplier to postpone the construction of these facilities when adequate source protection is provided and documented.

This symposium marks the first time drinking-water quality experts representing a wide variety of professions have pooled their resources to evaluate the concept and validity of source protection in a society that often relies on technology to purify the cheapest available and sometimes the most contaminated source of water. Probably the most important point was the realization that active source protection measures should always be considered as the first line of defense against potable water contamination.

Under no circumstances should there be an overreliance on treatment technology to remove the contamination. Instances were presented where the best available technology for drinking water treatment was unable to effectively remove certain organic chemicals from the water by using standard operational practices. However, these same contaminants were effectively eliminated by treatment at the source of contamination.

Another important point was the confirmation of the symposium's main objective, namely, that active source protection programs can help to reduce the costs of terminal drinking water treatment. However, no hard dollar figures were available to strengthen this claim. Whenever source protection is practiced, it must be confirmed with a careful monitoring program in case an unsuspected or unnoticed source is contaminating the water. Suggestions for monitoring and surveillance programs for both surface and groundwaters were presented during the symposium.

Present status

Source protection is often confused with the concept of purchasing or mandating a controlling interest in the area surrounding a particular water resource, then restricting or prohibiting the use of this area in the interest of maintaining water quality; there are many instances in the past when this did, in fact, happen. Source protection has since evolved into a more rational approach to the same goal.

A water quality enhancement program for any potable water source must be developed on a case-by-case basis. Each source is subjected to different forms of contamination and has differing capacities of assimilating these wastes. Once these factors have been appraised, a series of management options can be instituted on the source to prevent water quality degradation.

The historic posture of the water supply industry, itself, in protecting the source of potable water supply was presented by Chester A. Ring, 3rd, president of the American Water Works Association. Strict forms of source isolation have been practiced in the past to help prevent pollution of these most desirable water sources. Compromises from past practices have been made necessary to accommodate the changing conditions relative to multiple use of surface water sources. Increased use of new analytical techniques in conjunction with regular source surveys help the water utility to locate sources of potential water contamination and to deal with them effectively as part of their source protection program.

Any discussion of the viability of source protection must focus on the EPA's implementation of the Safe Drinking Water Act. Even though source protection is not specifically addressed in the Act as a means for enhancing and protecting the quality of all drinking water sources, the obvious need for adequate source protection measures is recognized. Basically, the law mandates two programs:

- public water system supervision programs
- protection of underground sources of drinking water.

Victor J. Kimm, EPA deputy assistant administrator, told the symposium that production of water that poses no threat to the consumers' health depends on continuous source protection. However, because of the human frailties associated with protection, adequate treatment should always be provided. Contaminated sources should not be used unless other sources are economically unavailable, and then only when personnel, equipment, and operating procedures can be depended on to purify and otherwise continuously protect the drinking water supply.

Section 1446 of the Act created a National Drinking Water Advisory Council to assist the EPA in the formulation of policies pursuant to the implementation of the Act. *ES&T*'s editor, Russell Christman, a representative of the Council, viewed the mechanisms the Council has adopted for accepting public input, evaluating agency plans, and communicating with the EPA administrator.

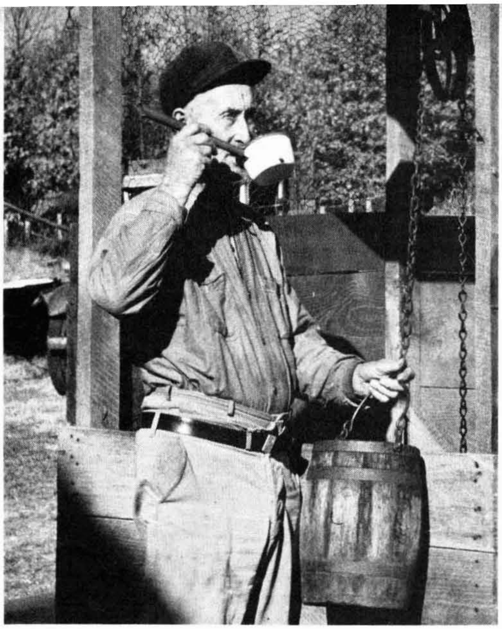
Over the past two years, attention has been given to determining the degree of human health risk associated with contamination of the drinking water. Whereas the adequacy and cost of present technological options intended to reduce contaminant exposure levels is of utmost concern, the Council is interested in obtaining input related to the adequacy of source protection measures in this regard.

Future status

Source protection options for the future were outlined by Daniel Okun of the University of North Carolina at Chapel Hill. These options fall into three categories:

- The contaminants can be eliminated at their source.
- The contaminants can be monitored and removed in treatment.
- Drinking water can be drawn from sources protected against contamination, such as upland streams or groundwaters, while contaminated waters can be used for the myriad of non-potable uses that pose no threat to the public health.

Because of the ubiquity of the contaminants in domestic and industrial wastewaters and in urban runoff, the first alternative is not very promising. The necessary resources in technology and qualified manpower are not available for the second option to be useful. Okun urged that the final option warrants further study by those responsible for planning public water supplies.



Unprotected. *This well may be an unsafe water source*

Regional differences

Many source protection efforts are conducted on a regional or statewide basis. Various approaches to the subject and the problems encountered were the topics of a number of symposium speakers.

Experiences with source protection in the highly populated Northeastern part of the U.S. was discussed by Floyd B. Taylor of the EPA Region I Water Supply Branch. In this region the general approach to source protection is that it provides the first line of defense in the production of potable water. Failure to protect the source places critical loads on terminal drinking water treatment.

One of the interesting problems that has surfaced in this region centers about the financial problems encountered by major private water purveyors who must face increased real estate tax payments on their large land ownership within the watershed and must cope with increasing regulatory pressures to construct or upgrade drinking water treatment facilities. Their efforts to relinquish their valuable land holdings to gain a source of revenue have met with intense suspicion and opposition from environmental and civic groups. Taylor pointed out that the proper resolution of these problems is essential to the protection and well-being of the region's people.

Charles T. Elly of the EPA Region V Surveillance and Analysis Division outlined a number of the water supply source protection practices used in the Great Lakes Basin. Among the programs discussed were the regionalization of water supply systems by using relatively pure sources, use of man-made "upground or offstream" reservoirs for surface water supplies, and increased use of natural and artificial recharge areas for enhancing overused groundwater supplies.

Recognition that state water supply protection programs are usually much better on paper than in reality was pointed out by Thomas G. Reeves of the EPA Region VII office. Many states have suffered from the lack of funds, lack of manpower, and in many cases, a low priority delegated to drinking water source protection. Prior to the passage of the federal environmental laws, many states had certain programs involving several state agencies, resulting in extensive overlapping of responsibilities, along with the conflicts this brings. Many changes are now taking place as the states begin to assume primacy for their implementation of the Act.

An example of what the states can do with regard to source protection is the recently instituted surveillance and monitoring program for Connecticut public water supply watersheds. These programs were developed as part of a unique effort involving waterworks industry representatives and the state regulatory officials. Anthony R. Castorina of the Bridgeport Hydraulic Company explained that the adopted guidelines:

- provide complete and accurate data on watershed areas
- provide a means to control acceptable land uses and prevent unacceptable uses
- serve a practical function for all size utilities in protecting their water sources
- provide the instrument of compliance to the State's implementation of the Act.

Within the guidelines a minimal drinking water source sampling program was specified that would monitor the effectiveness of the surveillance program.

Underground sources

Groundwater offers an immense potential source of drinking water. It has been estimated that global groundwater is more than 2000 times as plentiful as all fresh surface water combined. In the U.S., EPA estimates that nearly one-half of the population relies on underground sources for their drinking water. Of the total population, 29% use groundwater delivered by community systems and another 19% have their own domestic wells. Over 95% of rural domestic supplies are derived from subterranean aquifers.

Even though groundwater has such great potential, there are only a few areas where there is adequate data to determine the groundwater quality within a given aquifer. For much of the country, only when contamination of the aquifer is suspected is information on the groundwater quality collected. In the past 5–10 years, the number of major incidents of groundwater contamination have increased dramatically. These incidents involved chemical spills, municipal landfills, wastewater lagoon seepage, and industrial waste burial. An entire session at the symposium was devoted to methods of preventing contamination of the groundwater potable sources.

Section 1421 of the Safe Drinking Water Act calls for the establishment of requirements for state programs to protect underground drinking water sources from contamination by the injection of fluids. Thomas E. Belk of the EPA's Office of Water Supply described the recently developed State Underground Injection Control Program (40 CFR Part 146).

Within this program, underground injection practices will be regulated by permits issued for the following activities: industrial and municipal waste disposal; storage, subsidence control, mining, geothermal, barrier, and recharge wells; injection of brine or other fluids that are brought to the surface in connection with oil and gas production, and injection for the secondary or tertiary recovery of oil or natural gas; and injection by drainage wells. State programs offer potential as a source protection technique by prohibiting injection that endangers underground drinking water sources.

Problems with sludge disposal

Because other environmental regulations in the U.S. have reduced emissions to the atmosphere and surface waters, much of the municipal and industrial wastes have been disposed of on the land in the form of solids and sludges. Liquids associated with the wastes, in combination with natural precipitation, cause the formation of leachate. This leachate percolates into the soil and the unsaturated zone, carrying contaminants to the groundwater system. Often these contaminants move as a plume or slug with slow groundwater flow rates, being slowly diluted by diffusion, dispersion, and chemical or physical attenuation.

Olin C. Braids of Geraghty and Miller (Port Washington, N.Y.) discussed the effects of industrial hazardous waste disposal on the groundwater resource. He concluded that the effects of geochemical and geophysical processes cannot be accurately predicted without a hydrogeological study of the area and a characterization of the wastes in question. Potable groundwater

Water quality index

Drinking water consumers are not only interested in whether the water is safe to drink but also in the following questions: does it smell all right, does it taste all right, and, is the water source pretty to look at? In order to monitor their perception of water quality and to make political decisions on the desired quality and the means to achieve this goal, they need an index that can describe, in a single number, this elusive entity.

Conversion of this desire for a water quality index into a reproducible formula for calculating the index involves a series of judgments, which will eventually determine the form and utility of the index. Because the answers to these questions must also be expressed in subjective terms, one needs to use commonly measured parameters that will allow one to assign some objectively determined value to the quality of the water. Though the arithmetic mean is the obvious first choice, it has the shortcoming of failing to go to zero when the value of one of the parameters becomes poor to the point of rendering the water useless for drinking. One would wish for an index by which high contamination would cause the index to go to zero when 100 is ideal water quality.

A geometric mean has this property, and has the additional advantage that it is less affected by extreme values. If a geometric mean is to be employed, the water quality index would take the form:

$$\mathrm{WQI} = \left[\prod_{i=1}^{n} f_i^{a_i}(P_i)\right]^{1/\sum_{i=1}^{n} a_i}$$

where P_i = value of ith parameter
$f_i(P_i)$ = sensitivity function for ith parameter
a_i = weight attached to ith parameter
n = total number of parameters

Sensitivity functions must be assigned to each quality parameter. The sensitivity functions range from zero (completely unacceptable conditions) to one (ideal conditions). The functions are determined by the impact that a change in the value of the parameter has on water quality.

Because a change in value has more impact at lower concentrations for most substances than at higher concentrations, a negative exponential curve would best represent the sensitivity function for most quality parameters (odor, NO_2-N, color turbidity, coliform bacteria).

Temperature and pH, however, are represented by a parobolic sensitivity curve and dissolved oxygen by a linear log-log plot. Also, if certain water quality parameters were determined to be of greater interest, they can be weighted as shown in the equation.

Thus, if used properly, a water quality index can provide the citizenry with a meaningful way of evaluating the quality of its drinking water. The index can also furnish taxpayers with an idea of how well money spent on water quality maintenance is doing its job.

sources should be protected from surface disposal activities by a carefully managed monitoring system so that potential contamination can be detected and steps taken to remove or contain it. Land disposal of these hazardous wastes is a practice that, without proper controls, has the greatest potential for severe and large-scale contamination of groundwater.

Methods of minimizing the impact of the land disposal of municipal wastewater sludges on groundwater supplies were presented by Dennis Pennington of Richard S. Cowan & Associates (Quakertown, Pa.). Proper management of these sludges must be conducted within an institutional framework. Major elements of such a management program include the following: disposal site selection criteria; guidance to identify groundwater withdrawal areas, regions of aquifer overpumping, and critical recharge areas; a systematic monitoring and surveillance system; and the establishment of an operational control plan and an areawide long-range water supply plan.

Wetlands are areas that often have a high rate of groundwater recharge. These areas are particularly sensitive to contamination from the effects of urban encroachment, such as landfilling for roads and houses, increased contaminated storm runoff, and septic systems.

Walter S. Mulica of Interdisciplinary Environmental Planning (Wayland, Mass.) discussed means of evaluating wetlands with respect to their water quality improvement function. Once the wetlands have been evaluated, various alternatives must be used to protect significant wetlands and their associated water supplies. These alternatives include the direct purchase of wetland areas, enactment of land-use zoning in and/or adjacent to the wetland, and implementation of a protective buffer surrounding the wetland.

Joseph J. Delfino of the Wisconsin Laboratory of Hygiene discussed a number of actual instances of serious contamination of potable groundwater supplies in rural Wisconsin areas and speculated on their impact. Included in his presentation was nitrate contamination from farming activities and an accident resulting in a hazardous material spill (phenol). The institutional problems of dealing with this contamination and the means of preventing similar instances in the future were discussed.

If an aquifer serves as the sole or principal drinking water source for an area, the Act contains a provision that can protect the source from contamination that would create a significant hazard to public health. Mac A. Weaver of EPA's Region VI office discussed how the provisions of Section 1424(e) of the Act has led to the development of procedures that afford the maximum protection to the quality of water in the Edwards Underground Reservoir (Texas). The protection afforded to this aquifer does not prohibit reasonable development in the designated area. However, it does provide that there will be a careful review of all such projects with respect to protection of the quality of the water at the source.

Surface water sources

A majority of Americans still rely on surface waters as a potable water source. These water bodies vary tremendously in their chemical, physical, and biological characteristics, depending on their hydrological regime, climate, nature of the watershed, and their water uses. Consequently, water quality problems also vary and most must be dealt with on a case-by-case basis.

Contaminants may impact on surface water quality in various ways, depending upon the nature of the substance. Nutrients, such as derived from domestic sewage and commercial fertilizers, may cause accelerated eutrophication. Sediment from erosion-creating activities in the watershed may add to eutrophication problems or create unique problems in the absence of eutrophication. Toxic substances may contaminate water supply sources, interfere with normal aquatic biological activity, or otherwise render the water unfit for certain recreational activities.

The general approach to the enhancement of the quality of degraded surface waters must be twofold:

- restricting the input of contaminants to the water
- providing at-source treatment for the amelioration of the effects of these constituents.

Reducing or eliminating the sources of contaminants may be all that is necessary to enhance the quality of surface waters in which natural flushing aids are used in the self-purification process.

However, in many lakes, particularly those with long hydraulic retention times, at-source treatment or lake restoration schemes may also be required before significant water quality enhancement will be realized. The maintenance of high surface water quality is important when multiple use of the water is considered. Water quality management is essential if the water is to be used as a drinking water source without overreliance on elaborate terminal water treatment facilities.

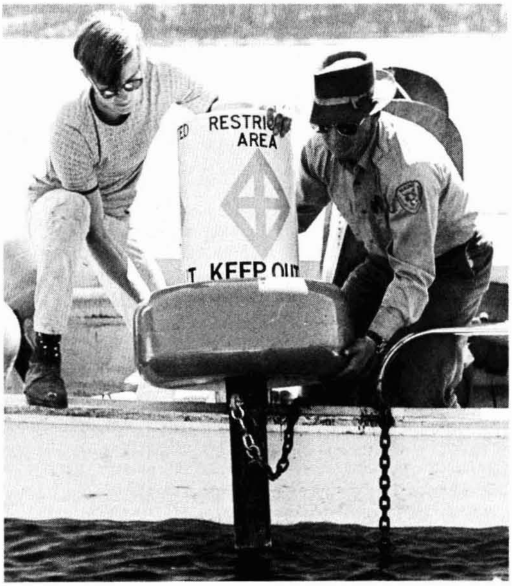
Multiple use of surface drinking water supplies is still a controversial subject. Jochen Kühner of Meta Systems (Cambridge, Mass.) pointed out that conflicts over the use of water supply watersheds and the reservoirs themselves are not new by any means. However, little progress has been made on developing rational means for resolving the differences in opinion. He proposed the assessment of existing methodologies for the evaluation and control of watershed land use in light of a literature review and a detailed examination of the historical context of water supply watershed land use.

The methodology that has evolved from this study involves an operational mathematical hydrological model designed to predict temporal and lateral transport, transformation, and the ultimate fate of contaminants through the watershed and water source itself. Pertinent methods of structural and nonstructural contamination control and the simulation of their effects are included in the modeling effort.

Recreational use

The demand for water-oriented outdoor recreation continues to increase, especially near urban areas. As this demand rises, source protection programs must give serious consideration to the recreational use of the land and water resources. Valid justifications for controls on the recreational uses must be provided, along with the strict enforcement of these controls. In this manner water quality can be maintained at the source.

Michael R. Alford of Urban Systems Research and Engineering (Cambridge, Mass.) reviewed the experience of providing recreation at water supply reservoirs. He also outlined the important planning and management considerations that help ensure that recreation is compatible with the production of safe drinking water. Many of the planning alternatives discussed served as the basis for the Council on Environmental Quality's handbook on increasing the recreational potential of water supply reservoirs.



Indicators. *Buoys will mark out a protected source*

Howard S. Peavy of Montana State University has conducted an extensive literature search on the specific effects of recreation on selected water quality parameters. He reported that the concern over the effects of multiple use may be justified at times. However, little quantitative data have been advanced to support rational decisions concerning the public use of water supply watersheds. An analysis of the literature with respect to the EPA's Primary Drinking Water Regulations indicates that most water supplies where multiple use is practiced will have to be treated to some extent to meet the standards before distribution to the consumers.

An exception of this generalization is Lake George (New York), which is used as a source of potable water by many residences and businesses around the lake, often with no treatment whatsoever. Community supplies that use this source only chlorinate the water as required by the state for disinfection. The interesting point made by Donald B. Aulenbach of Rensselaer Polytechnic Institute is that there are no restrictions on the recreational use of the lake. While the morphological characteristics of the lake contribute significantly to the high quality of the water within the lake, a key provision in maintaining the quality is the strict enforcement of sewage disposal regulations. The Lake George Association and the Rensselaer Fresh Water Institute have organized active public participation programs that have helped heighten the vigilance in controlling contamination of this popular lake.

Robert P. Grady of the Portland (Maine) Water District described his utility's developing source protection program on a large multi-purpose lake. From his experience, he conjectured on the ideal watershed management program, the establishment of a Resource Protection District. This would be a powerful group with controls over any activities that might adversely affect water quality. Water uses on all tributaries would also be controlled. It would have the authority to plan, zone, and enforce the provisions that are developed within the program. A key ingredient in the success of such a group is the solicitation of active public involvement.

A regional development project involving source protection of the City of Newark (N.J.) potable water supply was evaluated by Thomas J. Olenik of the New Jersey Institute of Technology. The "Penquannock Watershed Conservation and Development Plant" calls for increased residential development and recreational use of the watershed while maintaining the quality of water in the reservoirs. The planned urbanization of selected sections of this watershed must be carefully evaluated and controlled by a systematic program designed to quantify changes in water quality brought about by this development. If this is not done, major water quality changes could result.

Many reservoir systems have their sources in back-country water supplies. These remote systems are also the source of noncommunity supplies and trailside watering holes for the millions of people who use the wildland for recreational pursuits. Many of these historically pristine bodies of water are succumbing to the inevitable contamination from increased use of these recreational resources. Wildlife and occasionally domestic animals add to the contamination problems.

Sara H. Surgenor of the Appalachian Mountain Club described the efforts being made to resolve the potential conflict between these uses. The prime emphasis in the program is on adequate means of waste disposal in the high-use areas. This is often a difficult problem in remote rocky terrain of the White Mountain National Forest (New Hampshire), for example.

Organics

A major concern over the increased use of water that ultimately serves as a potable water source is contamination by toxic and carcinogenic substances. EPA chemists found 66 different organic chemicals in the New Orleans, La., drinking water by using a variety of analytical techniques. Levels of the trace contaminants were generally less than 1 ppb. However, EPA is uncertain about their long-term epidemiological effects with respect to total cancer mortality at these levels.

Herbert J. Brass of the EPA Office of Water Supply Technical Support Division explained that organic chemicals in drinking water can arise from the following sources:

- naturally occurring organic matter
- contaminants introduced as the result of water treatment
- synthetic chemicals from industrial point sources
- synthetic chemicals from nonpoint sources.

The measurement of organic compounds and the determination of the sources of contamination has been the goal of the National Organic Monitoring Survey (NOMS). The objective of this survey is to obtain data in support of the possible establishment of maximum contaminant levels of organic contaminants in drinking water. Once this information is obtained, sweeping efforts can be made to more adequately control these contaminants.

Natural organics in the water are primarily regarded as an aesthetic problem. However, these compounds can be converted into carcinogenic substances, such as chloroform, when chlorination is used for disinfection.

Bill O. Wilen, St. Petersburg, Fla., discussed a number of options for controlling the influx of natural, dissolved organic substance produced in the watershed. These options include a number of watershed management techniques and modifications in the design of the water supply intake systems.

Probably the most widely cited source of carcinogenic contaminants in drinking water sources is from point sources located on the water body. James F. Manwaring of the EPA Region III Office describes a unique pretreatment system that has been effectively used at a discharge point to reduce the concentration of organic contaminants. The system is based on destruction of organics rather than absorption. It is interesting to note that such a system was far more effective in eliminating the concentration of the organics than was an advanced carbon adsorption system installed at the drinking water treatment facility.

Water indices

When any program is undertaken to enhance the quality of water at the source, it is helpful to have a water quality index available with which to meter the program's success, although there are a number of these water quality indices available.

Frank L. Parker of Vanderbilt University has developed an index specifically for drinking water reservoirs. His index correlates the consumers' perception of the water quality with a scientifically determined index of the water quality. This index should be more useful to those people who must make decisions regarding the quality of the water used as a potable source.

Certainly a two-day symposium cannot begin to answer or even pose all the questions concerning drinking water quality enhancement through source protection. However, this gathering did take the first step toward increasing the level of discussion concerning this valid technological approach to the delivery of safe drinking water to the consumer. The symposium manuscripts, and others, will be published later this year by Ann Arbor Science Publishers. This expanded forum of information should provide EPA and regulatory agencies in other countries with the basis for including source protection programs in their regulations dealing with the quality of drinking water.

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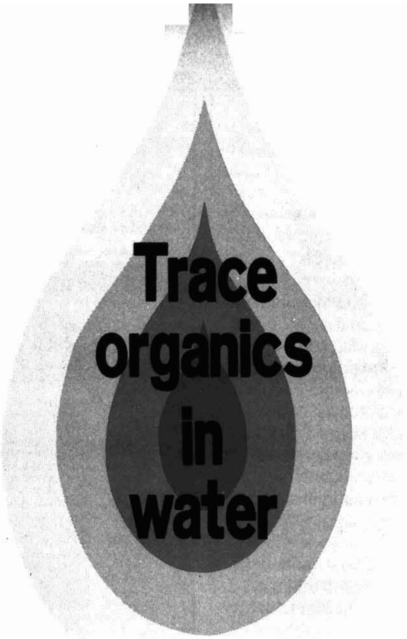
Coordinated by SSM and JJ



Trace organics in water

Refined methods are needed to document their occurrence and concentrations

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Scientific interest in trace organic chemicals in water has skyrocketed in the past two years. The indication of this growth has been a marked increase (over sevenfold since 1971) in the number of articles published annually on environmental applications of organic mass spectrometry, the most widely used tool for identifying organic compounds in waters.

This increased interest has resulted from improved capabilities for identifying and measuring large numbers of compounds at trace levels and from recognition that many organic compounds cause serious adverse effects (including cancer inducement) in laboratory test animals. Unfortunately, very little is known about the human health effects of trace quantities of organic chemicals in water. Basic to an assessment of human health effects is better documentation of the occurrence of trace organics as well as accurate measurements of their concentrations in natural waters.

Waterborne organic compounds

More than 2 million organic chemicals have been identified. The number of these compounds detected in a sample of water is related to the sensitivity of the measurement technique: as the detection level decreases by an order of magnitude, the number of compounds detected increases accordingly. Based on the number of compounds detected by current methods, one would expect to find every known compound at a concentration of 10^{-12} g/L or higher in a sample of treated drinking water (Figure 1). Therefore, to discuss the composition of water in a purely qualitative sense is meaningless, although many reports have listed compounds identified without concentration values.

For the "zero tolerance" proponents, it should be noted that 10^{-12} g/L is approximately 10^{10} molecules/liter; most water treated for domestic consumption contains about 10^{-3} g (10^{19} molecules) of organic material per liter. Drinking water will probably always contain large numbers of organic compounds. What we must do is determine which ones are there in concentrations significant enough to pose a hazard to human health.

A U.S. Department of Health, Education and Welfare Directory of toxic compounds lists 1500 suspected carcinogens. Of 6000 chemicals that have been tested for carcinogenicity, 1000 showed some carcinogenic activity. The important question, then, is what constitutes a significant concentration? To date, toxicologists are unable to determine no-effect levels of carcinogens in man by extrapolation from the no-measurable-effects level in laboratory test animals. Neither can they prove from an animal experiment that a substance is *not* carcinogenic to man.

The epidemiology of carcinogens and chemicals that are only toxic when present chronically is also difficult to delineate. Most relationships between human exposure to chemicals and development of cancer have been observed following occupational contact with such substances at much higher levels than those encountered normally. As the exposure concentrations approach levels encountered in non-occupational activities, the relationships begin to get lost in the "noise" created by other factors.

Two approaches have been used in selecting compounds in the environment that should have a high probability of being significant in respect to their cancer-causing potential. In one list of about 50 compounds, the major selection criteria were their known or suspected adverse health effects and their *predicted* occurrence, based largely on quantities manufactured and their uses. A second list of compounds was compiled based on the number of times any organic compound had *actually* been observed in water. All available literature and laboratory reports were examined in preparing this latter list, and data known to have been collected in a manner that would have biased the listing were rejected. For example, results of an extensive survey specifically for toxaphene would have been excluded. Many of the analyses were made by techniques that should have revealed the presence of most of the 50 compounds on the first list. Fifty-five hundred observations revealed 1296 different compounds occurring at the frequencies shown in Figure 2.

Although many of the 50 compounds from the first list, such as halomethanes, chloroform, and toluene, were among those most frequently observed, several others of the 50 were observed less than twice. Conversely, quite a few compounds that were not on the initial list were observed in environmental waters at relatively high frequencies. A comparison (see box) of some of the 50 that occurred infrequently is shown to some frequently occurring compounds that were not on the list but could be of concern based on their known toxicity or other characteristics.

There are several shortcomings in the manner in which the actual frequency of occurrence was developed. Concentrations were often not reported and were not considered, and no sampling program was designed specifically to provide frequency distribution. It is obvious, however, that many compounds must be considered in analyzing environmental samples. Some compounds occur frequently, but many occur only sporadically. Comparison of the two lists clearly indicates the difficulty of predicting what will be found in environmental waters without actually analyzing the water.

Surveying the chemicals

An important, and often overlooked, factor concerning trace organics in water is that, in nearly all cases, only those compounds that are volatile enough to pass through a gas chromatograph are identified and measured. In addition, the group of identified compounds usually is further restricted to those that can be extracted from water by a nonpolar solvent such as chloroform or hexane. Sometimes, in fact, only those that are sorbed by carbon and then extracted are identified. Because of these restrictions, only 10–20% of the total mass of organics in most waters are analyzed.

Polar and nonvolatile compounds are not measured because no practical methods of chemical analysis have been developed. The impact of this analytical limitation is dramatically demonstrated by the total absence of nonvolatile compounds from the list of 50 potentially significant compounds. Few, if any, of the 1296 compounds actually found in environmental waters would not pass through a gas chromatograph.

To determine which chemicals in the environment cause cancer or other adverse chronic health effects, a program should be developed to identify and measure organic compounds in all media, for selected geographic areas, in which a specific human health problem is significantly higher than normal; corresponding areas in which the same problem is significantly lower than normal should also be examined.

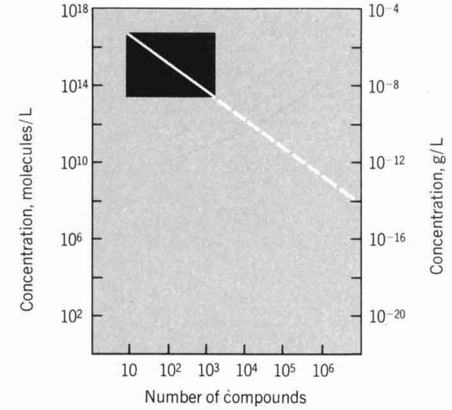
It is important that all compounds amenable to analysis be identified and measured—not just a limited number of preselected ones; otherwise the most significant compounds may be overlooked. This approach would provide at least some chance of identifying significant compounds that have been present long enough—for carcinogens this may mean a decade or two—for their effects to become obvious. To determine which compounds may now be causing health problems that will not be observed for several years, a survey of the entire nation is needed. Because so many compounds must be considered, a highly comprehensive analysis is obviously required.

Comparing predicted *(left)* and observed *(right)* organics

On the first list		*Not on the first list*	
Chemical	**Times observed**	**Chemical**	**Times observed**
Benzidine	2	**Acetaldehyde**	19
Dichlorobenzidine	0	**Aniline**	11
Diphenylhydrazine	2	**Benzothiazole**	18
Hexachlorocyclohexane	1	**Biphenyl**	28
Nitrosamines	0	**Chloral**	10
2,4-Dichlorophenol	2	**1,4-Dioxane**	15
2,4-Dimethylphenol	0	**Nitromethane**	10
Toxaphene	2	**Pyrene**	15
Acrolein	0	**Xylene**	91
Chlorinated naphthalenes	0	**Styrene**	23

FIGURE 1

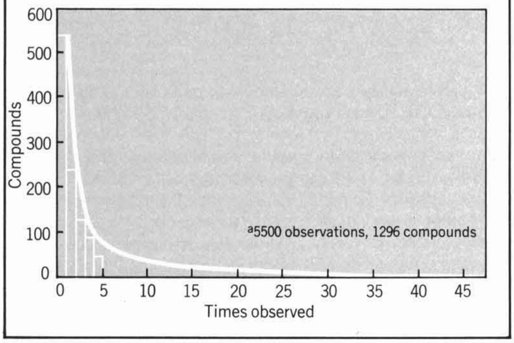
Detecting organic compounds in environmental waters[a]



[a] Compounds at concentrations of 10^{-5}, 10^{-6} and 10^{-7} g/L in drinking water were detected by GC—MS. The box represents the number and ranges of concentrations of compounds normally found in drinking water.

FIGURE 2

Occurrence of organic compounds in water[a]



The detection level adopted for this survey must be selected carefully because it determines the number of compounds that can be identified. The level must be low enough to reveal all important compounds, but not so low that it makes analysis unduly difficult. In drinking water, those compounds at the highest concentrations are usually present at 10^2 μg/L or less. At 10^{-2} μg/L, the analyst's ability to separate compounds is taxed. Therefore, a detection limit of 10^{-2} or 10^{-1} μg/L is usually selected for drinking water and for water from most lakes and streams. A higher level would probably be selected for wastewater effluents because their constituents are generally more concentrated.

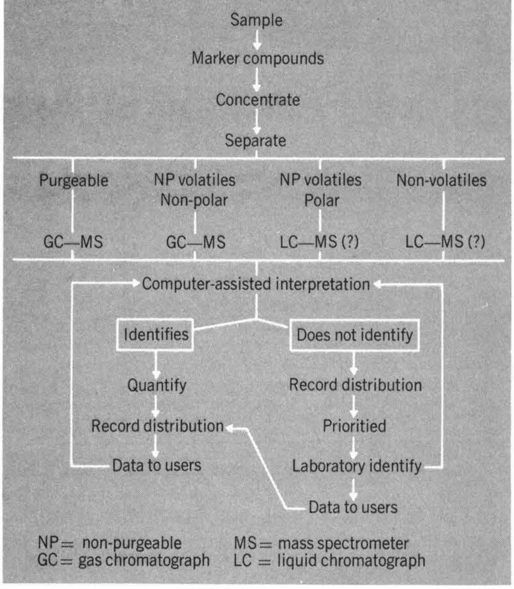
The analytical approach

Although the following techniques are not all fully developed, this approach to chemical analysis indicates what is involved in a comprehensive survey analytical scheme.

Samples can be collected either by "grabbing" a liter of the water of interest, or by passing a larger quantity through carbon- or macroreticular-resin accumulators (Figure 3). In the laboratory, some volatile compounds are purged from the sample with inert gas and sorbed onto a resin. The nonpolar compounds remaining in water or on accumulators are extracted sequentially with appropriate organic solvents to effect a preliminary separation. The next step involves concentration by evaporation of both the extracts and the polar compounds still in the water. Marker compounds to indicate retention time and provide quantitation references can be added prior to concentration.

FIGURE 3

Analyzing for organics in water



The concentrates are injected into gas chromatographs, or high-pressure liquid chromatographs, coupled to low-resolution mass spectrometers, which record spectra of all separated compounds. A central computer tentatively identifies sample components by matching their spectra with those of known compounds in a computer library. When the computer "identifies" a compound, it also selects an appropriate marker compound for automatic computation of concentration and relative retention time, which can help substantiate the tentative identification.

Spectra of compounds that are not in the computer file are listed separately by the computer and numbered to determine their frequency of occurrence, even though they are not identified. These compounds must be identified by generating and analyzing additional spectral information. Frequency of occurrence of unidentified compounds is a useful factor in ordering them for identification.

An analysis of the steps in the proposed approach reveals many unmet needs for research, beginning with the sampling process. Grab sampling is simple enough for stable, nonvolatile compounds, but improvements are needed to make certain that volatile compounds do not escape and that others do not decompose or interact during storage. The use of accumulators raises the need for further studies to determine appropriate accumulator materials, optimum flow rates, and removal efficiencies for all compounds or classes of compounds of interest. Development of a sampling device to accommodate accumulators and to meter flows is also required.

Solvent extraction from the accumulator or from the grab sample is often performed without adequate optimization of extraction conditions or adequate knowledge of recoveries. Sequential extraction from accumulators to effect preliminary separations should be investigated. The potential for separation by solvent extraction is far from being fully tapped. Marker compounds for quantitation and retention-time references should be added as early in the process as is practical to indicate recoveries through subsequent steps, but appropriate marker compounds must be developed for each class of compounds that behaves differently during extraction, concentration, separation, or detection.

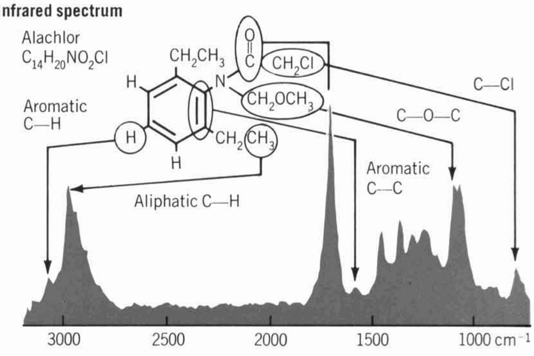
Concentration techniques for organic extracts are generally well established, but much needs to be done to determine the best means of concentrating polar compounds that remain in the aqueous phase during solvent extraction of grab samples.

Gas chromatography (GC), a technique that is continually being improved, is by far the best-established method for separating volatile compounds. Recent advancements in high-pressure liquid chromatography show considerable promise for separating the polar volatile and the nonvolatile compounds of moderate molecular weight.

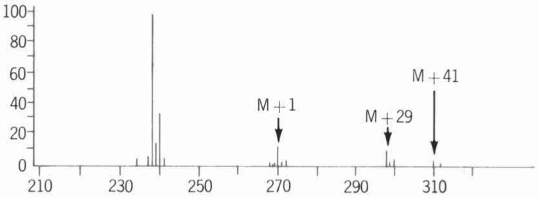
FIGURE 4

Piecing the puzzle together: identifying Alachlor

Infrared spectrum



Low-resolution chemical ionization spectrum



Appraising the techniques

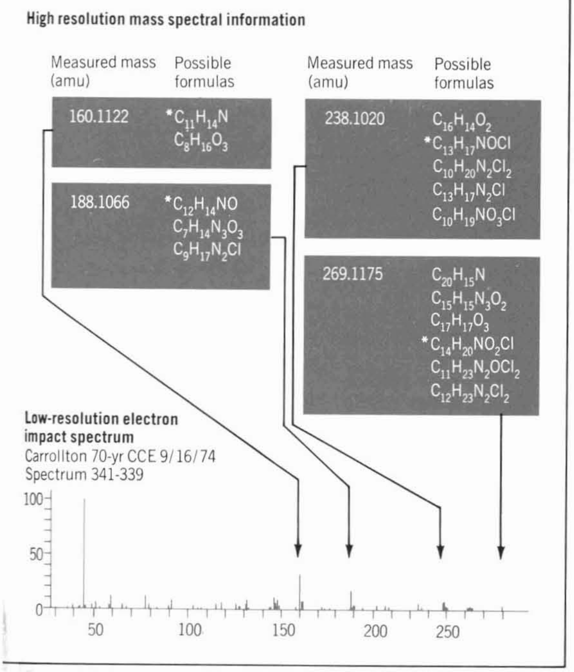
So little is known about the nature of high-molecular-weight materials in environmental waters that it is difficult to suggest approaches for their analysis. Obviously, however, the tedious task of characterizing these materials should be pursued to provide further insight into their nature and their significance as pollutants.

Rapid-scanning, low-resolution mass spectrometers have proved to be so effective in providing indentifying spectra that they are almost universally selected as the first-line approach to identifying separated compounds. Computer-assisted interpretation of spectra has advanced far enough to make it practically an integral part of organic mass spectrometry. Currently, most low-cost computerized spectra-matching programs are based on empirical matching and, therefore, require that the spectrum of the compound to be identified be stored in the computer. Files that are more relevant should be developed to further reduce cost and time for spectra matching.

For compounds that are not amenable to conventional mass spectrometry, techniques such as atmospheric-pressure-ionization mass spectrometry, Fourier-transform-infrared spectroscopy, nuclear-magnetic-resonance spectrometry, and Raman spectroscopy may be applicable and should be investigated. Information generated by these techniques will also be helpful to the analyst in identifying volatile compounds that cannot be identified from their mass spectra alone.

Ab initio identification of organic compounds (identifying them by piecing together and analyzing additional spectral information gained in the laboratory) is tedious and costly (Figure 4). If large numbers of compounds requiring such analysis are encountered, it will be worthwhile to develop a systematic, repetitive (although complex) approach to *ab initio* identification to make the process more efficient. Full advantage should be taken of computer-assisted analytical techniques in such a process.

Obviously a comprehensive qualitative and quantitative analysis is not necessary or practical for all samples. For example, once the identities of components in an industrial effluent are established, a GC retention time is adequate for subsequent identification. Extraction and concentration conditions can be simplified and tailored to the particular effluent.



Municipal wastes and water supplies vary in composition as a function of time, and GC retention times alone do not provide reliable identities for components in these samples. Surrogate methods, however, may provide a means of monitoring these systems. Surrogate methods do not measure specific chemicals; they respond to characteristics of the sample representing significant groups of chemicals that can be considered, as groups, from the standpoint of toxicity or control. For example, "purgeable organic chlorine" may be a significant parameter for water supplies because these compounds formed during chlorine disinfection represent a significant percentage of the mass of organics so formed. Conversely most compounds formed during chlorine disinfection of municipal sewage are nonpurgeable, which suggests "total organic chlorine" as a parameter for consideration.

In neither case is there sufficient information to establish the usefulness of such parameters. From the standpoint of toxicity; the same can be said of "total organic carbon" as a parameter because it would be influenced largely by the high concentrations of humic acids and lignins in natural waters. The Thermal Energy Analyzer is a highly sensitive detector for nitrosamines, most of which are considered to be potent carcinogens. This detector has been used effectively to demonstrate the *absence* of nitrosamines, but it is not exclusively specific; for example, it also responds to organic nitrates. Responses, therefore, cannot be considered as definite confirmations of the presence of nitrosamines. The major problem with surrogate methods is that not enough is presently known about the significance of the information they produce.

Summing up

Research is needed to improve capabilities to analyze samples comprehensively so that the significance of trace organics in the environment can be determined. But there is no need to wait until this research is completed to begin an extensive survey for these compounds in the environment. Comprehensive analysis of the extractable volatile compounds can be accomplished now and, in fact, is being done in commercial laboratories at costs under $2000 per sample.

After a survey program is established, improvements in quantitation techniques and in capabilities for separating nonvolatile compounds can be readily adopted. Eventually, with close collaboration among toxicologists and analytical chemists, we have a good chance to answer the question, "What is the human health significance of trace organic chemicals in water?"

Additional reading

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Keith, L. H. (Ed.), "Identification and Analysis of Organic Pollutants in Water," Ann Arbor Science Publishers, Inc., Ann Arbor, Mich., 1976.

Heller, S. R., McGuire, J. M., and Budde, W. L., "Trace Organics by GC/MS," *Environ. Sci. Technol.*, **9,** 210–213 (1975).

Griffiths, P. R., "Optimized Sampling in GC-IR," *J. Appl. Spectrosc.*, in press.

William T. Donaldson *heads EPA's program to develop techniques for identifying and measuring chemical pollutants in water and soils. He has been involved in the development of measurement techniques since 1948. Mr. Donaldson joined the federal government in 1966 after 18 years in industry.*

Coordinated by LRE

Monitoring the quality of ambient air

To set standards, assure compliance, develop controls and anticipate problems

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Monitoring of ambient air quality permits the quantification of pollutants and the documentation of their effects on man and his environment. This monitoring also quantitatively relates air quality and pollutant sources so that the efficacy of control measures, and thus compliance with standards, can be determined.

Air pollution measurements have been made for nearly 50 years. Most early air pollution efforts focused on smoke control. Before the middle 1950's, 13 U.S. cities made sporadic measurements of one or more gaseous pollutants, namely, hydrogen sulfide, oxides of nitrogen, ammonia, carbon monoxide, fluorides, oxidants, hydrocarbons, and aldehydes. In 1954, Los Angeles County established a 12-station continuous-air-monitoring network that measured particulate matter, carbon monoxide (CO), nitrogen oxide (NO), total oxides of nitrogen (NO_x), total oxidants, sulfur dioxide (SO_2), and hydrocarbons. Other cities soon implemented air-monitoring networks when federal financial assistance for state programs became available in 1963.

The Air Quality Act of 1967 underlies much of the current air pollution control effort: the development of air quality standards and the enforcement of these standards on a regional basis. The Clean Air Act Amendments of 1970 and subsequent amendments form the basis for current air pollution control activities and for necessary air pollutant measurement systems.

However, many of the monitoring efforts have resulted in less than adequate data, have not been cost effective and, in certain instances, have resulted in costly programs that provided questionable benefits. As they become available, new concepts and methodologies must be maximally utilized. Such concepts as integrated monitoring systems, new optimization techniques and state-of-the-art measurement devices, such as remote-sensing techniques, are becoming available for testing and application; failure to use them to their fullest capabilities will result in a loss of the opportunity to develop rational environmental assessment tools.

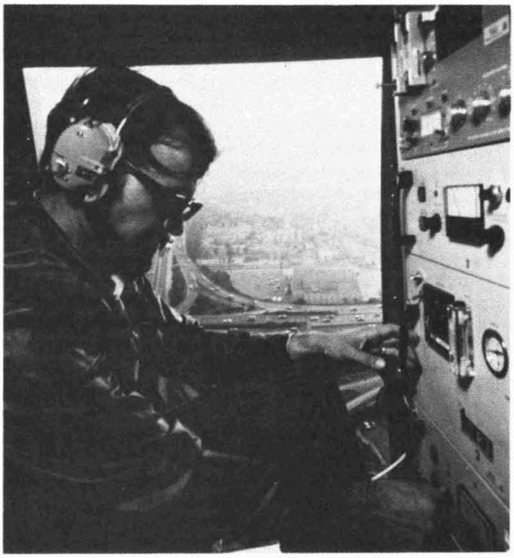
The ability to assess ambient air quality depends heavily on the availability and applicability of appropriate sensors. Until recently, most pollutant sensors capable of providing quantitative information were of the in-situ or contact type. Such sensors are restricted to measurement of a parameter at a single point or, when mounted on a mobile platform, at sequential points as a function of time. As a result of the difficulty in relating a point remote from the sensor to the collected data, great care must be taken in selecting the sensor placement site. Even the use of a dense array of sensors (a prohibitively expensive undertaking) provides information only between sensors, and then by interpolative techniques. This problem may be skirted by the appropriate application of remote sensors, which are generally capable of extremely rapid measurement of a profile or array of points.

Reasons for monitoring

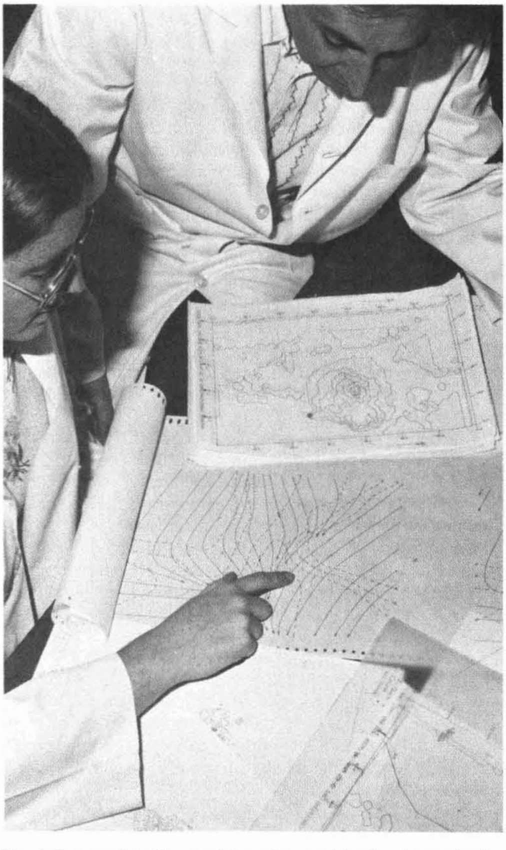
Monitoring for air quality is a very complex operation, one which requires a pollutant-specific systematic approach. Without an approach based on stated objectives and guidelines, proper ambient air quality assessment cannot be accomplished. Failure to recognize the complexities associated with ambient air quality has led to the present situation: the inability to document the relationship between sources and exposure, or between exposure and effects.

Nevertheless, once an air-monitoring network has been properly designed, it can furnish data to be used:

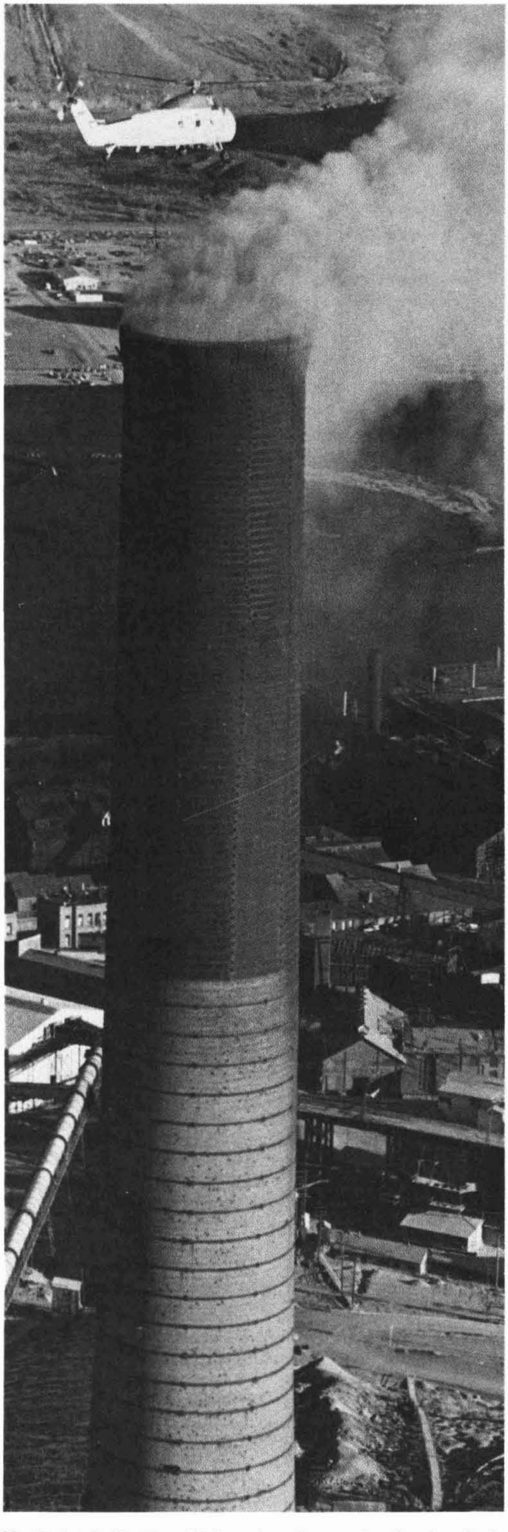
- to establish or revise standards
- to demonstrate that adequate progress is being made toward attainment of the standards
- to demonstrate that compliance with standards is maintained
- to furnish information during high-pollution episodes or accidental discharges and provide guidance on choice of subsequent actions
- to define air pollution problems for periodic determination



Airborne platforms. *This type of monitoring is efficient and cost effective for urban areas and long-range transport studies*



Simulation model. *The model can be used to site air-monitoring stations within an airshed through the development of pollution distribution maps*



Monitoring helicopter. *Well-equipped to monitor the six criteria pollutants, this helicopter is measuring sulfur dioxide in the plume from a copper smelter*

Major questions to consider in a monitoring system

- ***What is the area for which measurements are re-***

- ***What is the proper mix and location of fixed stations, movable stations, mobile stations, airborne stations, and what is the role of modeling in achieving the objectives?***
- ***What level or degree of errors is acceptable?***
- ***What is the importance of exposure monitoring in relation to air pollutants, or to those pollutants found in other media including the food chain?***
- ***What related meteorological data must be collected with air quality data?***
- ***What quality assurance program is necessary to assure that data are representative and legally and scientifically defensible?***
- ***What is the importance of sample averaging times to the network design?***
- ***What are the effects of physical and chemical transformations on the sampling location and network design; for example, for monitoring ozone or sulfates?***

of priorities for resource allocations, and to develop control programs.

Today's national air-monitoring program is an integrated effort involving local, regional, state and federal agencies; but the majority of the actual data are being collected by state and local agencies. In many cases, state and local agencies, possesssing detailed knowledge of local meteorology, topography, demography, pollutant sources, and emissions, have programs that exceed present EPA requirements.

The primary goal of state and local programs is to show compliance with national ambient air quality standards for particulate matter, SO_2, CO, nitrogen dioxide (NO_2), and photochemical oxidants. The primary goal of the federal monitoring program is to provide special air-monitoring data not furnished by state and local agencies, and to make available meteorological, aerometric and related data on a nationwide scale.

Present air monitoring must be expanded to provide an effective capability to detect and quantify ambient levels of toxic or nonregulated pollutants that may pose a threat to human health and welfare. In order to accomplish this, a priority list of toxic pollutants must be assembled. For those pollutants that are transported from one medium to another, an air-monitoring program must be developed in conjunction with other appropriate monitoring programs so that *total* exposure to important receptors may be quantified.

Establishing priorities for monitoring and controlling pollutants must be based on demonstrated effects, the probability that projected benefits will be commensurate with resources expended, and public concern. Some factors that should be considered in establishing pollutant priorities include: the severity of known or suspected effects on human health, soil, plants and other animals; the persistence and accumulation of the pollutant in man or his food chain; the availability of adequate measurement and control technology; and legal mandates.

Types of monitoring

Air-monitoring activities may be divided into permanent-fixed-site (trend) monitoring, exposure monitoring, ambient-source-linked monitoring, and biological monitoring.

Permanent-fixed-site (trend) monitoring is necessary to judge the attainment and maintenance of the present ambient air quality standards through the State Implementation Plans (SIP's). Monitoring of trends at permanent sites involves the measurement of pollutants and their effects over extended periods of time.

In urban or industrial areas, trend data are used to evaluate local, regional, and national long-term trends in pollutant levels and their effects on the ecosystem. These data are also necessary to determine the effectiveness of pollution control efforts as well as to alert epidemiologists to possible causes of adverse health effects.

Trend monitoring furnishes information of the impact of urbanized areas on remote or non-urban areas and is frequently referred to as baseline data. Subtle low-level changes in the baseline concentrations of pollutants yield the first indication of pollutants' effects on weather and climate modifications. These changes also identify pollutant pathways across the various media, identify regional and global transport, and identify the persistence and ubiquity of pollutants in the biosphere. Trend monitoring also involves the quantitative and qualitative evaluation, on a long-term basis, of emissions of pollutants from various sources.

Ambient-source-linked monitoring relates air quality to sources through modeling. But taken into consideration are other pertinent supporting data such as meteorology, demography, and topography. Several techniques, ranging from simple to complex, can be used.

A gross estimate of emission inventories can be derived from published data. For most urban and industrial areas, published statistics are available on quantities and types of fuels consumed, number and types of vehicles registered, population, types and number of industries, and typical emissions from each type. The most useful and complete type of source-emissions inventory involves actual measurements to obtain area and temporal variations.

Computer models are being used extensively to provide a mathematical relationship between emission sources and air quality. These models are normally validated on the basis of air quality measurements for a limited number of points and time periods, which are then used to extrapolate or predict the variations of pollutant concentrations at points and times that are not measured directly. Once models are validated they provide a basic tool for assessing the effectiveness of abatement strategies for immediate or long-term problems.

Models developed to date have been used with some degree of success, particularly when used to extend and interpret information on stable pollutants. Modeling can never completely replace direct measurements, but it can drastically reduce the number of monitoring sites necessary and thus significantly reduce costs.

Models have been developed for pollutants that undergo physical and chemical transformations, but these models presently lack proper field evaluation and validation. It is, therefore, necessary to carefully delineate the situations and problems for which valid models are available.

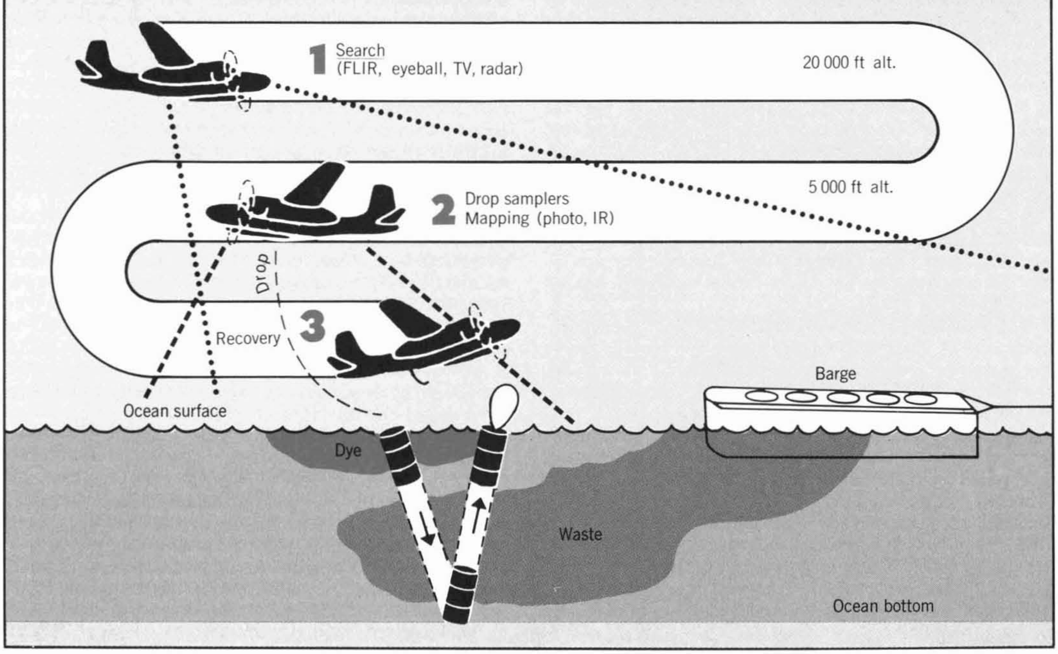
Much of research monitoring falls into the ambient-source-linked category. Projects that typically require significant monitoring support include studies of the movement, distribution, fate, pathways and effects of a specific pollutant entering a given environmental medium, and assessment of the effectiveness of experimental control systems or procedures.

Exposure monitoring should give a true picture of the impact of air pollution control on reduction of exposures and the resulting adverse effects on human health and welfare. An exposure-monitoring system is the preferred way of reporting progress toward cleaning the air and thus complying with the intent of the Clean Air Act.

Monitoring exposure systems measure pollutant concentration at locations where exposure may occur. The primary requirements for such systems are:

- The identification of critical receptors at risk and the pollutants that produce the adverse effects.

Air dropable/recoverable water samplers for ocean dumping monitoring



- The development of siting requirements and numbers of sites, including mobile and remote measurement systems, based on the time and variability of pollutant concentrations and the relevant receptor population.
- The integration of networks for estimating receptor exposure with networks for other purposes, such as standards attainment and maintenance.

Acute or chronic health effects may result from short-term peak exposure; repeated short-term high exposures; or a low-level, long-term exposure. The relationships between elevated short-term exposures or acute exposures and health effects are more easily recognized than are those for low-level exposure. Effects from chronic low-level exposures can be in the form of new disorders or aggravation of existing illnesses. There is a requirement for better estimates of human exposure to environmental levels of biological, chemical and physical agents as they relate to adverse health effects.

In order to adequately assess the impact of most pollutants on health, an integrated (multimedia) monitoring system is necessary to furnish an accurate estimate of exposure that can be used to determine the exposure- dose-response assessments needed for scientifically defensible environmental health criteria. When measuring the exposure of a receptor to chemical or physical agents, data from the integrated monitoring system should quantitate the contribution of each pathway and the chemical or physical form of the pollutant.

Biological monitoring can be an important part of an air-monitoring program. For many pollutants the major pathway from source to receptor is through the air. The monitoring of tissues and biological fluids collected from receptor plants, wildlife, domestic animals and humans can indicate levels, patterns and trends of atmospheric pollutants or their metabolites. For example, the first indication of air pollution damage is generally detected by adverse changes in living tissue. The health, growth and number of plants, or the accumulation of a pollutant within a plant, may be a useful indicator of an environmental pollutant that may adversely affect human health. Another example is that incidences of pollution are often detected by unusual changes or mortality in animal populations caused by pollutants such as DDT, mercury, cadmium, lead, fluorides, and arsenic. Valuable information on lead, cadmium, mercury and arsenic exposure may be furnished by the analysis of selected human tissues and fluids such as hair, teeth, fingernails and blood.

Components of a monitoring network

To provide valid data on pollutant concentrations, an air quality monitoring network must have the following essential components: a central laboratory facility; a manual sampling network; an automatic network; and support facilities.

No matter how sophisticated the facilities are in the field, a central laboratory is necessary to supply the following:

- analytical expertise for operating the total network
- quality control services for the total network
- primary standards for all pollutants
- preparation of reagents and filters for the manual sampling network
- laboratory analysis of samples from the manual sampling network
- primary standardization of systems used for field calibration of continuous monitors in the automatic network
- special surveys and analytical support (e.g., for emergency episodes)
- specialized personnel and instrumentation for research projects.

The manual network is the most efficient first step in establishing a total network. This system can provide basic data upon which a comprehensive network can be designed. The manual network provides 24-h integrated measurements of total suspended particulates, SO_2, and NO_2. A most important feature of this network is that valid data can be rapidly obtained with relatively simple and inexpensive field sampling equipment—the high-volume sampler and the manual gas sampler. Both of these samplers provide 24-h integrated samples for measurement of particulate burden and gaseous pollutant concentrations, respectively.

Atmospheric particulates are collected on the glass-fiber filter of the high-volume sampler, and the filter weight increase is a measure of the total particulate loading. The filter also provides sample aliquots on which analyses may be made for sulfate (acid aerosol) and toxic elements such as lead, cadmium, arsenic, beryllium, and mercury. Such filters may be stored in a sample bank for years for further historical analyses.

The high-volume samplers require some special associated equipment. Before and after sample collection, the glass-fiber filters must be conditioned in a controlled environmental chamber at a specified, controlled temperature and humidity.

In addition, a specially designed microbalance is required for gravimetric analysis of the filters. During sampling, the high-volume sampler flow rate must be controlled at a known value. Flow-rate calibration is performed by using devices such as calibrated orifices or wet-test meters.

The manual bubbler contains a pre-prepared gas absorber reagent for the collection of 24-h samples for SO_2 and NO_2 analysis. After contact with ambient air for a specified time, the aqueous samples are collected in the field and returned to the laboratory for analysis. Adequate wet-chemistry bubbler techniques such as the West-Gaeke and the EPA reference (arsenite modification) techniques are available for the analyses of SO_2 and NO_2, respectively. Twenty-four-hour bubbler techniques are not currently available for ozone, carbon monoxide, and hydrocarbons.

The automatic network will provide continuous in-situ measurements of pollutants. This is really the only feasible way to get peak and diurnal concentrations of pollutants. In the long run, the automatic network is the most accurate and economical means for measuring the usual spectrum of pollutants.

An automatic network does require, however, some major types of support equipment. A fully equipped mobile laboratory is required for calibration of field stations, for quality control functions, for pollutant-profile studies, and for interrelating monitoring systems. Meteorological support equipment is also needed at all stations. An automatic network for multipollutant monitoring represents an extensive investment and demands that site location, station design, instrument selection, instrument calibration, and data acquisition and handling be carefully considered.

Siting automatic stations

Automatic stations should be located at a site at which pollutant concentrations are representative of a given area of population exposure. Pollutant concentrations at the site should not be unduly influenced by local objects, such as nearly stationary emissions source, major traffic arteries, high walls or buildings, trees, or highly localized meteorological conditions. Ideally, the site should be located according to an atmospheric model that predicts concentration isopleths and the minimum number of stations required for area monitoring and model verification.

In the absence of all the information required to define an atmospheric model (emission inventories, emission factors, meteorological conditions, transformations, sinks), automatic stations should be located on a movable platform, such as a trailer, to facilitate relocation as required. Because of the sophisticated instrumentation contained in the station, the interior must be controlled within fairly narrow limits for temperature (±2.5 °C) and line voltage (±2 V). In addition, the station interior should have adequate space, including bench-top space, available for calibration systems, gas cylinders, and minor instrument service and repair.

The design of the air-sample inlet and manifold system requires special consideration. In general, the air sampling inlet should be located several meters above the ground to avoid street pollution, eddy currents, and ground-level sinks. The inlet should have a dust cap to prevent heavy particulates, precipitation, and insects from entering the manifold system. Sample air is pulled through the inlet and sample manifold by a high-speed blower or pump (100 L/min). Laminar flow through a wide diameter (50 cm or greater) inlet is desirable to avoid pollutant wall loss upstream of the inlet for the calibration gases. Provisions must be made for the dynamic introduction of calibration gases so as to be able to calibrate the complete sampling system from the manifold through individual instrument sampling tubes, filters, and valves, including the detector component of the instrument. Finally, the air-sample-inlet manifold should be easy to disassemble for cleaning purposes.

Valid pollutant concentration measurements cannot be made without adequate instrumentation; thus, the selection of instruments for individual pollutants must be given due attention. Instruments should meet certain guaranteed performance specifications for accuracy, sensitivity, zero and span drift, freedom from interferences, response time, and maintenance requirements. Fortunately, considerable information and expertise is available based on previous instrument evaluation programs. (The U.S. EPA equivalency document, 40CFR53, February 1975, is one such source). Such information may be used to provide guidelines on instrument performance to be expected for a given pollutant, and for performance specifications to be included in procurement contracts.

Many commercial sources of air pollution monitors are available. Based on extensive experience, EPA scientists have designated certain operational principles of measurement that have led to the development of instruments with proven performance in the field of monitoring. These are: for sulfur dioxide—coulometry, flame photometry; for ozone—chemiluminescence (gas-phase) or ultraviolet photometry; for carbon monoxide—non-dispersive infrared spectrometry, gas chromatography (conversion to CH_4) with flame ionization; for oxides of nitrogen—chemiluminescence; and for hydrocarbons—gas chromatography with flame ionization.

Handling the data, quality control

The continuous operation of an automatic station generates a copious amount of data. The acquisition, handling, storage, retrieval and utilization of such data require a large investment in data systems and manpower. Automatic-data-acquisition systems are necessary for handling such large amounts of data (*ES&T,* July 1976, p 632). In operation, the analog output of each instrument is sampled at periodic intervals (for example, once a minute). The analog data are converted to digital form and stored on magnetic tape for computer processing. The computer takes the digital data, compares it to calibration input, computes concentration units, makes corrections for zero and span drift, and makes computations such as 5-min, hourly, or 24-h averages.

Two major problems can occur with the automatic data acquisition system. Instrument malfunction may frequently cause anomalous outputs that can lead to serious errors in computer hourly or 24-h averages. Failures may also occur in the transmission of data from the instrument analog to the computer. This is particularly true when data are being "telemetered" from a remote location to a central-computer facility over telephone lines. For these reasons, it is most advantageous to have analog strip-chart recorders available for each instrument. These will serve as backup data acquisition systems and provide permanent records that may be used to validate the computer output.

A quality control program ensures that all the necessary steps are taken to assure that monitoring data and supporting information upon which decisions are based are legally and scientifically defensible. A quality control system is necessary if data generated by one network or one laboratory are to be comparable to similar data produced elsewhere at another time. It is only through such a program that the accuracy and precision of the data are known.

One of the major moves throughout various U.N. agencies involved in environmental monitoring, as well as OECD, SCOPE, and several individual countries, is to establish reference methods. Reference methods are those techniques that have been thoroughly studied and tested and about which we know the limitation, interferences, accuracy and precision. Once a method has been designated as a reference method, it is usually accepted by both the academic and industrial communities as being reliable and specific.

In some cases, the analytical chemist or engineer prefers to use state-of-the-art techniques instead of reference methods. This is acceptable provided the newer technique is statistically comparable to the reference method in the environment in which the measurements are to be made. This is necessary because sampling techniques, instrumentation, quality of chemical reagents and personal habits vary from one laboratory to another. During interlaboratory comparisons, many systematic discrepancies have been observed between results of measurements of the same pollutant concentrations in the same matrix.

It is necessary that all operational phases of a monitoring network system be considered in a quality control program; for example sampling, sample handling and storage, sample preparation, sample analysis, instrument performance, data calculations, data validation, data reporting, and data evaluation. In addition, any such quality control program must be applied in field operations for selection of sampling site, verification that the sampling site is directly representative of the area, size of sample collected, sampling rate, and frequency of sampling. All of these parameters must be specified so that resulting data fulfill the goals and objectives to the monitoring network system.

Guidelines and operational manuals for implementing and for operating a routine quality control program must be available for: laboratory construction; selecting qualified personnel; obtaining and testing environmental samples; and obtaining and handling the data correctly.

Future directions

Generally, the speed of airborne remote-sensing devices, which were referred to earlier in the article, is such that three-dimensional plots of the measured parameter are possible before any significant transport of pollutant can take place when appropriate data acquisition and processing equipment are used. A very persuasive case can be made for remote sensing, especially in terms of cost effectiveness. The principal handicap at present is the limited number of parameters capable of being measured remotely and quantitatively. Two parameters that can be measured are: particulate matter, by using airborne LIDAR, a system that is operational; and ozone, with a dual wavelength laser absorption system, which is in the testing phase.

Aggressive R&D programs are under way that address many other pollutants. Factors also under investigation include the feasibility of using ground-based lasers and networks of retroreflectors for multiple pass analysis in a horizontal direction. As these new devices become available, they should be incorporated into operational monitoring systems.

There is no doubt of the ever-increasing importance of remote sensing for EPA's monitoring programs. Yet these techniques will not replace contact monitors; rather they will supplement and improve monitoring methodology. As newer techniques and hardware become available to enhance our ability to monitor our environment we will be faced with the question: "What is the most cost-effective combination of fixed, mobile contact and remote sensors for a specific monitoring problem?"

In the past, environmental monitoring has been done in response to an already existing hazardous condition. Future monitoring systems must be able to detect potential problems and monitor the appropriate parameters before they reach crisis proportion. Some possibilities that might be explored are the use of biological exposure indicators as trend monitors to predict changes, and the development of personal dosimeters, most likely biochemical measurements that integrate the total exposure of an individual to a pollutant or class of pollutants. When we achieve accurate, valid and broadly applied exposure monitoring, we then shall have achieved the ability to truly and rationally manage our air resources.

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CURRENT RESEARCH

Rates of Direct Photolysis in Aquatic Environment

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Environmental Research Laboratory, U.S. Environmental Protection Agency, College Station Road, Athens, Ga. 30601

■ Equations are derived that describe the direct photolysis rates of pollutants in the aquatic environment. The equations translate readily obtainable laboratory data into "half-lives" for photolysis under sunlight. Photolysis half-lives are calculated as a function of season, latitude, time-of-day, depth in water bodies, and ozone layer thickness. Experimental verification of the computed half-lives is presented.

The importance of photochemical transformation in the atmosphere is well-documented (*1, 2*), but comparatively little is known about photolysis of pollutants in water where other competing processes such as biodegradation and hydrolysis occur. A number of different photochemical processes may account for transformation of pollutants in the aquatic environment. One of these processes, direct photolysis, involves direct absorption of light by the pollutant followed by chemical reaction. Other photochemical processes may be initiated via light absorption by natural substances (indirect or "sensitized" photolysis) (*3–5*). In pure water or saturated hydrocarbons, direct photolysis is the only mechanism for photochemical transformation. During the past 10 years there has been a virtual explosion of interest in the photolysis of pollutants in solution, especially pesticides. Most of these studies have involved the identification of products derived from direct photolysis.

We have employed an approach that is quite useful in judging the likelihood that direct photolysis of a substance is or will be important in the aquatic environment (*6*). This approach involves utilization of a series of equations and laboratory data to compute direct photolysis rates under sunlight. The term "photolysis rate" as used in this paper refers to conversion per unit time, not to the very rapid rate of a primary photochemical process that deactivates a molecule in its electronically excited state. The relative importance of direct photolysis under a given set of environmental conditions can be assessed by comparison of the photolysis rate either with rates of competing processes or with what is known about the persistence of the substance under comparable field conditions (*6*). A similar approach described by Leighton (*2*) has been a valuable aid in disentangling the complexities of photochemical smog formation.

The rates of all photochemical processes in a water body are affected by solar spectral irradiance at the water surface, radiative transfer from air into water, and the transmission of sunlight in the water body. These subjects are briefly discussed below with references to more detailed reviews. Equations used to compute direct photolysis rates, results of the calculations, and experimental verification of the results are discussed in the balance of the paper.

Experimental

Computer Program. All computations were performed on a Digital Equipment Corp. PDP-8/E minicomputer. The computed results are either printed out or plotted on a Calcomp 563 plotter. Required data inputs are: (1) the molar extinction coefficients of the pollutant at wavelengths >297.5 nm (>285 nm for computation of the effects of ozone reduction); (2) the attenuation coefficients and refractive index of the reaction medium (attenuation coefficients for distilled water as reported by Hulbert and Dawson (*7, 8*) have already been incorporated into the program); (3) the quantum yield(s) for reaction of the pollutant; (4) the solar declination, solar right ascension, and sidereal time for the date of interest (obtained from the American Ephemeris and Nautical Almanac); (5) the latitude and longitude; and (6) the average ozone layer thickness, $\overline{X}$, that pertains to the season and location of interest [from London's compilations (*9*)].

To compute the relationship between solar altitude and time of day, a rearranged version of an equation described by Green and coworkers (*10*) was used. The rearranged version computes times of day (in universal time) as a function of solar altitude. Universal time is then converted to local time by the appropriate time zone correction.

For routine computations the program automatically inputs representative midseason data for items (4) and (6) above. Assumed midseason solar declinations are +10° for spring, +20° for summer, −10° for fall, and −20° for winter. The program then computes midseason photolysis rate constants and half-lives as a function of local time of day for a given longitude and for any specified combination of depth, season, and latitude (ranging from 0° to 90°N in 10° increments).

Another subroutine in the program computes representative effects of variation in ozone layer thickness upon photolysis rates for three latitudes, 0°, 40°, and 73°N.

Solar Radiation Data. All values for intensity of ultraviolet radiation (297.5–380 nm) were derived from a report published by Bener (*11*). Sky intensity $H(\lambda, ho, \overline{X})$ was computed according to an empirical relation described by Bener (Equation 1)

$$\log H(\lambda, ho, \overline{X}) = \log H(\lambda, ho, Xo) - T(\lambda, ho)(\overline{X} - Xo) \tag{1}$$

where $H(\lambda, ho, Xo)$ is the sky intensity at solar altitude ho, wavelength λ, and a reference ozone value, Xo, and $T(\lambda, ho)$ is a coefficient. Parameters for each wavelength and solar altitude were computed from the extensive data in Bener's report. A similar equation was used to obtain the values of direct solar intensity as a function of ozone layer thickness. These data were converted from W cm^{-2} nm^{-1} to photons cm^{-2} s^{-1} nm^{-1} by Equation 2 where λ is the wavelength in nm.

$$I(\text{photons cm}^{-2}\text{ s}^{-1}\text{ nm}^{-1}) = I(\text{W cm}^{-2}\text{ nm}^{-1}) \times \lambda \times 5.035 \times 10^{15} \quad (2)$$

Approximate intensity values for visible solar radiation (390–800 nm) were calculated by computer using equations described by Leighton (*2*). Data used in these computations were derived from the following sources.

- Values for extraterrestrial solar irradiance were taken from Johnson's data (*12*).
- Atmospheric transmissivity with respect to scattering was computed using equations in Leighton's book (*2*).
- Absorption coefficients for ozone were obtained from a paper by Inn and Tanaka (*13*).

Experimental Procedures. The procedures and equipment used to measure the quantum yields for reaction have been discussed previously (*6*). All quantum yields used in the computations pertain to air-saturated water, hexane, or hexadecane. Electronic absorption spectra were obtained on Perkin-Elmer 602 or Perkin-Elmer 356 spectrophotometers. Since it was impossible to measure the spectra of highly water-insoluble compounds in water, the spectra were measured in water–acetonitrile.

Dilute solutions were exposed to sunlight in 1-cm-deep uncovered culture dishes that were filled to the brim and in stoppered quartz cells that were horizontal to the ground. The detailed studies with 1,1-bis(*p*-methoxyphenyl)-2,2-dichloroethylene (DMDE) were conducted in dishes using hexadecane as solvent. For those compounds that volatilized rapidly from the water, such as trifluralin, sunlight photolyses were conducted in the stoppered cells. The photolysis rates in the quartz cells were more rapid than those observed in the dishes, since internal reflection of sunlight in the cells increased the pathlength of the light. To correct for this effect, midday photolysis rates measured in the cells were multiplied by a factor that equaled the ratio of the midday photolysis rate of the pollutant in the dish to that in the cell, using hexadecane as solvent. In all cases discussed in this paper, no change in concentration occurred in dark controls during the period of sunlight exposure.

Results and Discussion

Solar Radiation at the Earth's Surface. Photolysis rates are strongly influenced by the intensity and spectral distribution of the light source. Detailed discussions of the nature of sunlight at the earth's surface appear elsewhere (*2, 10–11, 14–16*). Some highlights of these discussions that are pertinent to this paper are summarized below.

As sunlight passes through the atmosphere, its intensity is decreased through absorption by atmospheric gases, such as ozone, and by molecular and aerosol scattering. The transmittance of the atmosphere in the ultraviolet and visible region decreases with decreasing wavelength; essentially no light is transmitted at wavelengths <295 nm. The sharp decrease in intensity in the 280–320-nm region is due mainly to ozone absorption. This part of sunlight, often called UV-B radiation, causes sunburn and other biologic effects and is responsible for direct photolysis of many pollutants, including most commonly used pesticides.

The intensity and spectral distribution of sunlight on a horizontal surface change constantly. Generally, the intensity decreases with decreasing angular height of the sun. Thus, intensity decreases from midday to sunset, from summer to winter, and from the tropics to higher latitudes.

The decrease in UV-B intensity with decreasing solar altitudes is much more pronounced than the decrease in visible or UV-A (320–400 nm) intensity. The intensity of UV-B radiation is also strongly influenced by seasonal and geographic variations in atmospheric ozone amount. Increases in ozone amount occur with increasing northern latitude and from fall (minimum) to spring (maximum) (*9*). The intensity values used in the computations discussed below are based upon *average* ozone amounts at various latitudes and seasons as compiled by London (*9*). Deviations from the averages are discussed elsewhere (*9, 16*).

Atmospheric scattering increases with decreasing wavelength and is most pronounced in the blue and ultraviolet region. Scattered light illuminates the sky causing its blue appearance. The fraction of light from the sky exceeds 50% in the UV-B region. Thus, solar radiation at a given spot on the earth's surface is derived both directly from the sun and also from the sky.

Radiative Transfer from the Atmosphere into a Water Body. When a beam of sunlight encounters the surface of a water body, part is reflected at an angle equal to the angle of incidence, z, and part passes into the water body with a change in direction due to refraction (Figure 1). The fraction of direct sunlight that is reflected, RFD, can be computed by Fresnel's law and is less than 10% at all but very large values of z. Assuming the sky is uniformly bright, we computed that the reflected fraction of sky radiation, RFS, is about 0.07 (*17*). The values of RFD and RFS that were used in our calculations (Table I) were computed assuming that the refractive index, n, of water is 1.34, a value that pertains specifically to blue light (436 nm). Since the refractive index increases slightly with decreasing wavelength (*18*), the computed reflectivities are somewhat higher for ultraviolet light and somewhat lower for long wavelength visible light. The computed values agree closely with experimental data obtained from studies of natural water bodies (*19*).

Pathlengths of Sunlight in Water Bodies. The pathlength is defined as the distance traveled by a beam of sunlight as it passes through a horizontal layer of the atmosphere or a water body. Pathlengths of direct and sky radiation are used in equations that compute photolysis rates (see next section). In the atmosphere the pathlength of direct radiation is h sec z where h is the thickness of a horizontal layer (Figure 1). Underwater, the light is bent downward and assumes a pathlength, l_d, of D sec θ where D is the depth and θ is the angle of refraction. The relationship between the angles z and

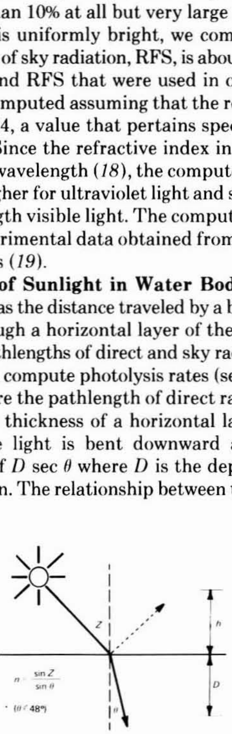

Figure 1. Diagram of passage of beam of sunlight through atmosphere into water body

Z = angle of incidence (solar zenith angle in case of direct sunlight); θ = angle of refraction

Table I. Intensities and Pathlengths of Solar Radiation in Atmosphere and Water Bodies

	Atmosphere[a]	Water body
Direct intensity on horizontal plane	$S \cos z$	$S \cos z\,(1\text{-RFD}) = I_d$
Sky intensity on horizontal plane	H	$H\,(1\text{-RFS}) = I_s$
Pathlength of direct radiation	$h \sec z$	$D \sec \theta = l_d$
Average pathlength of sky radiation	$2\,h$	$1.2\,D = l_s$

[a] Ref. *2*.

θ is defined by Snell's law (Figure 1). As the solar zenith angle, z, increases, so does the amount of refraction. Light coming from the horizon ($z > 85°$) is strongly bent, assuming an underwater angle, θ, of 48°.

Leighton has shown that the average pathlength for sky radiation in the atmosphere is close to $2\,h$ (*2*). Neglecting reflection and assuming that the sky is uniformly bright, it can be shown that the average pathlength for sky radiation underwater can be expressed by Equation 3 (*17*):

$$l_s = 2\,Dn\,(n - \sqrt{n^2 - 1}) \tag{3}$$

Assuming n is 1.34, the computed pathlength is $1.20\,D$. Taking reflection into account, the computed pathlength is $1.19\,D$ (*17*). Reflection has little effect on the computed value, because the most strongly reflected part of sky radiation (near horizon) contributes only a small fraction of the total sky intensity on a horizontal plane (*2*). Other workers have computed similar values for the underwater pathlength of sky radiation (*20–22*). Results discussed in this and the preceding section are summarized in Table I.

Light Attenuation in Natural Waters. As in the atmosphere, the intensity of sunlight is attenuated in natural waters through absorption and scattering (*23*). In the ocean, absorption is primarily due to water itself (*24*). Because water is most transparent in the blue region and scattering is relatively wavelength-independent, solar radiation in clear ocean water assumes a blue hue at great depths (*24*). Sunlight penetrates much more deeply into the ocean than into inland surface waters (*19*) where absorption is due mainly to dissolved natural organics (*24*). The attenuation coefficients, α_λ, that we measured for inland surface waters in the ultraviolet region are wavelength-dependent and can vary considerably from one water body to another (Figure 2). In Figure 2, $2/\alpha$ is the distance in which 99% of the incident intensity of a collimated beam of light is attenuated in passing through the water. Even in the relatively clear waters of the Savannah River, the attenuation coefficients are higher than those reported for distilled water in the ultraviolet region (*8*). Average attenuation coefficients for 10 river water samples collected in the Southeastern United States are shown in Figure 3. The average data should not be regarded as typical; variations were about ±95% in the UV-B region. Nonetheless, the general shape of the attenuation curve is representative. Attenuation of light intensity generally increases with decreasing wavelength in the visible and ultraviolet region.

Attenuation due to light scattering is less important than attenuation by absorption in most natural waters especially in the ultraviolet region (*16, 19, 23–24*). As a first approximation, scattering was ignored in the following considerations.

Equations Describing Direct Photolysis (25). Scientists realized long ago that only light which is absorbed can effect chemical change in a system. This basic law of photochemistry was first enunciated by Grotthus and then Draper in the nineteenth century. The average photolysis rate, $(-d[P]/dt)_\lambda$, at a certain wavelength λ in a completely mixed water body is directly proportional to the rate of light absorption by the pollutant per unit volume. The amount of light absorbed per unit time, I_λ, is defined by Lambert's law (Equation 4) where α_λ is the decadic absorption coefficient of the water body, l is the pathlength of the light, and I_o is the incident light intensity.

$$I_\lambda = I_{o\lambda}\,(1 - 10^{-\alpha_\lambda l}) \tag{4}$$

The average rate of absorption per unit volume, $I_{a\lambda}$, for underwater solar radiation in a layer of depth D is

$$I_{a\lambda} = \frac{I_{d\lambda}(1 - 10^{-\alpha_\lambda l_d}) + I_{s\lambda}(1 - 10^{-\alpha_\lambda l_s})}{D} \tag{5}$$

The pathlengths l_d and l_s can be computed as described above.

The addition of a pollutant to the water body changes its absorption coefficient to $(\alpha_\lambda + \epsilon_\lambda[P])$ where ϵ_λ is the molar extinction coefficient of the pollutant, and $[P]$ is its concentration. The fraction of light that is absorbed by the pollutant is $\epsilon_\lambda[P]/(\alpha_\lambda + \epsilon_\lambda[P])$. Since pollutant concentrations in water bodies are usually very low, $\epsilon_\lambda[P]$ is usually much smaller than α_λ, and $(\alpha_\lambda + \epsilon_\lambda[P]) \cong \alpha_\lambda$. Thus, the average rate of light absorption by a pollutant, $I'_{a\lambda}$, may be expressed as

$$I'_{a\lambda} = I_{a\lambda}\frac{\epsilon_\lambda[P]}{j\alpha_\lambda} \tag{6}$$

$$I'_{a\lambda} = k_{a\lambda}[P] \tag{7}$$

where $k_{a\lambda} = I_{a\lambda}\epsilon_\lambda/j\alpha_\lambda$ and j is a constant that converts the intensity units into units that are compatible with $[P]$ (j equals 6.02×10^{20} when $[P]$ is expressed in moles/liter and intensity is expressed in photons $\text{cm}^{-2}\,\text{s}^{-1}$).

The equation for $k_{a\lambda}$ simplifies under two circumstances:

- If $\alpha_\lambda l_d$ and $\alpha_\lambda l_s$ are both greater than 2, then essentially all the sunlight responsible for photolysis is absorbed by the system and the expression for $k_{a\lambda}$ becomes

$$k_{a\lambda} = \frac{W_\lambda \epsilon_\lambda}{jD\alpha_\lambda} \tag{8}$$

where W_λ equals $(I_{d\lambda} + I_{s\lambda})$. Values of W_λ for midday and midseason at latitude 40°N are summarized in Table II. This equation shows that at depths greater than that of the photic zone, the average photolysis rate is inversely proportional to depth.

- If $\alpha_\lambda l_d$ and $\alpha_\lambda l_s$ are both less than 0.02, then $k_{a\lambda}$ becomes independent of α_λ and can be approximately expressed as:

$$k_{a\lambda} = \frac{2.303\,\epsilon_\lambda(I_{d\lambda}l_d + I_{s\lambda}l_s)}{jD} \tag{9}$$

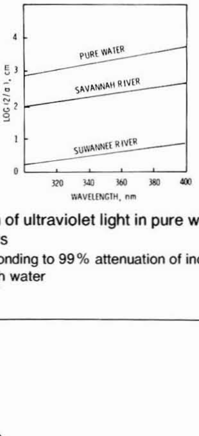

Figure 2. Attenuation of ultraviolet light in pure water and in water obtained from two rivers

$2/\alpha$ is distance corresponding to 99% attenuation of incident intensity of beam of light traveling through water

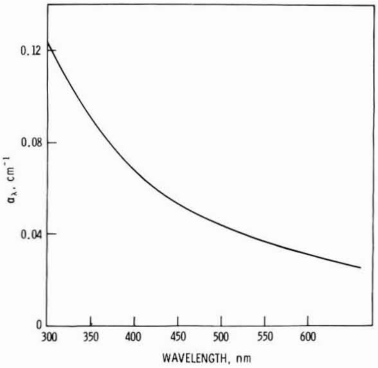

Figure 3. Average attenuation coefficients for 10 river water samples collected in southeastern U.S.

Table II. W_λ and Z_λ Values for Latitude 40°N

Wavelength (nm)	Spring	Summer	Fall	Winter
		W_λ values Photons (cm^{-2} s^{-1} 2.5 nm^{-1})		
297.5	0.240E + 12	0.648E + 12	0.786E + 11	0.000E + 00
300.0	0.105E + 13	0.219E + 13	0.434E + 12	0.601E + 11
302.5	0.369E + 13	0.657E + 13	0.185E + 13	0.300E + 12
305.0	0.106E + 14	0.163E + 14	0.555E + 13	0.139E + 13
307.5	0.195E + 14	0.274E + 14	0.112E + 14	0.369E + 13
310.0	0.325E + 14	0.444E + 14	0.173E + 14	0.698E + 13
312.5	0.510E + 14	0.643E + 14	0.308E + 14	0.145E + 14
315.0	0.683E + 14	0.836E + 14	0.410E + 14	0.222E + 14
317.5	0.867E + 14	0.103E + 15	0.532E + 14	0.296E + 14
320.0	0.103E + 15	0.121E + 15	0.663E + 14	0.408E + 14
		Photons (cm^{-2} s^{-1} 3.75 nm^{-1})		
323.1	0.193E + 15	0.226E + 15	0.119E + 15	0.740E + 14
		Photons (cm^{-2} s^{-1} 10 nm^{-1})		
330.0	0.669E + 15	0.762E + 15	0.421E + 15	0.279E + 15
340.0	0.778E + 15	0.875E + 15	0.500E + 15	0.341E + 15
350.0	0.835E + 15	0.938E + 15	0.533E + 15	0.363E + 15
360.0	0.895E + 15	0.100E + 16	0.568E + 15	0.383E + 15
370.0	0.997E + 15	0.112E + 16	0.623E + 15	0.418E + 15
380.0	0.110E + 16	0.124E + 16	0.679E + 15	0.450E + 15
390.0	0.133E + 16	0.148E + 16	0.895E + 15	0.646E + 15
400.0	0.191E + 16	0.212E + 16	0.129E + 16	0.931E + 15
410.0	0.251E + 16	0.279E + 16	0.170E + 16	0.123E + 16
420.0	0.258E + 16	0.287E + 16	0.175E + 16	0.127E + 16
430.0	0.249E + 16	0.277E + 16	0.170E + 16	0.123E + 16
440.0	0.295E + 16	0.327E + 16	0.201E + 16	0.146E + 16
450.0	0.332E + 16	0.368E + 16	0.227E + 16	0.164E + 16
460.0	0.335E + 16	0.372E + 16	0.230E + 16	0.167E + 16
470.0	0.347E + 16	0.384E + 16	0.238E + 16	0.172E + 16
480.0	0.355E + 16	0.394E + 16	0.244E + 16	0.177E + 16
490.0	0.336E + 16	0.372E + 16	0.231E + 16	0.168E + 16
500.0	0.343E + 16	0.380E + 16	0.236E + 16	0.171E + 16
525.0	0.362E + 16	0.401E + 16	0.251E + 16	0.181E + 16
550.0	0.377E + 16	0.418E + 16	0.262E + 16	0.188E + 16
575.0	0.380E + 16	0.423E + 16	0.265E + 16	0.190E + 16
600.0	0.385E + 16	0.427E + 16	0.268E + 16	0.192E + 16
625.0	0.387E + 16	0.428E + 16	0.271E + 16	0.196E + 16
650.0	0.389E + 16	0.429E + 16	0.273E + 16	0.199E + 16
675.0	0.388E + 16	0.427E + 16	0.273E + 16	0.200E + 16
700.0	0.384E + 16	0.422E + 16	0.272E + 16	0.200E + 16
750.0	0.369E + 16	0.404E + 16	0.261E + 16	0.193E + 16
800.0	0.354E + 16	0.387E + 16	0.252E + 16	0.187E + 16
		Z_λ values Photons (cm^{-2} s^{-1} 2.5 nm^{-1})		
297.5	0.274E + 12	0.716E + 12	0.949E + 11	0.000E + 00
300.0	0.120E + 13	0.240E + 13	0.524E + 12	0.733E + 11
302.5	0.419E + 13	0.723E + 13	0.223E + 13	0.368E + 12
305.0	0.121E + 14	0.181E + 14	0.670E + 13	0.170E + 13
307.5	0.223E + 14	0.305E + 14	0.135E + 14	0.450E + 13
310.0	0.372E + 14	0.495E + 14	0.208E + 14	0.854E + 13
312.5	0.584E + 14	0.717E + 14	0.371E + 14	0.177E + 14
315.0	0.780E + 14	0.933E + 14	0.494E + 14	0.271E + 14
317.5	0.992E + 14	0.115E + 15	0.641E + 14	0.362E + 14
320.0	0.117E + 15	0.135E + 15	0.800E + 14	0.498E + 14
		Photons (cm^{-2} s^{-1} 3.75 nm^{-1})		
323.1	0.221E + 15	0.252E + 15	0.144E + 15	0.906E + 14
		Photons (cm^{-2} s^{-1} 10 nm^{-1})		
330.0	0.761E + 15	0.846E + 15	0.508E + 15	0.342E + 15
340.0	0.880E + 15	0.963E + 15	0.604E + 15	0.420E + 15
350.0	0.942E + 15	0.103E + 16	0.645E + 15	0.449E + 15
360.0	0.101E + 16	0.110E + 16	0.687E + 15	0.479E + 15
370.0	0.112E + 16	0.122E + 16	0.754E + 15	0.520E + 15
380.0	0.124E + 16	0.135E + 16	0.822E + 15	0.562E + 15
390.0	0.149E + 16	0.161E + 16	0.108E + 16	0.805E + 15
400.0	0.213E + 16	0.231E + 16	0.156E + 16	0.116E + 16
410.0	0.280E + 16	0.302E + 16	0.206E + 16	0.154E + 16
420.0	0.288E + 16	0.310E + 16	0.212E + 16	0.159E + 16
430.0	0.277E + 16	0.298E + 16	0.205E + 16	0.154E + 16
440.0	0.327E + 16	0.351E + 16	0.244E + 16	0.184E + 16
450.0	0.368E + 16	0.394E + 16	0.275E + 16	0.208E + 16

Table II. Continued

Wavelength (nm)	Spring	Summer	Fall	Winter
		Photons ($\text{cm}^{-2}\ \text{s}^{-1}\ 10\ \text{nm}^{-1}$)		
460.0	0.371E + 16	0.398E + 16	0.279E + 16	0.211E + 16
470.0	0.384E + 16	0.411E + 16	0.289E + 16	0.219E + 16
480.0	0.392E + 16	0.420E + 16	0.296E + 16	0.225E + 16
490.0	0.371E + 16	0.396E + 16	0.281E + 16	0.213E + 16
500.0	0.378E + 16	0.404E + 16	0.287E + 16	0.218E + 16
525.0	0.398E + 16	0.426E + 16	0.305E + 16	0.232E + 16
550.0	0.413E + 16	0.442E + 16	0.318E + 16	0.241E + 16
575.0	0.417E + 16	0.446E + 16	0.322E + 16	0.243E + 16
600.0	0.421E + 16	0.450E + 16	0.326E + 16	0.247E + 16
625.0	0.422E + 16	0.450E + 16	0.329E + 16	0.252E + 16
650.0	0.424E + 16	0.451E + 16	0.332E + 16	0.256E + 16
675.0	0.423E + 16	0.448E + 16	0.333E + 16	0.259E + 16
700.0	0.419E + 16	0.443E + 16	0.330E + 16	0.258E + 16
750.0	0.401E + 16	0.423E + 16	0.318E + 16	0.250E + 16
800.0	0.385E + 16	0.405E + 16	0.306E + 16	0.242E + 16

Equation 9 applies even if $\epsilon_\lambda[P]$ exceeds α_λ as long as $(\alpha_\lambda + \epsilon_\lambda[P])$ is less than 0.02; i.e., less than 5% of the light is absorbed by the system. By substituting the equations defining pathlengths l_d and l_s (Table I) into Equation 9, Equation 10 is obtained:

$$k_{a\lambda} = 2.303\ \epsilon_\lambda j^{-1} Z_\lambda \tag{10}$$

where

$$Z_\lambda = I_{d\lambda} \sec\theta + 1.2\ I_{s\lambda} \tag{11}$$

This equation is approximately applicable to shallow depths in any natural water and depths up to one-half meter in distilled water. Midday, midseason values of Z_λ for latitude 40°N are presented in Table II.

The values shown in Table II correspond to wavelength intervals centered at the specified wavelength. For example, the Z_λ value for 350 nm corresponds to the 10-nm interval from 345 to 355 nm. Extinction coefficients, ϵ_λ, used in calculations are averaged over the wavelength intervals that correspond to those in the table.

The second law of photochemistry, the Stark-Einstein law, states that one molecule is activated for each light quantum or photon absorbed in a system. Thus, photolysis rates are proportional to the total number of photons absorbed per unit time, not the total energy absorbed. After a molecule absorbs a photon, it is unstable and will undergo a variety of competing *primary processes*, such as chemical reaction, light emission, or physical deactivation, to return to a stable state. The fraction of photons absorbed that results in a certain primary process is called the *primary quantum yield*, Φ, for the process. A corollary of the Stark-Einstein law is that the sum of the primary quantum yields of all the processes that deactivate an excited molecule equals unity. The primary quantum yield of a photochemical process in solution sometimes differs from the experimentally measured quantum yield for reaction, ϕ. For example, secondary thermal reactions such as free radical chain reactions can cause the value of ϕ to exceed unity, or reversal of a photochemical cleavage can cause the observed quantum yield to be much lower than the primary quantum yield. It is unlikely that chain reactions initiated by direct photolysis of a pollutant are important at the very low concentrations of pollutants that are found in lakes and rivers. Most inland waters contain phenolic humic materials, and phenols inhibit chain reactions. Thus, quantum yields for direct photolysis in the aquatic environment are not likely to exceed unity. More detailed discussions of quantum yields and their measurement appear elsewhere (*26, 27*).

The average photolysis rate is also proportional to the quantum yield for reaction, ϕ. The kinetic expression for direct photolysis is

$$-\left(\frac{d[P]}{dt}\right)_\lambda = \phi_\lambda k_{a\lambda}[P] \tag{12}$$

The quantum yield for reaction of complex molecules in solution is usually not wavelength-dependent (*28*). Accordingly, the complete rate expression is

$$-\frac{d[P]}{dt} = \phi k_a [P] \tag{13}$$

where k_a equals $\Sigma k_{a\lambda}$, the sum of the $k_{a\lambda}$ values for all wavelengths of sunlight that are absorbed by the pollutant. This expression has the form of a first-order rate equation in which the photolysis rate constant, ϕk_a, is expressed in units of reciprocal time. The concentration-independent half-life, $t_{1/2}$, inherent to direct photolysis is

$$t_{1/2} = \frac{0.693}{\phi k_a} \tag{14}$$

Since the value of ϕ is not likely to exceed unity, it follows that

$$t_{1/2} \leq \frac{0.693}{k_a} \tag{15}$$

Some sunlight photolysis rates reported in the literature have been measured under experimental conditions in which the pollutant absorbs much more light than the solvent, i.e., $\Sigma\epsilon_\lambda[P] \gg \Sigma\alpha_\lambda$. Under these conditions, if *all* the incident light is absorbed, the photolysis kinetics become zero order, and the half-life (Equation 16) becomes dependent on the initial pollutant concentration, $[P_o]$, and depth, D.

$$t_{1/2} = \frac{jD[P_o]}{2\ \phi \Sigma W_\lambda} \tag{16}$$

Thus, half-lives measured at high pollutant concentrations can be much longer than those observed at concentrations similar to those found in the aquatic environment.

Results of Calculations. We have developed a computer program written in Fortran IV that uses the above-mentioned equations and intensities of solar radiation to compute direct photolysis rates. The program, which is available on request, will be described in more detail elsewhere.

To illustrate the results of the calculations, photolysis rates were computed for carbaryl, a widely used carbamate insecticide, and trifluralin, a popular preemergent herbicide.

Carbaryl, a naphthalene derivative, absorbs UV-B radiation most strongly, and trifluralin, a dinitroaniline derivative, absorbs sunlight strongly in the visible region (Figure 4). The $k_{a\lambda}$ values shown in Figure 4 were computed for a shallow depth (see Equation 9) and apply to midsummer and midday at latitude 40°N. The quantum yields for reaction of carbaryl and trifluralin in air-saturated water are similar, 0.006 (313 nm) and 0.002 (366 nm), respectively (*29*). However, the sunlight absorption rate of trifluralin is about 400 times larger. Consequently, direct photolysis of trifluralin is over two orders of magnitude more rapid than photolysis of carbaryl.

The computed midday photolysis half-lives (near-surface) of the two pesticides depend upon season and latitude (Figure 5). The results in Figure 5 were computed as relative values, where the half-life of each pesticide for midsummer at latitude 30°N was assigned a value of unity. Seasonal variations occur for both pesticides at the midlatitudes with minimum half-lives occurring during summer, the period of maximum pesticide use, and maximum values occurring during winter. Both the half-lives and the amplitude of their seasonal variation increase with increasing northern latitude. In the tropical zone, photolysis rates are approximately constant throughout the year. However, in the midlatitudes the amplitudes of seasonal variation are much larger for carbaryl than for trifluralin. Latitudinal variation is relatively small during the summer. The seasonal variations shown for carbaryl are similar to those computed for most commonly used pesticides.

As the intensity of sunlight increases and then decreases throughout the day, so do the photolysis rates (Figure 6). The computed rates in Figure 6 are relative to photolysis rates at midday and midsummer and apply to shallow depths only. Because UV-B "sunrise" and "sunset" lags and precedes, respectively, visible sunrise and sunset, the period of photolysis for carbaryl is shorter than that for trifluralin. In comparing photolysis rates with rates of other processes such as hydrolysis or volatilization, the photolysis rates are integrated over the entire period of a day (*6*).

As sunlight passes down through a water body, its intensity decreases, and marked changes in its spectral distribution occur. The decrease in photolysis rate with increasing depth depends upon the magnitude and spectral distribution of: the attenuation coefficients of the water body, the molar extinction coefficients of the pollutant, and the intensity values of sunlight. The computed depth dependence of the direct photolysis of carbaryl and trifluralin at midday and midsummer (latitude 40°N) is shown in Figure 7. Results were calculated using attenuation coefficients of pure water and "average river water" shown in Figures 2 and 3. The photolysis rates of both pesticides drop off much more rapidly in the river water than in pure water. In lake or ocean water, the depth dependence is usually similar to that shown for pure water. Since UV-B radiation is absorbed more strongly than visible light in both pure and river water, the photolysis rate of carbaryl decreases more rapidly with increasing depth than that of trifluralin. Note, however, that the rate of decrease with increasing depth becomes identical for both pesticides once the depth corresponding to the photic zone is exceeded (see Equation 8). The underwater pathlength of direct sunlight lengthens, and depth dependence increases as the sun moves lower in the sky. Consequently, the depth dependence becomes more pronounced with increasing northern latitude (*6*) and from summer to winter in the midlatitudes.

All of the above computations for carbaryl were based upon average UV-B intensities for each season and latitude circle. Natural variations in the ozone layer (*9*, *16*) can cause significant deviations from the average intensity values. Moreover, there is growing evidence that certain anthropogenic activities may lead to a depletion of the ozone layer (*30*). The effect of

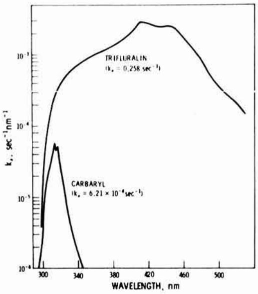

Figure 4. Specific sunlight absorption rates of carbaryl and trifluralin as function of wavelength at midday and midsummer, latitude 40°N

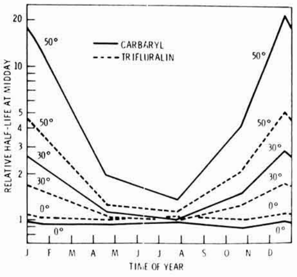

Figure 5. Relative midday half-lives for direct photolysis of carbaryl and trifluralin at midseason for several northern latitudes

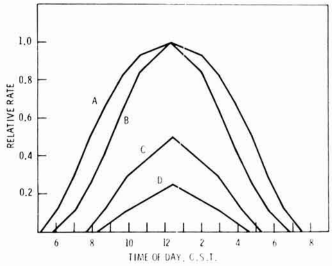

Figure 6. Diurnal variation of direct photolysis rates of trifluralin and carbaryl at latitude 40°N, longitude 90°W

A, trifluralin, 7/24/75; B, carbaryl, 7/24/75; C, trifluralin, 1/21/75; D, carbaryl, 1/21/75

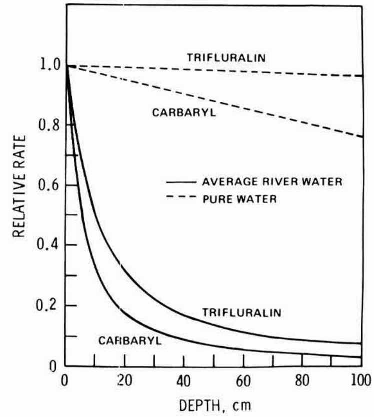

Figure 7. Computed depth dependence of direct photolysis of carbaryl and trifluralin at midday and midsummer, latitude 40°N

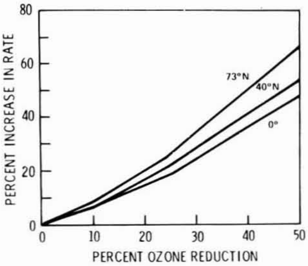

Figure 8. Effect of ozone reduction upon direct photolysis of carbaryl at selected northern latitudes

Ozone thickness assumed for zero reduction: lat 0°, 0.248 cm; lat 40°N, 0.319 cm; lat 73°N, 0.366 cm. Solar altitudes assumed: lat 0° and 40°N, 60°; lat 73°N, 40°

ozone reduction upon the photolysis rates of carbaryl at three latitudes is shown in Figure 8. The photolysis rate of trifluralin is essentially unaffected by ozone variation because ozone is transparent to wavelengths of sunlight that are strongly absorbed by trifluralin.

Experimental Verification. Studies by Hedlund and Youngson (*31*) of the photolysis of the pesticide, picloram, under sunlight have verified that:

- Photolysis in dilute solution obeys a first-order rate expression (Equation 13). Thus, the photolysis half-life is concentration-independent in dilute solution.
- The photolysis half-life increases with increasing depth.
- At shallow depths, direct photolysis rates are the same regardless of the nature of the water, be it distilled or of natural origin (Equation 9).

To check the results of our calculations, we have determined the photolysis rates of several pesticides and organomercury compounds (*32*) at shallow depths under sunlight in Athens, Ga. (latitude 34°N). The direct photolysis of DMDE (*33*) was examined in some detail. DMDE was chosen because it photodegrades very rapidly under sunlight and, like most pesticides, absorbs UV-B radiation most strongly (Figure 9). Dilute solutions of DMDE (1.00×10^{-7} M) in uncovered dishes were exposed to sunlight for 1–1.5 h at different times of the day in an open field. The solutions were analyzed, and average photolysis rate constants (ϕk_a values) were computed for each time-of-day. The experimental values for two days in June agreed closely with the values computed using the above equations (Figure 10). During both days the mornings were clear, but increasing cloudiness occurred in the afternoon.

Experimental midday half-lives for the direct photolysis of DMDE from spring to winter during 1975 agreed reasonably well with computed values (Figure 11). The rapid increase in half-life during November and December is attributed to the sharp decline in UV-B intensity during this period.

Computed half-lives were in reasonable agreement with the experimental values for photolysis of pesticides and pesticide derivatives ranging in half-life from 3 min to 168 h (Figure 12). Generally, the computed half-lives were within ±30% of the experimental values.

Conclusions

The technique described above provides a simple method for computing direct photolysis rates of aquatic pollutants. The rates are computed from reproducible, readily obtainable data, the quantum yield for reaction and the electronic absorption spectrum of the pollutant. Even in the absence of quantum yield data, the mininum photolysis half-life and its variation with season, latitude, time-of-day, and depth can be computed from the absorption spectrum (Equation 15).

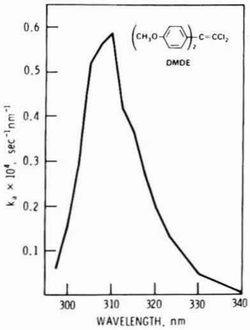

Figure 9. Absorption of solar radiation by 1,1-bis(*p*-methoxyphenyl)-2,2-dichloroethylene (DMDE) at midday, midsummer, latitude 40°N

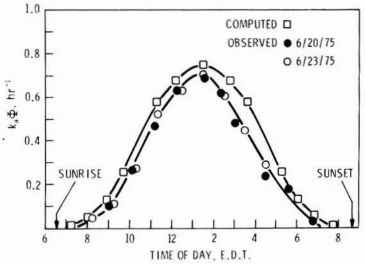

Figure 10. Time-of-day dependence of direct photolysis of DMDE at Athens, Ga.

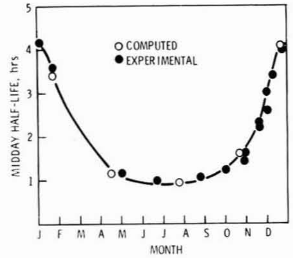

Figure 11. Seasonal variation of direct photolysis of DMDE at Athens, Ga., during 1975

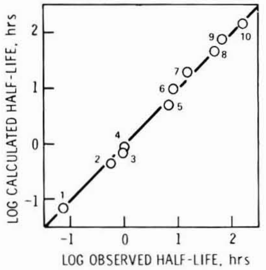

Figure 12. Comparison of calculated and observed half-lives for direct photolysis of several pesticides and pesticide derivatives (quantum yields parenthesized)

1, *N*-nitrosoatrazine in water (ϕ = 0.30); 2, trifluralin in water (ϕ = 0.0020); 3, DMDE in water (ϕ = 0.30); 4, DMDE in hexadecane (ϕ = 0.20); 5, DDE in hexadecane (ϕ = 0.26); 6, diphenylmercury in water (ϕ = 0.27); 7, phenylmercuric acetate in water (ϕ = 0.25); 8, 2,4-D-butoxyethyl ester in hexadecane (ϕ = 0.17); 9, carbaryl in water (ϕ = 0.0060); 10, 2,4-D-butoxyethyl ester in water (ϕ = 0.056)

Some limitations of the computations are discussed below.

- Exposure to the sun and whole sky at sea level is assumed. Clouds reduce the UV-B intensity about 50% under overcast conditions (*2, 10, 15*). Intensity increases about 15–20% per kilometer increase in elevation (*11*).
- Daily variations in atmospheric ozone amount can be as high as 30% at midlatitudes (*30*). These variations can cause deviations from the computed rates, since they are based upon average ozone amounts (Figure 8). Pollutants that absorb sunlight most strongly at wavelengths >320 nm are little affected by ozone variation.
- The computations assume that the natural organics in a water body act only as photochemically inert "sunscreens". This assumption is valid only with respect to the direct photolysis process. Recent studies have shown that these natural substances are not photochemically inert, but may act as "sensitizers" that cause other photochemical processes to occur (*3, 4, 6, 33*).
- The effects of light scattering in water bodies are ignored. Scattering is likely to have an important effect upon the computed depth dependence in turbid lakes and rivers (*23*).
- In computing the average photolysis rate at a given depth, we have assumed that the pollutant is isotropically distributed and that all the pollutant in the water layer is exposed to the same amount of light during a given period of time. The latter assumption is always valid at depths in which only a small fraction of the incident light is absorbed (up to several meters in clear lakes and the ocean). However, if at the depth considered, all of the light is absorbed in the upper part of the water column, the assumptions are valid only if mixing is more rapid than entry of the pollutant into the upper layer of the water body through industrial discharge, atmospheric fallout, etc.; or loss of the pollutant from the upper layer through photolysis, vaporization, and other processes. If entry to the upper layer is more rapid than mixing, then the pollutant concentration will be highest near the surface. There is some evidence that this is the case in deep water bodies. For example, the concentration of CCl_3F, a chemically inert substance, declines with increasing depth in the ocean (*34*). On the other hand, Hedlund and Youngson have shown that lack of complete mixing can slow photolysis when the pollutant is, initially, uniformly distributed in the water column (*31*).

Despite the above limitations, our experiments at shallow depths have indicated that the computed rates are very close to those in the photic zone, which is usually well mixed. The computed rates should be a useful tool in evaluating the behavior of pollutants in the aquatic environment.

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Method for Determining Acute Toxicity of an Acid Waste and Limiting Permissible Concentration at Boundaries of an Oceanic Mixing Zone

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■ A new method is described for determining mortality of bioassay organisms attributable to acidic and nonacidic constituents of an acid waste and for using these measurements to derive a limiting permissible concentration for the whole waste at boundaries of an oceanic mixing zone. The method reports mortality attributable to the acidic constituent in terms of its direct cause—hydrogen-ion concentration ($\{H^+\}$) of bioassay water. Titration of acid waste into a representative sample of seawater from the mixing zone is then performed to obtain a limiting permissible concentration for the whole waste that recognizes the dominant role of neutralization in reducing concentration and toxicity of the acidic constituent in the zone. The method, which is demonstrated for a by-product hydrochloric acid with the copepod *Acartia tonsa* as the bioassay organism, can be modified for use with alkaline wastes.

The Ocean Dumping Final Regulations and Criteria (*1*) require that concentration of a waste material or chemical constituent in receiving waters shall not, after reasonable allowance for initial mixing in the mixing zone, exceed 0.01 of a concentration shown to be toxic to appropriate sensitive marine organisms in bioassays conducted in accordance with approved United States Environmental Protection Agency (USEPA) procedures. Presently approved procedures (*2*) specify that 96-h static acute bioassays be conducted in media of 20–30‰ salinity and that results be reported as the estimated concentration of waste material or chemical constituent that causes 0.50 mortality of test organisms (LC_{50}).

Ocean dischargers, who are responsible for conducting bioassays on their own wastes, presently report LC_{50} values to USEPA on a "dilution" basis, i.e., volume of whole waste per volume of bioassay water (ppm) that produces LC_{50}. USEPA then determines limiting permissible concentration of waste at boundaries of the mixing zone by multiplying LC_{50} by the 0.01 application factor. These procedures appear to be appropriate for such commonly discharged wastes as sewerage sludge, cellar dirt, dredging spoil, and most industrial wastes. Toxicity of these materials is directly related to the volume of whole waste that is added per volume of bioassay or mixing-zone water because dilution is the primary factor that reduces waste concentration in aquatic systems.

Acid wastes, however, are unique among materials that are discharged into the ocean. Toxicity of acidic materials is only indirectly related to the volume of whole waste that is added per volume of bioassay or mixing-zone water since much of this acid is instantaneously removed by the carbonate buffer system. Toxicity, on the other hand, is directly related to the concentration of unneutralized acid ($\{H^+\}$) to which organisms are exposed. Because the importance of this distinction is widely recognized (*3–5*), bioassays of effects of acids and highly acidic wastes on organics almost invariably report results as $\{H^+\}$ or equivalent pH of bioassay water. Bioassays in which mortality is reported as volume of whole waste that is added per volume of bioassay water are useful for the limited purpose of comparing toxicity of two or more acidic materials under identical laboratory conditions. These results, however, do not identify the direct cause of mortality and therefore cannot be meaningfully extrapolated to the environment—the major reason for conducting bioassays.

The Ocean Dumping Final Regulations and Criteria recognize that neutralization in the marine environment must be realistically accounted for when determining limiting permissible concentration of an acid waste at boundaries of a mixing zone. Section 227.71 of the Regulations specifies that "reasonable allowance [must be made] for initial mixing in the mixing zone" of a waste material or chemical constituent. This mandate can only be interpreted as meaning that all major processes that reduce concentration of an acid waste or its constituents during mixing must be evaluated when determining a limiting permissible concentration for the waste. Limiting permissible concentrations that are derived by multiplying dilution-based LC_{50} values by 0.01 are incapable of realistically accounting for neutralization of the acidic constituent of an acid waste in the mixing zone. This is because mixing zone water often has a greater neutralizing capacity than bioassay water and, even if neutralizing capacities were equal, $\{H^+\}$ of a buffered medium does not increase proportionately with volume of added waste. The dilution method, because of these defects, is inconsistent with the provisions of the ocean dumping regulations.

The method that we propose for determining acute toxicity of an acid waste and limiting permissible concentration at boundaries of an oceanic mixing zone is based on a bioassay design that identifies, in technically appropriate terms, LC_{50}'s attributable to acidic and nonacidic constituents of the waste; calculation of limiting permissible concentrations of acidic and nonacidic constituents of the waste at boundaries of the mixing zone; and determination of a total limiting permissible concentration for the whole waste that is derived by titrating a sample of waste into a representative sample of seawater from the mixing zone and which, therefore, realistically accounts for neutralization of the acidic constituent in the zone.

Demonstration of Method

The method is demonstrated for a by-product hydrochloric acid with normality of 9.04 and pH of 0.2. Nonacidic components of the waste and their approximate concentrations were: chlorides, 290 000 ppm; fluorides, 10 000 ppm; oil and grease, 1 ppm; arsenic, 475 ppb; zinc, 140 ppb; lead, 130 ppb; vanadium, 110 ppb; nickel, 105 ppb; copper, 95 ppb; mercury, 85 ppb; chromium, 60 ppb; selenium, 27 ppb; and cadmium, 13 ppb.

The copepod, *Acartia tonsa*, which for this particular acid waste is the most sensitive of three indigenous species selected for testing by Region II, USEPA, was used as the bioassay organism. Adult animals were collected by plankton net from Big Lagoon, near Bionomics Marine Research Laboratory in Florida, and acclimated at 19‰ salinity and 21 ± 1 °C for 48 h. Mortality was <4% during acclimation, and animals ap-

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peared in excellent condition at the time bioassays were initiated.

Static 96-h bioassays were conducted in closed containers (110-ml Erlenmeyer flasks with ground glass stoppers) to ensure that $\{H^+\}$ of bioassay water—the expected major cause of mortality—would not vary significantly during the experiments, as required by bioassay protocol. (Extreme decreases in $\{H^+\}$, caused by evasion of carbon dioxide from bioassay water to air, occur over a 96-h period in bioassays conducted in open containers.) For each bioassay that was performed, 30 animals, equally distributed among three containers, were exposed to 10 concentrations of toxicant (plus a control) under unaerated conditions. Toxicant concentrations were prepared with filtered (1.2 μm) natural seawater, with salinity of 19‰, and maintained at 21 ± 1 °C. Measurements of pH were taken with a combination glass electrode and Orion Digital 109 pH meter at the start and finish of the 96-h period. Conversion from pH to $\{H^+\}$ of bioassay water was accomplished by the formula: ppb $\{H^+\} = 1.008\,\rho^{-1}\,10^{(9-\mathrm{pH})}$, where ρ = density of seawater (g/l.). Mortality of *A. tonsa* at the end of 96 h was corrected for mortality in control containers by use of Abbott's (*6*) formula: $M_c = [(X - Y)/X](100)$, where M_c = corrected mortality (%), $X = 1 -$ control mortality, and $Y = 1 -$ observed mortality.

Throughout this demonstration, subscript A, used in the terms LC_{50A} and LPC (limiting permissible concentration)$_A$, refers to the acidic constituent of acid waste as measured in ppb $\{H^+\}$ of bioassay or mixing-zone water. Subscript NA, employed in the terms LC_{50NA} and LPC_{NA}, refers to the nonacidic constituent of the waste as measured in ppm acid waste added to bioassay or mixing-zone water. The nonacidic constituent includes all components of the waste—chlorides, fluorides, oil and grease, and heavy metals—that do not undergo neutralization upon contact with seawater. LPC_T is the limiting permissible concentration for the whole waste as measured in ppm acid waste added to mixing-zone water.

Determination of LC_{50} for Acidic Constituent of Acid Waste. A 96-h static bioassay was conducted with *A. tonsa* with reagent-grade hydrochloric acid equivalent in normality (8.96 N) to acid waste (Table I). Slight decreases in pH of bioassay water, attributable to carbon dioxide produced by respiration of organisms, occurred for most concentrations of acid by the end of the 96-h testing period.

Mortality of *A. tonsa*, corrected for mortality in control test containers (*6*), is plotted as a function of initial pH of bioassay water in Figure 1. Regression equation ($Y = 4.493 - 0.633\,X$) is a weighted, least-squares linear fit of empirical data located between the 0.16 and 0.84 mortality marks on the *Y*-axis of the figure. Inverse variance of observed mortality is used as the weighting factor (*7, 8*). The weighted correlation coefficient (r_w) of 0.869 indicates that approximately 80% of increase in mortality can be explained by decrease in pH of bioassay water.

LC_{50A} is the hydrogen-ion equivalent of the pH represented by intersection of the regression line and 0.50 mortality mark of Figure 1. This value (0.488 ppb $\{H^+\}$) is a conservative estimate of acute toxicity of the acidic waste constituent since it is based on a regression in which mortality of organisms is plotted against initial pH of bioassay water, rather than the slightly lower final pH to which animals were exposed during at least part of the bioassay.

Use of reagent-grade acid equivalent in normality to acid waste accurately identifies mortality attributable to the acidic constituent of the waste. In a similar study to determine acute effects of acidity on white suckers (*4*), two different acids, hydrochloric and sulfuric, were used interchangeably to establish pH levels in test containers.

Determination of LC_{50} for Nonacidic Constituent of Acid Waste. A 96-h static bioassay was conducted with *A. tonsa* using acid waste (Table II). Small decreases in pH of bioassay water again occurred for most concentrations of material that were tested.

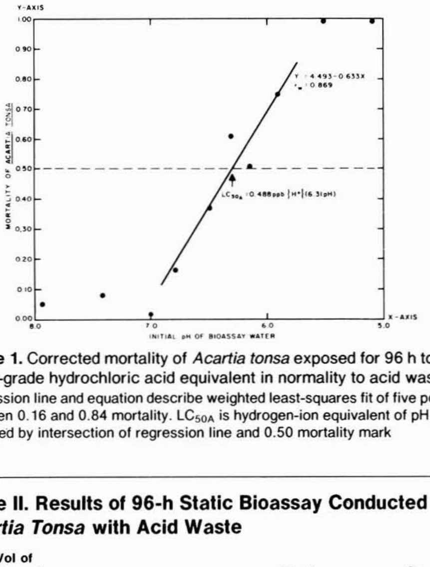

Figure 1. Corrected mortality of *Acartia tonsa* exposed for 96 h to reagent-grade hydrochloric acid equivalent in normality to acid waste
Regression line and equation describe weighted least-squares fit of five points between 0.16 and 0.84 mortality. LC_{50A} is hydrogen-ion equivalent of pH represented by intersection of regression line and 0.50 mortality mark

Table I. Results of 96-h Static Bioassay Conducted on *Acartia Tonsa* with Reagent-Grade Hydrochloric Acid Equivalent in Normality to Acid Waste

Vol of acid added to bioassay water, ppm	pH of bioassay water		Obsd 96-h mortality, %	Corr 96-h mortality, % [a]
	Initial	Final		
Control	8.00	7.17	5	0
1	7.92	7.21	10	5
10	7.46	6.95	13	8
20	7.10	6.78	3	0
30	6.79	6.60	20	16
40	6.50	6.38	40	37
50	6.31	6.22	63	61
60	6.15	6.10	53	51
70	5.92	5.88	77	75
80	5.65	5.64	100	100
90	5.24	5.27	100	100

[a] Mortality is corrected for control mortality by use of Abbott's (*6*) formula.

Table II. Results of 96-h Static Bioassay Conducted on *Acartia Tonsa* with Acid Waste

Vol of acid waste added to bioassay water, ppm	pH of bioassay water		Obsd 96-h mortality, %	Corr 96-h mortality, % [a]
	Initial	Final		
Control	8.00	7.26	5	0
1	7.91	7.23	3	0
10	7.45	6.99	13	8
20	7.04	6.81	20	16
30	6.72	6.60	43	40
40	6.56	6.46	43	40
50	6.40	6.34	57	54
60	6.25	6.18	73	72
70	6.04	6.02	90	89
80	5.73	5.76	100	100
90	5.45	5.47	100	100

[a] Mortality is corrected for control mortality by use of Abbott's (*6*) formula.

Corrected mortality of *A. tonsa* is shown as a curvilinear function of volume of waste added to bioassay water (Figure 2). Corrected mortality of *A. tonsa* exposed to hydrochloric acid of equivalent normality (Table I; Figure 1) is also presented in Figure 2 on a dilution basis. Chi-square goodness-of-fit tests between midsections of the eye-fitted curvilinear regression lines and corresponding empirical data indicate that regression lines reasonably approximate observed mortality (Table III).

Mortality of *A. tonsa* attributable to the nonacidic constituent of the acid waste is described as a weighted, least-squares linear regression ($Y = -0.344 + 0.245 \log X$) of the difference between mortalities at the center of the curvilinear regression lines for acid waste and hydrochloric acid. The weighted correlation coefficient (r_w) of 0.703 suggests that about 50% of increase in mortality can be explained in terms of increased concentration of the nonacidic constituent of the waste. A more exact relationship cannot be expected because, in part, of lack of exact correspondence between $\{H^+\}$ of bioassay water (the major cause of mortality) produced by equal volumes of acid waste and hydrochloric acid (Tables I and II).

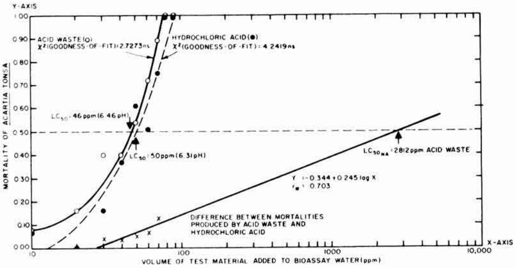

Figure 2. Corrected mortality of *Acartia tonsa* exposed for 96 h to acid waste and reagent-grade hydrochloric acid of equivalent normality

Linear regression line and equation describe mortality produced by nonacidic constituent of acid waste as weighted least-squares fit of difference between mortalities at centers of two curvilinear regression lines. LC_{50NA} is value on *X*-axis of graph represented by intersection of linear regression line and 0.50 mortality mark

LC_{50NA} (2812 ppm acid waste) is graphically determined as the point on the X-axis of Figure 2 that is represented by intersection of the linear regression line and the 0.50 mortality mark. LC_{50NA} is a corrected value which discounts that part of the LC_{50} for acid waste that represents toxicity of the waste's acidic constituent, which is accounted for in the LC_{50A}. LC_{50NA}, because it is derived from the difference between mortalities produced by equal volumes of acid waste and hydrochloric acid of equivalent normality, measures synergistic as well as primary effects of the nonacidic constituent, i.e., mortality attributable to nonacidic components acting in an acid medium.

LC_{50NA} cannot be determined with high precision and therefore must be viewed in context with supplemental information to establish its authenticity. Two factors account for the imprecision of LC_{50NA}. Firstly, LC_{50NA} is highly sensitive to changes in slope at midsections of the acid waste and hydrochloric-acid regression lines (Figure 2). These lines theoretically must diverge with increasing concentration of test material. Parallel lines would imply that mortality caused by the nonacidic constituent of the waste remains constant with increasing concentrations of nonacidic components. Converging regression lines would denote the even less likely possibility that mortality due to the nonacidic constituent decreases as concentrations of nonacidic components increase. Secondly, LC_{50NA} is an extrapolated parameter and, thus, is greatly dependent upon the scale selected for the *X*-axis of Figure 2.

LC_{50NA}, although not characterized by high precision, is a classically derived and, in all likelihood, a scientifically accurate estimate of acute toxicity of the nonacidic constituent of acid waste. The regression line from which LC_{50NA} is determined describes a linear relationship between mortality of organisms and dosage ($\log_{10}$ of the concentration of tested material). In bioassay interpretation, LC_{50} values are standardly obtained by straight-line interpolation between mortality points plotted against dosage. This practice usually normalizes the distribution of an organism's tolerance to toxic materials and therefore is based on sound biological theory. Linear extrapolation on a logarithmic scale is also routinely employed when applying application factors, such as the 0.01

Table III. Chi-Square Goodness-of-Fit Tests of Midsections of Curvilinear Regression Lines Illustrated in Figure 2 and Observed Mortality

Vol of test material added to bioassay water, ppm	Observed mortality[a]			Expected mortality detd from regression line[a]		χ^2 1 degree of freedom[b]
	Dead	Alive	Total	Dead	Alive	
			Acid waste			
30	12	18	30	8	22	2.7273
40	12	18	30	12	18	0.0000
50	16	14	30	16	14	0.0000
60	22	8	30	22	8	0.0000
70	27	3	30	27	3	0.0000
Total	89	61	150	85	65	2.7273 (5 df)
			Hydrochloric acid			
30	5	25	30	7	23	0.7453
40	11	19	30	11	19	0.0000
50	18	12	30	15	15	1.2000
60	15	15	30	19	11	2.2966
70	22	8	30	22	8	0.0000
Total	71	79	150	74	76	4.2419 (5 df)

[a] Observed and expected mortality and survival are reported as number of individuals, rather than as corresponding proportions as shown in Figure 2. [b] All individual and total χ^2 values are nonsignificant at the 95% confidence level [tabulated $\chi_{0.05}^2$ values for 1 and 5 df (maximum df appropriate for testing of an extrinsic hypothesis) are 3.84 and 11.0, respectively]; thus, it can be assumed that the two regression lines reasonably approximate observed data.

factor specified in the ocean dumping regulations, to LC_{50} data.

Reasonableness of the LC_{50NA} parameter can be verified by conducting a bioassay with preneutralized acid waste. Such a bioassay was performed with *A. tonsa* using by-product hydrochloric acid adjusted to a pH of 7.0 by addition of reagent-grade sodium hydroxide. The resulting LC_{50} for that test is 3950 ppm acid waste. It is to be expected that an LC_{50} which measures primary and synergistic effects of nonacidic components of a waste, as is the case with LC_{50NA}, will have a slightly lower value than an LC_{50} which measures only primary toxicity of nonacidic components, as in a test with preneutralized waste.

Reasonableness of the LC_{50NA} parameter can also be evaluated by comparing it to published accounts of bioassay mortality caused by similar types and concentrations of toxic materials. For example, the total concentration of heavy metals in the by-product hydrochloric acid used for this demonstration was approximately 1240 ppb. If a waste that contains 1240 ppb heavy metals is tested in a bioassay at a concentration of 2812 ppm (derived value for LC_{50NA}), the heavy metal concentration to which organisms are exposed is about 3.5 ppb. Yet, USEPA (*5*) states that, based on 96-h LC_{50} values for the most sensitive aquatic species, a concentration in marine waters of less than 10 ppb of lead (one of the more toxic heavy metals) constitutes a minimal risk of deleterious effects.

Finally, it should be noted that, at least in the case of the by-product hydrochloric acid used in this demonstration, the value of LC_{50NA} has only a marginal effect on LPC_T of acid waste at boundaries of the mixing zone. If LC_{50NA} were about one-half of the calculated value (1500 as compared to 2812 ppm), LPC_T would decrease by only approximately 7%.

Calculation of Limiting Permissible Concentrations of Acidic and Nonacidic Constituents of Acid Waste at Boundaries of Mixing Zone. LPC_A and LPC_{NA} are obtained by multiplying LC_{50A} and LC_{50NA}, respectively, by 0.01 as specified in the ocean dumping regulations. LPC_A calculated in this manner = 0.00488 (or 48.8×10^{-4}) ppb $\{H^+\}$ and LPC_{NA} = 28.1 ppm acid waste.

Determination of Total Limiting Permissible Concentration of Acid Waste at Boundaries of Mixing Zone. Both LPC_A and LPC_{NA} place constraints on the volume of acid waste that can be discharged into the mixing zone. Each, however, applies to only one of the two basic constituents of the waste. Therefore, a total limiting permissible concentration—LPC_T (ppm acid waste)—must be derived that satisfies the relationship (*9*):

$$\frac{C_A}{LPC_A} + \frac{C_{NA}}{LPC_{NA}} = 1.0 \qquad (1)$$

where C_A and C_{NA} represent concentrations of waste constituents in the mixing zone as estimated by titrating a sample of acid waste into a representative sample of seawater from the acid-waste dumping grounds. LPC_T, as is apparent from the above equation, imposes more stringent limitations on dumping activity than either LPC_A or LPC_{NA} and, because it is based on titration with a representative sample of seawater from the mixing zone, is an empirically derived value that realistically accounts for initial mixing of an acid waste in the mixing zone.

A titration curve describing acidity attributable to addition of by-product hydrochloric acid to a representative sample of seawater from the acid waste dumping grounds of New York Bight is illustrated in Figure 3. Acid waste was incrementally added to 1 l. of seawater sample, which was gently stirred for several seconds to ensure complete mixing. Measurements of pH of seawater sample were then taken and converted to $\{H^+\}$. Those values were corrected for ambient $\{H^+\}$ of sample to obtain estimates of acidity of seawater sample attributable to acid waste. Any point on the straight line drawn through points representing LPC_A on the *Y*-axis and LPC_{NA} on the *X*-axis of the titration-curve graph would satisfy the relationship described by Equation 1. LPC_T for by-product hydrochloric acid is the value on the *X*-axis of the graph obtained by drawing a line parallel to the *Y*-axis from the point at which the titration curve and straight line intersect. LPC_T for the acid waste at boundaries of the mixing zone is 4.6 ppm of whole waste.

Titration procedures probably result in a conservative estimate of the volume of acid waste that can be discharged into the mixing zone according to ocean dumping regulations. Seawater sample was not vigorously stirred during titration; hence immediate release of CO_2 into the atmosphere and subsequent reduction of $\{H^+\}$ in the water did not occur to the extent that would be expected in the mixing zone. Also, during actual dumping, acid waste is released at high concentrations in the center of the mixing zone, establishing in all likelihood a significantly elevated CO_2 gradient between the water–air interface. This gradient would result in substantial numbers of hydrogen-ions being neutralized before the acid–water mixture is convected to boundaries of the mixing zone. This phenomenon cannot be accounted for under laboratory conditions.

Conclusions

This new method for determining acute toxicity of an acid waste and limiting permissible concentration at boundaries of an oceanic mixing zone conforms with the letter and intent of the ocean dumping regulations (*1*) and with regional USEPA procedures (2) for conducting bioassays. The method, which can be modified for use with alkaline wastes, is superior in three major ways to the dilution method presently used by dischargers of acid wastes.

Firstly, the new method uses a bioassay design that is based on sound scientific principles and precedents since: toxicity of acidic and nonacidic constituents of acid waste are separately determined; bioassays are conducted in closed test containers, in which $\{H^+\}$ of bioassay water is maintained at relatively constant levels throughout the bioassay; and toxicity of the acidic constituent of acid waste is reported as $\{H^+\}$ of bioassay water. Separate determination of toxicity of the two primary waste constituents represents a refined chemical approach in conducting bioassays that is needed to analyze

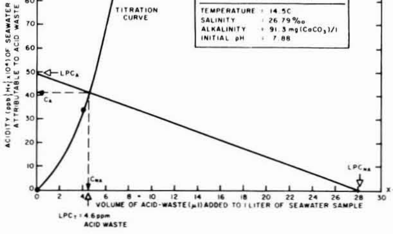

Figure 3. Titration curve describing acidity attributable to addition of acid waste to representative sample of seawater from acid-waste dumping grounds of New York Bight

LPC_T, which is 4.6 ppm acid waste, satisfies equation: $C_A/LPC_A + C_{NA}/LPC_{NA} = 1.0$, where C_A and C_{NA} are titration-based estimates of acidic and nonacidic waste constituents in mixing zone individual toxicants of a waste and properly interpret their effects (*10*). Maintenance of relatively constant levels of toxicants during static bioassays is a standard requirement, as is the reporting of effects of acidic materials as $\{H^+\}$ of bioassay water.

Secondly, the new method obeys the provisions of the ocean dumping regulations. Since LPC_T for acid waste is derived from titration of waste into a representative sample of seawater from the mixing zone, neutralization of the acidic waste constituent in the mixing zone is accounted for in a realistic manner.

Lastly, the new method offers a potentially valuable tool to authorities responsible for enforcing ocean-dumping regulations. LPC_T is represented in ppb $\{H^+\}$ of mixing-zone water, as well as in ppm of acid waste, on the titration-curve graph (Figure 3). Therefore, the pH that cannot be exceeded at boundaries of the mixing zone can be determined by adding ambient $\{H^+\}$ in the mixing zone to the $\{H^+\}$ designated as "C_A" on the graph, and converting this sum to pH. This pH value can be easily monitored at mixing-zone boundaries to ensure that dumping conveyances do not discharge their contents at impermissibly rapid rates. Regulatory monitoring cannot be readily implemented if LC_{50}, and subsequently, LPC of an acid waste are reported solely on the basis of volume of acid waste added to bioassay water.

The new method results in a LPC_T of by-product hydrochloric acid at boundaries of the mixing zone that is 10 times greater than the limiting permissible concentration that would be generated by the dilution method—4.6 ppm acid waste as compared to 0.46 ppm if LC_{50} value shown for acid waste in Figure 2 were multiplied by the 0.01 application factor. The reason for this, as has been previously stressed, is the inability of the dilution method to realistically account for the neutralization that occurs to the acidic constituent of acid waste in bioassay and mixing-zone waters.

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Nutrient Regeneration from Aerobic Decomposition of Green Algae

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■ A laboratory study of the aerobic decomposition of batch unialgal cultures (*Chlorella vulgaris* and *Selenastrum capricornutum*) was conducted in an attempt to quantify the rate and extent of regeneration of phosphorus and nitrogen. The above algae were grown in a synthetic medium until they reached biomass values of 15–60 mg/l. (dry weight). The cultures were then inoculated with a natural bacterial community (control cultures maintained bacteria-free) and placed in the dark. Bacteria-free cultures remained viable after 70 days in the dark with no net P regeneration occurring. The extent of P regeneration in the bacteria-inoculated cultures varied from 31 to 95% (mean, 74%) with higher percent release associated with excess initial cellular phosphorus. The P regeneration rates during active decomposition varied from 0.06 to 0.39 μg P/mg algae-day. The conversion of particulate organic nitrogen to NH_3 ranged from 51 to 94% (mean, 74%) for the bacteria-inoculated cultures. The dark incubation periods required for stabilization of the system varied from 29 to 55 days.

The effect of aerobic decomposition of algal blooms on the cycling of phosphorus and nitrogen is a very important process in aquatic ecosystems. It is axiomatic that when an algal cell dies and decomposes, some of the nutrients which it has taken up during growth are released to the surrounding medium. Along with many other parameters, this nutrient regeneration can have a marked effect on the dynamic seasonal succession of phytoplankton in a lake as well as the total biomass at any point. The rate and extent of nutrient regeneration must also be considered as a component in the mathematical modeling of the biochemical processes in aquatic ecosystems.

Previous emphasis on the remineralization of nutrients like phosphorus and nitrogen has been placed on this occurrence at the sediment-water interface. While there is no question that this site of regeneration is important, it is possible that, depending on certain factors, a significant amount of aerobic decomposition of algae may occur in the water column. The concurrent regeneration of nutrients would make them available for reuse during the same growing season.

The fact that bacteria as well as other microorganisms can mediate nutrient cycling is well established (*1–4*). More recently some evidence has been presented to support the hypothesis that these microorganisms cannot only decompose algae and thereby remineralize nutrients but that they can under certain circumstances be the causative agent in the termination of an algal bloom (*5–8*). This study provides indirect proof of this hypothesis.

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With respect to the rate and extent of aerobic decomposition of algae, Jewell and McCarty (*9*) observed that decay rates were a function of culture age and were higher for young cultures ($k = 0.01$ to 0.06 day^{-1}) than for older cultures ($k = 0.01$ to 0.03 day^{-1}). The previous literature on the nutrient regeneration associated with this phenomenon is not very extensive. Grill and Richards (*10*) and Kamatani (*11*) studied phosphorus, nitrogen, and silicate remineralization using marine diatoms in laboratory cultures. Otsuki and Hanya (*12*) studied the decomposition of dead green algal cells (*Scenedesmus* sp. killed by freeze-drying). Probably the most comprehensive nutrient regeneration studies on the microbial decomposition of live, freshwater algae to date have been performed by Jewell (*13*), Foree et al. (*14*), and Foree and Barrow (*15*).

Several parameters which may affect the rate and extent of nutrient regeneration by aerobic decomposition of algae are: light, temperature, pH, dissolved oxygen, nutrient content of algal cells and the medium, cell sinking rates, the algal species of interest, and the microbial decomposer population. The work reported herein emphasizes the important role of bacteria in nutrient regeneration as well as the relative short time periods necessary for significant regeneration. It will also be seen that the nutrient content of the algal cells at the time of decomposition is a critical parameter in the rate and extent of mineralization. Note that the initial P and N concentrations in the medium, and to a certain extent the algal biomass, closely approximate those values observed in eutrophic lake waters.

Experimental Procedure and Analytical Methods

The basic procedure used in this study was to grow unialgal cultures in batch culture vessels under controlled laboratory conditions and to then place these same vessels in the dark for further incubation. This procedure allowed for strict control of environmental changes from growth to decomposition. Some cultures were maintained bacteria-free, whereas others were inoculated with a decomposer population. During the dark incubation period the vessels were monitored to observe changes in the various forms of phosphorus and nitrogen as well as COD, suspended solids, and algal and bacterial densities.

Growth Procedure. Two unialgal species of green algae were used for the study: an axenic culture of *Chlorella vulgaris* (Carolina Biological Supply Co.) and a unialgal culture of *Selenastrum capricornutum* (Pacific Northwest Environmental Research Lab, Corvallis, Ore.). Six runs were made with *Chlorella* (two bacteria-free), and two runs were made with *Selenastrum*. The algae were cultured and decomposed in stoppered, 5-gal pyrex bottles which were continually supplied with humidified, filtered air at a rate of 3 scfh (0.084 m^3/h). These vessels could be sampled from a sampling tube extending to within 2 in. of the bottom of the culture by clamping an air pressure release tube.

Continuous light was supplied to the algal cultures during the growth period by 20-W cool white fluorescent bulbs. The light intensity, measured at the outside surface of the culture vessels, was 800 ft-*c*. (8611 lm/m^2). The temperature of the culture systems was maintained at 25 ± 3 °C during both the growth and decomposition phases of the study.

The same synthetic medium was used to grow all the algal cultures with the exception that phosphate and nitrate concentrations were lowered for two experimental runs. The medium used in this study was the NAAM medium, designed for use in EPA algal assay procedures (*16*). This medium was designed so that phosphorus is the growth-limiting nutrient. To ensure bacteria-free systems, the entire culture vessel with medium (18 l. of medium in each vessel) was autoclaved at 121 °C for 80 min prior to inoculation, by use of aseptic techniques, from a stock algal culture.

Decomposition Procedure. When the algal cultures had reached the desired stage of growth, the entire vessel was moved into a completely darkened room. All other environmental parameters were held constant. Just prior to placing the vessels in the dark (day 0), they were sampled to obtain a baseline for all parameters monitored. At this time designated cultures were inoculated with bacteria.

Two different methods for obtaining a bacterial inoculum were used in this study. First, a natural bacterial inoculum was obtained by concentrating the bacteria in a large volume of water from the 3-m depth of a eutrophic lake (Stone Lake, Cassopolis, Mich.). The concentration process consisted of passing the lake water through a 35-μm nylon mesh followed by loosely packed glass wool. Having removed practically all zooplankton and algae, the filtrate was then centrifuged at 8000 rpm for 20 min to pellitize the bacteria. The second method for obtaining a bacterial inoculum was the centrifugation of the remainder of the culture in the experimental culture vessels after decomposition had taken place.

As mentioned earlier, eight different decomposition runs were conducted in this study. Table I is a summary of the variation in experimental parameters in these eight runs. Note that runs 2 and 4 were maintained bacteria-free throughout the decomposition period. Also, two runs (5 and 7) were begun with lower phosphate and nitrate concentrations than the other six runs.

Table I. Summary of Experimental Conditions for Decomposition Studies

Run no.	Initial nutrient concn in medium		Algal species	Culture age at darkening, days	Bacterial inoculum
	PO_4, μgP/l.	NO_3, μgN/l.			
1	186	4200	*Chlorella*	7	Bacteria concentrated from 2.5 l. of Stone Lake water
2	186	4200	*Chlorella*	7	Bacteria-free
3	186	4200	*Chlorella*	7	Bacteria concentrated from 10 l. of Stone Lake water
4	186	4200	*Chlorella*	7	Bacteria-free
5	80	1600	*Chlorella*	5	Bacteria concentrated from 2.5 l. of water from vessel 1 after 68 days in dark
6	186	4200	*Chlorella*	9	Same as run no. 5
7	80	1600	*Selenastrum*	4	Bacteria concentrated from 2.5 l. of water from vessel 3 after 42 days in dark
8	186	4200	*Selenastrum*	4	Same as run no. 7

As runs 5–8 proceeded in the dark, it became evident that the bacterial inocula from previous culture vessels did not contain sufficient viable bacteria to cause decomposition in a reasonable length of time. The bacteria counts were comparatively low, and little growth was observed. For this reason, these four cultures were reinoculated after varying periods in the dark with bacteria concentrated from 2.5 l. of Stone Lake water. For runs 5 and 6 the reinoculation took place after 31 and 28 days in the dark, respectively. For runs 7 and 8 the reinoculation was performed after 21 days in the dark.

Analytical Procedures. The culture vessels were sampled at irregular intervals, which ranged from one to seven days, depending on the activity in the cultures. Chemical analyses for the various phosphorus and nitrogen forms, chemical oxygen demand, and suspended solids were performed in accordance with procedures given in "Standard Methods" (*17*) with few variations. Cellular inorganic phosphorus was considered to be the acid-hydrolyzable fraction of the particulate phosphorus, while cellular organic P was calculated as the difference between the total particulate P and the acid-hydrolyzable fraction.

Periodic quantitative estimates of the bacterial densities in the decomposition vessels were made to correlate bacterial densities with decomposition and to monitor bacteria-free cultures. Direct microscopic counts were made on membrane filter concentrated samples using an erythrosine staining technique patterned after Jannasch (*18*).

Results and Discussion

Decomposition Run Nos. 1 and 2. Experimental runs 1–4 were intended primarily to demonstrate the importance of bacteria in the decomposition of algae and the subsequent nutrient regeneration. The time variation of suspended solids, COD, phosphorus, and nitrogen for run 1 is shown in Figure 1. Recall that the only difference between runs 1 and 2 was that run 2 was not inoculated with bacteria. Although space limitation prevents showing the time variation of run 2, its behavior will be described in the remainder of this section.

In both runs there appeared to be an initial decrease in algal biomass which occurred within the first five days of dark incubation. This drop in suspended solids corresponds to an endogenous respiration phase, during which the algae must obtain energy heterotrophically from their own biomass. These results are consistent with a number of other researchers that axenic algal cultures often have high initial oxygen utilization rates when placed in the dark (*19, 20*).

After 22 days of dark incubation the two cultures began to differ dramatically. Very little change was occurring in culture no. 2, whereas it was visually evident by the color change from green to brown that active decomposition was taking place in culture no. 1. As is evident from Figure 1b, breakdown of organic matter is taking place during the first three weeks although it is not obvious until the end of that period that the bacteria were dominating the system. By day 30 a microscopic examination revealed very few intact algal cells in culture no. 1, whereas culture no. 2 remained green and viable until the pair of runs were terminated after 70 days. Although much less than run 1, there was some biomass decrease (38% reduction in COD) in culture no. 2, which is consistent with the hypothesis that some organic matter was being used for respiration and cell maintenance.

The pattern of nutrient regeneration for runs 1 and 2 was consistent with the amount of decomposition taking place. A number of interesting points can be made about the phosphorus dynamics in run 1. First, even though there was initially a substantial decrease in algal biomass, there was no

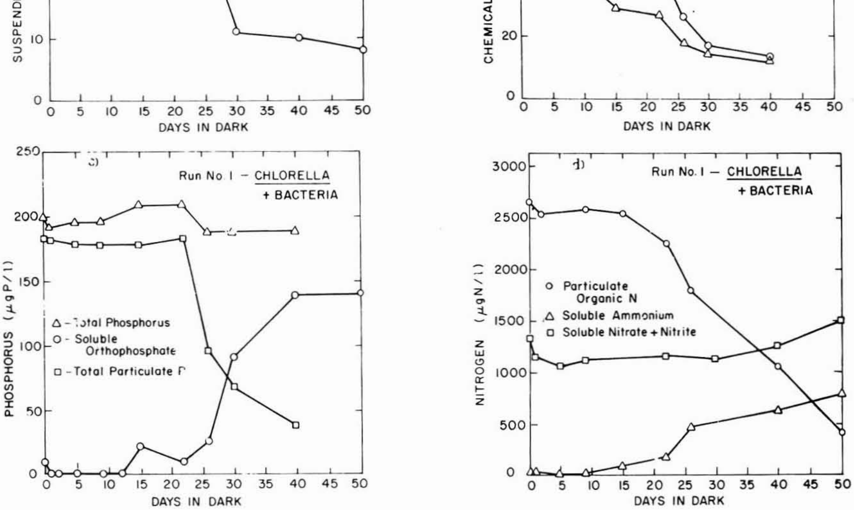

Figure 1. a) Suspended solids, b) chemical oxygen demand, c) phosphorus, and d) nitrogen vs. time in dark for decomposition run no. 1

detectable increase in soluble phosphorus in the culture vessel. If soluble P was released during the initial biomass decline, then the remaining viable organisms (algae and/or bacteria) must have rapidly taken up this fraction. The conditions of these experiments made it impossible to differentiate between algal-related particulate phosphorus and bacterial-related particulate P; however, it is unlikely that the comparatively small bacterial biomass could have accounted for this entire phosphorus fraction. Second, no net phosphorus release occurred until the viable algal population had been significantly reduced. Note that substantial soluble P release is not evident in run 1 until after day 22. Also note the corresponding decline in total particulate phosphorus. Finally, Figure 1c indicates that after the 22-day lag time, about 75% of the initial cellular phosphorus was released as soluble orthophosphate within an 18-day period. On the other hand, no net soluble orthophosphate release was observed in the bacteria-free culture during the entire dark incubation period.

The nitrogen regeneration in this study followed the expected pattern of cellular organic nitrogen being released as ammonia, which in turn, may or may not be converted to nitrite and nitrate, depending upon the nitrifying bacterial population. An accurate nitrogen balance could not be obtained in these culture vessels because of the potential loss of ammonia due to vigorous aeration. Consequently, the best measure of nitrogen regeneration is the decrease of particulate organic N in the cultures. A comparison of runs 1 and 2 illustrates that nitrogen regeneration can take place either by algal endogenous respiration or by active decomposition of algae. Although decrease in particulate organic N occurred in both cultures, culture no. 1 (Figure 1d) displayed a much greater and more rapid nitrogen release, most of which took place during the active decomposition period. Culture no. 2 did exhibit a 38% reduction in particulate organic N, which was consistent with the amount of COD reduction. There is also evidence that nitrification is beginning to take place in vessel no. 1 about eight days after the rapid ammonia release, whereas there was no apparent nitrification in the bacteria-free culture.

Evidence of the important role played by bacteria in the algal decay is presented in Figure 2, a plot of bacterial density in culture vessel no. 1 vs. days of incubation in the dark. It is interesting to note that the peak bacterial population coincided with the onset of soluble phosphorus release. Table II substantiates the premise that a certain bacterial density must be achieved before the decomposers exert a significant impact on the system. In every culture except no. 5, the maximum bacterial density occurred either during or just prior to the onset of rapid phosphorus regeneration.

Decomposition Run Nos. 3 and 4. Runs 3 and 4 were intended as a confirmation of the findings in the first two runs, except that an attempt was made to cut down the lag time by using a larger (and more representative) bacteria inoculum. In this case, the bacteria concentrated from 10 l. of lake water comprised the inoculum for the 18-l. culture no. 3. A comparison of the nutrient dynamics in runs 3 and 4 can be seen in Figure 3. Apparently due to the larger bacterial inoculum, run 3 exhibited a much shorter lag time (10 days) before active decomposition and nutrient regeneration were evident. In this run 95% of the initial cellular phosphorus was regenerated in less than 30 days of dark incubation. The most probable explanation for the time differential between runs 1 and 3 is that the peak bacterial density during run 3 was almost three times that for run 1 (Table II). Again the "bacteria-free" culture, run 4, remained green for the duration of the study, and again no net phosphorus regeneration was observed.

The pattern of nitrogen regeneration exhibited in run 3 is probably more indicative of what is occurring in a natural lake ecosystem than that of run 1. Organic nitrogen was released as ammonia, which peaked for about five days until a sufficient nitrifying bacterial population could develop to rapidly oxidize it to nitrate. The larger bacterial inoculum in this culture probably accounts for the more rapid and thorough nitrification in run 3 than in run 1.

Decomposition Run Nos. 5–8. Runs 5–8 were designed to investigate the effect of initial cellular phosphorus conditions on the regeneration of this nutrient (Figure 4). Also, runs 7 and 8 used a different green algal species (*Selenastrum capricornutum*). To obtain algal cultures with different initial cellular phosphorus content, the concentrations of phosphorus and nitrogen in the culture media for runs 5 and 7 were reduced to about 80 μg PO_4-P/l. and 1600 μg NO_3-N/l. Phosphorus was still the limiting nutrient in the medium; therefore, the decreased nitrate level did not seriously affect the nitrogen status of the cells. The growth phase of these four runs was then terminated at much lower algal biomass (15–21 mg/l. dry wt.) than the first four; hence, the difference in the initial medium phosphate levels showed up in the internal cellular phosphorus. The *Chlorella* in culture vessel no. 5 had an initial cellular phosphorus content of 0.48% (dry wt) (0.24% organic and 0.24% inorganic), whereas the *Chlorella* in vessel no. 6 had an initial cellular phosphorus content of 1.21% (dry wt) (0.48% organic and 0.73% inorganic). The *Selenastrum* in culture vessels 7 and 8 had initial cellular phosphorus levels of 0.38% (dry wt) (0.21% organic and 0.17% inorganic) and 0.85% (dry wt) (0.30% organic and 0.55% inorganic), respectively. Note that most of the excess phosphorus in cultures 6 and 8 was stored as inorganic P.

Although the rate and extent of organic decomposition for these four runs were approximately the same, they do differ in the realm of phosphous regeneration (Figure 4). Runs 6 and 8 exhibited about the same phosphorus release pattern as the earlier bacteria-inoculated runs. Runs 5 and 7, on the other hand, displayed a much lower percent phosphorus regeneration during the same time period as their paired counterpart,

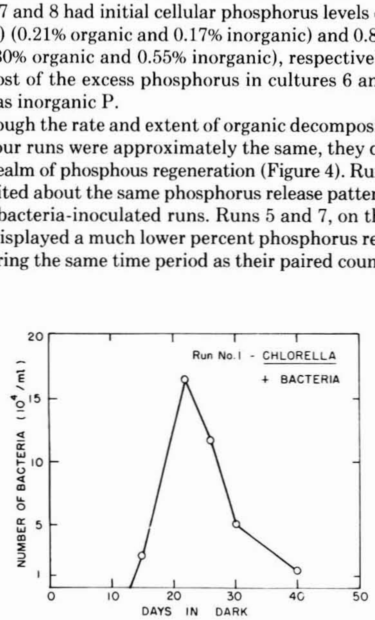

Figure 2. Bacterial density vs. time in dark for decomposition run no. 1

Table II. Maximum Bacterial Densities in Decomposition Vessels

Run no.	Max bacterial density, no./ml	Incubation time at max density, days	Onset of rapid phosphorus regeneration, days
1	1.63×10^5	22	22
3	4.70×10^5	13	10
5	1.44×10^5	8	24
6	1.81×10^5	29	22
7	2.55×10^4	35	35
8	2.42×10^6	23	12

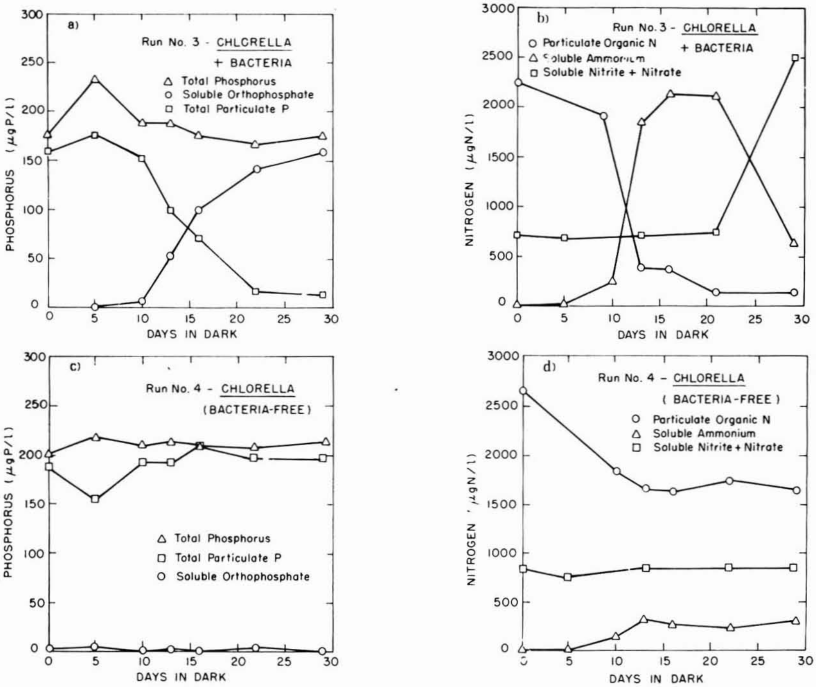

Figure 3. Nutrient dynamics for decomposition run nos. 3 and 4: a) phosphorus in no. 3, b) nitrogen in no. 3, c) phosphorus in no. 4, d) nitrogen in no. 4

which was apparently a reflection of the low initial cellular phosphorus. A plausible explanation lies in the fact that, irrespective of the initial particulate phosphorus upon darkening, an absolute amount of P (20–40 μg P/l.) remained insoluble at the completion of the experiments rather than a constant fraction of the initial amount. This quantity of phosphorus remaining is, therefore, probably not entirely refractory in nature. It is more likely associated not only with detritus but with the decomposer population in the cultures; hence, given more time, more phosphorus release would occur.

Summary of Results. This study has illustrated the two general mechanisms by which algae populations may decay under dark, aerobic conditions—endogenous respiration by the algal cells themselves and decomposition by microconsumers. Active bacterial decomposition proved to be the far more important mechanism in this study, especially for phosphorus regeneration. Furthermore, the rate and extent of the active decomposition of algae appeared to be highly dependent on the magnitude of the bacterial population. The extent of organic decomposition in bacteria-inoculated vessels (as measured by percent reduction of particulate COD) in this study varied from 53 to 95% (mean, 76%) (Figure 5). These results compare favorably with the average fraction decomposition of 73% found by Jewell and McCarty (*9*) in their studies of axenically grown *Chlorella* cultures. In contrast, the average percent reduction of particulate COD in the two uninoculated cultures was only 33.5%, pointing out the obvious role played by bacteria in this process. Rates of decomposition reported in the literature vary from 0.01 to 0.08 mg O_2/mg SS/day (*9, 19, 21*). The decomposition rates observed in this study varied from 0.014 to 0.083 mg O_2/mg SS/day.

The phosphorus regeneration in this study followed a pattern which indicated three stages: 1) after the algae are subjected to a darkened environment, there is a rapid release of P to solution associated with endogenous respiration followed by an immediate absorption by the remaining cells; 2) this stage is followed by a stationary lag phase lasting several days, during which there is a buildup of bacteria and no net phosphorus regeneration; 3) finally, when the viable algal population has been significantly reduced, there is an associated active phosphorus regeneration with a net release of orthophosphate to solution. In this study, the third stage lasted between 20 and 45 days, during which an average of 74% (range, 31–95%) of the initial cellular phosphorus had been regenerated in the bacteria-inoculated cultures (Figure 6). By contrast, the third stage never began in the uninoculated cultures.

Foree and Barrow (*15*) observed a similar pattern of phosphorus regeneration, except they observed an average of only 54% phosphorus regeneration under aerobic conditions after 200 days in the dark. Their studies differed greatly from this investigation, however, in one respect. The suspended solids of the algae cultures which they used for decomposition ranged from 130 to 1380 mg/l. In cultures this concentrated, an extremely large bacterial population would be required to bring about active decomposition and nutrient regeneration. Moreover, the extracellular substances produced by such a concentrated algal population may have had an inhibitory effect on the bacteria.

A further observation on the phosphorus regeneration in this study revealed that its rate and extent were dependent upon the phosphorus content of the algal cells. Close observation of the form of cellular phosphorus regenerated revealed two types of phosphorus regeneration based on the form of internal P being considered. For the organic cellular phosphorus the regeneration was proportional to the degree of decomposition of the cellular organic matter. On the other hand, when excess phosphorus (luxury uptake) was present in the cells at the onset of decomposition (runs 1, 3, 6, and 8), then excess regeneration occurred with this luxury inorganic phosphate being released rather rapidly following cell lysis.

To demonstrate that the form and amount of cellular phosphorus affect its regeneration, a plot was made of the inorganic/organic cellular phosphorus ratio just prior to active decomposition (during stationary stage 2) vs. the ultimate phosphorus release per dry weight of algae (Figure 7). Recall that excess cellular phosphorus is stored in an inorganic form; therefore, algal systems in a luxury state would tend to have a larger ratio of cellular inorganic P to organic P than those systems in a phosphorus-deficient state. It may be only coincidental that the data in Figure 7 appear to yield a straight line; however, the trend of more phosphorus regeneration under conditions of higher excess inorganic cellular phosphorus is obvious.

The rate of phosphorus regeneration during the active decomposition phase (stage 3) also appeared to depend on the initial algal phosphorus levels. Runs 5 and 7, which had significantly lower initial cellular phosphorus levels than runs 1, 3, 6, and 8, produced phosphorus regeneration rates of 0.08 and 0.06 μg P/mg algae (dry wt)/day, respectively. On the other hand, the rates for the other four runs ranged from 0.16 to 0.39 μg P/mg algae (dry wt)/day with an average of 0.24 μg P/mg algae/day.

The nitrogen regeneration pattern in this study seemed to be less complicated than that for phosphorus. It appeared that all organic nitrogen regenerated appeared first as ammonia, followed by a conversion of a portion of the ammonia to nitrate by nitrification. The most striking observation about nitrogen regeneration comes from a comparison of nitrogen regeneration with organic decomposition for each culture as presented in Figure 5. Note that the nitrogen regeneration in all cases—even bacteria-free—was almost identical to the amount of organic decomposition as reflected by the particulate COD reduction. This result strongly suggests that, unlike phos-

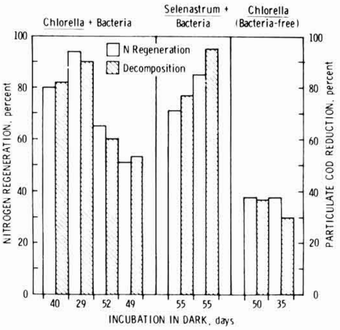

Figure 5. Comparison of the extent of decomposition and nitrogen regeneration for all eight runs

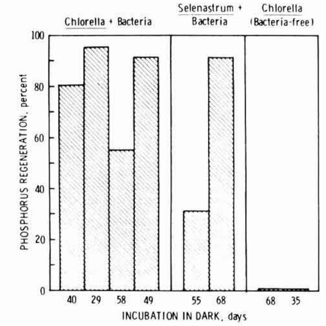

Figure 6. Extent of phosphorus regeneration under aerobic conditions for all eight runs

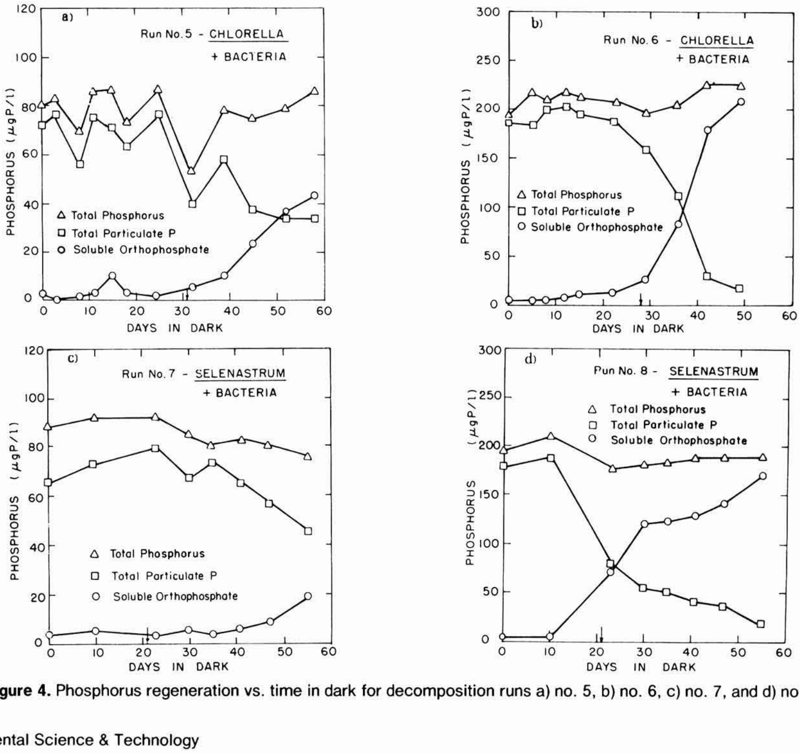

Figure 4. Phosphorus regeneration vs. time in dark for decomposition runs a) no. 5, b) no. 6, c) no. 7, and d) no. 8

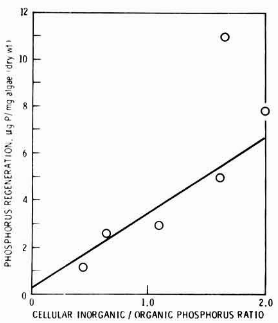

Figure 7. Extent of phosphorus regeneration as function of cellular inorganic/organic phosphorus ratio

phorus regeneration, nitrogen regeneration is a direct function of the amount of organic decomposition.

Conclusion

Although it has been previously reported that viable algal cells are generally not susceptible to attack by bacteria, this investigation suggests otherwise. The only difference between the cultures which rapidly decayed and those which remained viable for more than 70 days in the dark was the presence and absence of a bacterial-inoculum, respectively. In some manner, the bacteria contributed to the early lysis and decay of the algal cells, which did not occur in their absence. This phenomenon represents one possible explanation for the often observed rapid decline of algal blooms in lakes.

It has been demonstrated that a relatively large fraction of algal-related organic material can be decomposed under aerobic conditions within a 2-month period in the dark (about one-third of which is bacterial lag time). The nutrient regeneration in this study took place rapidly enough to suggest that this phenomenon may have a significant impact on soluble nutrient recycle in the metalimnion of stratified lakes. It is thought, therefore, that this phenomenon can have important ramifications in the calculation of nutrient budgets, prediction of seasonal phytoplankton succession, mathematical modeling of lake ecosystems, and any attempt at lake rehabilitation.

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Particle Collection Efficiencies of Air Sampling Cyclones: An Empirical Theory

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■ A new empirical cyclone collection theory is presented in which cyclone efficiency is expressed as a function of flow rate and particle diameter. The four empirical constants in the new equation are reported for four small cyclones calibrated in this laboratory by use of monodisperse aerosols of aerodynamic mass median diameters between 0.2 and 8 μm, and for three cyclones of Stairmand's design studied by others.

The cyclone separator has been used extensively for many years for industrial air cleaning. Since Harris and Eisenbud (*1*) used a 2-in. diameter cyclone as a precollector for a high-volume filter sampler, other small cyclones such as the 10-mm nylon cyclone and several sizes of steel and brass cyclones have been used in two-stage samplers (*2, 3*). The subject of respirable mass sampling has been reviewed by Lippmann (*4*), and established sampling criteria have also been discussed in the AIHA Guide (*5*). Four small cyclones were calibrated in this laboratory at a wide range of flow rates and particle sizes using γ-tagged monodispersed Fe_2O_3 particles. Particle retentions in the cyclones and backup filters were measured by γ-counting (*6, 7*).

In addition to specifying the appropriate flow rates for respirable dust sampling to match recommended sampler acceptance criteria (*5*), the small cyclone efficiency data obtained in our laboratory permit a critical evaluation of cyclone theories. The test aerosols used were monodisperse, stable, neutral in electrostatic charge, dilute in concentration, and nonhygroscopic. Effects due to electrostatic image forces and coagulation were therefore absent. The data of Beeckmans (*8*) and Ayer and Hochstrasser (*9*) for 19-mm and 6-in.

Stairmand-type cyclones are also presented, since their calibrations were also done under stable, controlled, and well-characterized conditions.

Particle Collection in Cyclone

Particle collection in the cyclone is primarily an inertial process with some complications due to the turbulent nature of the flow field inside the cyclone. Incoming air spirals downward from the inlet along the cyclone wall, then reverses direction, and flows upward along the axis through the outlet. Thus, some of the airborne particles are thrown to the cyclone wall or fall into the dust collector. The collection efficiency of a cyclone depends on various parameters including the flow rate and the aerodynamic mass median diameter of the particles (i.e., the equivalent diameter of a unity density sphere having the same settling velocity as the particle under consideration). The mass median aerodynamic diameter (MMAD) for a spherical particle is simply MMAD = $\sqrt{\rho} \times$ MMD, where MMD is the mass median diameter. This particle density dependence is important for most inertial collectors.

The aerodynamics inside the cyclone is generally described as a double vortex with a low-pressure, highly turbulent inner vortex. Flow near the cyclone wall is assumed to be laminar, although it is usually somewhat turbulent. Between the two vortices, there is a transitional boundary of zero vertical or horizontal velocity. This boundary is of great importance since it permits mass transport between these turbulent vortices. The phenomenon was noted by Hejma (*10*) as strong turbulence, by Wagner and Murphy (*11*) as short circuit flows, and by Fuchs (*12*) as turbulent mixing. Velocity profiles were measured in large cyclones by Ter Linden (*13*) and others. Semiempirical expressions for the velocity components were derived by Marinianscky and Cheng (*14*) based on the Navier-Stokes equations. However, none of these expressions is satisfactory since none reflects the effects of turbulence. Early investigators such as Ter Linden (*13*) and Ranz (*15*) noted that the derived expressions give maximum possible collection efficiencies. Only Beeckmans (*16*) considered mass transport between these turbulent zones.

Recent studies in the understanding of the particle collection behavior in cyclones have led Ayer and Hochstrasser (*9*) to propose a new "laminar core" flow field model for the air sampling cyclones. Their model accounts for the existence of a stagnant ring region near the bottom of the cyclone and the decrease of collection efficiency when the exit flow field becomes turbulent. The new model explains the ring deposits in most of our cyclones and the sudden pressure-flow discontinuities at the transitional region.

Review of Theories and Comparison with Experimentally Determined Efficiencies

There are at least 10 different cyclone theories in the literature which can be classified into four categories. A summary of these theories is given in Table I.

Type I. Conventional theories based on first principles assume that the flow field is laminar and that the cyclone wall is a perfect collection surface for particles. These theories have a general form of $D_{pc} = K_1 Q^{-1/2}$, where D_{pc} is the particle cut size (defined as the aerodynamic diameter of particles with a collection efficiency of 0.5 at a given flow rate); Q, the flow rate; and K_1, a characteristic cyclone parameter based on physical dimensions. Particle inertia is considered to be the only deposition force, and particle reentrainment is assumed to be negligible. The number of turns a particle makes within the cyclone is an important parameter in these equations and must be estimated. This usually limits the accuracies of the computed efficiencies. Rosin et al. (*17*), Lapple (*18*), Davies (*19*), and Barth (*20*) have described variants of this type of theory. Their theories are usually satisfactory in describing particle collection behavior in cyclones only if the particle trajectories follow the rules of classical particle dynamics.

Table I. Summary of Cyclone Collection Theories

Category	Theory and year	Form of equation	Ref	Assumptions	Features
I. Conventional	Rosin, 1932	$D_{pc} = K_1 Q^{-1/2}$	*17*	Inertial forces predominant in particle collection and cyclone wall as perfect sink for collection	No. of turns particles made has to be estimated
	Lapple, 1951		*18*		
	Davies, 1952		*19*		Calculations straight-forward
	Barth, 1956		*20*		
II. Semiempirical	Leith & Licht, 1972	$\eta = 1 - e^{f(Q,D_p)}$	*22*	Empirical fit of cyclone collection efficiency data vs. particle size at single flow rate	Good fit of data by adjusting coefficient but weak dependence of D_{pc} to Q predicted
	Sproull, 1970	$\eta = 1 - e^{f(Q,D_p)}$	*21*		
III. Theoretical	Beeckmans, 1973	$\eta = 1 -$ {infinite series with algebraic and exponential terms}[a]	*24*	Turbulent deposition predominant, negligible vertical velocity component	Computer solution required
	Soo, 1973	$\eta = 1 - e^{f(Q,D_p)}$	*25*	Initial deposition including electrostatic charge effects and adhesive forces on collector	Empirical constants required
IV. Empirical	Wagner,[b] 1971		*11*	Direct correlation of D_{pc} vs. Q	Provides good means of interpolation and extrapolation of data for useful applications
	Mercer, 1973	$D_{pc} = K_2 Q^{-n}$	*26*		
	Lippmann & Chan, 1974	$\eta = f[\tanh(Ax + Bx^2)]$ where $x = f(D_p, D_{pc})$	*6*		
	Beeckmans, 1976	$\eta = f(\mathrm{Re}^a \mathrm{Stk}^b)$	*28*		Suggests significance of flow field and particle inertia in the particle deposition process

[a] Solution to differential equations. [b] Correlated for liquid cyclones.

However, respirable particles are small enough so that their motions are affected by fluid turbulence and molecular forces. Particle inertia is no longer the only deposition force.

Type II. Semiempirical theories such as those of Sproull (*21*) and Leith and Licht (*22*) make an analogy to electrostatic collection of particles, and cyclone collection data are fitted against particle sizes at a single flow rate. A good fit can be obtained by adjusting various coefficients (*23*). Complete backmixing of particles in the cyclone is assumed in the Leith and Licht theory, but the predicted weak dependence of D_{pc} on flow rate does not agree with the small cyclone data as shown in Figure 1.

Type III. A theoretical approach by Beeckmans (*16, 24*), which assumes turbulent diffusion as the predominant particle collection mechanism, results in second order differential equations. Computer solutions of the Beeckmans theories can be written in the form of $\eta = 1 - \{$infinite series with algebraic and exponential terms$\}$. Soo's treatment (*25*) is similar but he includes effects of electrostatic charge, splashing, and adhesive properties of the collection surfaces within the cyclone. Such effects, however, are difficult to assess separately, and since they can be accounted for in the "sticking probability" term, Soo's equation can be reduced to a simpler form similar to the Leith and Licht equation by dropping the electrostatic terms.

Type IV. A direct empirical correlation of cyclone data relating cut size to flow rate in the form of $D_{pc} = K_2Q^n$ has been used by Wagner and Murphy (*11*) for liquid cyclones and by Mercer (*26*) for respirable dust samplers. The correlation of the 10-mm cyclone data by Mercer differs slightly from our own as illustrated in Figure 2, since his cyclone data are collected from various sources including one which contained data of questionable accuracy (*27*). If cyclone collection efficiencies can be determined at a few flow rates, these correlations permit better extrapolations in describing cyclone collection behavior. Another empirical fit which belongs to this category was described by Lippmann and Chan (*6*) and by Blachman and Lippmann (*7*) who fit cyclone retention to a hyperbolic tangent function of the normalized particle size. This kind of curve fitting is useful in examining the overall shape of the characteristic cyclone efficiency curve.

Recently, Beeckmans (*28*) obtained a new empirical correlation by relating cyclone efficiency to a product of the Reynolds and Stokes numbers each raised to a certain power, i.e., $\eta = f(\mathrm{Re}^a\mathrm{Stk}^b)$. Excellent correlation was shown using his own experimental data and those of Lippmann and Chan (*6*) and Blachman and Lippmann (*7*). Although there is no theoretical explanation of the new parameter $\mathrm{Re}^a\mathrm{Stk}^b$, it is certainly an indication that particle inertia in a specific flow field play a crucial role in the particle deposition process in a cyclone.

A comparison of several cyclone theories to the 10-mm nylon cyclone experimental data is presented in Figure 1.

Experimental Methods

The cyclone calibration apparatus has previously been described (*6*). It consists of a test chamber with multiple cyclone sampling ports. Filter holders are mounted after each cyclone with precalibrated orifice meters downstream of each filter. The test aerosols greater than 1 μm used were γ-tagged monodispersed ($\sigma_g \leq 1.10$) iron oxide particles with a density of 2.56 g/cm^3 (*29*) produced with a spinning disc aerosol generator, and the submicron particles were produced with an atomizer-impactor aerosol generator (ERC Model #7300). The particle size distribution of each test run with particles larger than 1 μm was analyzed optically by a 100× apochromatic oil immersion objective and a filar micrometer eyepiece. A spiral centrifuge (*30*) was used to determine the aerodynamic size distributions of the submicron particles. Radiometric counting was done with an array of scintillation detectors mounted inside a low background chamber. The counting efficiencies were predetermined with known sources to permit accurate determination of collection efficiencies. This technique is ideal for calibration purposes since sampling time is short, and the removal of particles from the cyclone is unnecessary. The cyclones used in the study were checked for dimensional and pressure drop deviations prior to use and were rejected if they exceeded ±5% (*6*).

Development of New Empirical Cyclone Efficiency Equation

While no theory can adequately describe particle collection in all cyclones under all conditions, a new empirical equation has been developed which enables one to predict cyclone collection efficiencies under various limited operating conditions. The basis of this new equation is the hyperbolic tangent equation used previously (*6, 7*) in fitting our cyclone data and a direct correlation of D_{pc} to Q, the flow rate through a cyclone. The original empirical expression is in the form of $\eta = 0.5 + 0.5 \tanh{(AX^2 + BX)}$ where η is the collection efficiency, and X is the normalized particle size defined as $X = (D_p - D_{pc})/D_{pc}$. Substitution of KQ^n for D_{pc} leads to an empirical expression of cyclone efficiency as a function of D_p and Q only. The correlation of D_{pc} and Q is straightforward. D_{pc}'s, the particle cut sizes, are interpolated from cyclone efficiency curves at different flow rates from the experimental cyclone data and plotted against Q on a log-log scale. The resulting straight lines, as shown in Figure 2, have correlation

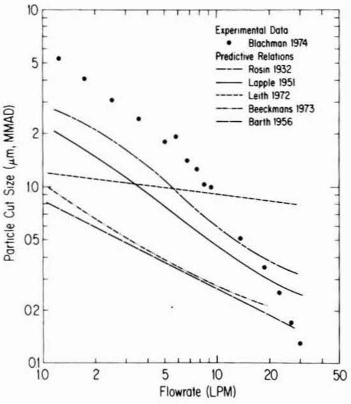

Figure 1. Comparison of experimental data vs. theoretical predictions for 10-mm nylon cyclone

Data from Blachman and Lippmann (1974). Data for Beeckmans' theory obtained from Beeckmans (1974)

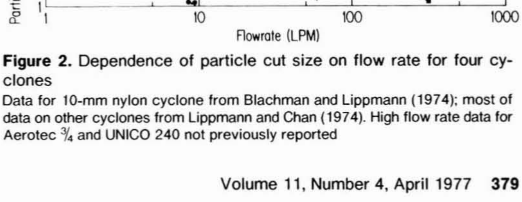

Figure 2. Dependence of particle cut size on flow rate for four cyclones

Data for 10-mm nylon cyclone from Blachman and Lippmann (1974); most of data on other cyclones from Lippmann and Chan (1974). High flow rate data for Aerotec ¾ and UNICO 240 not previously reported coefficients better than 0.95, and the values of K and n are different for each cyclone. The complete expression is therefore:

$$\eta = 0.5 + 0.5 \tanh \left[B \left(\frac{D_p}{KQ^n} \right)^2 + (A - 2\,\mathrm{B}) \frac{D_p}{KQ^n} + B - A \right]$$

The empirical constants A, B and K, n can be obtained from the least-squares fitting program of the original equation and the direct correlation of D_{pc} and Q, respectively. Plots of calculated and experimental values for six different cyclones are shown in Figures 3–8. Agreement between calculated and experimental data is quite good. A summary of the empirical constants for the cyclones is given in Table II.

Although the present form of the hyperbolic tangent equation is superior in fitting all our cyclone data, the expression has a maxima at $D_p/KQ^n = 1 - A/2\,B$ due to the quadratic form of the equation. The equation is therefore no longer valid when $D_p/KQ^n > 1 - A/2\,B$, conditions which arise either at very low flow rates, generally considered to be outside of the realistic operating ranges for cyclone separators, or with very large particles.

Discussion and Conclusions

It is apparent from Figure 1 that most cyclone efficiency equations overestimate the collection efficiencies for the 10-mm nylon cyclone. In comparing various theories to the experimental data, equations of Rosin et al. (*17*) and Lapple (*18*) seemed better than more recent theories. This is so only because we are able to examine the buildup of spiral deposits

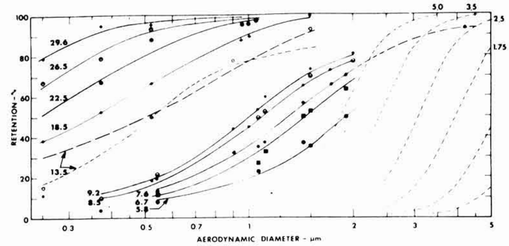

Figure 3. Collection efficiency of 10-mm nylon cyclone

Solid and dashed line curves computed by empirical theory. Data at flow rates >5 lpm from Blachman and Lippmann (1974)

Courtesy of American Industrial Hygiene Association

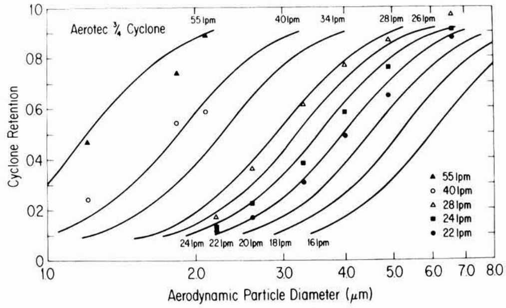

Figure 4. Collection efficiency of Aerotec ¾-in. cyclone

Data below 28 lpm from Lippmann and Chan (1974). Solid line curves computed from empirical theory

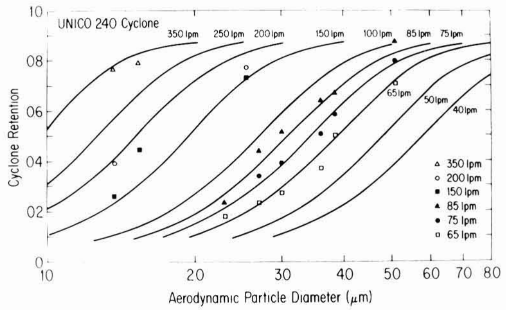

Figure 5. Collection efficiency of UNICO 240 cyclone

Data below 85 lpm from Lippmann and Chan (1974). Solid line curves computed from empirical theory

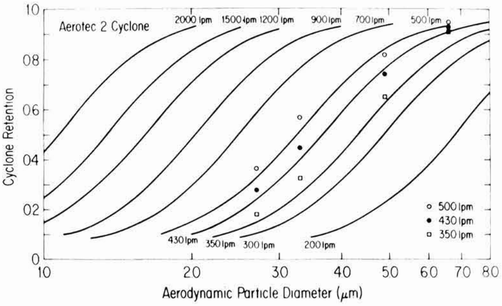

Figure 6. Collection efficiency of Aerotec 2-in. cyclone

Data from Lippmann and Chan (1974). Solid line curves computed from empirical theory

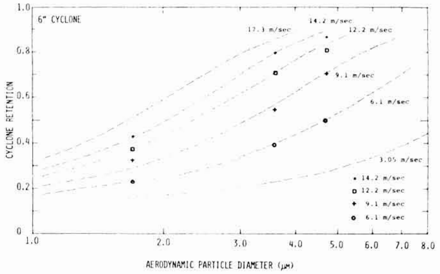

Figure 7. Collection efficiency of 6-in. cyclone

Data from Beeckmans (1976). Dashed line curves computed from empirical theory. Inlet velocities shown

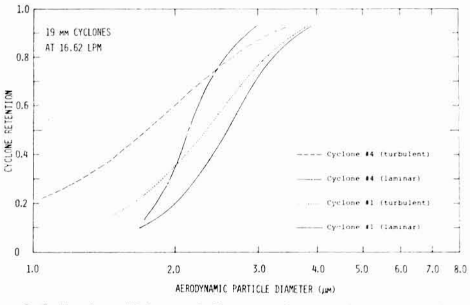

Figure 8. Collection efficiency of 19-mm cyclones at flow rate of 16.62 lpm showing effect of outlet diameter and "pseudolaminar" vs. turbulent operating conditions

Line curves computed by empirical theory with data from Hochstrasser (1976) at different flow rates. Outlet pipe interior diameters of cyclones #1 and #4 are 9.52 and 7.95 mm, respectively; other dimensions identical

Table II. Empirical Constants for Small Cyclones

Cyclone	D_{pc}, µm, AED	Q, lpm	K	n	A	B	Ref
Aerotec 2	2.5–4.0	350–500	468.01	−0.80	2.02	−0.68	*6*
UNICO 240	1.0–5.0	65–350	123.68	−0.83	1.76	−0.82	
Aerotec 3/4	1.0–5.0	22–65	214.17	−1.29	2.04	−0.77	
10-mm nylon	1.8–7.0	0.9–5.0	6.17	−0.75	3.07	−0.93	*7*
	1.0–1.8	5.8–9.2	16.10	−1.25	1.19	−0.59	
	0.1–1.0	18.5–29.6	178.52	−2.13	0.74	−0.07	
6-in. cyclone	0.6–5.0	1150–2700	4591.0	−0.98	0.914	−0.111	*8*
19-mm cyclone							
#1 laminar			15.46	−0.636	2.927	−0.849	*38*
#1 turbulent	1.9–5.0	9.9–23.3	21.69	−0.792	2.151	−0.385	
#4 laminar			16.69	−0.731	4.117	−2.459	
#4 turbulent			31.88	−1.033	1.438	−0.265	

inside the cyclones and thus estimate the exact number of turns a particle makes in the cyclone. The lack of this information can often reduce the calculated D_{pc}'s by at least a factor of two. Other theories tested such as the Leith and Licht (*22*), Barth (*20*), and Beeckmans (*24*) theories seem unsatisfactory. Beeckmans attributed the difference between theoretical and experimental data to the presence of a boundary sublayer which is resistant to mass transport at the wall of the cyclone (*31*). Another possible explanation is the reentrainment of particles collected on the walls of the cyclone. Evidence of this was reported by Jotaki (*32*) and Mori et al. (*33*) for industrial cyclones. Although the high dust loading favors such a process in the air cleaning cyclones, particle rebound must be considered as part of the particle reentrainment process in these air sampling cyclones at low dust concentrations. The magnitude of the inlet velocities for all the cyclones described here exceeds conditions favoring particle reentrainment reported by Dahneke (*34, 35*) and Cleaver and Yates (*36*).

The problem in developing a theoretical cyclone efficiency theory lies in the treatment of the complicated flows fields in the cyclone. Type I theories assumed laminar flow fields, and other theories of Type II and III considered turbulence with complete mixing. Then, there is the newly proposed laminar core theory of Ayer and Hochstrasser (*9*) which permits some qualitative explanations of previously anomalous experimental observations. Empirical correlations of Beeckmans (*28*) using the $\mathrm{Re}^a\mathrm{Stk}^b$ parameter and the $D_{pc} = KQ^n$ relationship presented here seem satisfactory in describing particle collection in the cyclone. It is of interest to note the values of n in the $D_{pc} = KQ^n$ correlation given in Table II. All values of n are less than the −0.5 predicted by the Type I theories, and the magnitude of n is an indication of the degree of turbulence in a cyclone. There are two distinctly different flow regimes in the 10-mm nylon cyclone with n values of −0.75 and −1.25 corresponding to a transition to more turbulent flows (Figures 1 and 2). The abrupt change in the slope from −0.75 to −1.25 is in agreement with a similar sudden change in pressure drop across a cyclone reported by Ayer and Hochstrasser (*9*) as the flow fields change from laminar to turbulent in the outlet pipe. Based on the n values alone, the cyclone #1 of Ayer and Hochstrasser and the dual inlet 1- and 2-in. cyclones can be considered to be operated in "pseudolaminar" or low turbulent regimes, whereas the Aerotec ¾-in. and the 6-in. cyclones studied by Beeckmans were operating in a more fully turbulent flow regime.

The effect of turbulence and outlet diameter for the #1 and #4 19-mm cyclones at a flow rate of 16.62 lpm is also shown in Figure 8. The computed curves were based on the data reported by Hochstrasser (*38*) who established the "laminar" and turbulent conditions by flow measurements. It is clear from Figure 8 that a decrease in the outlet pipe size (from 9.52 mm i.d. for cyclone #1 to 7.95 mm for cyclone #4) results in a sharper cutoff at the laminar region. The effect of turbulence is more significant for the cyclone #4 with an "n" value of −1.033. The efficiency curves are less sharp under turbulent conditions.

The empirical theory presented here enables one to predict cyclone performance at various operating conditions based only on a few experimental runs. The basic $D_{pc} = KQ^n$ correlation has been applied in the design of a multicyclone sampler which is now used in classifying urban particulates (*37*). The sampler is capable of determining trace constituents and their respective size-mass distributions in the urban particulates.

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Mechanism for Olefin–Ozone Reactions

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■ The gas-phase reaction of 2-butene with ozone is investigated. By use of experimentally obtained disappearance and formation rates, intermediates are proposed that when modeled explain the nonstoichiometric behaviors of olefin–ozone reactions. The oxidation of SO_2 in the presence of O_3 and 2-butene is also investigated. A biradical is not needed in the oxidation of SO_2. Instead, the SO_2 can be explained solely by its reaction with intermediates such as OH, O_2H, and CH_3O_2 that are produced in ozone–olefin reactions.

The production of ozone from the photooxidation of simple hydrocarbons in the presence of oxides of nitrogen is well recognized (*1*). The product, ozone, is also recognized as a principal reactant with the olefinic hydrocarbons in polluted atmospheres. Interest in recent years has been the determination of the rate constants and stoichiometry of olefin–ozone reactions. Knowledge of the stoichiometry of these reactions is necessary if a photochemical model is to be written to mathematically describe the manifestations arising from the production of photochemical smog.

The reaction investigated in this study was that of ozone with *trans*-2-butene. This was done for two reasons: the 2-butene is the simplest of the internally double-bonded olefins, and the compound is symmetrical through the double bond. This gives rise to only one biradical, thus simplifying the mechanism.

In attempting to arrive at the overall mechanism for the ozonolyses of 2-butene, the results and postulates of Demerjian et al. (*2*) as well as those of Niki et al. (*3*) were considered. A major difference between these two groups is the relative importance of HO_2 or OH resulting from the reaction of the biradical with oxygen.

Experimental

Two separate experimental systems were used for the study of the ozonolysis of *trans*-2-butene.

The first system employed a Teflon bag of 300–400 l. for the reaction chamber. The bag was filled with a measured volume of zero grade tank air which had passed through a pen ray mercury lamp ozonator. Thus, the volume of air and concentration of ozone could be controlled. Once the specific concentration of ozone and volume was established, *trans*-2-butene was injected into the bag with a gas tight syringe. The puncture hole was immediately sealed with tape, and the bag was kneaded to assure complete mixing. The amount of *trans*-2-butene to be injected was calculated from the volume of air in the bag and concentration that was to be obtained. The *trans*-2-butene was research grade and was used without further purification. The ozone concentration was monitored on a Bendix ozone–ethylene chemiluminescence instrument. The *trans*-2-butene was monitored by gas chromatography with flame ionization detection. A 10-ml air sample was chromatographed on a 12 ft × ⅛ in. outside diameter stainless steel column containing 60–80 mesh Pora pac Q, which was maintained at 115 °C, with a helium carrier gas flow of 40 ml/min. *Trans*-2-butene was monitored every 2.5 min while the ozone was monitored continually. Ozone decay in the Teflon bag in the absence of olefin was less than 1%/h. The only product analysis with this system was acetaldehyde by use of the above column.

The second system used two Teflon bags of 400-l. volume. One contained ozone, and the other *trans*-2-butene each in zero tank air. The contents of these bags were drawn into a large cylindrical chamber of 700 l. volume via two manifold systems of the chamber. The chamber consisted of six 1.25-m-long glass sections, 0.31 m in diameter. Manifold inlets were located between the sections. The chamber was evacuated to less than 1 torr pressure, and both ozone in air and *trans*-2-butene in air filled the cell at about the same rate. The chamber was filled in about 4.5 min. Time "0" was taken when the chamber had filled to 1 atm.

In the experiment with SO_2, a measured amount of *trans*-2-butene and SO_2 mixed in air was injected into the chamber at ½ atm. Ozone in air from the Teflon bag was added to bring the chamber to 1 atm. When the chamber pressure reached 1 atm, time "0" was recorded. The chamber contained internal optics for multipass path reflections that enabled in situ infrared measurements. Measurements were made with a rapid scan Fourier transform spectrometer that uses a Michelson interferometer with liquid nitrogen-cooled detectors covering the spectral range of 700–3400 cm^{-1} (*4*). Path lengths of 500 m were used. Products observed during the ozonolysis of *trans*-2-butene were carbon monoxide, acetaldehyde, formaldehyde, formic acid, methanol, and ketene. Carbon dioxide may also be a product. Small changes of carbon dioxide in the chamber could not be detected since some of the optical system between the interferometer and chamber and between the chamber and detectors is open to room air in which the carbon dioxide concentration does not remain constant. The ozone decay in the LPIR cell was 4.5%/h. Sulfur dioxide was measured from its absorption bands at 1135 and 1165 cm^{-1}.

Results and Discussion

Runs were made for olefin-to-ozone ratios of 1:1 (Figure 1), 1:3 (Figure 2), and 3:1 (Figure 3). Initial concentrations were on the order of a few parts per million (v/v). The experimental results illustrate: when olefin and ozone were present in equal amounts, more ozone than olefin was consumed; when ozone was in excess, slightly more ozone was consumed; and when the olefin was in excess, more olefin than ozone was consumed. These observations are at least in qualitative agreement with those of Japar et al. (*5*) and Williamson (*6*).

The measured products arising from the ozonolyses of *trans*-2-butene are shown in Figure 4. Products acetaldehyde, formaldehyde, carbon monoxide, and methanol were all followed with the long path IR system. Ketene was also observed spectroscopically, but its concentration was not quantified. Trace amounts of formic acid observed experimentally are not shown in this figure.

Model simulations for the three olefin-to-ozone ratios were made. The modeled curves are also shown in Figures 1–3. Although the modeling was not specific for either *cis*- or *trans*-2-butene, the rate constants for the initial ozone–2-butene reaction were the same as for the experimentally determined *trans*-2-butene–ozone reaction. The products arising from the model are shown in Figure 4. Ketene, carbon dioxide, and formic acid were plotted separately as modeled (Figure 5) since these values were not measured experimentally. From the model the concentration of CO_2 was considerable, but its correctness with the experiments could not be confirmed. Also not plotted but of considerable importance are hydrogen peroxide, and to a lesser extent, water. Small concentrations of H_2O_2 were obscured by H_2O absorption, and small concentration changes in H_2O could not be determined since the external path containing H_2O changed more drastically than the changes expected in the reaction cell.

In accordance with the Criegee mechanism, the proposed overall mechanism between ozone and 2-butene initially gives rise to a biradical and acetaldehyde. A molozonide was first invoked as an intermediate specie which unimolecularly rearranges in accordance with the O'Neal-Blumstein mechanism (*7*). This involves alpha-H and beta-H abstraction and a sequence leading to Criegee products and products characteristic only of the O'Neal-Blumstein mechanism. Upon mod-

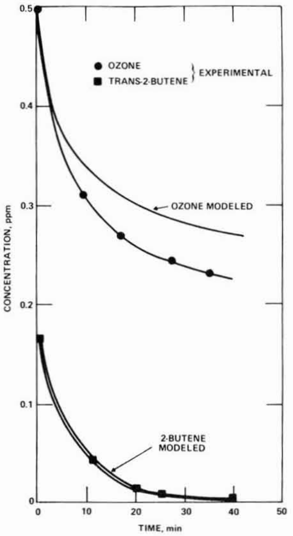


Figure 2. Experimental and modeled results of *trans*-2-butene ozonolysis, 0.5 ppm ozone, and 0.17 ppm *trans*-2-butene

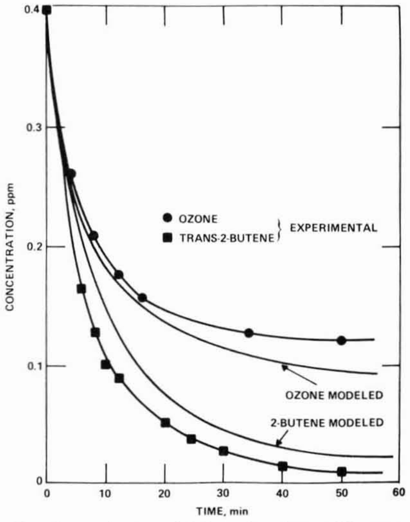


Figure 1. Experimental and modeled results of *trans*-2-butene ozonolysis, ozone, and *trans*-2-butene initially both 0.4 ppm

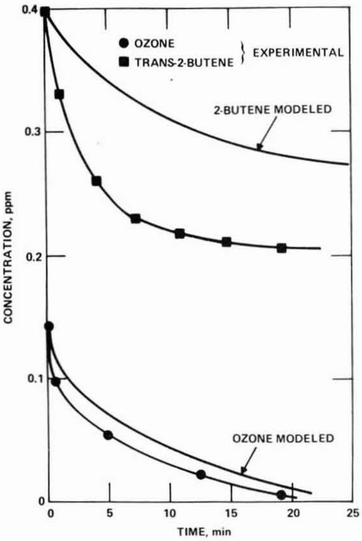


Figure 3. Experimental and modeled results of *trans*-2-butene ozonolysis, 0.14 ppm ozone, and 0.4 ppm *trans*-2-butene

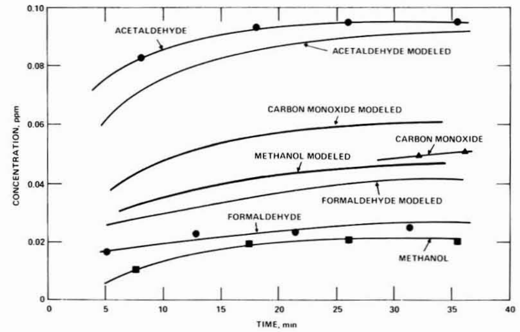


Figure 4. Products measured experimentally and modeled from ozonolysis of 0.4 ppm ozone and 0.4 ppm *trans*-2-butene

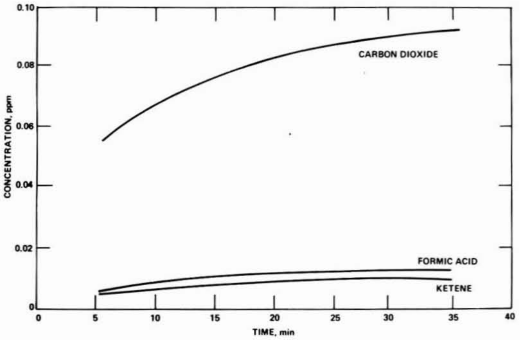


Figure 5. Other modeled products for ozonolysis of 0.4 ppm ozone and 0.4 ppm *trans*-2-butene

eling the experimental results, the Criegee mechanism was all that was required to explain the results when utilizing the O'Neal-Blumstein and Criegee mechanisms together as advocated in ref. 7. This, however, in no way negates the O'Neal-Blumstein mechanism. It only implies that our results could be explained without introducing this mechanism.

To obtain a fast decay for ozone, it was necessary to introduce a fast reaction between CH_3O_2 and O_3 which produces CH_3O and O_2. The rate constants for this reaction and others are given in the Appendix. The rate constants of some of the reactions when not available were derived from the techniques of Benson (*8*).

The reaction mechanism and rates that best describe the experimental results are shown below:

$$CH_3CH{=}CHCH_3 + O_3 \rightarrow CH_3\dot{C}HOO\cdot + CH_3CHO \quad (1)$$

$3.9 \times 10^{-1}\ ppm^{-1}\ min^{-1}$

(From this study initial *trans*-2-butene decay with equal amounts of ozone–*trans*-2-butene)

$$CH_3\dot{C}HOO\cdot \rightarrow CH_3CO_2H^* \quad (2a)$$

$1.0 \times 10^{5}\ min^{-1}$

(Calculated)

$$CH_3\dot{C}HOO\cdot \rightarrow HCO_2CH_3^* \quad (2b)$$

$2.3 \times 10^{4}\ min^{-1}$

(Calculated)

$$CH_3\dot{C}HOO\cdot + (O_2) \rightarrow CH_3CO_2 + O_2H \quad (3a)$$

$1.37 \times 10^{5}\ min^{-1}$

(*2*)

$$CH_3\dot{C}HOO\cdot + (O_2) \rightarrow CH_3CO_3 + OH \quad (3b)$$

$3.15 \times 10^{2}\ min^{-1}$

(*3*)

$$CH_3COOH^* \rightarrow CH_3OH + CO \quad (4a)$$

$8.4 \times 10^{13}\ min^{-1}$

(Calculated)

$$CH_3COOH^* \rightarrow CH_2{=}C{=}O^* + H_2O \quad (4b)$$

$4.4 \times 10^{13}\ min^{-1}$

(Calculated)

$$CH_2{=}C{=}O + (O_2) \rightarrow HCO_2H + CO \quad (5)$$

$1.5 \times 10^{10}\ min^{-1}$

(Calculated)

$$CH_2{=}C{=}O^* + (M) \rightarrow CH_2{=}C{=}O + (M) \quad (6)$$

$1.2 \times 10^{10}\ min^{-1}$

(Calculated)

$$HCO_2CH_3^* \rightarrow CH_3OH + CO \quad (7)$$

$1.8 \times 10^{13}\ min^{-1}$

(Calculated)

$$CH_3CO_2 \rightarrow CH_3 + CO_2 \quad (8)$$

$1.3 \times 10^{12}\ min^{-1}$

(*2*)

$$CH_3 + (O_2) \rightarrow CH_3O_2 \quad (9)$$

$1 \times 10^{8}\ min^{-1}$

(*2*)

$$CH_3CHCHCH_3 + OH \rightarrow CH_3CHOHCHCH_3 \quad (10)$$

$7.5 \times 10^{4}\ ppm^{-1}\ min^{-1}$

(*2*)

$$CH_3CHOHCHCH_3 + O_2H + (O_2) \rightarrow CH_3CHOHCHOCH_3 + OH + O_2 \quad (11)$$

$5.4 \times 10^{3}\ ppm^{-1}\ min^{-1}$

(*2*)

$$CH_3CHOHCHOCH_3 \rightarrow CH_3CHO + CH_3CHOH \quad (12)$$

$6.0 \times 10^{13}\ min^{-1}$

(*3*)

$$CH_3CHOH + (O_2) \rightarrow CH_3CHO + O_2H \quad (13)$$

$3.2 \times 10^{2}\ min^{-1}$

(*3*)

$$CH_3CHCHCH_3 + OH + (2O_2) \rightarrow CH_3CHO + HCHO + HCO_2 + H_2O \quad (14)$$

$3.0 \times 10^{4}\ ppm^{-1}\ min^{-1}$

(*2*)

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O \quad (15)$$

$2.2 \times 10^{4}\ ppm^{-1}\ min^{-1}$

(*2*)

$$HCHO + OH \rightarrow HCO + H_2O \quad (16)$$

$2.1 \times 10^{4}\ ppm^{-1}\ min^{-1}$

(*2*)

$$CH_3CO + (O_2) \rightarrow CH_3CO_3 \quad (17)$$

$2.1 \times 10^{9}\ min^{-1}$

(*2*)

$$HCO + (O_2) \rightarrow O_2H + CO \quad (18)$$

$5.3 \times 10^{7}\ min^{-1}$

(*2*)

$$\mathrm{HCO + (O_2) \rightarrow HCO_3} \tag{19}$$

$2.1 \times 10^{7}\ \mathrm{min}^{-1}$

(*2*)

$$\mathrm{2CH_3CO_3 \rightarrow 2CH_3CO_2 + O_2} \tag{20}$$

$3.8\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$

(*2*)

$$\mathrm{CH_3CO_3 + O_2H \rightarrow CH_3CO_2 + OH + O_2} \tag{21}$$

$3.9 \times 10^{1}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$

(*2*)

$$\mathrm{2HCO_3 \rightarrow 2HCO_2 + O_2} \tag{22}$$

$3.8\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$

(*2*)

$$\mathrm{HCO_3 + O_2H \rightarrow HCO_2 + OH + O_2} \tag{23}$$

$3.9 \times 10^{1}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$

(*2*)

$$\mathrm{HCO_2 \rightarrow H + CO_2} \tag{24}$$

$1.5 \times 10^{10}\ \mathrm{min}^{-1}$

(*2*)

$$\mathrm{H + (O_2) \rightarrow O_2H} \tag{25}$$

$3.6 \times 10^{8}\ \mathrm{min}^{-1}$

(*2*)

$$\mathrm{2O_2H \rightarrow H_2O_2 + O_2} \tag{26}$$

$8.3 \times 10^{3}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$

(*9*)

$$\mathrm{H_2O_2 + OH \rightarrow O_2H + H_2O} \tag{27}$$

$1.2 \times 10^{3}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$

(*2*)

$$\mathrm{2CH_3O_2 \rightarrow 2CH_3O + O_2} \tag{28}$$

$5.0 \times 10^{2}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$

(*10*)

$$\mathrm{CH_3O_2 + CH_3CO_3 \rightarrow CH_3O + CH_3CO_2 + O_2} \tag{29}$$

$3.9 \times 10^{1}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$

(*2*)

$$\mathrm{CH_3O_2 + O_2H \rightarrow CH_3O + OH + O_2} \tag{30}$$

$5.0 \times 10^{2}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$

(*10*)

$$\mathrm{CH_3O_2 + O_3 \rightarrow CH_3O + 2O_2} \tag{31}$$

$1.6 \times 10^{1}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$

(Calculated)

$$\mathrm{CH_3O + (O_2) \rightarrow HCHO + O_2H} \tag{32}$$

$5.0 \times 10^{3}\ \mathrm{min}^{-1}$

(*2*)

$$\mathrm{O_2H + O_3 \rightarrow OH + 2O_2} \tag{33}$$

$2.3\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$

(*9*)

Addition of SO_2. Experiments were conducted with added SO_2. With the addition of 0.4 ppm of SO_2 to equal amounts of *trans*-2-butene and ozone (both 0.4 ppm), the following set of reactions had to be added to the above reaction scheme.

$$\mathrm{SO_2 + OH \rightarrow HSO_3} \tag{34}$$

$1 \times 10^{3}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$

(*10*)

$$\mathrm{SO_2 + O_2H \rightarrow SO_3 + OH} \tag{35}$$

$1.4\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$

(*11*)

$$\mathrm{SO_2 + CH_3O_2 \rightarrow SO_3 + CH_3O} \tag{36}$$

$7.0\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$

(Calculated)

The observed oxidation of SO_2 was approximately 0.031 ppm for 31 min. This amounts to approximately 7.6% reaction. The above reactions over a period of 30 min when modeled can account for 0.17% for OH, 2.84% for O_2H, and 13.8% for CH_3O_2. These three reactions can, therefore, account for all of the SO_2 oxidation. The reaction with the biradical, i.e., $SO_2 + CH_3\dot{C}HOO\cdot \rightarrow CH_3CHO + SO_3$ has a rate constant of $4 \times 10^{5}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$ derived from the slope-intercept method of Cox and Penkett (*12*). This value for the rate constant is much too high and will give an extremely high percent SO_2 conversion. Although the calculated rate for Reaction 36 may be too high, it is doubtful that the contribution of the biradical to SO_2 oxidation is important. Since the product distribution is altered when SO_2 is added to an olefin–ozone system (*13*), it is possible that SO_2 does react with the biradical. However, the observed oxidation rates strongly imply that the SO_2-biradical rate constant is considerably smaller than $4 \times 10^{5}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$; if the reaction rate constant of CH_3O_2 with SO_2 is even close to correct, the total SO_2 oxidation can be accounted for without invoking any reaction with the biradical. This is obviously an area that requires additional investigation.

Summary

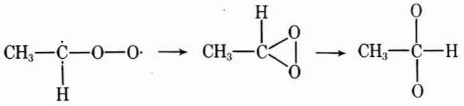
The experimental data show a definite nonstoichiometry in the reaction of ozone with *trans*-2-butene. This stoichiometry is variable depending upon the initial reactant ratios. The results can be explained by incorporating free radical reactions into the reaction scheme. The oxidation of SO_2 in an olefin–O_3 system can be explained solely with the reactions of OH, O_2H, and CH_3O_2. A reaction of the biradical is not necessary to explain the rate of disappearance of SO_2.

Appendix

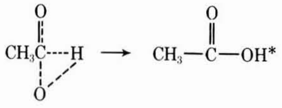
Derivation of selected rate constants illustrative of the techniques used is shown below:

$$\mathrm{CH_3\dot{C}HOO\cdot \rightarrow CH_3CO_2H^{*}} \tag{2a}$$

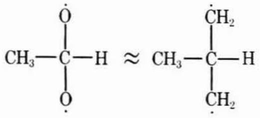
By analogy with ab initio calculations of the methylene peroxide biradical $\cdot CH_2OO\cdot$, which can rearrange to $CH_2\dot{O}\dot{O}$ and then to formic acid (*14*), a similar series of reactions can be postulated for $CH_3\dot{C}HOO\cdot$.



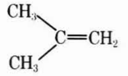
The dioxyethane biradical then rearranges to produce a very hot acetic acid.



In estimating a rate constant for the above process, the methylene group is substituted for the isoelectronic oxygen atom, i.e.,



This rearranges (*8*) to produce



The driving force is the formation of the double bond with an A factor of $10^{13}\ \mathrm{s}^{-1}$ and an activation energy of 11 kcal (*8*). However, the symmetry of the biradical is twofold less than the trimethylene. Also, the OH bond energy is approximately 2 kcal less than that of CH_2—H. The rate constant for Reaction 2a is, therefore;

$$k_{2a} = 5 \times 10^{12}\, e^{-21} \cdot 6\ \mathrm{s}^{-1} \approx 1 \times 10^{5}\ \mathrm{min}^{-1}$$

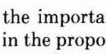
Decomposition of Hot Acetic Acid (4a). The decomposition of the hot acetic acid to methanol and CO involves a 1,2 shift of OH from a carbonyl to carbon or a 1,2 shift of a methyl group to carbon. The three-center transition state will be taken as the same for cyclopropane forming propylene. We recognize, of course, that this is not completely correct but is convenient as we can arrive thereby at the values quickly for the A factor and Ea from Benson (*8*). The values are $A = 6 \times 10^{14}\ \mathrm{s}^{-1}$ and $Ea = 61$ kcal/mol. Since a hot molecule is being considered, the approximation will use the RRK method. For simplicity the effective vibrational degrees of freedom S will be taken as ⅔ the total number of vibrational degrees of freedom. Since there are eight atoms in acetic acid, the effective number S is ⅔ [3 (8) − 6] or 12. Therefore,

$$k = A\left(\frac{E^* - Ea}{E^*}\right) S - 1$$

where A and S have been defined, Ea is the usual activation energy, and E^* is the excess energy contained in the hot molecule or 144 kcal/mol in this case.

$$k = 6 \times 10^{14}\left(\frac{83}{144}\right)^{11}\ \mathrm{s}^{-1}$$

$$= 8.4 \times 10^{13}\ \mathrm{min}^{-1}$$

for  $\longrightarrow$ CH_3OH + CO

$$\text{for}\ \ CH_3\overset{\overset{\displaystyle O}{\|}}{C}O^*H^* \longrightarrow CH_3OH + CO$$

The reaction $CH_3COOH^* \rightarrow CH_3 + COOH$ was not considered in the model. The rate constant for this reaction was calculated at $7.4 \times 10^{13}\ \mathrm{min}^{-1}$. This reaction is competitive with Reactions 4a and b. However, since the products are the same as 3a and 8, the deletion of this reaction will have only a qualitative effect similar to raising the rate constants of Reaction 3a.

Because of the importance of the $CH_3O_2 + O_3$ reaction (Reaction 31) in the proposed mechanism, the derivation of this rate constant will be given.

$$CH_3O_2 + O_3 \rightarrow CH_3O + 2O_2 \qquad (31)$$

$$k_{31} = \text{to be determined}$$

$$O_2H + O_3 \xrightarrow{k_{33}} OH + 2O_2$$

$$k_{33} = 2.3\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}\ (\mathit{10})$$

$$2O_2H \xrightarrow{k^1} 2OH + O_2$$

$$k^1 = 5.3\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}\ (2)$$

$$2CH_3O_2 \xrightarrow{k_{28}} 2CH_3O + O_2$$

$$k_{28} = 5 \times 10^{2}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}\ (\mathit{10})$$

$$\left(\frac{k_{31}}{k_{33}}\right)^2 = \frac{k_{28}}{k^1} = 94.3$$

$$k_{31} = 2.2 \times 10^{1}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$$

$$\text{also}\ CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$k^a = 9.1 \times 10^{2}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}\ (2)$$

$$O_2H + NO \rightarrow OH + NO_2$$

$$k^b = 2 \times 10^{2}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}\ (2)$$

$$\frac{k_{31}}{k_{33}} = \frac{k^a}{k^b} = 4.55$$

$$k_{31} = 1.05 \times 10^{1}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$$

Take k_{31} as the average = $1.6 \times 10^{1}\ \mathrm{ppm}^{-1}\ \mathrm{min}^{-1}$.

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Large Particle Collection Characteristics of Ambient Aerosol Samplers

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■ Large particle sampling effectiveness of commercially available and prototype particle collectors was determined by wind tunnel testing. Included in the tests were the standard 1 CFM Andersen and a specially modified version of it which utilizes a weatherproof, directionally insensitive inlet; the standard Hi-Volume sampler; a Prototype Dichotomous sampler; and a prototype sampler which utilizes the 20 CFM Andersen with a rotating cowl inlet. The tests were performed using particles ranging in size from 5 to 50 μm, approach velocities from 5 to 15 ft/s (1.5–4.6 m/s), turbulence levels of <1 and 8%, and orienting the samplers at different directions to the flow. By use of a base condition for comparison purposes of 15 ft/s (4.6 m/s), a 15-μm aerosol, and an 8% level of turbulence intensity approaching the samplers in the wind tunnel, the following sampler effectivenesses (aerosol deposited on collection substrates of the particular sampler to that detected by an isokinetic sampling system) were noted: commerically available 1 CFM Andersen 2%; modified 1 CFM Andersen with the special inlet, 50%; standard Hi-Volume sampler 55% (wind at 45° to the ridge of the roof); Prototype Dichotomous sampler 45%; and the 20 CFM Andersen with a rotating cowl inlet 82% (tested at 5 ft/s, 1.5 m/s).

The goal of this study was to ascertain quantitatively the capability of commercially available and prototype ambient air samplers to determine in an unbiased manner the particle cloud concentration consisting of 5–50 μm (micrometer) diameter particles. The investigation was performed in a wind tunnel under conditions similar in flow velocity and turbulence intensity to those that the samplers would encounter in routine operation in the atmospheric boundary layer. The resulting data will assist persons concerned with ambient air particle sampling to more accurately interpret their data.

Background and Commercial Instruments Tested. Pursuant to the 1970 Amendments to the Air Quality Act, the Environmental Protection Agency has placed primary emphasis on the control of small particles (<5 μm) since the potentially deleterious health effects are better correlated with the small sizes. Also, submicron particles play the greatest role in scattering light in the atmosphere and exist in an airborne state for long periods of time. However, as efforts increase to exploit natural resources in search of alternate sources of energy, the emission of large particles (>5 μm) will increase from mining efforts, oil shale usage, and fuel transportation and utilization operations. The environmental impact of energy related phenomena in the form of damage to materials and welfare will necessitate that control considerations also be directed to the larger particles in the future.

At the present, little effort has been devoted to the development of instrumentation with the capability of collecting unbiased samples of the larger fraction of ambient particles. The increased inertia associated with large particles poses significant internal transport problems for any collection apparatus. Particles may also impact on the sampler inlet or upon surfaces of fractionation elements within the sampler.

It was the primary purpose of this study to evaluate the ambient air samplers to determine the capabilities of these devices for effective collections of the larger particles. The resulting data can be used not only for future judgments in aerosol sampler selection, but also for interpretation of previously acquired data. For example, Hi-Volume samplers have been used extensively for sampling in situations in which large wind-blown dust particles are present. The efficiency with which these larger particles are drawn into the samplers has not been known.

There are two basic sampling approaches incorporated into commercial instruments that are currently widely used for collection and subsequent physical and chemical analysis of atmospheric particulate matter. The first is exemplified by the standard Hi-Volume sampler (*1, 2*) which employs an absolute filter and a vacuum source and provides an assessment of total aerosol mass concentration. For the wind tunnel experiments, the sampler tested was made by General Metal Works and represents the standard version adopted by EPA (*3*). The second approach utilizes the impaction principle to introduce a size-fractionation capability. The basic commercial instrument employed in tests was a 1 CFM eight-stage system introduced by Andersen (*4*).

Prototype Instruments Tested. Another instrument tested which utilizes an impaction system is the virtual impactor, first introduced by Houman and Sherwood (*5*). A version of this device, a Prototype Dichotomous sampler (*6*), was examined in the wind tunnel tests. This sampler is designed to permit two size fractions of particles to be collected separately with the cut point being near 3 μm. This point is suggested by the bimodal nature of the mass distribution of urban aerosol (*7*) with the lower fraction being associated with potential health hazards and the upper size with materials damage. The size segregation is affected by inertial impaction across a virtual surface into a chamber of relatively stagnant air with the large particles penetrating into the chamber and the small particles being diverted around it. Both size fractions are then collected on filters. The particular dichotomous sampler tested has a total inlet flow of 220 lpm, 14 lpm of which are brought through the two-stage virtual impaction fractionator. For more details of the system, see Dzubay and Stevens (*6*).

In addition to the particles collected in the fractionation system, the Dichotomous sampler tested also has accommodations to collect a total particle sample. The system operates in parallel with the fractionation apparatus and consists simply of a 127-mm glass-fiber filter.

A second prototype instrument developed and tested was designed to improve the sampling effectiveness of the 1 CFM Andersen. Specifically, two modifications were introduced which consisted of the inclusion of an all weather sampler inlet (AWSI), and the replacement of the original Andersen stages 0 and 1 with revised stages denoted by A and B and the use of a conically shaped connector between the inlet and sampler (Figure 1). Stages A and B had only 36 jets each, with the jet inlets tapered. The collection plates were modified to allow the flow to go through the center of the plates as well as around them. For more details, see McFarland et al. (*8*). With reference to the inlet housing, for a sampling rate of 0.47 l/s. (1 CFM) the flow enters at a velocity of 15 ft/min (0.076 m/s). Once inside the unit the flow is decelerated, flows vertically upward through a stilling chamber, and then through a set of 24 holes, each ½ in. (1.27 cm) in diameter, into the internal inlet for transport to the impaction stages.

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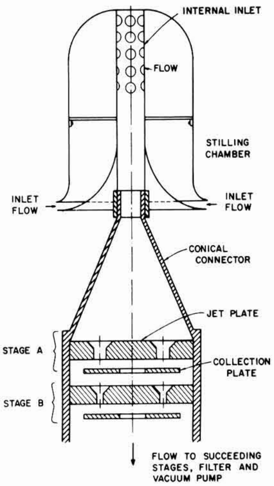

Figure 1. Configuration of modified 1 CFM Andersen with all weather sampling inlet and revised stages A and B

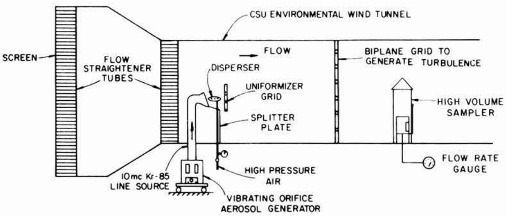

Figure 2. Wind tunnel experimental system

The other prototype instrument tested was the Sehmel Rotating Cowl and Impactor system (*9*)) which consists of a 20 CFM Andersen equipped with a special housing that orients a 6-in. (15.24 cm) diameter cylindrical inlet directly into the wind. The inlet velocity is 0.52 m/s and upon passing through the cylinder, the particles enter the 20 CFM Andersen head for fractionation and collection.

Experimental Procedure

Wind Tunnel Tests. The five samplers—commercially available and prototype—1 CFM Andersen impactors, the General Metal Works Hi-Volume sampler, the Prototype Dichotomous sampler, and the Sehmel Rotating Cowl and Impactor system were placed one at a time in the Environmental Wind Tunnel facility at Colorado State University (shown schematically in Figure 2). The tunnel has a 3.65-m-wide test section with a roof that can be adjusted up to 2.44 m in height—a feature which allows the tests to be conducted with a zero pressure gradient in the direction of flow. The present series of tests was performed with a 1.83-m ceiling height which was also sufficient to preclude blockage effects.

The samplers were tested under a variety of field-realistic conditions using monodisperse aerosols of 5–50 μm in aerodynamic diameter, longitudinal components of approach flow turbulence intensity <1% (tunnel background) to 8%, and flow rates up to 15 ft/s and at different inlet orientations to the flow. Referring to Figure 2, aerosol was generated by a vibrating orifice type atomizer (*10*) and was injected into the tunnel through a 15-cm diameter pipe. A uniform concentration profile for the particle cloud was obtained by first dispersing the freshly injected aerosol with a series of jets placed normal to the flow. Second, the expanded particle cloud was passed through a biplane grid to generate turbulence and increase mixing and homogeneity and then into the test section. The aerosol concentration was determined prior to and subsequent to each test of the various samplers using an isokinetic sampling manifold fitted with six isokinetic sampling nozzles attached to absolute filters. The manifold was approximately 90 cm in width with the six isokinetic sampling nozzles spaced at equal intervals (~15 cm) on the same plane. The sampling effectiveness of the instruments was then determined by comparing the quantity of aerosol deposited on the collection substrates of a particular sampler to that detected by the isokinetic sampling system with appropriate corrections for differences in sampling volumes.

The turbulence level of 8% was achieved by introducing a biplane grid approximately 10 mesh diameters upstream of the sampler placement area in the wind tunnel. Note that the wind tunnel tests were primarily a test of inlet effectiveness.

Sample Analysis. The particles used in the studies were formed from the atomization of an oleic acid solution tagged with uranine dye, the latter used for increasing mass sensitivity through fluoroscopic analysis. Analysis was performed by washing the collection substrates (or filters) from the particular sampler being tested in pure ethanol. The resulting solution was diluted 1:1 with distilled water. One drop of 1 N NaOH was added to a 4-ml aliquot of each sample solution to stabilize and maximize fluorescence. These aliquots were quantified in terms of fluorescent content with the aid of a calibrated Turner Model 111 fluorometer.

Special Tests. Certain tests were performed on some instruments in addition to the wind tunnel tests described. The internal wall losses of the original and modified upper stages of the 1 CFM Andersen impactor were examined by direct sampling of the test aerosol of 5-, 10-, and 15-μm aerodynamic diameter. Internal losses were determined by comparing the quantity of material on the collection substrates (Mylar or Teflon surfaces) with the total deposited on all surfaces.

Also, tests were performed on the Prototype Dichotomous sampler to determine transport losses. In this case, the total particle mass deposited on the walls and elements of the fractionation stages was divided by that collected by the 127-mm filter (with appropriate correction for flow rate) to obtain the fractional wall losses.

Test Results and Discussion

Original and Modified 1 CFM Andersen. The reduced data for the 1 CFM Andersen are shown in Tables I and II. With reference to Table I, the results of the special tests reveal that a considerable reduction in internal losses was made

Table I. Internal Wall Losses of Original and Modified 1 CFM Andersen Samplers

	Particle diameter, μm		
	5	10	15
Original design	10%	32%	41%
Modified design	4%	9%	18%

Table II. Sampling Effectiveness of Original and Modified 1 CFM Andersen Samplers

	Particle diameter, μm		
	5	15	30
Original design	67%	2%	0%
Modified design	97%	50%	22%

possible by the modified design. For example, the losses for a 10-μm particle are 32% for the original Andersen and 9% for the modified Andersen. Note that the AWSI mentioned earlier was not used for the tests presented in Table I.

Table II shows the results from the wind tunnel tests using the AWSI. The comparative data illustrate the substantial increase in sampling effectiveness realized by the modified version. For the base condition of 15 ft/s (4.6 m/s), 8% approach flow turbulence, and a 15-μm diameter particle, the original Andersen had a sampling effectiveness of 2% as compared to 50% for the modified 1 CFM Andersen. Tests reflect both inlet and stages A and B sampling effectiveness.

The effect of approach flow turbulence upon sampler effectiveness is negligible over the range of parameters tested (Figure 3). In addition, the data shown in Figure 4 indicate that velocity also has relatively little effect upon the system performance for particles of 15 μm diameter. The effectiveness of the modified system is 55% in a 5 ft/s wind and 48% in a wind of 15 ft/s. Figures 3 and 4 are essentially tests of the sampler inlets.

Hi-Volume Sampler. The results from tests with the Hi-Volume sampler are presented in Table III for 5-, 15-, 30- and 50-μm particle sizes at 15 ft/s (4.6 m/s) and for two different sampler orientations, 0° and 45°. In this case 0° is defined as the situation with the Hi-Volume roof ridge parallel to the flow. The Hi-Volume is extremely sensitive to the angle of approaching wind and is more efficient at 45° than 0°. This may be explained by the fact that with a 0° orientation the particles are approaching an inlet which requires that they must negotiate a sharp turning angle to enter the sampler. Indeed, for larger particles there was visible evidence of losses (recorded on film) on the stagnation face of the sampler housing. With reference to Table III, only at the 5-μm particle size does the sampling effectiveness approach 100% and sampler orientation ceases to be important.

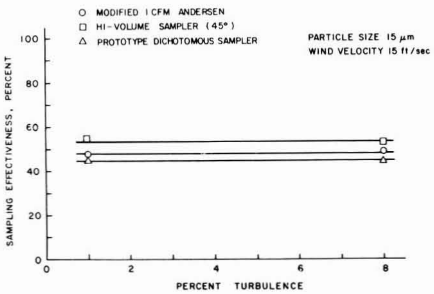

Figure 3. Influence of approach flow turbulence upon effectiveness of various samplers

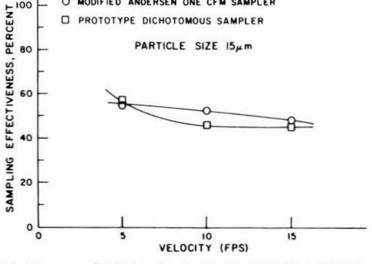

Figure 4. Influence of wind velocity upon sampling effectiveness of modified Andersen and Prototype Dichotomous samplers

Table III. Sampling Effectiveness of Hi-Volume Sampler at 15 ft/s

Particle diameter, μm							
5		15		30		50	
Sampler orientation, °							
0	45	0	45	0	45	0	45
97%	100%	35%	55%	18%	41%	7%	34%

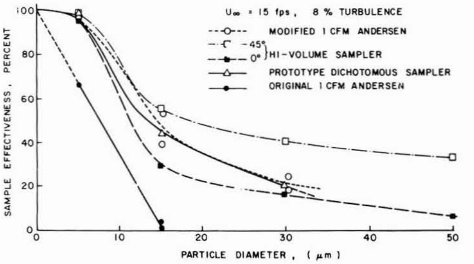

Figure 5. Comparison of effectiveness of ambient samplers

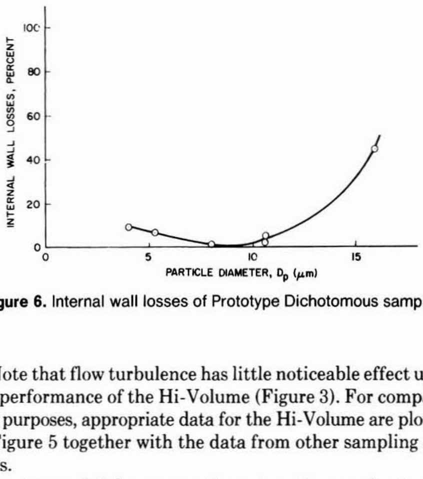

Figure 6. Internal wall losses of Prototype Dichotomous sampler

Note that flow turbulence has little noticeable effect upon the performance of the Hi-Volume (Figure 3). For comparative purposes, appropriate data for the Hi-Volume are plotted in Figure 5 together with the data from other sampling systems.

Prototype Dichotomous Sampler. The results for the Dichotomous sampler are presented in Figures 6 and 7. The internal transport losses given in Figure 6 are defined as the mass collected on the walls of the fractionation nozzles and housing of the virtual impaction system to that collected on the 127-mm filter. Significant loss occurs for particles less than 5 μm and greater than 10 μm. For particles 15 μm and greater, the losses approach 50%.

Figure 7 is essentially a plot of the effectiveness of the sampler inlet since it is based upon the ratio of the aerosol concentration determined with the 127-mm filter to that determined with isokinetic probes. On this basis, it may be inferred that a large fraction of particles greater than 20 μm does enter the unit. The base condition for comparison (15 ft/s to 4.6 m/s, 15 μm, 8% approach flow turbulence) shows a sampling effectiveness of 45%. Note that neither approach flow turbulence nor velocity appreciably affects the sampler capabilities (Figures 3 and 4). The variation of effectiveness with particle size for this sampler may be compared with that for other systems by referring to Figure 5.

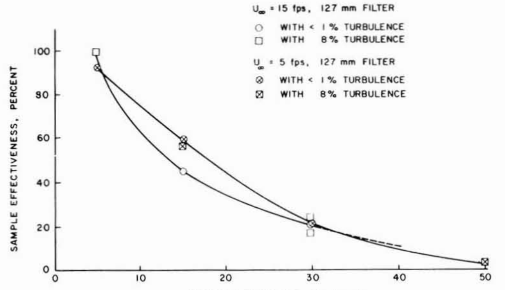

Figure 7. Influence of particle size upon effectiveness of Prototype Dichotomous sampler

Rotating Cowl and Impactor. This system, developed by G. A. Sehmel, was the most effective sampler tested. For a velocity of 5 ft/s and 8% approach flow turbulence, the sampler inlet was 82% effective up to a 15-μm particle size. Without the turbulence generating grid, the inlet system was essentially 100% effective and the overall capability limited only by the inherent losses in the 20 CFM Andersen head.

Conclusions

Through this research effort, the sampling effectiveness of five commercially available or prototype instruments was compared. The 1 CFM Andersen with redesigned impaction stages and a new inlet was found to be essentially independent of wind speed [up to 15 ft/s (4.6 m/s)], turbulence intensity (up to 8%), and wind direction. The modifications permitted a substantially increased capability to collect large particles in the 5–15-μm diameter size range. For example, the base condition of a 15-μm diameter particle, 8% turbulence, and 15 ft/s (4.6 m/s) yielded a sampling effectiveness of 50% for the modified version and 2% for the original Andersen.

All of the instruments tested showed similar trends of sampler effectiveness as a function of particle size—namely that the effectiveness is gradually reduced as particle size is increased. Ideally, a sampler intake should demonstrate a sharp fractionation curve with near zero effectiveness above a selected particle cutpoint. Thus, these data emphasize the need for better inlet design.

Tests with the Hi-Volume yielded results which show a great variation of effectiveness with sampler orientation.

The Dichotomous sampler tests revealed relatively small effects of wind speed and direction but rather excessive losses in internal transport and fractionation efficiency.

The Rotating Cowl system tests showed that a properly oriented cylindrical inlet performs well even though the sampling velocity was far from isokinetic.

Over the range of turbulent intensities employed in the experiments, 1 and 8%, turbulence has no appreciable effect upon the performance of the samplers tested.

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Asbestos in Raw and Treated Water: An Electron Microscopy Study

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■ Recovery and identification of asbestos fibers from the Southern end of Lake Michigan reaffirm the concept that asbestos is present in Lake Michigan, which is used as the water supply for Chicago and other cities. The Chicago Water Filtration Plants remove most of the asbestos fibers present in the lake. A brief summary of problems associated with asbestos and methods for collection, preparation, and identification is given. The authors recommend continued monitoring of these fibers.

Studies indicate that asbestos fibers are a common part of most people's environment. An examination of lung sections of people living and working in New York City has shown some fibers in the lungs of every person examined (*1*). Similar results probably could be found in any other large city in the nation. In addition, recent studies indicate that asbestos occurs naturally in much of the drinking water in the U.S. Environmental exposure to it is increased by filtration of certain beverages and pharmaceuticals through asbestos filters (*1*). Cunningham and Pontefract found that Canadian beer and tap water contained chrysotile asbestos fibers (*2*). They also found, through the use of the electron microscope, that some beers, sherries, port, vermouths, soft drinks, and drinking water contained millions of fibers per liter of asbestos (*3*). Cancer from asbestos is an occupational health hazard for people who work around large amounts of asbestos dust for a long period of time (*1*). Few people will argue about the dangers of breathing asbestos fibers; there is too much evidence which supports the belief that it is harmful.

The evidence, however, is not so one-sided when we speak of the hazards of ingesting asbestos fibers. What effect does eating and drinking material which contains asbestos fibers have on our health? Nobody can say for sure, because what little evidence exists is often contradictory. Davis could detect no asbestos passing through the stomach or intestinal walls of rabbits fed asbestos fibers (*1*). However, Pontefract injected an asbestos sample directly into the stomachs of laboratory animals and was able to detect about 0.1% of his sample in the epidermis (*1*). Kuschner et al. state that asbestos can cause granulomatous and fibrotic reactions in the lungs, but there is no evidence that it does so in the gastrointestinal tract (*4*). At the same time Chatfield wrote that there is some evidence of increased incidence of gastrointestinal carcinoma where individuals have been exposed to asbestos fibers over a long period (*5*). The staff of the Ontario Ministry of Health concluded in 1973 that, based on information available at that time, there was no evidence that asbestos in water had an effect on health (*3*). In short, we have to conclude that we really do not know what effect, if any, ingested asbestos fibers have on people. The primary reason for this is the very long time between initial exposure and evidence of biological effects, perhaps as long as 25–35 years (*1*). Another problem is the lack of data over a number of years, which is necessary to gauge the long-range impact of asbestos fibers in water on the general public.

Objective of Study

Much concern has recently been voiced, both in the public media and in scientific circles, over the possible health hazards associated with asbestos fibers in drinking water. This became especially significant following the Reserve Mining disclosure and its potential effect on the water supply at Duluth, Minn. In an effort to investigate the possibility of asbestos in Chicago's water supply, the Microscopy Unit of the Water Purification Laboratory of the Chicago Bureau of Water Operations initiated asbestos studies of both raw and treated water early in 1973. Data were obtained in the southern end, along the western shore of Lake Michigan by monitoring and recording the number of fibers in both raw and treated water.

A search of early photographic files in the Unit revealed that needle-like objects which resembled asbestos fibers have been found in Lake Michigan water since 1960. At that time the presence of these fibers was not reported because the fibers were not confirmed as asbestos, nor were they then considered important (Figure 1).

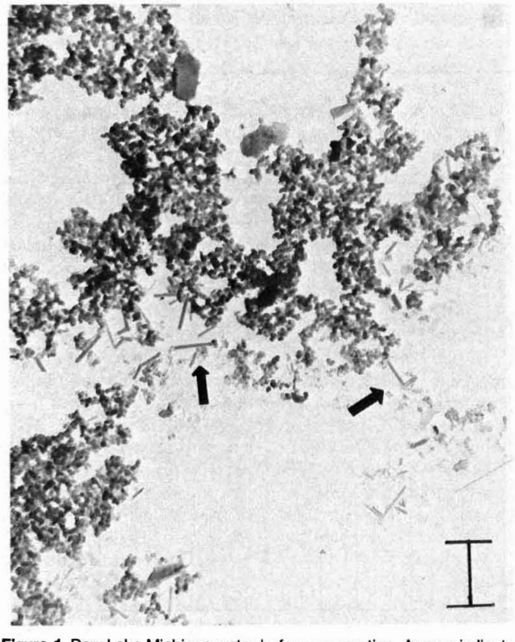

Figure 1. Raw Lake Michigan water before preparation. Arrows indicate possible asbestos fibers. Photomicrograph taken in October 1962. Bar represents 1 μm

The raw water samples are collected from various points along the shore and from crib intakes located 2½ miles from the shoreline. Additional samples are collected up to seven miles out into Lake Michigan. The treated water samples come from various clearwells, outlets, and distribution points (Figure 2). Each sample is collected in a 1-l. bottle which is cleaned, rinsed, and partially filled with triple distilled water which has been passed three times through a 0.22-μm membrane filter. A control bottle is run with each sample to determine the number of fibers in the sample count which may

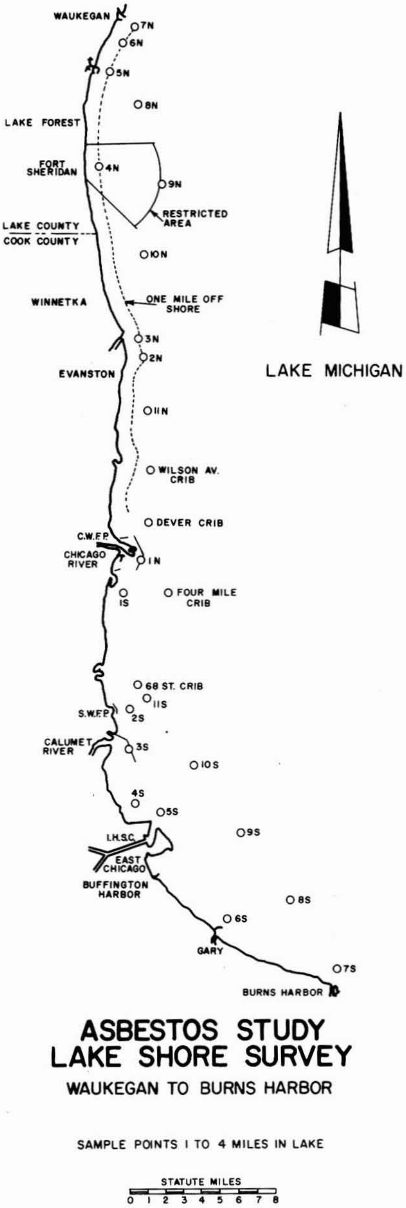

Figure 2. Points of sample collection along shore of Lake Michigan

be due to contamination during collection, preparation, and examination. This method has been used for several years, and contamination in the control bottles was essentially negative, and when detectable, its numerical value did not significantly affect the sample data listed in Figure 3.

Sample Preparation

Since the asbestos fibers are usually suspended throughout the water sample, it is necessary to concentrate the fibers by filtration so that they can be counted. A 200-ml portion of the sample is passed through a 0.22-μm membrane filter which is 47 mm in diameter, has a 35-mm effective filtration diameter, and an effective filtration area of 9.62 cm^2. All filtrations are performed under a controlled filtered atmosphere hood, which has a laminar air flow to reduce the possibility of airborne contamination. Occasionally, it is necessary to dilute a raw water sample with the corresponding control water if the raw turbidity is relatively high, about 2.50 FTU's or more. This is done to make the suspended material less concentrated, which in turn makes the fibers more visible and easier to count.

Identification and Counting Fibers

A transmission electron microscope was used exclusively during this study, due to the sublight microscopic size of the fibers: 2.0–8.0 μm in raw water and 0.1–6.0 μm in treated water. Approximately 50% of fibers in Lake Michigan raw water range from 2.0 to 5.0 μm in length, and 50% of the fibers in the finished water are between 0.5 and 2.0 μm long. The width of all fibers does not exceed 1.0 μm. (Figures 4–6).

There are difficulties involved in accurate size measurements. A useful analogy is to visualize the asbestos particles as a rope. The rope can be measured as one complete unit or may be separated into the individual strands and bits of material which make up the rope. The various stages of collection, preparation, and examinations may break down the large bundles of asbestos into the individual fibers. Therefore, it is difficult for the researcher to determine if he is measuring a complete bundle of asbestos, one single fiber, or just a broken splinter of one fiber. This problem obviously makes accurate measurements of fiber lengths very difficult.

Other researchers have reported a large range of fiber sizes. Chatfield states that no detailed study of fiber lengths has yet been made, but the peak of the number distribution appears to be about 1–2 μm, with fibers ranging from 0.2 to 30 μm (*6*). Chatfield examined asbestos in both air and water for his figures.

Cunningham and Pontefract state that most of the fibers found in Canadian beer and in filtered city water were less than 1.0 μm in length. Most of the samples of wine, American beer, and unfiltered melted snow or river water contained a considerable number of asbestos fibers ranging from 1 to 15 μm in length (*7*).

An EPA examination of western Lake Superior raw water indicated 55% of the amphibole fibers were between 0.4–1.7 μm long. For chrysotile fibers, 62% were between 0.3–1.3 μm in length (*8*).

To accurately count and identify the fibers present, it is necessary to remove the inorganic particles, diatoms, organic debris, and other extraneous material which may obstruct or cover the fibers. The removal of interferences is desirable when using x-ray or electron microscopy techniques (*9*). One-half of the membrane filter is placed on a sidearm condensation washer (Figure 7). Some authors (*10*) claim that substantial fiber loss occurs during preparation in the condensation washer. In our laboratory a number of samples were examined on several different occasions to determine the reproducibility of this procedure. The variation of the fiber count within each sample was less than 10%. This repeatability is good, considering the high multiplication factor involved. This device uses acetone as a solvent to dissolve the membrane, leaving just the suspended material in the sample on previously prepared carbon-coated copper screens with a 0.25% formvar film composed of the resin and ethylene dichloride. The sample is refluxed for 4 h. After drying, the screens are ready for electron microscopic examination. The second method is to place the other half of the membrane filter

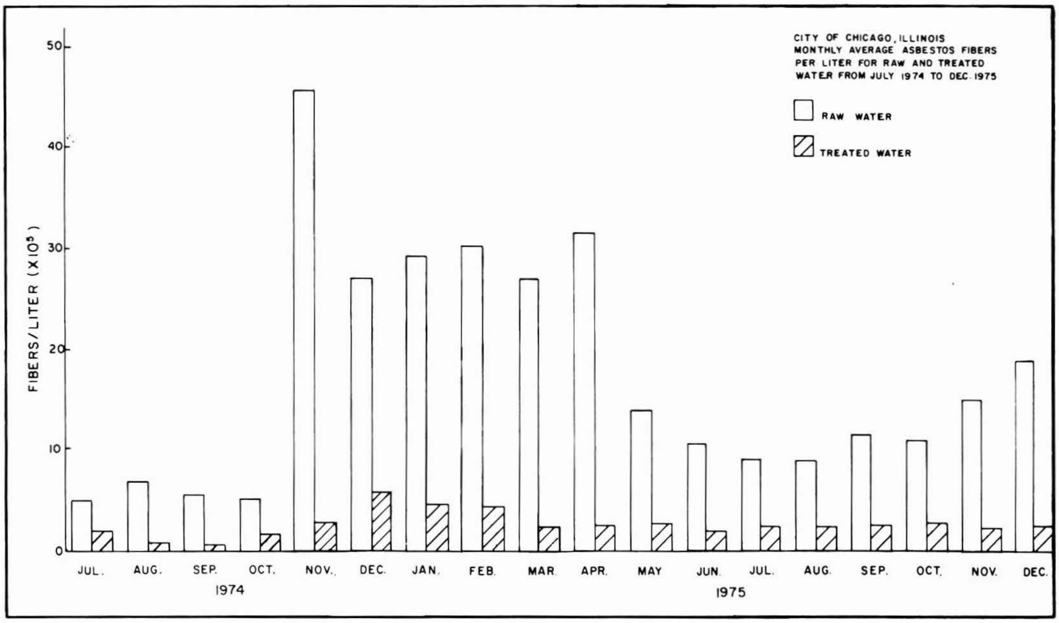

Figure 3. Graph of asbestos fibers per liter in raw and treated water from July 1974 to December 1975, using condensation washer

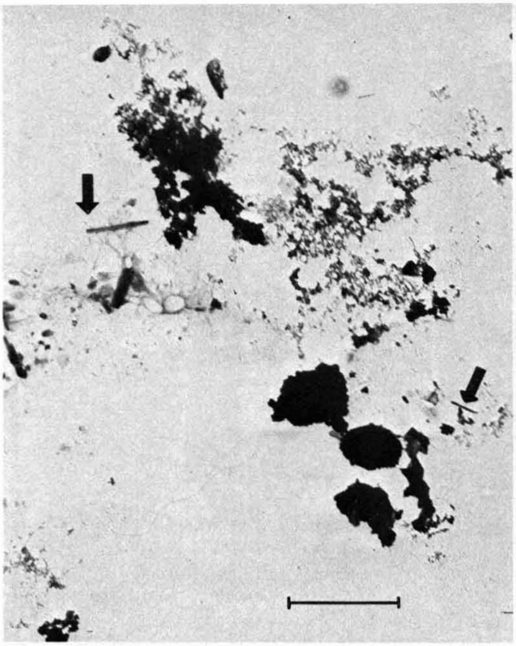

Figure 4. Raw lake water before preparation. Arrows indicate asbestos fibers. Bar represents 1 μm

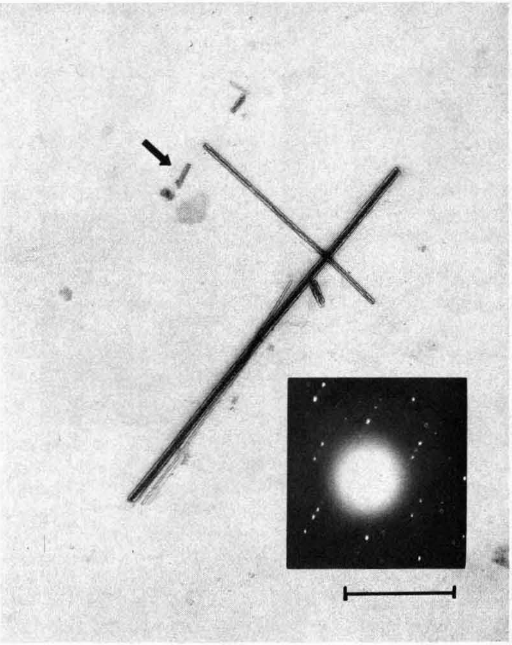

Figure 5. Chrysotile asbestos in raw water sample after ashing (insert). Selected area diffraction pattern. Bar represents 1 μm

in a ceramic crucible and to ash it at a temperature not to exceed 600 °C for 4 h. The ashed residual in the ceramic crucible is diluted with 10 ml of the corresponding control water and placed in an ultrasonic device for 30 min to disperse the residual. The suspended ashed material is then refiltered through a 13-mm diameter filter which has an effective filtration area of 60 mm^2 and a 0.22-μm pore size. Screens are prepared using the sidearm condensation washer as described above. The electron microscope is again used for final verification.

This is done only on raw water samples since organic matter and other suspended material make it difficult to obtain a fiber count. The fibers are left essentially intact and are more easily counted and identified. The treated water, having a turbidity of >0.20 FTU's, does not require ashing to remove the organic material. Only the method employing the condensation washer was used on the treated samples. On those occasions when both methods were used, the fiber counts obtained were reasonably close.

The following methods for identification and counting fibers are similar to the procedures used by the Environmental Protection Agency at the Taft Center in Cincinnati, Ohio (*11*). Standard samples, which are obtained commercially, of known asbestiform groups are suspended in known concentrations and examined under the electron microscope. There are two major groups known: chrysotile (serpentine) and amphibole (crocidolite, anthrophyllite, tramolite, and amosite) (*5*). Microphotographs of the various types were taken for future reference. The fibers were measured for both length and width, and their distinctive electron diffraction patterns were obtained. Similar methods were reported by Richards (*12*). Unknown fibers resembling asbestos are compared against these known standards for confirmation.

There is some interest as to which type of asbestos fibers, chrysotile and/or amphibole, is present in the water supply.

Durham and Pang indicated that the majority of fibers examined during 1973 from the central portion of Lake Superior were chrysotile (*2*). Fairless also reported various levels of amphibole fibers in his potable water intake investigation of the western arm of Lake Superior (*13*). Other researchers indicate a combination of chrysotile with fewer, but, still significant, amounts of amphibole also present at Duluth, Minn. (*8*).

The majority of fibers in our study, perhaps as much as 80% of the total, appear to be chrysotile. It should be emphasized that this assumption is based only on the raw water collected at the southwestern corner of Lake Michigan and does not necessarily apply to Lake Michigan as a whole.

To count the asbestos fibers using only the first method, two rows of open screen areas are counted. This is accomplished by counting 10 areas vertically and another 10 grids horizontally for a total of 20 open areas. The formula for counting the fibers using this method for the total count per liter is equal to the total number counted in 20 open areas multiplied by 3720.

To count the asbestos fibers using the second method, we follow this procedure: Because the opening of each square area used in this study is 85 μm on a side, the total open size of each area is (85 μm)^2 or 0.007225 mm^2. Likewise, the effective Millipore filter area is (4.4 mm)^2 × 3.14 or 60.8 mm^2. With these figures and the average fiber count per grid, the number of fibers per liter can be calculated with the following formula (similar to EPA methods of Cincinnati, Ohio) (*11*):

$$\text{fibers/liter} = \frac{\text{av per open area} \times 60.8\ \text{mm}^2 \times 1000\ \text{ml}}{0.007225\ \text{mm}^2 \times \text{sample vol (usually 200 ml)}}$$

fibers/liter = total number of fibers in 20 fields × 4.1 × 10^3 (for a 200-ml sample) or fibers/liter = av fibers per open area × 8.2 × 10^4 (for a 200-ml sample).

Graph and Interpretation

The graph (Figure 3) gives the counts of asbestos fibers per liter of water. The raw water was considered those samples collected at the crib intakes, shore intakes, and headers.

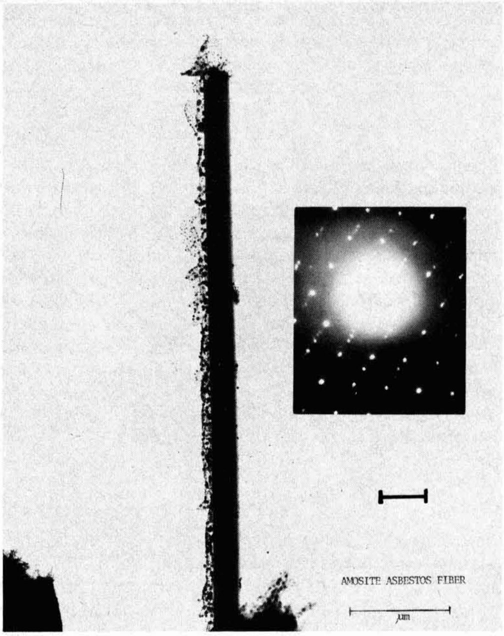

Figure 6. Amphibole asbestos fiber in raw water sample after ashing (insert). Selected area diffraction pattern. Bar represents 1 µm

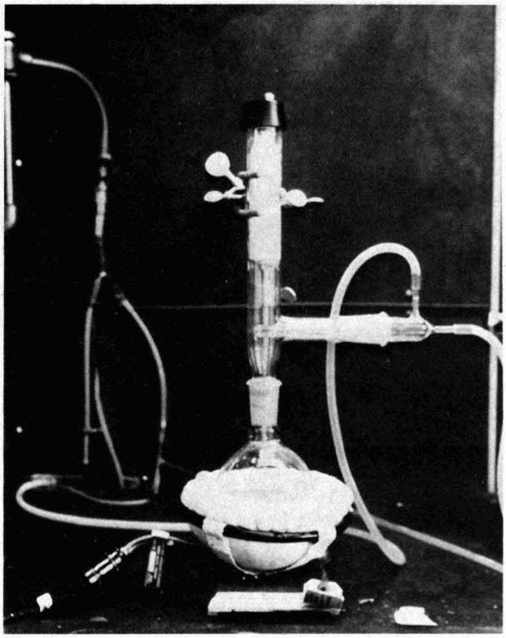

Figure 7. Condensation washer apparatus used for sample preparation

The treated water was considered those samples collected at the outlets, clearwells, and distribution system after the filtration process was complete. A somewhat bell-shaped curve resulted with the peak from November to April. During this time span the raw water count averaged about 3 million fibers per liter. During the rest of the year the raw water count was slightly less than 1 million fibers per liter (F/l.). The average count for the entire year was about 1.8 million F/l. The highest raw water count recorded during the test period was 4.2 million F/l.; the lowest count was 420 000 F/l.

The treated water counts generally followed the raw water fluctuations. The highest recorded treated water count was about 550 000 F/l.; the lowest treated water count was about 80 000 F/l. with an average treated water count of about 230 000 F/l.

Since data have not yet been collected over an extended length of time, we cannot state positively that this seasonal fluctuation is a yearly occurrence. However, we can state that the flocculation, sedimentation, and filtration process used at the Chicago Water Filtration Plants does remove from 70 to 90% of the asbestos fibers present in the raw water of Lake Michigan.

Summary

Asbestos fibers in both raw and treated water of the Chicago water system have been monitored and recorded weekly from July 1974 to the present.

Photographic files indicate possible asbestos fibers in Lake Michigan water for at least 15 years.

The health hazards of breathing asbestos dust are well documented, but not enough research has yet been done to determine possible health dangers from the ingestion of asbestos fibers.

Both raw and treated water samples are collected weekly, and several methods of sample preparation for examination by the electron microscope are utilized.

Data indicate a somewhat seasonal variation in the number of fibers in raw water, with the highest period from November to April, with a yearly average of about 1.8 million F/l. Treated water figures generally tend to follow the raw water curve, with a yearly average of about 230 000 F/l. The filtration process eliminates 70–90% of the fibers found in the raw water sample.

It is recommended that the presence of asbestos fibers in both raw and treated water continue to be monitored and recorded to build up a data base for future interpretation.

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Synthesis and Evaluation of Potential Atmospheric Eye Irritants

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■ The existence of several substituted peroxybenzoyl nitrate (PBzN) compounds was established by synthesis and by characterization through physical and chemical methods. The stabilities of these compounds were determined in the long-path infrared cell under simulated atmospheric conditions, and the eye irritation reactivities were determined in a smog chamber. The compounds studied were: *o*-, *m*-, and *p*-methyl PBzN, 2,4- and 2,5-dimethyl PBzN, and 2,4,6-trimethyl PBzN. From the data generated in this study and aerometric data in the literature, substituted PBzN compounds probably do not contribute significantly to atmospheric eye irritation. However, a final assessment of their importance must await aerometric data of substituted PBzN concentrations.

Photochemical smog, as found in Los Angeles, is manifested by several chemical, physical, and physiological symptoms. Among these are the oxidation of nitric oxide to nitrogen dioxide, oxidant formation, visibility reduction, and eye irritation. The chemical species responsible for these phenomena have been identified in some cases. In the specific case of eye irritation, formaldehyde, acrolein, and peroxyacetyl nitrate (PAN) are the known eye irritants identified in urban atmospheres (*1*). However, the substances responsible for eye irritation in photochemical smog have not been completely defined (*2*). In this regard, a compound of the PAN type, peroxybenzoyl nitrate (PBzN), has been synthesized in our laboratory and has been shown to be about 200 times more powerful an eye irritant than formaldehyde (*3*). Although the presence of PBzN in the ambient atmosphere has not been reported to date, very low concentrations of this material are sufficient to produce significant eye irritation.

To further characterize atmospheric eye irritation, several irritants of the PBzN type have been investigated. The existence of the compounds was established by synthesis, and their atmospheric stabilities were estimated by following their disappearance under irradiation conditions. Their eye irritation properties were then determined to ascertain their possible importance in photochemical smog formation. The substituted PBzN's studied were *o*-, *m*-, and *p*-methyl, 2,4- and 2,5-dimethyl, and 2,4,6-trimethyl compounds. Of these compounds, the *o*-, *m*-, and *p*-methyl PBzN's were isolated and characterized by various physical and chemical methods. Additionally, the preparation of peroxycyclohexanecarboxy nitrate and β-phenyl PAN was attempted.

Experimental

Apparatus. The eye irritants were synthesized in a 3-m base-path multiple-reflection cell. The course of the reaction was followed by infrared spectrophotometry with a modified Perkin-Elmer Model 21 instrument. The cell is equipped with a number of black-light fluorescent bulbs as the source of near ultraviolet radiation. Details of the cell and the irradiation system have been given previously (*4*). Eye irritation measurements were made in an 8.5×10^3 l. smog chamber (*5*).

Chemicals. *o*-, *m*-, and *p*-Methyl benzaldehydes and cyclohexanecarboxaldehyde, 2,4-dimethyl-, and 2,4,6-trimethylbenzaldehydes were products of the Aldrich Chemical Co. *o*-, *m*-, and *p*-Methylstyrene, 2,4-, 2,5-dimethyl-, and 2,4,6-trimethylstyrene were products of the Chemical Samples Co. Nitric oxide (Matheson) was purified by passage through an Ascarite bed, followed by repeated bulb-to-bulb distillations on a vacuum line. Nitrogen dioxide was prepared, as needed, by the thermal oxidation of nitric oxide. Ozone was obtained from a Welsbach generator, and nitrogen pentoxide was prepared in situ by the reaction of nitrogen dioxide and ozone.

Procedures. The potential eye irritants were prepared in the long-path infrared cell by the reaction of the corresponding aldehyde with N_2O_5. The procedure for preparing and isolating the eye irritants has been described previously (*3*). Final purification was afforded by distillation at a pressure of 0.15 torr.

Densities were estimated by weighing known volumes of the liquids added from a 10-μl syringe. Liquid-phase infrared spectra were obtained in hexane solution with a Perkin-Elmer Model 337 grating instrument. Ultraviolet spectra were obtained with a Cary Model 15 spectrophotometer.

Eye irritation measurements were carried out in the smog chamber using the photooxidation of the corresponding styrene in the presence of NO as the method of preparation for the various PBzN-type irritants (*3*). The details of the eye irritation measurement procedure have been given before (*3*).

Analysis. The concentrations of the various PBzN-type irritants, present during the eye irritation experiments, were determined by the method of Appel (*6*). This method involves the conversion of the PBzN to the corresponding methyl benzoate by bubbling the sample through a methanolic NaOH solution. The sample solution was then concentrated by blowing a stream of N_2 over the sample at 0 °C. The final sample size was then determined by weighing (the normal sample size was about 1.0 cc). The methyl benzoate content of the sample was then determined by gas chromatography on a 183 × 0.32 cm column containing 10% Ucon (U-C-W 9880-1005), with an FID. The column temperatures ranged from 85 to 115 °C, depending on the degree of aromatic ring substitution. The gas chromatographic procedure was calibrated with mixtures of known concentrations of the pure esters in methanol. With a 60-l. air sample size, as little as 10 ppb of the various PBzN compounds could be measured.

Since the photooxidation of styrenes in the presence of NO produces formaldehyde and PAN (known eye irritants), it was necessary to analyze for these irritants as well. Formaldehyde was measured by the chromotropic acid procedure, whereas PAN was determined by gas chromatography with an electron-capture detector (*3*). Concentrations of formaldehyde and the substituted PBzN were determined by collecting samples for the last hour of irradiation at a flow rate of 0.017 l. s^{-1}. PAN concentrations were determined just prior to the eye irritation tests.

Results and Discussion

Of the potential eye irritants, only *o*-, *m*-, and *p*-methyl PBzN could be isolated. Available evidence for the existence of each of the compounds is given in the succeeding paragraphs.

***o*-, *m*-, and *p*-Methyl PBzN.** *o*-, *m*-, and *p*-Methyl PBzN were pale yellow liquids with densities of 1.30, 1.28, and 1.26 g cc^{-1}, respectively. These values can be compared to the density of PBzN itself, 1.31 g cc^{-1} (*3*).

The purities of the methyl isomers were determined by converting them to the corresponding methyl benzoates by reaction with methanolic sodium hydroxide solution (*3*) and measuring the ester concentration with ultraviolet spectrophotometry. The purities determined in this fashion were 98.1 and 97.0% for *o*- and *m*-methyl PBzN, respectively. The purity of the *p*-isomer could not be determined in this fashion because of the presence of an impurity that interfered with the determination of methyl *p*-toluate. It is estimated from infrared spectra of *p*-methyl PBzN that the purity is similar to that of the *o*- and *m*-isomers.

The vapor-phase infrared spectra of these compounds were determined in the long-path infrared cell at a concentration of 2.0 ppm in 760 torr nitrogen. The complete spectra are given in Table I along with the absorptivities of the major peaks. The corresponding data for PBzN itself are included for reference. The spectra given in Table I have striking similarities both in band position and absorptivity. The bands at 5.5, 5.7, 7.7, and 12.6 μm are common to all these spectra. Bands also appear in the regions 8.0–8.2 and 10.1–10.3 μm in all the spectra with similar intensities.

The liquid-phase infrared spectra of these compounds were entirely comparable to the vapor-phase spectra except for small shifts in band position as was noted earlier for PBzN (*3*).

The liquid-phase ultraviolet spectra and absorption coefficients of the monomethyl-PBzN isomers are given in Table II along with the corresponding data for PBzN itself. Comparison of the ultraviolet spectral data for the methyl-substituted PBzN compounds with that for PBzN demonstrates that similar molecular structures are present. Both the band positions and absorption coefficients are quite comparable.

Based on the weight of the physical and chemical evidence given above, the products isolated from the reactions of *o*-, *m*-, and *p*-methyl benzaldehyde with N_2O_5 are *o*-, *m*-, and *p*-methyl peroxybenzoyl nitrates, respectively.

2,4-Dimethyl and 2,4,6-Trimethyl PBzN. The products of the reactions of 2,4-dimethyl and 2,4,6-trimethyl benzaldehydes with N_2O_5 could not be isolated from the long-path cell. The products apparently adsorb strongly on the cell surfaces. Heating the cell to reduce adsorption proved fruitless, since this procedure led to increased product decomposition. Infrared spectra of the gaseous products present in the cell were obtained, and the major product band positions are given in Table III. Comparison of the band positions given in Table III with those given in Table II indicates that the major structural elements of PBzN are present in the products in question. Subsequent experiments have shown that photooxidation of 2,4-dimethyl and 2,4,6-trimethylstyrene in the presence of NO produces products which react with methanolic NaOH solutions to form methyl 2,4-dimethyl and 2,4,6-trimethylbenzoates. Since the formation of methyl benzoate (*3*) or methyl toluates, as shown here, on reaction with methanolic NaOH is indicative of the presence of PBzN or a methyl-PBzN, 2,4-dimethyl- and 2,4,6-trimethyl PBzN are apparently formed in the photooxidation of the corresponding styrene.

The circumstantial evidence given above suggests that the spectra given in Table III are those of 2,4-dimethyl and 2,4,6-trimethyl PBzN, and therefore, these compounds do exist.

Peroxycyclohexanecarboxy and β-Phenylperoxyacetyl

Table I. Vapor-Phase Infrared Spectra [a] and Absorptivities of *o*-, *m*-, and *p*-CH_3PBzN and PBzN [b]

o-CH_3PBzN		*m*-CH_3PBzN		*p*-CH_3PBzN		PBzN	
λ (μm)	$10^4 \times a$ (ppm^{-1} m^{-1})	λ (μm)	$10^4 \times a$ (ppm^{-1} m^{-1})	λ (μm)	$10^4 \times a$ (ppm^{-1} m^{-1})	λ (μm)	$10^4 \times a$ (ppm^{-1} m^{-1})
3.28 (VW)		3.35 (W)		3.34 (W)		3.27 (W)	
3.38 (W)		3.42 (VW, Sh)		5.55 (S)	6.9	5.54 (S)	6.9
5.52 (S)	7.6	5.54 (S)	5.9	5.75 (VS)	22.8	5.75 (VS)	22.8
5.75 (VS)	30.5	5.75 (VS)	22.0	6.19 (M)		6.23 (W)	
6.21 (VW)		6.26 (W)		7.69 (S)	8.8	6.90 (M)	
7.69 (VS)	9.9	7.69 (S)	8.8	8.15 (VS)	15.6	7.65 (VS)	8.8
8.20 (S)	7.8	7.96 (VS)	9.8	8.47 (S)	7.5	8.07 (M, Sh)	
8.87 (W)		8.49 (M, Sh)		9.77 (W)		8.17 (VS)	15.6
10.29 (S)	9.0	8.56 (S)	6.4	10.05 (VS)	9.7	8.47 (M)	
12.59 (VS)	10.9	9.65 (M)		10.18 (VS)	9.6	8.55 (M, Sh)	
13.62 (M)		9.94 (M)		11.98 (M)		9.65 (W)	
		10.14 (M)		12.59 (VS)	9.5	10.13 (VS)	17.8
		10.74 (W)		13.40 (M)		12.0 (W)	
		11.64 (M)				12.67 (VS)	9.5
		12.61 (VS)	10.4			13.4 (W)	
		13.64 (W)				13.5 (W)	
						14.4 (M, Br)	

[a] The intensity estimations are: (VS) very strong, (S) strong, (M) medium, (W) weak, and (VW) very weak. (Sh) indicates a shoulder and (Br) a broad peak. [b] Ref. *3*.

Table II. Ultraviolet Spectra and Absorption Coefficients for *o*-, *m*-, and *p*-CH_3PBzN [a] and PBzN [b]

o-CH_3PBzN		*m*-CH_3PBzN		*p*-CH_3PBzN		PBzN	
λ max (nm)	ε (l. mol^{-1} cm^{-1})	λ max (nm)	ε (l. mol^{-1} cm^{-1})	λ max (nm)	ε (l. mol^{-1} cm^{-1})	λ max (nm)	ε (l. mol^{-1} cm^{-1})
279	2.4×10^3	280	1.5×10^3	272	1.0×10^3	276	1.2×10^3
		288	1.3×10^3	282	7.2×10^2	284	9.2×10^2
233	1.1×10^4	236	1.0×10^4	242	1.4×10^4	233	1.7×10^4

[a] Liquid-phase spectra determined in *n*-hexane solution at 23 °C. [b] Ref. *3*.

Table III. Vapor-Phase Infrared Spectra of Various Substituted PBzN's [a]

2,4-Dimethyl PBzN λ (μm)	2,4,6-Trimethyl PBzN λ (μm)
5.57	5.56
5.75	5.76
7.68	7.68
8.18	8.45
10.23	
12.66	12.67

[a] Measured in situ after preparation of the PBzN compound.

Table IV. Vapor-Phase Infrared Spectra of Various Peroxyacyl Nitrates [a]

Peroxycyclohexanecarboxy nitrate λ (μm)	β-Phenyl PAN λ (μm)
5.47	5.45
5.75	5.72
7.69	7.66
9.46	9.65
10.03	10.15
12.58	12.62

[a] Measured in situ after preparation.

Nitrates. The products of the reactions of cyclohexanecarboxaldehyde and β-phenylacetaldehyde with N_2O_5 could not be isolated from the long-path cell, owing to rapid decomposition. However, infrared spectra of the products could be obtained and the major product bands are given in Table IV. Comparison of these band positions with those of PBzN (Table II) indicates that the lower wavelength band in the carbonyl region occurs at a lower wavelength than the corresponding band in the PBzN spectrum. This observation is consistent with the fact that the expected products are PAN derivatives. The similarity of the bands at 5.5, 5.7, 7.7, and 12.6 μm is consistent with those of PAN (7). Supportive evidence for the existence of these peroxynitrates is provided by the nature of their decomposition products, identified by infrared spectrophotometry. The cyclohexane derivative yields cyclohexyl nitrate and CO_2, while the benzene derivative yields, primarily, benzyl nitrate and CO_2, with some benzaldehyde and PBzN. PBzN probably arises from the subsequent conversion of some of the benzaldehyde in the presence of excess N_2O_5. PAN, itself, decomposes to methyl nitrate and CO_2 (7). The evidence given suggests that peroxycyclohexanecarboxy and β-phenylperoxyacetyl nitrates do exist, albeit for only short periods of time.

Stability of Peroxynitrates Under Irradiation Conditions. The importance of an eye irritant in photochemical smog formation is dependent on the product of the eye irritant reactivity and its concentration where the concentration is dependent on its lifetime under atmospheric conditions. As a means of estimating the atmospheric lifetimes of the irritants studied, the half-lives of approximately 1.0 ppm of the irritants in air were determined at a light intensity corresponding to $k_D = 6.7 \times 10^{-3}\ s^{-1}$. In the case of irritants which could not be isolated, decompositions of the product mixtures were studied after complete conversion of the reactant aldehydes. The half-lives, in 10^3 s, were 1.2, 3.1, and 3.2 for *o*-, *m*-, and *p*-methyl PBzN, respectively, and 0.90 and 2.5 for 2,4-dimethyl and 2,4,6-trimethyl PBzN, respectively. The half-life of PBzN under similar conditions was 3.4×10^3 s (3). It is estimated that β-phenyl PAN and peroxycyclohexanecarboxy nitrate had half-lives of about 0.1 and 0.3×10^3 s, respectively. Note that the above values are only approximations to atmospheric lifetimes because of heterogeneous decomposition pathways present in our experimental system which are not directly comparable to the pathways available in the atmosphere.

Eye Irritation Reactivities. Eye irritation tests were originally attempted by direct injection of the methyl-PBzN compounds into the smog chamber. Such tests were unsuccessful due to the slow evaporation rate of these involatile compounds. An in situ method was adopted whereby the photooxidation of the various styrenes was studied at a concentration of 1.0 or 2.0 ppm with 1.0 ppm NO in air. The concentrations of the substituted PBzN, formaldehyde, and PAN formed during the photooxidation are given in Table V, along with the eye irritation intensities. The data given in Table V are the averages of duplicate runs where the average deviation of the eye irritation intensities for duplicate experiments is about 30%. The precision of the concentration measurements is about 10–15%, depending on the compound.

To use the data of Table V to calculate the eye irritation reactivity of a specific irritant, it is necessary to correct the intensity measurements for the presence of the known irritants, formaldehyde and PAN. The corrections are made assuming that eye irritation intensity is proportional to irritant concentration, and eye irritation from a mixture of irritants is linearly additive. The proportionality constant in the first assumption is the eye irritation reactivity, ε. The values of ε for formaldehyde and PAN were 4.4×10^{-4} and 4.1×10^{-4} ppb^{-1}, respectively, by a multiple regression analysis of the data of our previous investigation (3). With these values the values of ε for the substituted PBzN compounds were calculated and are given in Table VI. The values for formaldehyde, PAN, and PBzN are included for reference. The corrections for formaldehyde and PAN to the eye irritation intensities

Table V. Irradiation of Various Substituted Styrenes in Air with NO [a]

Styrene	(HCHO) ppb	(PAN) ppb	(Subst. PBzN) ppb	Eye [b] irritation
o-Methyl	350	2	90	1.0
m-Methyl	300	1	16	0.8
p-Methyl	400	2	31	1.0
2,4-Dimethyl	670	20	78	1.2
2,5-Dimethyl	720	16	150	0.9
2,4,6-Trimethyl	460	58	17	1.3

[a] The experimental conditions were as follows: 1.0 ppm of the monomethyl styrenes and 2.0 ppm of the di- and trimethyl styrenes, HC/NO ratio of 2.0, 155 torr O_2, 605 torr N_2, temperature of 35 °C, and a light intensity corresponding to $k_D = 6.7 \times 10^{-3}\ s^{-1}$. [b] Corrected for blank response.

Table VI. Eye Irritation Reactivities of Various Eye Irritants [a]

Irritant	ε (ppb^{-1})
Formaldehyde	0.00044 [b]
PAN	0.00041 [b]
PBzN	0.10 [b]
o-Methyl PBzN	0.0099
m-Methyl PBzN	0.041
p-Methyl PBzN	0.027
2,4-Dimethyl PBzN	0.011
2,5-Dimethyl PBzN	0.0038
2,4,6-Trimethyl PBzN	0.062

[a] Assuming eye irritation intensity is proportional to irritant concentration. [b] Calculated from the data of ref. *3*.

varied from 14 to 36%, averaging 21% with formaldehyde contributing over 94% of the total correction.

The eye irritation reactivities of PBzN and the methyl-substituted PBzN compounds are much larger than those of the known atmospheric irritants, formaldehyde, acrolein, and PAN. Substitution of a methyl group on the benzene ring of PBzN decreases the eye irritation reactivity of the irritant, with substitution at the ortho-position exhibiting the greatest effect. Substitution of a methyl group at the 2-position of *m*- or *p*-methyl PBzN decreases the eye irritation reactivity, the effect being more pronounced with the meta isomer. Looking at these data in another way, however, shows that substitution of a methyl group at the 4-position of *o*-methyl PBzN has no effect on the eye irritation reactivity, whereas substitution at the 5-position decreases the eye irritation reactivity by more than a factor of two. The relatively large difference in eye irritation reactivity between the 2,4- and 2,5-dimethyl PBzN compounds implies that the chemistry of eye irritation by PBzN derivatives is a very sensitive function of molecular structure. Whereas the effect of substituting a methyl group at the ortho-position in a *p*-methyl PBzN is a reduction in eye irritation reactivity, the addition of a second methyl group at the other ortho-position yielding 2,4,6-trimethyl PBzN is a substantial increase in eye irritation reactivity. The possibility of the formation of some unknown irritant or irritants in the photooxidation of 2,4,6-trimethylstyrene is suggested by the increased PAN formation in this system (indicative of increased rupture of the benzene ring). Thus, the eye irritation readings may not be strictly due to 2,4,6-trimethyl PBzN alone. Of course, the presence of undetected eye irritants in our experiments cannot be ruled out without more exhaustive analyses than were performed in this investigation.

Importance of Substituted PBzN Irritants in Atmospheric Eye Irritation. Since PBzN compounds have not been observed in polluted atmospheres, an indirect approach has been used to assess their importance to eye irritation in photochemical smog. The concentrations of the aldehyde precursors were obtained from the literature and the steady-state concentrations of the PBzN compounds were then calculated by a simplified kinetic analysis of the probable reaction scheme. Then, by use of the measured eye irritation reactivities in Table VI, the eye irritation contributions of the substituted PBzN compounds were calculated. Since the only substituted benzaldehydes reported in urban air are the *o*-, *m*-, and *p*-methyl benzaldehydes (tolualdehydes), the following discussion is limited to the corresponding PBzN compounds.

In February 1974 Jones (*8*) found tolualdehyde concentrations of 0.05–0.28 ppb for a 16-h period in Columbus, Ohio, air. To the author's knowledge, this is the only report of aerometric measurements of substituted benzaldehydes. Presumably, the concentration of such species would be higher in more polluted environments such as Los Angeles. However, the reported values should serve as a lower limit to tolualdehyde concentrations in polluted atmospheres.

The conversion of benzaldehydes to PBzN compounds has been modeled by studying the photolysis of benzaldehyde–NO_2 mixtures. In this system the PBzN concentration increases to a maximum value and then decreases slowly thereafter. The reaction scheme can be formalized as follows:

$$\phi\text{CHO} \rightarrow \text{PBzN} \tag{1}$$

$$\text{PBzN} \rightarrow \text{products} \tag{2}$$

At the maximum PBzN concentration,

$$k_1(\phi\text{CHO}) = k_2(\text{PBzN})_{\max} \tag{3}$$

Therefore, measurement of the maximum PBzN concentration and the benzaldehyde concentration at the same time permits an evaluation of the ratio k_1/k_2. The photooxidations of 1.0 ppm ϕCHO with 0.5 ppm NO_2 in air and 0.6 ppm ϕCHO with 0.5 ppm NO_2 in air were studied. The two experiments yielded k_1/k_2 values of 0.146 and 0.147, respectively. Assuming that the same type of reaction scheme is operative in photochemical smog formation, that the substituted PBzN is in a steady state, and that k_1/k_2 is relatively insensitive to molecular structure, then the steady-state concentration of the substituted PBzN can be evaluated from the ambient tolualdehyde concentration with Equation 3. In this fashion, methyl-PBzN concentrations of 0.008–0.042 ppb were obtained.

The eye irritation indices corresponding to these concentrations are 0.0003–0.0014, obtained by using the average eye irritation reactivity for the ortho-, meta-, and para isomers given in Table VI. As a point of reference, the eye irritation index of formaldehyde at a typical (*9*) Los Angeles atmospheric concentration (41 ppb) was calculated to be 0.018, using the eye irritation reactivity given in Table VI. It would appear, therefore, that the contribution of methyl-substituted PBzN compounds to the eye irritation burden of polluted atmospheres would be negligible. However, since the above estimated values are lower limits, a more positive assessment of the importance of substituted PBzN compounds to eye irritation in photochemical smog formation must await more detailed aerometric analyses.

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Simple Device for Reduction of Pollution from Motor Vehicles

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■ A simple retrofit device is developed to reduce the exhaust emission from a spark ignition internal combustion engine, and complies with the U.S. Federal 1973 requirements and the current European maximum emission levels. The device aims at improving the vaporization and atomization of the air/fuel mixture fed to the engine by incorporating a second venturi and an air bleed under the existing carburetor. No fuel or power penalties are incurred; in fact, fuel savings and increased drivability are in evidence. Other benefits such as decoking of the engine and a reduction in wear accrue from the use of the device.

The effort being made to reduce pollution from the exhaust of petrol-fueled internal combustion motor vehicles can be categorized conveniently into four main areas (*1*):

- Induction system improvements
- Exhaust system improvements
- Combustion and combustion chamber modifications
- Total engine redesign and alternative fuels and power sources.

While undoubtedly the latter category holds the ultimate answer to the problem of pollution from motor vehicles, it will require considerable effort and cost to effect the optimum solution. Further, there will be some appreciable time delay before the developments accruing from this approach are available on the road and actually contributing to a reduction in motor vehicle pollution (*2*). Even then it will be a number of years beyond that point before the full benefits of these developments are realized as the current units are replaced or phased out. The same observations are true for combustion chamber modifications which have proved to be effective in meeting the required pollution standards.

The first two categories provide the possibility of fitting some pollution control device on an already operating vehicle. But while this retrofit approach presents difficulties, mainly through the sheer magnitude of the number of operating vehicles involved, it is workable and does provide a quicker and therefore more realistic approach to the immediate pollution problem arising from motor vehicles. The cleanup of tail-pipe gases should be used only as a last resort when all else fails because it would appear to be more logical, in light of the current fuel crisis, to burn the fuel more efficiently in the first place and thus avoid forming the major portion of the pollutants. Furthermore, the thermal processes so far devised to treat tail-pipe gases appear to be expensive and possess a limited operational life (*2*).

Advances with the use of catalytic converters have enabled several systems that appear practical to be developed, usually in conjunction with exhaust gas recirculation. For example, the new Volvo has a three-way catalyst system which was developed by Engelhard Industries and satisfied EPA requirements. The catalytic system is reported to cost $50 per vehicle, but its operational life may be as limited as other similar catalytic converters (*3–5*). Indeed, it may be more logical as some workers have pointed out (*5–7*) to seek the solution to motor vehicle pollution by directing attention to the air and fuel fed to the engine even if only to relieve the load on the catalytic converter.

Better fuel preparation results in more complete combustion within the cylinders and hence in a reduction in both the fuel usage and the concentration of pollutants in the exhaust (*8–14*). Moreover, it is possible to operate such an engine on higher air/fuel ratios than normal with a further reduction in pollutant concentration in the exhaust without loss of drivability (*14–18*). By extension of this basic reasoning, work was undertaken to endeavor to develop a simple device, which when fitted to an operating vehicle, will reduce pollution without adverse side effects.

Experimental

Several units were developed and tested on stock motor vehicles. All vehicles under test were first checked out to make sure all components of the engine, particularly the fuel and electrical systems and the tires, conformed to the manufacturer's specification. Also the carburetor was set to the requirements laid down by the manufacturer before any test work was done. Emission tests were done according to the procedures and driving cycles laid down under the U.S. Federal 1970 test procedure, the ADR 27 (ECE 15 test) procedure, and the ADR 27A (U.S. Federal 1973) procedure. Fuel economy tests were conducted on the highway on the same vehicle using the same driver with and without the device. Bench tests were made on an engine set to the manufacturer's specification in the normal way.

The first unit tested, illustrated schematically in Figure 1, was an air preheater operating off the vehicle electrical system. It consisted of an 8-A electrical heater placed in the inlet to the air cleaner to preheat the incoming air in a confined space. It developed 100 W and could raise the temperature of the incoming air typically about 12 °C. Details of the unit are given elsewhere (*19*). The vehicle was driven over 160 km on the road in between tests in order to run in the unit. Subsequently, a second unit was built and tested. The unit is illustrated in Figure 2 and consisted of a second venturi located under the carburetor. Secondary air was admitted through a

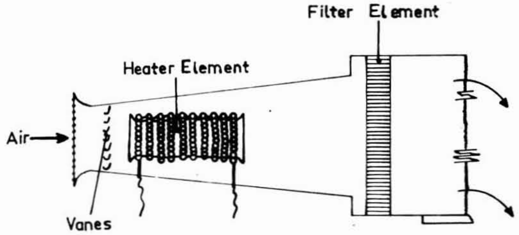

Figure 1. Air preheater unit

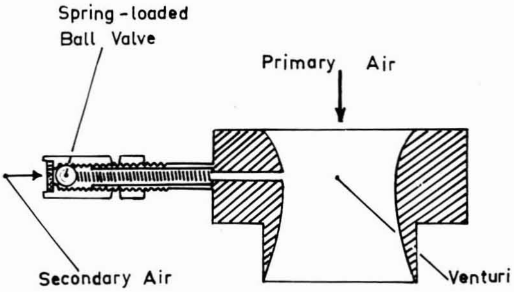

Figure 2. Venturi air bleed unit

vacuum-controlled valve located at the throat of the second venturi. The venturi throat was of fixed dimensions so that the volume of secondary air admitted varied between 0 and 6 l./s with the vacuum generated by the engine.

Results

The results of the air preheater are given in Table I. Additional work on a test bed engine and road evaluation tests showed that the air preheater gave a reduction of 10–30% in fuel usage, with no reduction in total power while carbon buildup was eliminated from the engine and exhaust system. There was a noticeable increase in drivability, a 30–40 °C lowering of the exhaust gas temperature, and a 10% increase in air intake.

The results of the U.S. Federal 1970 tests for the venturi air bleed unit are detailed in Table II. The results of the tests following the Australian ADR 27 and ADR 27A procedure are given in Table III. Additional work showed that the venturi air bleed unit removed carbon buildup from the engine and exhaust system, increased both drivability and total power output, achieved a fuel saving of 10–30%, and reduced the octane number requirements of the motor.

Discussion

The results detailed in Tables I and II followed the U.S. Federal 1970 procedures and therefore can be criticized in that they are not accurate in the absolute sense, but they do provide a reasonable measure of the relative reduction in pollution which was achieved using the units. It is clear from the test results in Table I that the air preheater gave a modest reduction in all tail-pipe pollutants. Independent test work by other organizations has confirmed these results (*20, 21*). Optimization of the size of the air preheater was carried out to give maximum pollution reduction. Figure 3 shows that an average temperature rise of 12 °C of the incoming air achieved by the 8-A heater gave maximum pollution reduction without causing any loss of power.

Subsequent work has revealed that the mechanism of operation of the preheater unit was through the increased vaporization of the fuel droplets in the mixture fed to the cyl-

Table I. Average Concentration and Reduction in Tail-Pipe Pollution from Motor Vehicles Fitted with Air Preheater

Vehicle					CO		H/C		NO	
Make	Engine size, l.	Compression ratio	Cylinders	Meterage, km	ppm	% Reduction	ppm	% Reduction	ppm	% Reduction
GM Holden 1969	3.0	9.4/1	6	120 700	23 000	41.5	1070	16.0	1000	15.5
GM Holden 1968	3.0	9.4/1	6	28 200	7 700	35.7	1260	8.9	820	11.0
GM Holden 1968	5.0	9.4/1	8	128 700	16 800	48.3	1580	13.7	26	12.2
GM Holden 1971	3.0	9.4/1	6	6 500	25 300	19.0	1600	11.3	110	16.0
Ford Falcon 1969	3.6	9.1/1	6	41 800	24 500	52.2	1700	14.4	15	13.6
Ford Falcon 1969	3.6	9.1/1	6	68 700	12 700	33.7	1200	19.3	220	63.3
			Average		18 300	40.1	1400	13.9	365	21.9

Table II. Average Concentration and Reduction in Tail-Pipe Pollution from Motor Vehicles Fitted with Venturi Air Bleed Device

Vehicle					CO		H/C		NO	
Make	Engine size, l.	Compression ratio	Cylinders	Meterage, km	ppm	% Reduction	ppm	% Reduction	ppm	% Reduction
GM Holden	3.0	9.4/1	6	6 400	3000	90.0	260	76.0	30	91
GM Holden	3.0	9.4/1	6	7 400	3730	88.0	257	77.0	37	90
BMC Marina	1.75	9.1/1	4	9 600	2300	90.0	95	82.0	30	90
BMC Mini	1.0	8.3/1	4	20 600	2760	92.0	150	79.0	39	89
			Average		2950	90.0	190	78.5	34	90

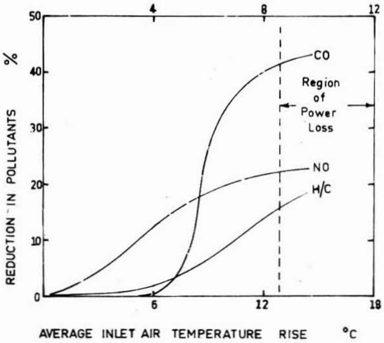

Figure 3. Effect of inlet air temperature on reduction in tail-pipe pollutants (GM 6-cylinder vehicle—U.S. Federal 1970 procedure)

Table III. Average Concentration and Reduction in Tail-Pipe Pollution from Motor Vehicles Fitted with Venturi Air Bleed Device [a]

		CO		H/C		NO_x	
Test	Vehicle cylinders	g/test	% Reduction	g/test	% Reduction	g/test	% Reduction
ADR 27	6	30	78.7	5.4	40.0	. . .	. . .
(ECE 15)	6	41	77.1	4.9	49.0	. . .	. . .
		g/km		g/km		g/km	
ADR 27A (U.S. Federal 1973)	6	17.8		1.75		1.63	

[a] Three Ford Falcon and three GM Holden vehicles used (similar to those shown in Table I).

inders. This mechanism has been suggested by other workers at various times to explain a similar effect found with preheated inlet manifolds and hot spots (*22, 23*). The normal petrol engine operates on a mixture of air, vaporized fuel, and fuel droplets. It is these latter which cause maldistribution and stratification in multicylinder engines, resulting in the end cylinders in the engine block being fed a rich mixture and the other center cylinders a lean mixture. Elimination of a major portion of the gross fuel droplets by providing heat in the incoming air for their vaporization and atomization evens up the air/fuel distribution to the cylinders. Liimatta et al. (*24*) and others (*14*) also have observed this effect, while Ogasawara et al. (*25*) claim fuel vaporization and atomization provide a more reactive mixture in the combustion zone.

All this implies that it is possible to run the gasoline engine on a leaner mixture when proper fuel vaporization and atomization are achieved without burn-out of exhaust valve occurring. Tests showed this was the case for the preheater units, and other workers (*26*) have demonstrated similar findings. However, with the air preheater, any increase in the air rate caused by leaning the mixture resulted in an electric power demand which was beyond that of the vehicle's existing power system. A modification to the power system was attempted to enable a leaner mixture to be fed to the engine and was found to give an additional reduction in the tail-pipe pollution concentration. Such a modification was not consistent with our basic philosophy of a simple attachment to an operating vehicle and was considered to be too major to be of practical worth. The same was considered to be true of exhaust gas heat exchangers such as the Vapipe (*27*) and similar devices (*28*).

The reduction in pollution given by using the air preheater could be improved by inclusion of other simple antipollution devices to make a more acceptable system. For example, a new design of spark plug and the use of gaskets which eliminate dead areas in the quench zone of the cylinders (*29*) when included on a vehicle fitted with the air preheater give an 80% reduction in carbon monoxide and a 40% reduction in hydrocarbons. Details of tests performed using the U.S. Federal 1970 test procedures are given in Table IV.

Detailed analysis of cumulative samples from the engine showed that the supercharging effect was due to increased scavenging of the cylinders (*30*). Inone et al. (*31*) found a similar supercharging effect with alteration of spark timing apparently caused by increased scavenging. Apparently the venturi air bleed device, and to a limited extent the air preheater, partially remove the film of unburned fuel which accumulates on the walls of the cylinder in the quench zone. In the normal vehicle this film of liquid fuel partially evaporates as the air/fuel mixture is drawn in under vacuum. Thus, it limits the amount of air/fuel taken into the cylinder by reducing the vacuum created in the cylinder through the normal rotation of the engine. If the film of liquid within the cylinder is removed, evaporation will not occur during the charging stroke, and the pressure difference between the cylinder and the outside air will be greater, thus allowing more air to be drawn into the cylinder.

It was felt that while the air preheater was interesting in that it showed the way to other developments, it was of itself a device which only could achieve, at the best, modest improvements in tail gas analysis. However, by use of the basic reasoning arising from the operation of the air preheater, it was thought that it would be more realistic to achieve vaporization by passing the air/fuel mixture through a reduced pressure region created by a second venturi set under the carburetor. The result was the venturi air bleed unit which achieved far better results than the air preheater. The first series of tests shown in Table II was of interest but could not give any positive indication as to how the unit performed regarding current U.S. limits. Consequently, the results for the venturi air bleed were confirmed by independent tests carried out by Bendix Corp. of Australia.

The first series of tests shown in Table III was carried out following the Australian ADR 27 procedure which is the same as the ECE 15 test. The maximum allowable levels for the tests are 152 g for carbon monoxide and 10.1 g for hydrocarbons per test. It is observed, therefore, that the device meets these requirements with ease. The second series of tests shown in Table III was carried out following the Australian ADR 27A procedure which is the same as the U.S. Federal 1973 test procedure. The maximum allowable levels which applied up until the end of 1974 for these tests are 2.1 g/km for hydrocarbon emissions, 24.2 g/km for carbon monoxide, and 1.9 g/km for nitrogen oxides. The results show that the device meets the requirements of the U.S. Federal emission levels for 1974. Additional data on the effect of idle setting on the results are detailed in Figure 4.

The venturi air bleed unit simultaneously suppressed carbon monoxide hydrocarbons and nitrogen oxides in the engine exhaust. The literature shows this aspect of the unit's operation to be unusual but by no means unique (*32–35*). Most antipollution devices record a rise in nitrogen oxides as, for example, found by Gompf (*36*). However, as Matthes and McGill (*14*) have been at pains to point out, the manner in which mixture preparation influences emissions and the combustion process is not well understood. Further work needs to be carried out on the venturi air bleed to explore the reason for the suppression of all three major pollutants. It appears that the presentation of a more reactive mixture to the engine contributes in some measure to the reduction in pollutants, particularly nitrogen oxides. This observation is in line with suggestions made by other workers (*37, 38*), but the literature is by no means in agreement on this subject.

Another important aspect of the results of the venturi air bleed is the increasing drivability and total power, and a reduction in the octane number requirement of the engine. These benefits may well be important in that they leave room to make simple changes in the engine, such as carburetor and

Table IV. Average Concentration and Reduction in Tail-Pipe Pollution from Motor Vehicles Fitted with Air Preheater and Various Other Simple Antipollution Devices[a]

Vehicle					CO		H/C		NO	
Make	Engine size, l.	Compression ratio	Cylinders	Meterage, km	ppm	% Reduction	ppm	% Reduction	ppm	% Reduction
Ford Falcon	3.6	9.1/1	6	45 800	28 700	44.1	1730	13.3	18	−6.5
Ford Falcon	3.6	9.1/1	6	51 600	51 000	0.8	1820	8.7	17	−0.6
Ford Falcon	3.6	9.1/1	6	57 500	10 300	80.0	1195	40.0	16	+5.3

[a] In order, the tests are 1, new spark plugs only; 2, wide gaskets only; and 3, preheater and new spark plugs and wide gaskets.

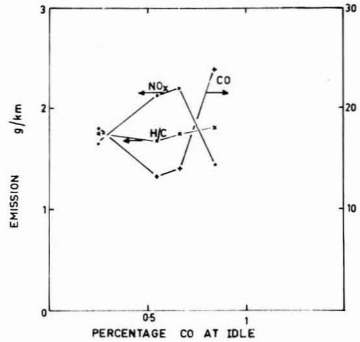

Figure 4. Effect of idle CO setting on tail-pipe pollutant concentrations (Ford 6-cylinder vehicle—U.S. Federal 1973 procedure)

timing adjustments (*39, 40*) and spark plug modification (*41*) which can lead to further reductions in pollutant concentrations without a reduction in engine performance in some way. In any event, the reduction in carbon buildup and octane requirement of the fuel may be useful in extending the operational life of catalytic mufflers.

Partial optimization of the venturi dimensions and air bleed rate indicated that the venturi throat diameter is the critical variable. Venturi length, on the other hand, had no pronounced effect on CO levels. An adverse effect on hydrocarbons was noted if the venturi length was too short, while an excess of secondary air beyond the optimum level raised the hydrocarbon and NO_x concentration but reduced the CO concentration of the exhaust gases.

Note that the venturi air bleed is by no means properly optimized at present, and further reductions in pollutant concentration, particularly in hydrocarbons, can be achieved by attention to this area.

A systems approach using retrofit devices can give further reductions in pollution levels. For example, combining the air preheater and the venturi air bleed unit leads to further reductions in pollution levels.

Another development which arose from a logical progression of ideas from these two units has shown that it is possible to reduce pollution levels below those given in Table III. This will be the subject of a later paper.

Conclusions

Several retrofit units have been developed which reduce tail-pipe emissions of motor vehicles to comply with the 1974 U.S. Federal emission levels. These units have the additional advantage that they lead to a modest increase in fuel economy without adversely affecting other vehicle operational and driving characteristics. Some of the latter characteristics would be useful in extending the life of catalytic converter units currently used on motor vehicles.

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Atmospheric Chemistry of *N*-Nitroso Dimethylamine

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■ Gaseous dimethylamine, $(CH_3)_2NH$, reacts in air with gaseous nitrous acid, HONO, to yield *N*-nitroso dimethylamine, $(CH_3)_2NNO$. Long path infrared spectroscopy is used to monitor these reactions at concentration levels of parts-per-million. The measured reaction rate shows that a small degree of nitrosation of dimethylamine vapor might take place during the night in a heavily polluted urban atmosphere. Nitrosation reactions would essentially cease after sunrise because the nitrous acid would be destroyed by photolysis. The *N*-nitroso dimethylamine vapor is also destroyed by sunlight, the half-life under full sun being about 30 min. By midday any nighttime accumulation of nitrosamine would be rather fully destroyed. Any *N*-nitroso dimethylamine detected in the air in the afternoon could not be the result of the reaction of precursors. It could only be the result of direct emissions of the pollutant.

Two questions to be answered about nitrosamines are: will they form in the ambient air, and how long will they last in the presence of sunlight? *N*-nitroso dimethylamine is a principal candidate for concern. Nitrous acid and dimethyl amine react to yield the nitrosamine and water (*1*).

$$(CH_3)_2NH + HONO \rightarrow (CH_3)_2NNO + H_2O \qquad (1)$$

Nitric oxide and nitrogen dioxide are two other pollutant species that are said to nitrosate dimethylamine, but the mechanisms by which they react are obscure. The reactions of NO, NO_2, and HONO with dimethylamine have been examined in this work.

Nitroso compounds are light sensitive. They absorb ultraviolet radiation and may dissociate or isomerize. It is worth noting that many past years of study of the photochemistry of atmospheric organic compounds and nitrogen oxides have not shown nitroso compounds to be reaction products. It is therefore necessary to establish the behavior of *N*-nitroso dimethylamine under actual sunlight conditions.

Experimental Technique

Measurements were made of the rate of formation of *N*-nitroso dimethylamine from dimethylamine and nitrous acid in air. The nitrosation was carried out in a cylindrical glass reaction chamber 9 m long and 0.3 m in diameter. The reaction chamber is surrounded by 96 fluorescent lamps to allow study of the photochemical behavior of the reactants and products. The chamber contains a multiple-pass mirror system to allow in situ analysis of reactants and products by infrared absorption spectroscopy. The absorption path length was 360 m, allowing monitoring of gases at concentrations down to 0.1 part-per-million (ppm) in air. Spectra were recorded by a Fourier transform spectrometer. The system is diagrammed in Figure 1.

Dimethylamine liquid was purchased from Fisher Chemical Co. *N*-Nitroso dimethylamine was prepared by mixing in a glass vessel 20 torr of dimethylamine vapor and 20 torr of nitric oxide, and then admitting room air until the total pressure reached 1 atm. A mist of products formed. Volatile components were pumped out of the vessel, leaving liquid nitrosamine. The nitrosamine was then vaporized into the reaction chamber. Figure 2 shows the spectrum of approximately 10 torr of dimethylamine in a 10-cm absorption cell. This is equivalent to 3.7 ppm in the 360-m cell. Figure 3, upper portion, shows the spectrum of *N*-nitroso dimethylamine at a concentration of between 1 and 3 ppm in the 360-m cell. The spectrum in the upper portion of Figure 3 is similar to the spectrum of liquid *N*-nitroso dimethylamine reported in the "Aldrich Library of Infrared Spectra" (*2*).

The photolysis of *N*-nitroso dimethylamine was studied both in the laboratory reaction chamber and in a 25-ft^3 Teflon bag exposed to real sunlight.

Results

Nitrosation experiments were carried out with a dry NO-NO_2 mixture in nitrogen, as well as with a nitrous acid-NO-NO_2 mixture in room air at normal humidity. When 1 ppm dimethylamine was mixed with 1 ppm NO_2 and 4 ppm NO in dry nitrogen, the amine reacted at a rate of about 1%/min. Assuming the product to be entirely *N*-nitroso dimethylamine allowed the calculation of an upper limit for the rate of nitrosation by either NO or NO_2. It does not seem appropriate to present numbers for these rate constants because the mechanisms of reaction are unknown. The observed slow reaction may well have been the result of traces of nitrous acid in the system. It seems sufficient to say that these upper limit rates are too slow to allow for an appreciable degree of nitrosation by NO or NO_2 in real ambient atmospheres.

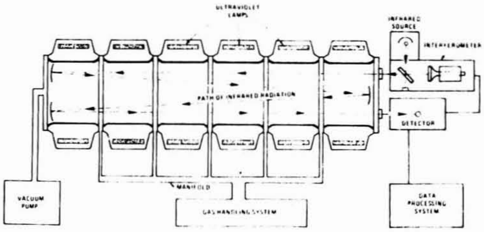

Figure 1. Apparatus used in study of *N*-nitroso dimethylamine

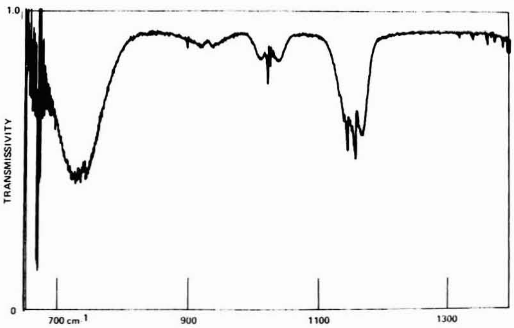

Figure 2. Portion of infrared spectrum of 10 torr of dimethylamine in 10-cm cell

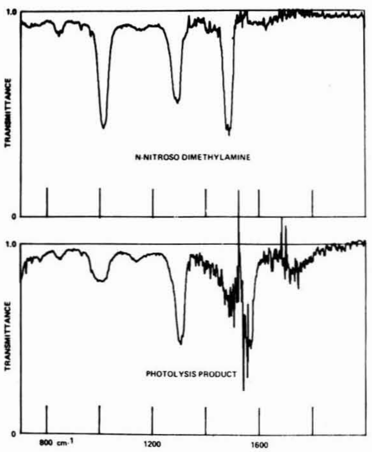

Figure 3. Top: *N*-nitroso dimethylamine vapor between 1 and 3 ppm in dry nitrogen; 360-m cell. Bottom: Same sample as top, photolyzed 1 h with ultraviolet fluorescent light filtered through Pyrex glass (simulated solar radiation)

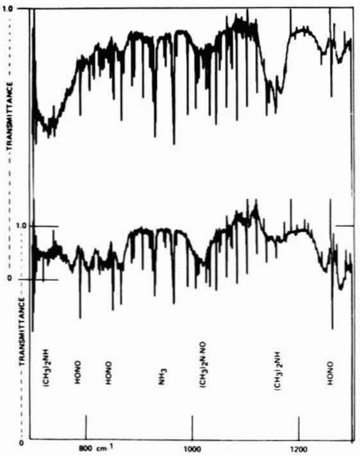

Figure 4. Top: mixture of 5 ppm dimethylamine, 0.7 ppm NH_3, and 0.6 ppm HONO (in equilibrium with 4 ppm NO_2, 6 ppm NO, and 13 000 ppm H_2O) in room air; 360 m. Bottom: same mixture 45 min later, showing conversion to *N*-nitroso dimethylamine

When 1 ppm dimethylamine was mixed with 0.5 ppm nitrous acid vapor in equilibrium with about 2 ppm NO, 2 ppm NO_2, and 13 000 ppm H_2O in room air, the amine was reacted at a rate of about 4%/min. Figure 4 shows infrared absorption spectra of a reactant mixture at the beginning of the reaction and 45 min later. The spectrum at the start shows bands due to dimethylamine, nitrous acid, and some ammonia impurity. The spectrum after reaction shows dimethylamine nearly completely reacted, while the nitrous acid and ammonia are slightly reduced from their starting amounts. This spectrum also shows a new band at 1020 cm^{-1} due to the *N*-nitroso dimethylamine.

From the intensity of the 1020 cm^{-1} band, it is estimated that there was only a 10–30% yield of gaseous nitrosamine. Products unaccounted for may have been on the vessel walls or in an aerosol. Whether the unseen material was nitrosamine is not known.

Glasson (*3*) has repeated some of the work reported herein and has confirmed the observations on the rate of loss of amine. In his experiment, however, the rate of nitrosamine formation appeared to be only about 1% of the rate of amine loss. He has stated that it appears likely that the rate is controlled by a reaction at the wall of the cell. This apparent complexity of the reaction makes extrapolations to real atmospheric conditions rather doubtful. Only an upper limit of the rate of reaction can be estimated, assuming a homogeneous reaction.

For the photolysis experiments in the laboratory, the nitrosamine was mixed with air in the reaction cell and irradiated with a bank of ultraviolet lamps for periods up to 1 h. Figure 3 shows the spectrum before and after irradiation. Note that in 1 h the nitrosamine was nearly fully converted to a new compound that has a distinctly different set of absorption bands. This new compound has not been identified, but some information has been derived from the spectrum. There is no OH stretching absorption band in the spectrum, and the CH stretching frequency in the new spectrum is considerably weaker than in the spectrum of the original *N*-nitroso dimethylamine. Other photolysis products seen when the spectrum is recorded at higher resolution include nitric oxide, carbon monoxde, and formaldehyde.

The samples photolyzed in the large Teflon bag were analyzed in the infrared absorption cell before and after their exposure to sunlight. An inert tracer compound, Freon 11, was added to the sample to indicate any dilution or loss of sample in handling. The nitrosamine concentrations before and after irradiation were determined as ratios to the Freon 11 concentrations. These sunlight photolyses were carried out on two different days. On a cloudy day between 11:00 a.m. and 12:00 noon, half the *N*-nitroso dimethylamine was destroyed in 1 h. On a clear sunny day between 11:00 a.m. and 11:30 a.m., half the *N*-nitroso dimethylamine was destroyed in ½ h.

Discussion

The experiments have shown that in dry air, NO gas and NO_2 gas do not react with dimethylamine vapor at a rate that could be appreciable in the atmosphere. When water vapor is present in the air, however, the formation of *N*-nitroso dimethylamine does proceed at a significant rate. This result most clearly is due to the gas-phase formation of nitrous acid.

$$NO + NO_2 + H_2O \rightarrow 2HNO_2$$

This equilibrium has been well documented. Recently, Calvert et al. (*4*) have given the following value for the equilibrium constant at 23 °C:

$$K_{eq} = \frac{P_{HNO_2^2}}{P_{NO} \cdot P_{NO_2} \cdot P_{H_2O}} = 1.5 \times 10^{-6}\ \text{ppm}^{-1}$$

From this constant, the amounts of nitrous acid reacting with dimethylamine were calculated. Knowledge of the HNO_2 concentration, the dimethylamine concentration, and the rate of disappearance of dimethylamine, combined with an assumption of the bimolecular reaction expressed above in Equation 1, allows a rate constant to be calculated for the expression:

$$-\frac{d(CH_3)_2NH}{dt} = k \cdot P_{(CH_3)_2NH} \cdot P_{HONO}$$

The value obtained is $k = 0.08\ \text{ppm}^{-1}\ \text{min}^{-1}$. This is the apparent rate in the large glass reaction vessel, assuming a gaseous reaction. If the rate is actually wall-controlled, the atmospheric rate is likely to be slower.

Assuming a homogeneous reaction, with a 100% yield of *N*-nitroso dimethylamine, an upper limit formation rate under assumed atmospheric conditions can be calculated. At a moderate level of urban air pollution, the sum of NO and NO_2

might equal 0.05 ppm. If it is assumed that NO and NO_2 are equal in concentration and that the amount of water vapor present is 13 000 ppm, the concentration of nitrous acid would be 0.0035 ppm in the dark. Any trace of dimethylamine introduced into such an atmosphere would react at a rate of about 2%/h. For heavier urban pollution, the reaction rate would be correspondingly higher.

The above calculations apply only in the dark. When the sun rises, the nitrous acid is destroyed by photolysis much faster than it can be reformed by the relatively slow termolecular reaction of NO, NO_2, and H_2O. Nitrosation therefore cannot take place in the daylight.

The same light that stops the nitrosation process will destroy the accumulated *N*-nitroso dimethylamine. As reported above, at full sunlight half the nitrosamine will be destroyed in ½ h. Between 8:00 a.m. and noon, any *N*-nitroso dimethylamine accumulated during the night would be reduced to less than one-half of 1% of its starting concentration. After 10 h of daylight, only one molecule in one million will remain.

The study of photolysis products is not complete. To date, the results have shown that the destroyed *N*-nitroso dimethylamine is replaced by a mixture of nitric oxide, carbon monoxide, formaldehyde, and an unidentified compound whose spectrum is shown in Figure 3. A weakening of the C—H band indicated that this latter compound may only contain a small fraction of the starting material. The spectrum of products does not exhibit any O—H stretching frequency, thus indicating that a molecular rearrangement to an oxime does not take place. In this respect, the gas-phase photolysis differs from the liquid-phase photolysis reported by Chow (*5*).

The large nitric oxide yield indicates that the photolysis breaks the N—N bond:

$$(CH_3)_2N{-}NO + h\nu \rightarrow (CH_3)_2N + NO$$

The radical $(CH_3)_2N$ most likely gives up methyl radicals that are further oxidized to the CO and H_2CO seen as products. It seems possible that the unidentified compound is the result of oxidation and/or recombination of such radicals as $(CH_3)_2N$, CH_3N, and CH_3.

Conclusions

It seems reasonable to conclude that atmospheric formation of *N*-nitroso dimethylamine should not be regarded as a serious general problem. This conclusion is based on two factors. First, the reaction between dimethylamine and nitrous acid will only occur to an appreciable extent while the amine is confined to a region of heavy urban air pollution. The second factor to be considered is that dimethylamine is not a generally distributed air pollutant; the problem will arise only in the vicinity of manufacturing plants that release the amine.

The indicated nonformation of the nitrosamine during the daylight hours requires that any nitrosamine detected in the air in the afternoon must have emitted as nitrosamine rather than in the form of precursors.

The destruction of *N*-nitroso dimethylamine by sunlight will prevent day-to-day accumulation of the compound in the air. It seems reasonable to assume that any *N*-nitroso dimethylamine that may be present in particles in the air will also be destroyed by photolysis.

Formation of *N*-nitroso dimethylamine would take place more readily in industrial atmospheres than in the ambient air, because indoor illumination does not have sufficient ultraviolet intensity for photolytic destruction of either the nitrous acid reactant or the nitrosamine product.

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Interphase Transfer Processes. II. Evaporation Rates of Chloro Methanes, Ethanes, Ethylenes, Propanes, and Propylenes from Dilute Aqueous Solutions. Comparisons with Theoretical Predictions

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Two theoretical models for predicting the rate of evaporation of slightly soluble materials from aqueous solution have been published recently (*1–3*). In a continuation of our work on the evaporation of low-molecular-weight chlorohydrocarbons from dilute aqueous solution [Part I (*4*)], we have measured the evaporation rates of 27 chlorohydrocarbons from water to test these two theoretical models. Preliminary work (*4*) had indicated that the earlier model (*1*) was inadequate since neither absolute nor relative predicted rates were in agreement with the experimental rates. In the present work the evaporation rates of all of the chloro methanes, ethanes, and ethylenes, and a few of the chloro propanes and propylenes were measured to carry out a more extensive test.

Experimental

The same hollow fiber-mass spectrometric procedure as reported previously (*4*) was used to determine the evaporation rates. A schematic diagram which shows the geometry and approximate degree of turbulence of the solution is shown in Figure 1. Two to five compounds were run simultaneously in the same solution. The initial concentration of each component was 1.0 ppm (weight basis). Typical data are shown in Figures 2 and 3. The ion-peak height was correlated with concentration by extrapolation of the decay portion of the curves in Figures 2 and 3 to zero time. This extrapolated concentration at zero time was taken as 1.0 ppm. Successive

■ The evaporation rates of 27 of the title compounds from dilute (~1 ppm) aqueous solutions were determined, and the data were used to test two theoretical models. Most of the rates followed first order kinetics for the first 2–5 half-lives. Under the experimental conditions [200 rpm stirring (shallow pitch propeller), ~25 °C, still air (<0.2 mph), solution depth 6.5 cm], the half-lives ranged from 17 min for 1,1,1-trichloroethane to 56 min for 1,2,3-trichloropropane. The experimental half-lives correlated reasonably well with those calculated by the methods of Mackay and Leinonen and Liss and Slater, especially for series of compounds run simultaneously in the same solution. The experimental half-lives did not correlate with those calculated by the method of Mackay and Wolkoff.

half-lives were determined from the decay portion of the curves and are reported in Table I. The rising portion of the curve for the higher molecular-weight compounds, e.g., CCl_3CCl_3 (Figure 3), is due to the time required for diffusion of the compound through the silicone rubber hollow fiber.

Results and Discussion

The measured half-lives for evaporation, $t^{e}_{1/2}$, of the chlorohydrocarbons from dilute (1 ppm) aqueous solutions are shown in Table I. Under the experimental conditions which included 200 rpm stirring of the solution with a shallow-pitch propeller stirrer, ~25°, still air (<0.2 mph air currents), and an average solution depth of 6.5 cm (Figure 1), the half-lives ranged from 17 min for CH_3CCl_3 to 56 min for $CH_2ClCHClCH_2Cl$. Most of the rates followed first order kinetics as shown by the constancy of the first 2–5 half-lives.

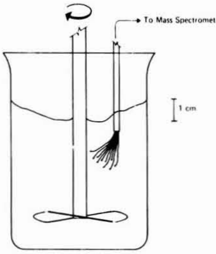

Figure 1. Vessel (250-ml beaker) used to determine evaporation rates

Approximate positions of stirrer and hollow fiber-mass spectrometer probe are indicated. Approximate degree of turbulence of solution is indicated by upper liquid contour

The more recent theoretical model by Mackay and Leinonen (*2*) employed liquid and vapor-phase mass transfer coefficients for exchange between the ocean and the atmosphere reported by Liss and Slater (*3*). Various parameters involved in this treatment are shown in Table I. The partition coefficients, *H*, or Henry's law constants, were calculated by using Equation 1

$$H = \frac{C_{\text{air}}}{C_{\text{water}}} = \frac{16.04\,PM}{TS} \tag{1}$$

where C_{air} and C_{water} are the equilibrium concentrations in the air and water phases, respectively, *P* is the vapor pressure of the pure solute in mm of Hg, *M* is the gram molecular weight of the solute, *T* is the temperature in K, and *S* is the solubility of the solute in water in mg $l.^{-1}$ (~ppm). Equation 1 is derived simply by using the ideal gas law to calculate C_{air} while C_{water} is equal to *S* in the appropriate units so that *H* is dimensionless. Values for *S* and *P* were obtained from published data and other sources and are noted in Table I. The agreement in values of *P* among various workers is quite good, but there are wide discrepancies in values of *S* for some of the compounds, e.g., the value for $CH_2{=}CHCl$ (see Table I). For purposes of calculation, we chose values of *S* on the basis of agreement among various workers or the most recent data. Experimentally determined values of the partition coefficients are in reasonably good agreement with the calculated values in most cases. Calculated partition coefficients were used for calculating the evaporation rates. The overall liquid exchange

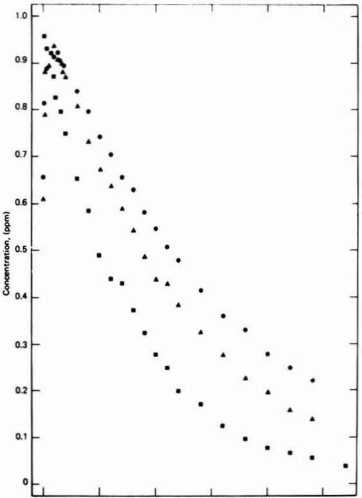

Figure 2. Evaporation rates of $CH_2{=}CHCH_2Cl$ (■), CH_2ClCCl_3 (▲), and $CHCl_2CHCl_2$ (●) from water

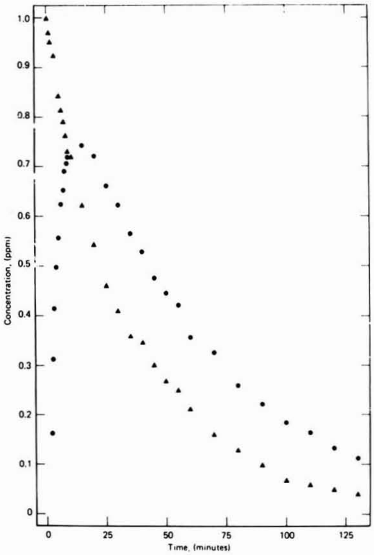

Figure 3. Evaporation rates of $CH_2{=}CCl_2$ (▲) and CCl_3CCl_3 (●) from water

Table I. Calculated and Experimental Evaporation Parameters and Rates of Chlorohydrocarbons from Water[a]

No.	Compound	Solubility in water, ppm, S	Vapor pressure, mm Hg, P	Partition coeff H		Overall liquid exchange constant, cm min^{-1} K_l	Resistance in liquid phase $\%r_l$	Approx. initial concn[b] ppm, C_0	Successive exptl evap half-lives[c] min, $t_{1/2}^{e}$	Evap half-lives, min		
				Calcd	Found					Calcd by Equation 5, $t_{1/2}^{M}$	Calcd by Equation 4, $t_{1/2}^{L}$	Exptl, (av), $t_{1/2}^{e}$
1	CH_3Cl	5380^{d}	e	0.38		0.303	97.4	1.00	27.1, 28.5, 27.3	0.599	14.9	27.6
		$6270^{f,g}$	e,f	0.33^{f}	$0.30^{f,h}$							
2	$CH_2Cl_2^{\,i}$	19400^{j}	438^{k}	0.10	0.11^{l}	0.218	90.8	0.99	23.2, 24.7, 27.2, 25.7	2.23	20.7	25.2
								0.93	17.2, 17.8, 21.5, 24.9, 22.3			20.7
								0.99	18.2, 18.2, 16.2, 18.2, 21.1			18.4
		$22700^{m,n}$	$158^{m,k}$	0.034^{m}		0.184^{m}	76.8^{m}	0.98	22.8, 38.7, 43.1^{o}		24.5^{m}	34.9^{o}
3	$CHCl_3^{\,i}$	7840^{p}	192^{q}	0.16	0.13^{l}	0.190	93.8	0.96	22.7, 26.0, 26.2, 27.8	1.46	23.7	25.7
								0.95	17.1, 18.8, 22.9, 21.4, 20.8			20.2
								0.98	18.4, 18.7, 18.2, 17.7, 19.6			18.5
		$10300^{m,n}$	$66^{m,n}$	0.045^{m}		0.164^{m}	81.1^{m}	0.98	24.3, 37.6, 41.5^{o}		27.4^{m}	34.5^{o}
4	CCl_4	800^{p}	113^{r}	1.2	0.87^{l}	0.177	99.1	0.90	27.7, 30.6, 24.7, 32.1	0.20	25.5	28.8
5	CH_3CH_2Cl	5700^{s}	t,u	0.46		0.269	97.8	0.99	21.1, 26.3, 23.7, 21.1	0.50	16.7	23.1
6	CH_3CHCl_2	5100^{v}	226^{w}	0.24		0.213	95.8	0.96	22.0, 38.8, 35.9	0.98	21.2	32.2
7	CH_2ClCH_2Cl	8700^{x}	82^{y}	0.050	0.040^{l}	0.184	82.9	0.99	28.4, 28.2, 27.5	4.5	24.5	28.0
8	$CH_3CCl_3^{\,i}$	720^{z}	$124^{a'}$	1.2		0.190	99.2	0.97	21.2, 26.7, 23.6, 28.2	0.19	23.7	24.9
								0.95	16.3, 19.8, 19.9, 21.1, 16.5			18.7
								0.93	17.8, 17.3, 19.1, 15.3, 17.2			17.3
		$730^{f,z}$	$99^{f,b'}$	1.0^{f}	$1.4^{f,h}$							
		$880^{m,z}$	$40^{m,c'}$	0.36^{m}		0.186^{m}	97.2^{m}	0.96	23.6, 33.2, 33.8^{o}		24.2^{m}	30.2^{o}
9	$CH_2ClCHCl_2$	$4420^{d'}$	23^{w}	0.038		0.150	78.3	0.74	36.3, 34.5, 32.7, 36.9	6.1	30.1	35.1
10	CH_2ClCCl_3	$1100^{e'}$	$13.9^{f'}$	0.11		0.156	91.6	0.94	43.5, 41.1	2.01	28.8	42.3
11	$CHCl_2CHCl_2$	$3000^{g'}$	6.5^{w}	0.019		0.111	67.2	0.92	55.7, 54.6	12	40.5	55.2
12	$CHCl_2CCl_3$	$480^{h'}$	4.5^{w}	0.10		0.141	90.7	0.90	48.0, 44.9	2.3	32.0	46.5
13	CCl_3CCl_3	$8^{i'}$	0.33^{w}	0.05		0.12	83	0.72	43.6, 37.9, 40.7	4	38	40.7
14	$CH_2{=}CHCl$	$60^{j'}$	e	43	$50^{j'}$	0.280	99.98	0.89	25.2, 29.6, 27.9, 27.6	0.0054	16.1	27.6
		$2700^{k'}$	e	0.95		0.277	98.9			0.243	16.3	
15	$CH_2{=}CCl_2$	$400^{l'}$	$598^{m'}$	7.8		0.224	99.9	1.00	21.6, 31.1, 28.0, 27.9	0.029	20.1	27.2
		$400^{f,l'}$	$497^{f,m'}$	6.6^{f}	$6.3^{f,h}$							
16	*cis*-$CHCl{=}CHCl$	3500^{p}	206^{w}	0.31		0.217	96.7	0.97	18.0, 17.6, 20.4, 19.2, 21.6	0.75	20.7	19.4
17	*trans*-$CHCl{=}CHCl$	6300^{p}	326^{w}	0.27		0.216	96.3	0.99	23.1, 25.2, 25.6, 20.8, 25.3	0.85	20.8	24.0
18	$CHCl{=}CCl_2^{\,i}$	$1100^{n'}$	74^{y}	0.49		0.189	97.9	0.96	22.7, 24.3, 24.5, 22.6	0.47	23.8	23.5
								0.95	17.4, 19.9, 18.2			18.5
								0.94	18.2, 17.8, 16.9, 17.9			17.7
		$1100^{f,n'}$	$59^{f,o'}$	0.40^{f}	$0.365^{f,h}$							
		$1000^{m,n'}$	$23^{m,w}$	0.17^{m}		0.181^{m}	94.1^{m}	0.93	28.9, 31.4, 35.3^{o}		24.8^{m}	31.9^{o}

(*Continued on page 408*)

Table I. Continued

No.	Compound	Solubility in water, ppm, S	Vapor pressure, mm Hg, P	Partition coeff H Calcd	Partition coeff H Found	Overall liquid exchange constant, cm min^{-1} K_l	Resistance in liquid phase $\%r_l$	Approx. initial concn[b] ppm, C_0	Successive exptl evap half-lives,[c] min, $t_{1/2}^e$	Evap half-lives, min: Calcd by Equation 5, $t_{1/2}^M$	Evap half-lives, min: Calcd by Equation 4, $t_{1/2}^L$	Evap half-lives, min: Exptl, (av), $t_{1/2}^e$
19	$CCl_2=CCl_2$[i]	140[p']	18.6[y]	1.2	0.50[l]	0.170	99.1	0.92	24.5, 28.3, 26.8, 28.7	0.20	26.5	27.1
								0.92	22.2, 25.5, 27.3, 26.6			25.4
								0.92	20.6, 19.4, 20.2, 20.5			20.2
		120[f,p']	14.2[f,y]	1.0[f]	0.82[f,h]							
		130[m,q']	4.8[m,w]	0.35[m]		0.167[m]	97.1[m]	0.90	36.8, 38.1[o]		27.0[m]	37.5[o]
20	$CH_2ClCHClCH_2Cl$	1900[r']	3.1[s']	0.013		0.101	55.3	0.92	53.2, 58.9	18	44.7	56.1
21	$CH_2ClCCl_2CH_2Cl$	[t']						0.85	47.7, 51.4			49.6
22	$CH_2=CHCH_2Cl$	3370[u']	361[v']	0.44		0.247	97.7	0.96	26.5, 28.4, 24.9	0.520	18.2	26.6
23	$CH_2=CClCH_3$	[t']						0.99	29.7, 33.9, 35.8			33.1
24	$CHCl=CHCH_3$	[t']						0.95	16.0, 17.0, 20.1, 20.1, 16.5			17.9
25	$CH_2=CClCH_2Cl$	2150[w']	53[x']	0.15		0.196	93.4	0.94	19.3, 19.8, 20.9, 20.2	1.6	23.0	20.1
26	*cis*-$CHCl=CHCH_2Cl$	2700[y']	43[z']	0.095		0.189	90.1			2.4	23.8	
								0.97[a'']	28.4, 31.4, 29.1			29.6[a'']
27	*trans*-$CHCl=CHCH_2Cl$	2800[y']	34[z']	0.072		0.184	87.4			3.2	24.6	
28	$CHCl=CClCH_2Cl$	[t']						0.78	45.2, 45.1			45.2

[a] All data for 25° unless specified otherwise. [b] Initial concentration used for determining the first half-life. [c] The first decimal place is somewhat uncertain. [d] Average of data in refs. *5* and *6*. [e] The vapor pressure of the solute in equilibrium with the solution for the cited solubility was 760 mm. [f] At 20°. [g] Datum from ref. *5*. [h] Data from refs. *7* and *8*. [i] Results from three separate experimental runs are given. [j] Datum from ref. *9*. [k] By interpolation of data in ref. *10*. [l] Datum from ref. *11*. Vapor phase was nitrogen; liquid phase was Mississippi River water. [m] At 1.5°. [n] By interpolation of data in ref. *9*. [o] At *1–2*°. [p] Datum from ref. *12*. [q] Average of values obtained by interpolation of data in refs. *7–9*. [r] Average of values obtained by interpolation of data in refs. *7–9* and *13*. [s] Value reported in refs. *14* and *15* at 20° and 17.5°. [t] The vapor pressure of the solute in equilibrium with the solution for the cited solubility was presumably ~760 mm. [u] See also ref. *16*. [v] Average of values obtained by interpolation of data in refs. *9* and *17*. [w] Average of values obtained by interpolation of data in refs. *9* and *18*. [x] Average of values obtained by extrapolation of data in refs. *7–9, 14,* and *17* using average temperature dependence in refs. *14* and *17*. [y] Average of values obtained by interpolation of data in refs. *7–9,* and *18*. [z] Average of values obtained by extrapolation of data in refs. *7, 8, 19,* and *20* using temperature dependence in ref. *17*. [a'] Average of values obtained by interpolation of data in refs. *7–9, 18,* and *21*. [b'] Average of data in refs. *7–9, 18,* and *21*. [c'] Average of values obtained by interpolation of data in refs. *9, 18,* and *21*. [d'] Average of values obtained by interpolation and extrapolation of data in refs. *12, 14,* and *17*. [e'] By interpolation of data in ref. *17*. [f'] By interpolation of data in ref. *18*. [g'] Average of values obtained by interpolation of data in refs. *12, 14,* and *17*. [h'] Average of values obtained by extrapolation of data in refs. *12* and *17* using temperature dependence in ref. *12*. [i'] Average of values obtained by extrapolation of data in refs. *22* and *23* using temperature dependence in ref. *23*. [j'] Value reported in refs. *7* and *8* at 10°. [k'] Datum from ref. *24*. [l'] Value reported in refs. *7–9* at 20°. [m'] Average of values obtained by interpolation of data in refs. *7, 8,* and *10*. [n'] Average of values obtained by extrapolation of data in refs. *7, 8, 12,* and *14* using temperature dependence in ref. *12*. [o'] Average of data in refs. *7–9* and *18*. [p'] Average of values obtained by extrapolation of data in refs. *7, 8, 12,* and *23* using temperature dependence in ref. *23*. [q'] Average of values obtained by extrapolation of data in refs. *7, 8, 12,* and *23* using temperature dependence in ref. *12*. [r'] Average of values in refs. *19, 25,* and *26* at 20° and 30°. [s'] Average of values obtained by interpolation of data in refs. *14* and *25*. [t'] No solubility data available. [u'] Average of values obtained by interpolation and extrapolation of data in refs. *19* and *27–29* using temperature dependence in ref. *29*. [v'] Data from refs. *27* and *28*. [w'] By extrapolation of data in ref. *29*. [x'] Average of values obtained by interpolation and extrapolation of data in refs. *19* and *30*. [y'] Value reported in ref. *31* at 20°. [z'] Datum from ref. *19*. [a''] A mixture of *cis* and *trans* isomers was used.

constant, K_l, in cm min^{-1} was calculated by Equation 2, where k_l and k_g are the exchange constants

$$K_l = \frac{Hk_lk_g}{Hk_g + k_l} = \frac{221.1}{\left(\frac{1.042}{H} + 100.0\right)M^{1/2}} \tag{2}$$

for the liquid and gas phases, respectively (*3*). The liquid and gas-phase exchange constants for the chlorohydrocarbons were evaluated by the procedure described by Liss and Slater (*3*) in which

$$k_l = k_l^{CO_2}\,(M_{CO_2}/M)^{1/2},$$

$$k_g = k_g^{H_2O}\,(M_{H_2O}/M)^{1/2},\ k_l^{CO_2} = 0.33 \text{ cm min}^{-1}$$

and $k_g^{H_2O} = 50$ cm min^{-1}. The resistance in the liquid phase, $\%r_l$, is given by Equation 3, where R_l is the total resistance

$$\%r_l = \frac{100\,r_l}{R_l} = \frac{10^4}{100.0 + \frac{1.042}{H}} \tag{3}$$

expressed on a liquid-phase basis (*3*). The solute evaporation half-life, $t_{1/2}^L$, in minutes was calculated by Equation 4 where d is the solution depth (*2, 32*).

$$t_{1/2}^L = \frac{0.6931\,d}{K_l} \tag{4}$$

A correlation of the half-lives for evaporation, $t_{1/2}^L$, calculated by Equation 4 with the experimental values, $t_{1/2}^e$, is shown in Figure 4. The reasonably close agreement between the calculated and experimental half-lives is somewhat fortuitous since the calculated values depend on the exchange constants, k_l and k_g (*3*), whereas the experimental values depend on the stirring rate, air currents, and other factors (*4*).

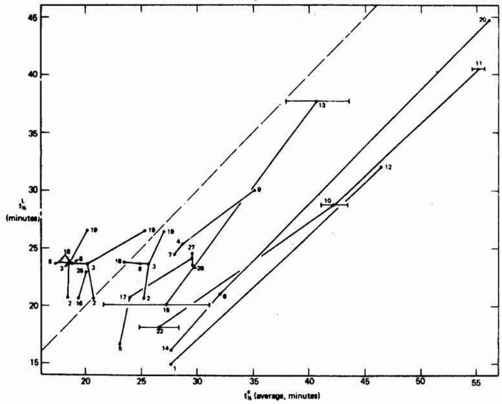

Figure 4. Correlation of evaporation half-lives, $t^L_{1/2}$, calculated by Equation 4 with experimental half-lives, $t^e_{1/2}$

Numbers refer to compound numbers in Table I. Compounds run in same solution are indicated by lines which connect data points. Error bars for compounds 10, 11, 13, 15, and 22 are for total variation of experimental half-lives. Other error bars are omitted for clarity. Dashed line is 1:1 correlation line

A more significant test of the model is a comparison of the relative values of the two sets of data. For compounds which were run in the same solution, an approximately linear relationship with an intercept near the origin was observed in most cases (Figure 4). The variation among different runs was apparently due to some uncontrolled variables in the experiments (*4*).

One experiment was run at 1–2° (Table I). The increased half-lives at the lower temperature are predicted by Equations 2 and 4. The increase in the calculated half-lives is due to a decrease in H with the decrease in temperature. However, on lowering the temperature the experimental half-life increased more than the calculated half-life did, possibly because k_l and k_g were assumed to be independent of temperature (*2*).

One interesting feature of Equation 2 involves the effect of changes in H on the exchange constant, K_l, and thus on the half-life, $t^L_{1/2}$. For values of H greater than about 0.1 (>90% liquid-phase resistance), there is relatively little change in K_l with major changes in H. For example, the forty-fivefold variation in the two values of H for $CH_2{=}CHCl$ in Table I leads to only a 1% change in K_l and $t^L_{1/2}$. Thus, for compounds with $H > \sim 0.1$, i.e., most but not all of the chlorohydrocarbons in this study, the calculated half-life, $t^L_{1/2}$, is almost directly proportional to the square root of the molecular weight and is nearly independent of H.

The earlier theoretical model by Mackay and Wolkoff (*1*) leads to Equation 5 where $t^M_{1/2}$ is the solute evaporation

$$t^M_{1/2} = \frac{0.01797\, GP_w S}{EPM} \tag{5}$$

half-life in minutes, G is the weight of water in grams, P_w is the partial vapor pressure of water in mm of Hg, and E is the weight of water in grams which evaporates per day. In our experiments at ~25°, $G = 200$, $P_w = 23.76$, and $E = 20$. Calculated values of $t^m_{1/2}$ are listed in Table I. Comparison of the values of $t^M_{1/2}$ with the experimental values, $t^e_{1/2}$, shows that Equation 5 fails to predict both the absolute and relative half-lives for evaporation. The possible reasons for this failure of Equation 5 have been discussed previously (*2, 4*).

A recent comparison of experimental evaporation half-lives with those calculated by the two methods described in this paper led to conclusions similar to ours (*32*).

Acknowledgment

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Received for review June 1, 1976. Accepted November 5, 1976. Presented at the Division of Industrial and Engineering Chemistry, 172nd Meeting, ACS, San Francisco, Calif., August 29–September 3, 1976; Abstracts of Papers, No. INDE 8.

INDUSTRY TRENDS

Chemical Separations Corp. (Oak Ridge, Tenn.) will construct and install a fixed-bed ion-exchange system for water demineralization at the Bellefonte Nuclear Power Plant (1332 MW) near Scottsboro, Ala.

EMA, Inc. is the new name of the firm formerly known as Environmental Management Associates, Inc. The firm is located at St. Paul, Minn.

The Bionetics Corp. (Hampton, Va.) has been awarded a potential $750 000 contract by the EPA to set up a support laboratory for the Quality Assurance Branch, Environmental Monitoring and Support Laboratory, at Cincinnati, Ohio.

Norsk Hydro (Norway) will supply its nitrophosphate fertilizer-making process to the U.S.S.R. The plants to be supplied will meet strict air pollution control standards, and almost totally suppress water pollution.

Asplundh Environmental Services (Willow Grove, Pa.) has opened a Midwest Regional office at Ann Arbor, Mich. Asplundh has contracts in environmental studies for electric power transmission rights-of-way.

Standard Havens, Inc. (Kansas City, Mo.) has supplied fabric filtration systems to Huron Cement (Alpena, Mich.) to clean 195 000 acfm at about 280 °F, and operate at an air-to-cloth ratio of 5.5:1.

Hercules Inc. (Wilmington, Del.) has renamed its Environmental Services Division as the Water Management Chemicals Division of Hercules' Industrial Systems Department, to reflect the firm's heavy involvement in waterborne waste treatment work.

Proler International Corp. (Houston, Tex.), a leading processor of metals for recycling, has begun construction of two plants at Coolidge, Ariz., to recover tin, and to convert ferrous scrap into precipitation iron.

Union Carbide (Tarrytown, N.Y.) will provide "Ucarsep" reverse osmosis units to Commonwealth Edison Co., to handle radioactive laundry wastes.

The Chemical Industry Institute of Toxicology (Research Triangle Park, N.C.) announced that Standard Oil Co. (Ohio) and Mobil Chemical Co., have become Institute members.

Airco Industrial Gases (Murray Hill, N.J.) will install its F^3O wastewater treatment system to increase wastewater treatment capacity at Wayne, N.J. from 1 mgd to 1.8 mgd.

Fairfield American Corp. was formed at Middleport, N.Y. to make a line of insecticide products that were formerly made by the Agricultural Chemical Division of FMC Corp.

Dow Chemical U.S.A. (Midland, Mich.) has formed a task force to review the distribution and safe handling of soil fumigants that Dow manufactures.

Newport News Shipbuilding (Va.) and Globtik Tankers U.S.A. signed a letter of intent for construction of up to three 600 000-deadweight ton nuclear-powered oil tankers. Estimated base price is $325 million/ship, not counting inflation.

Resources Conservation Co. (Renton, Wash.) has received $3.1 million worth of contracts for brine concentrators to treat cooling tower wastes at power plants in the western U.S., and in Canada.

UOP Inc. has licensed **Mitsui Toatsu Chemicals, Inc.** (Tokyo) to make and market thermal and catalytic incinerators in Japan and in other Far East countries.

Research-Cottrell, Inc. will design and supply a fabric filter system, to handle 255 800 acfm at 360 °F, to the United Power Association, Elk River, Minn.

The Aeroacoustic Corp. (Copiague, N.Y.) has supplied the first of a new line of gas turbine silencers that have suppressed excess community noise and low-frequency vibrations at a New York metropolitan area utility plant.

Neptune International Corp. has been awarded a nearly $600 000 contract by Fluor Nederland, B.V., to supply two water treatment systems for gas conditioning plants in Iran, to produce 500 000 gpd of processed water, and 300 000 gpd of potable water.

Zurn Industries, Inc.'s Fluid Handling Division has received an American Society of Mechanical Engineers "N" Stamp certifying the division's qualifications to supply equipment to nuclear power plants.

Flack & Kurtz Energy Management Corp. (New York, N.Y.) has created a computerized system to monitor heating, ventilation, and air conditioning (HVAC) in buildings. This "Census Program for Energy Conservation" is aimed at optimizing building energy use/savings.

General Motors has completed the first portion of a program to expand its vehicle emission test/certification facilities at its proving grounds at Milford, Mich., and Mesa, Ariz.

Sebring Vanguard, Inc. (Columbia, Md.) has delivered the first two electric CitiVans to the U.S. Postal Service's R&D center at Rockville, Md. Each CitiVan has a suggested retail price of $3988, f.o.b. Sebring, Fla.

InterOcean Systems and its subsidiaries have recently moved to new facilities near San Diego, Calif. InterOcean makes water quality monitoring systems, and a whole line of oceanographic instruments.

The Electric Power Research Institute (Palo Alto, Calif.) has funded studies of response of model nuclear power plant structures to simulated earthquake ground motions.

Camp Dresser & McKee has announced a merger with Harvey O. Banks, Consulting Engineer, Inc. (Belmont, Calif.).

Fluor Corp. announced that the trans-Alaska pipeline's marine terminal and pumping stations are 85% complete, and hydrotesting of piping elements at these facilities has passed the 50% completion mark. Fluor Alaska, Inc. is in charge of these projects.

American Electric Power Service Corp. (New York, N.Y.), Babcock & Wilcox, Ltd. (England), and STAL-LAVAL Turbine AB (Sweden) have begun a joint study of the feasibility of building a full-scale demonstration plant for pressurized fluidized-bed coal combustion.

Donaldson Co., Inc. (Minneapolis, Minn.), manufacturer of air pollution control equipment, is to establish a wholly-owned subsidiary, Donaldson Torit B.V., at Haarlem, The Netherlands.

Ingersoll-Rand (Woodcliff Lake, N.J.), which is providing heavy equipment for the Valley Forge, Pa., wastewater project, said that the project is running 40% ahead of schedule.

UNIBRA s.a. (Brussels, Belgium) is leading a group of companies in developing a fluidized-bed fuel desulfurization process that would increase absorption of sulfur by a factor of 5. Combustion temperatures would be 600–900 °C; fixed-bed applications are possible.

Stanley Consultants, Inc. (Muscatine, Iowa) is one of three companies working on the planning and design of a commercial-scale coal gasification plant planned for northeastern Missouri.

Hyde Products Inc. (Cleveland, Ohio) has reached agreement with J. Arthur Moore Co., to market the "Bailey" oil content monitor, developed in England, in conjunction with Hyde's gravity-media oil-water separator.

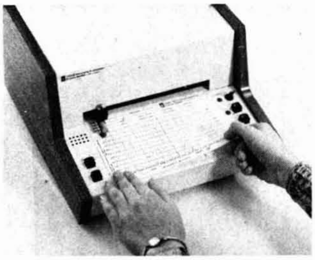
NEW PRODUCTS

Chrome, nickel recovery systems

This 20 gal/h evaporative system recovers chrome or nickel from electroplating processes. When the recovered solution of plating chemicals reaches a pre-set concentration the solution is automatically drained into a storage tank for later use as plating bath make-up. Corning Glass Works **101**

Tertiary filter

Filters the "clear" effluent from chemically treated wastewater systems. Concentrations of metal hydroxides are reduced from a range of 1–3 mg/L to less than 0.5 mg/L. It is designed primarily for plating treatment systems with continuous effluent discharges of up to 5000 gpd. Motor Guard **102**



Recording audiometer

Designed to provide rapid, automatic hearing tests and to produce a permanent record of the results on 5 × 8-in. audiogram form. The unit is ideal for ongoing monitoring for hearing conservation programs. GenRad **103**

Dew point/temperature monitor

The system, designed for field application, provides an accuracy of ±0.5 °C over a dew point and temperature range of −50 to +50 °C. EG&G **104**

Pump supports

These are to be used with diaphragm proportioning pumps in applications where water treatment or process chemicals are pumped directly from shipping containers (55-gal drums). These supports are available in three configurations. Neptune Chemical Pump Co. **105**

Filter Fluorimeter

This unit is designed for ppt trace analysis in liquid chromatography for detecting naturally fluorescent compounds and fluorescent derivatives. Minimum detectable concentrations are: polynuclear aromatics, 50 ppt range and aflatoxins, 20 ppt. Varian **106**

Electrochemical analysis system

The system, composed of one or all of the three modules for pH, O_2/temperature, and/or conductivity determinations, allows the operator to select one or any combination of two functions. The pH module features automatic temperature compensation and accepts a wide range of sensors; the conductivity unit's measurement range is 0–140 000 μmhos/cm^2. Beckman Instruments **107**

Liquid grab sampler kit

The kit comes equipped with polyvinylchloride-clear autoclavable bottles that are able to contain an 8-oz effluent sample with up to 0.25-in. solids. After collecting an uncontaminated sample, the bottle can be unthreaded from the sampler unit and capped for transport to the laboratory. Fluid Kinetics **108**

Subsurface sludge applicator

Three- and five-knife models for applying municipal sludges, lime slurries and industrial wastes are available. The knives are designed to open and close most soil to a depth of 6–8 in. The applicator injects 600–800 gal of waste material/min at speeds up to 6 mph. Big Wheels **109**

Electrical thermometer

The portable unit will accept up to 4 inputs from remote temperature sensors. The sensor's measuring range is 50–480 °F. Tempkey Inc. **110**

Self-cleaning liquid filter

The filter, according to the manufacturer, handles large volumes of liquid ladened with suspended solids and oils. It features low-micron particle separation, produces no back-flushing effluent and is self-cleaning. The filter is positioned at the point of suction, and comes in several sizes and capacities. Applied Products **111**

Water quality monitoring system

Designed for the acquisition of oceanographic and limnological field data. The underwater probe operates to depths of 1000 m and will sense and transmit a total of up to eight water parameters. Inter-Ocean **112**

Gas monitoring system

The 8-channel system can continuously and simultaneously monitor up to 8 detection points and as many as 4 different types of gases. Sensors to monitor hazardous atmospheres in sewage treatment facilities and refineries can be placed up to a mile from the instrument. International Sensor Technology **113**

Portable calibration system

The instrument is designed to field calibrate ambient level H_2S and SO_2 sensors. Veekay Limited **114**

Gas sampling bags

The "Teflon" and "Tedlar" bags do not absorb gaseous products and are suitable for chemical sampling; the collected gaseous samples can then be analyzed by chromatographic techniques. Carborundum **115**

PCB isomers kit

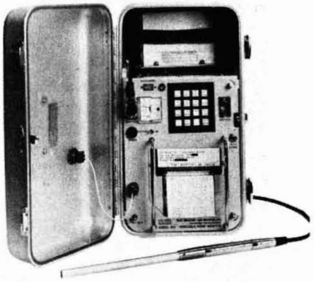
Developed for environmental testing of commonly encountered PCBs, the kit contains 5 mg each of 14 different PCB isomers and 6 interference pesticides that are used as reference standards. Analabs, Inc. **116**

Calibrator/potentiometer

The miniaturized device can be used for testing, calibrating and trouble-shooting electronic equipment such as recorders, indicators, pH meters and controllers. Transmation, Inc. **117**

PCB substitutes

The new dielectric fluids, termed Dielektrol I and II, are claimed to have the performance characteristics of PCB and are environmentally compatible. They are biodegradable, nonpersistent and nonbioaccumulative. General Electric **118**



Noise monitor

Measures and prints out L-percentile noise level data. The instrument also prints out time. Sound level range without range switching is 30–130 dBA; timing accuracy is ±10 s/24 h. BBN Instruments **119**

Dry electrostatic precipitator

The modular construction permits modules to be combined in either series or parallel to provide the required efficiency or capacity. Operating temperatures of up to 650 °F are permissible. The unit can handle gases with high-moisture and high-sulfur content. There are no moving parts. MikroPul Corp. **120**

Condensing unit

Designed for the recovery of gasoline vapors at service stations, the automatically controlled unit reduces pollution. The gasoline vapors are recovered at the point of delivery—the pump and service station tanks—and are collected at a central location for reuse. Edwards Engineering **121**

Solids dewaterer

The belt-filter presses can be used for treating sludges with input loadings as thin as 0.5% solids, at throughput rates of 100 gpm. Cake concentrations between 15–50% can be obtained. The Ralph B. Carter Co. **122**

Inkless recorder

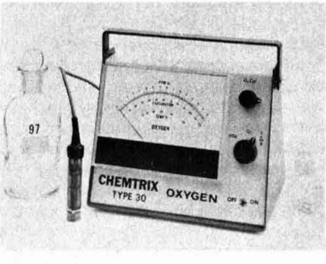
The two-pen, 250 mm (10 in.) recorder is designed so that both channels write the full chart width. Accuracy is 0.25% while pen speed is 0.30 s full scale; 16 input spans from 1 mV–100 V and 20 chart speeds are features of the recorder. Soltec Corp. **123**

Ozone meter

The meter, designated as a reference method by the EPA, uses the photometric detection of the chemiluminescence resulting from the reaction of ethylene gas with ozone. A refrigerated enclosure houses the photomultiplier tube, electrometer, and associated circuitry. Six selectable ranges from 0.001–10 ppm are possible. Columbia Scientific Industries **124**

Microbicide

The high-potency diamine is free from toxic phenol compounds, but still controls the growth of many algae and bacteria to be found in open recirculating cooling systems. Dearborn Chemical **125**



Dissolved oxygen meter

The unit measures dissolved oxygen in liquids and air with a range of 0–25 ppm. The meter also measures temperature between 0–50 °C. Dissolved oxygen is measured by the polarographic technique. Chemtrix **126**

Pesticide sampling head

The 4-in. diameter head is designed to be used with the company's high-volume air sampler in pesticide studies. The head uses a fixed charge of ion-exchange resin; after the sampling period, the resin is removed from the head and poured into a bottle for later analysis in the laboratory. Microchemical Specialties **127**

Data acquisition system

The system features 16-channel capability, an A/D converter, crystal clock, digital display and variable scan rate control. The storage medium is a tape cassette. Climatronics **128**

Formaldehyde monitor

The unit has a range of 0–0.5 ppm full scale with a detectable limit of 10 ppb expandable to a full-scale range of 0–10 ppm. The instrument can be adapted to other wet chemical techniques, including SO_2, NO_2 and NO_x. CEA Instruments **129**

Sodium ion recorder/analyzer

The selective ion electrode unit is designed to continuously measure and record sodium concentrations from 0.1–10 000 ppb in water. Calgon **130**

Diaphragm valve

The valve is helium-tight and cannot leak to the environment when installed under proper conditions. It is designed to be used within the containment vessel and in other critical areas of nuclear plants. Dresser Industries **131**

Gas sampling pump

The pump offers adjustable flow rates from 1–20 L/h and is small enough to be worn on the operator's person. Calibrated Instruments **132**

Atomizing nozzle

The nozzle is to be used for incinerating petrochemicals, refinery wastes, methanol, water/alcohol solutions, sewage sludge and other liquid and viscous wastes. The nozzle is self-cleaning. Sonic Development Corp. **133**

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NEW LITERATURE

Heat recovery. Bulletin, "Waste Heat Recovery Units," tells how enough fuel can be saved to permit possible 1–2 year payback of investment. Beltran Associates, Inc. **151**

Sanitary chemicals. Booklet SAN-300-13 is a revised list of sanitary chemicals, including cleaning agents, surfactants, deodorants, and antiseptics. Other applications are listed. Rohm and Haas Co. **152**

Waste treatment. Brochure describes chemicals and services for complete wastewater treatment, including sludge, oil emulsions, foam, odor, and other problems. Dearborn Chemical (U.S.) **153**

Environmental equipment. Catalog/directory/buyers' guide produce listings cover air and water pollution control equipment catalog listings by product. Three pages of listings. Koch Engineering Co., Inc. **154**

Dust collector. Bulletin 4000 describes high-efficiency jet-pulse fabric filter with two-thirds less moving parts. Engineering features are fully discussed. American Precision Industries Inc. **155**

Ocean equipment. Catalog lists and describes ocean water samplers, instruments, pressure vessels, camera systems, and other equipment for oceanographic applications. Benthos, Inc. **156**

Surveying calculator. Bulletin No. 5952-9128 describes surveying calculator system and programming for field use and mapping. Land-use applications possible. Hewlett-Packard **157**

Microbiocide. Two technical papers explain how chlorine dioxide can be successful biocide for cooling towers and oxidant for wastewater treatment. Presented at WWEMA conference, Houston, Tex., March. Olin Corp. **158**

Mud remover. Company has information as to how mud fouling in cooling water systems can be eliminated with commensurate cost savings. Metropolitan Refining Co., Inc. **159**

Zeta potential control. Bulletin 149 tells how zeta reader is used to read zeta potential and facilitate small particulate settling in liquid wastes, especially in the paper industry. Komline-Sanderson. **160**

Filtration. Information packet discusses fully applications, installation, and maintenance of filter housings, drains, tubes, and related products. Balston, Inc. **161**

Fly ash collection. Technical paper features a selection of fly ash collection systems. Designs and effects of particle size and fly ash loading characteristics on performance are covered. UOP Inc. **162**

Recovered water. Booklet explains how to obtain distilled water from wastewater-soluble emulsions and other discarded industrial solutions. Hoffman Filtration Systems **163**

Noise analysis. Brochure describes a new model community noise analyzer, especially suited to baseline evaluation. Resolution 0.25 dB with digital readout. B&K Instruments, Inc. **164**

Analytical chemicals. Analytical Chemicals Catalog, focused on classical wet chemical methods and special products, is now available. Hach Chemical Co. **165**

Aeration costs. Bulletin 450 charts performance and costs of aerated-facultative lagoons. Oxygen transfer/dispersion data, and design details for U.S. and Canadian installations are given. Hinde Engineering Co. **166**

Sewer pipes and fittings. Brochure TRX-11 describes the company's PVC gravity sewer pipes and fittings for conveying domestic sanitary sewage. Johns-Manville **167**

Three-gas sampler. Bulletin 2441 shows a sampler that can sample up to three different pollutant gases simultaneously, and features a unique thermoelectric system for maximum SO_2 sample accuracy. Research Appliance Co. **168**

Refuse control. Booklet A-1821 explores factors in refuse handling from source to final disposal, and shows many aspects of solid waste management. Booklet A-1818 is a guide to proper equipment selection. John Deere **169**

Analytical instruments. Fall/winter issue of *Instrument News* has articles on gas chromatography, infrared NMR, fluorescence, and many other types of precise analytical instrumentation. Perkin-Elmer **170**

Fabric filter. Brochure shows Norfelt HE Fabric Filter, explains how it is engineered, and lists many applications. Envirotech/Buell **171**

Pumps. Pump bulletin features top-of-the-line pumps, including the Varistaltic, Cassette, and Dispenser Pumps, along with applications. Manostat Corp. **172**

Strip-chart recorder. Catalog lists strip-chart recorders that can provide readouts of humidity, pH, dissolved oxygen, voltages, and many other parameters. One recorder has 24 channels. Galvanometric and servo. Gulton Industries, Inc. **173**

Waste treatment. Bulletin TXAR-EA-75 describes waste treatment plants with hopper-type clarifiers, 10 000–25 000 gpd, for small subdivisions, mobile home parks, and the like. Factory assembled. Can-Tex Industries **174**

Spectroscopy. Application Note AN-40 explains the use of silicon-barrier detectors for improved timing and energy-resolution performance in heavy-ion and fission-fragment spectroscopy. Ortec Incorporated **175**

Textile size recovery. Brochure describes recovery of synthetic sizing agents such as polyvinyl alcohol and carboxymethyl cellulose from desize wastes by unique ultrafiltration method. Abcor Inc. **176**

Instruction in analysis. Bulletin SEO-5698 describes 54 audio-visual instruction courses with equipment and accessories for analysis, including pH, enzymology, ultraviolet and infrared, and spectrography. Beckman Instruments, Inc. **177**

Tank level readouts. Data sheet describes tank level reading instrumentation, with alarming subsystems, even for levels of hazardous (Class I) substances. Metritape, Inc. **178**

Recycled water use. Case history tells how maker of elemental phosphorus was able to switch from fresh water to recycled water during production. Vibra Screw Incorporated **179**

Laboratory instruments. "What's New for the Laboratory" No. 98 lists "tall" pH meters, pipetting systems, environmental chambers for microbiology, and balances. SGA Scientific **180**

Power transmission. Bulletin GPC-76 describes gear reducers, clutches, and other power transmission devices used in paper-making, sewage treatment, chemicals, and other applications. Flender Corp. **181**

Sludge collectors. Bulletin 315-65 describes non-metallic chain sludge collector that wears better than cast chain

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and eliminates the need for two men with block and sledge hammer (*ES&T*, December 1976, p 1198). Envirex **182**

Power plant optimization. Brochure PSG-4786 tells how to reduce unscheduled downtime at fossil power plants. Combustion Engineering, Inc. **183**

Oil reclamation. Data sheet on Petro-Clar PI-1010 outlines applications and design features of 300–600 gph oil reclamation systems. Velcon Filters Inc. **184**

Fabric filters. Three brochures explain in detail the new line of Pulse Jet Fabric Filters the company is offering for dust control. Construction details and operating features are given. Johnson-March Corp. **185**

Scale inhibition. Two data sheets describe a non-phosphate, non-chromate corrosion inhibitor for cooling systems, and chelating agents for scale inhibition in boilers. Alken Murray Corp. **186**

Ball valves. Bulletin No. 1208 describes ball valves that combine long wear life and leak-tight shutoff for low- and high-pressure saturated steam, superheated steam, and hot water. Hills-McCanna Co. **187**

Multi-stage pumps. Bulletin 722.9 describes Low Flow–High Head Multi-Stage pumps for petrochemicals, hydrocarbons, reverse osmosis, and other low-flow applications. Goulds Pumps, Inc. **188**

Continuous weighing. Bulletin 460 describes "Weightometer" belt scale and Model DS digital weight measurement system. Merrick Scale Manufacturing Co. **189**

GC/MS. Pub. 23-5952-5808 describes gas chromatograph/mass spectrometer (GC/MS) data system, and gives steps for analysis of a lake water sample. Hewlett-Packard **190**

Slurry equipment. Brochure describes slurry trench and diaphragm wall equipment and supply information. Company supplies complete slurry construction equipment systems. Resource Management Products **191**

Line filters. Catalog SF-11 announces heavy-duty hydraulic line filter installable between valve outlet and tank, or between tank and pump inlet. Works to 300 psi and −60 to +300 °F. The Lenz Co. **196**

EIS. Brochure outlining rapid, economic methods for writing environmental impact statements (EIS) for major construction projects is available. The Research Corporation of New England. **197**

Solvent recovery. Technical brochure outlines activated carbon adsorption process for solvent recovery for reuse of air pollution control. In many cases, investment pays off. American CECA Corp. **198**

Oil spills. Report No. 7/76 describes spillages from oil pipelines in Western Europe. Stichting CONCAWE, Van Hogenhoucklaan 60, The Hague 2018, The Netherlands (write direct).

Ground water modeling. Prediction of ground water resource behavior. USGS Circular 737. Branch of Distribution, USGS, 1200 South Eads St., Arlington, VA 22202 (write direct).

The Wash Water Storage Scheme, a report on the ecological studies. The Wash is a bay on the North Sea coast of England. Natural Environment Research Council, Alhambra House, 27/33 Charing Cross Road, London WC2H OAX, England (write direct).

Noise definition. Documentation of research into noise pollution and its minimization. Office of Information, Air Force Systems Command, Andrews AFB, MD 20334 (write direct).

Clean Communities. Redesigned Clean Community System Bulletin illustrating behavioral approach. Keep America Beautiful, Inc., 99 Park Ave., New York, NY 10016 (write direct).

BOOKS

The Health of the Oceans. Edward D. Goldberg. 172 pages. The Unesco Press, 7, Place de Fontenoy, 75700 Paris, France. 1976. $9.25, paper.

This book takes a somewhat different look at ocean pollution by asking what should be known in relation to what is presently known, concerning alteration of the ocean's chemistry by man. It covers many types of marine pollution, and considers monitoring, prediction, and short- and long-term strategies for diagnosing and combatting pollution problems.

Environmental Monitoring. Stanton S. Miller, Ed. 197 pages. American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. 1976. $8.50 paper; $13.50, hard cover.

This work is a collection of features, "Outlook" stories, currents, interviews, and editorials concerning monitoring, that have appeared in Volume 7–10 of *ES&T* (1973–1976). It includes air and water, U.S. and international activities, businesses, techniques, and recommended books, as well as other related topics. Many aspects of monitoring are available virtually "at a glance."

Strategy of Pollution Control. P. Mac Berthouex and Dale F. Rudd. ix + 579 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1977. $18.95, hard cover.

This textbook emphasizes a problem-solving approach by innovation and planning, rather than simply surveying the pollution problem. It discusses fundamental concepts, strategic use of industrial chemistry, systems integration, separation systems, policy studies, and various other pertinent topics.

Oil Power. Carl Solberg. x + 326 pages. New American Library, Education Department, 120 Woodbine St., Bergenfield, N.J. 07621. 1976. $1.95, paper.

U.S. dependence on oil is all too well known. The author explains how this dependence arose, how the oil industry built such a tremendous empire, and why he believes that the "imminent fall" of this empire will occur.

Handbook of Industrial Noise Management. Richard K. Miller. 210 pages. The Fairmont Press, 134 Peachtree St. N.E., Suite 822, Atlanta, Ga. 30303. 1976. $19.95, hard cover.

Noise-abatement rules become ever more stringent. Thus, a book is needed that tackles subjects such as when noise control is not feasible; what a company should do in the face of an OSHA citation; how to estimate noise-control expenditures; workmen's compensation; and related matters. The author is frequently retained by companies needing solutions to noise-control problems.

IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Vol. 10. 353 pages. World Health Organization, 49 Sheridan Ave., Albany, N.Y. 12210. 1976. $15.20, paper.

This book discusses various naturally occurring substances that may present a carcinogenic threat. It is the outgrowth of a working-group session that met at Lyon, France, in October 1975.

Air Pollution. 3rd edition. Vol. III. Arthur C. Stern, Ed. xx + 799 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1976. $42.50, hard cover.

The third of five volumes, this work concerns itself with sampling and analysis, ambient air surveillance, and source surveillance. It covers particulate matter, hydrocarbons, sulfur compounds, nitrogen compounds, radionuclides, and other substances. Many aspects of monitoring, analysis, data handling, and modeling are exhaustively discussed.

Environmental Legislation. Mary Robinson Sive, Ed. xxxiv + 561 pages. Praeger Publishers, 200 Park Ave., New York, N.Y. 10017. 1976. $35, hard cover.

Over the last decade, environmental laws have become more extensive, complex, and involved. This book discusses many federal and state laws on air, water, noise, land use, and toxic substances, the National Environmental Policy Act, and other legislation, and explains them in easily understood terms.

Toxic Metals. Marshall Sittig. vii + 350 pages. Noyes Data Corp., Mill Rd. at Grand Ave., Park Ridge, N.J. 07656. 1976. $39, hard cover.

Toxic metals in the general environment and in the workplace are coming under accelerating regulation. This state-of-the-art book defines "toxic metals," and outlines removal techniques from air and water. It also provides a full discussion of metals from antimony through cadmium, lead, mercury, and zinc; other metals are covered as well.

Encyclopedia of Environmental Science and Engineering. J. R. Pfafflin and E. N. Ziegler, Eds. Vols. 1 and 2, 1091 pages, total. Gordon and Breach, 1 Park Avenue, New York, N.Y. 10016. 1976. $180, hard cover.

What was needed was to bring all key environmental areas into one single, readily available work. This encyclopedia fulfills that task, and covers many topics from Air Pollution Meteorology to Water Treatment. The advisory board and contributors comprise top authorities in many environmental fields.

Betz Handbook of Industrial Water Conditioning. 7th ed. Betz. 344 pages. Betz Laboratories, Inc., Somerton Road, Trevose, Pa. 19047. 1976. $15, hard cover.

While there are a number of books concerning water reuse, chemical treatment, cooling systems, and other water-conditioning topics, this book is prepared by a company with at least 50 years of experience in the field. It is illustrated with many photographs, flow diagrams, charts, and graphs, and is written in plain language by people with a practical industrial outlook.

Biological Monitoring of Water and Effluent Quality. Special Technical Publication 607. 242 pages. ASTM, 1916 Race St., Philadelphia, Pa. 19103. 1977. $24.25; add 3% for shipment.

This book evaluates present and future needs for biological monitoring, and for solving watershed monitoring problems. It assesses the current state-of-the-art, and aims at stimulating research in biological monitoring techniques. Work at many world laboratories is represented.

Resource Recovery and Conservation. James G. Abert and Harvey Alter, Eds. Quarterly journal. Elsevier/North-Holland Inc., 52 Vanderbilt Ave., New York, N.Y. 10017. $40.50/year.

This journal's scope includes many aspects of recovery of materials and energy from solid and fluid wastes. Water reuse is also covered. The editors are with the National Center for Resource Recovery (Washington, D.C.). Knowledgeable authors are invited to submit manuscripts to the editors.

Dust Extraction Technology. Wilhelm Batel; R. Hardbottle, translator. 272 pages. Radley Communications Limited, 509 Madison Ave., Suite 412, New York, N.Y. 10022. 1976. $31.25, postpaid.

Dust and particulate removal is an important aspect of health protection. This book covers dust removal technology as a unit process, explains processes occurring in dust removers, and describes all sort of dust extractors. Much practical application information is given, as are specific industry processes.

Refuse Separation at the Household Level: Effluent Charges. 17 pages. Center for the Study of Environmental Policy,

225 Pond Lab, University Park, Pa. 16802. 1977. $2.50.

Solid waste collection and processing would be greatly eased if different types were separated at the household level. Ellen Garvey and Glenn Harris, the authors, who are students at The Pennsylvania State University, suggest how this might be approached, and how charges could be levied upon those who fail to separate wastes. They explain how resource recovery could be enhanced and labor costs cut.

A Question and Answer Explanation in Lay Language of the Toxic Substances Control Act. Manufacturing Chemists Association, Publications Services, 1825 Connecticut Ave., N.W., Washington, D.C. 20009. $0.75.

This booklet explains the new Act, and lists who will be affected. General and specific actions necessary to comply with the law are outlined. Toxicological and premarket notification and testing, and other pertinent topics are discussed.

Recovery and Restoration of Damaged Ecosystems. John Cairns, Jr. et al., Eds. 448 pages. University Press of Virginia, Box 3608 University Station, Charlottesville, Va. 22903. 1977. $20 (Virginia residents add 4% sales tax).

In this work, international scientists contribute present theories, case histories, and questions related to restoration and recovery of damaged ecosystems. Among topics covered are stream/lake restoration; effects and cleanup of oil spills; plant and wildlife reintroduction; political problems of environmental legislation; and other pertinent subjects.

Water Treatment Plant Design. R. L. Sanks, conference director. 730 pages. Department of Civil Engineering & Engineering Mechanics, Montana State University, Bozeman, Mont. 59715. 1976. $20, three-ring binder.

This work comprises proceedings of the Fifth Environmental Engineers' Conference held last June. Subjects include water quality monitoring; ion exchange; design blunders; equipment selection; design criteria; reverse osmosis; coagulation and sedimentation; and other matters related to water treatment. Several points of view are expressed.

Genetics of Human Cancer. John J. Mulvihill et al., Eds. 523 pages. Raven Press, Publishers, 1140 Avenue of the Americas, New York, N.Y. 10036. 1977. $20.

One talks of environmentally-caused cancers, but is there some kind of predisposition? Are there genes gone awry? Here, some of the approximately 200 single-gene traits involving neoplasia are discussed, and concept of "cancer families" is addressed. Application of these ideas to population and clinical genetics is covered, in order to lead to a more basic understanding of carcinogenesis.

MEETING GUIDE

April 18–21 Atlanta, Ga.
Fifth Annual Industrial Pollution Conference. Water and Wastewater Equipment Manufacturers Association (WWEMA)

Write: Alan Krigman, Technical Program Coordinator, WWEMA, 7900 Westpark Dr., Suite 304, McLean, Va. 22101

April 20–22 Chicago, Ill.
Water Quality Surveys for 208: Data Acquisition and Interpretation of Nonpoint Runoff. Metropolitan Sanitary District of Greater Chicago and the Association Metropolitan Sewerage Agencies

Write: Andrew Ellicott, Association Metropolitan Sewerage Agencies, 1015 18th St., N.W., Washington, D.C. 20036

April 21–22 Pittsburgh, Pa.
Eighth Annual Pittsburgh Conference on Modeling and Simulation. University of Pittsburgh and others

Write: William G. Vogt or Marlin H. Mickle, Modeling and Simulation Conference, 348 Benedum Engineering Hall, University of Pittsburgh, Pittsburgh, Pa. 15261

April 23–27 Los Angeles, Calif.
23rd Annual Technical Meeting and Equipment Exposition. Institute of Environmental Sciences

Theme is "1977 Environmental Technology." *Write:* B. L. Peterson, Institute of Environmental Sciences, 940 E. Northwest Hwy., Mount Prospect, Ill. 60056

April 25–26 Oakland, Calif.
Eighth Annual Western Solid Waste Symposium. Governmental Refuse Collection and Disposal Association

Write: Robert Lawrence, City of San Leandro, 835 E. 14th St., San Leandro, Calif.

April 25–27 Lake Lanier Islands, Ga.
7th Annual Symposium on the Analytical Chemistry of Pollutants. American Chemical Society Divisions of Analytical and Environmental Chemistry, EPA and others

Write: Mrs. Elaine McGarity, Environmental Protection Agency, Environmental Research Laboratory, College Station Rd., Athens, Ga. 30601

April 25–27 Chicago, Ill.
1977 TAPPI Environmental Conference. Technical Association of the Pulp and Paper Industry (TAPPI)

Write: W. H. Cross, One Dunwoody Park, Atlanta, Ga. 30341

April 25–28 Madison, Wis.
Conference on Mechanics of Lake Restoration. University of Wisconsin–Extension

Write: Program Committee, Environmental Resources Unit, University of Wisconsin–Extension, 1815 University Ave., Madison, Wis. 53706

April 25–28 Boston, Mass.
1977 American Occupational Health Conference. American Occupational Medical Association and the American Association of Occupational Health Nurses.

Write: Howard N. Schulz, Conference Manager, American Occupational Health Conference, 150 N. Wacker Dr., Chicago, Ill. 60606

April 25–29 Valley Forge, Pa.
Filtration Day '77. Filtration Society

Write: Filtration Society, P.O. Box 126, Mount Holly Springs, Pa. 17065

April 25–29 Dallas, Tex.
Spring Convention and Exhibit. American Society of Civil Engineers

Environmental topics will be discussed. *Write:* American Society of Civil Engineers, 345 E. 47th St., New York, N.Y. 10017

April 26 Houston, Tex.
Enhanced Recovery of Oil and Gas: Potential and Prospects. The Energy Bureau, Inc.

Write: Robert W. Nash, Executive Director, The Energy Bureau, Inc., 101 Park Ave., New York, N.Y. 10017

April 26–28 Houston, Tex.
1977 National Conference on Treatment and Disposal of Industrial Wastewaters and Residues. U.S. EPA, the University of Houston, Gulf Coast Waste Disposal Authority and Information Transfer, Inc.

Write: Harold Bernard, Conference Manager or Susan Fields, Conference Coordinator, Information Transfer, Inc., 1160 Rockville Pike, Rockville, Md. 20852

April 26–29 Chicago, Ill.
First International Electric Vehicle Exposition and Conference. The Electric Vehicle Council

Write: Jerry Van Dijk, Charles Snitow Organization, 331 Madison Ave., New York, N.Y. 10017

April 27–29 Anaheim, Calif.
49th Annual Conference. California Water Pollution Control Association

Write: Michael Donovan, c/o Trotter-Yoder & Associates, 3730 Mt. Diablo Blvd., Lafayette, Calif. 94549

April 27–29 Syracuse, N.Y.
Ninth Annual National Waste Management Conference: Food, Fertilizer and Agricultural Residues. Cornell University

Write: Waste Management Conference, Cornell University, 207 Riley-Robb Hall, Ithaca, N.Y. 14853

May 1–4 Pittsburgh, Pa.
1977 Coal Convention. American Mining Congress

Write: American Mining Congress, 1100 Ring Building, Washington, D.C. 20036

May 2–4 Bethesda, Md.
Comparative Metabolism & Toxicity of Vinyl Chloride Related Compounds. National Institute of Environmental Health Sciences (NIEHS)

Write: Ms. Janet Riley, NIEHS, P.O. Box 12233, Research Triangle Park, N.C. 27709

May 2–5 Houston, Tex.
9th Annual Offshore Technology Conference. American Society of Mechanical Engineers (ASME) and others

Write: Gail T. Jannon, Manager, Industry Dept., ASME, 345 E. 47th St., New York, N.Y. 10017

May 2–6 Gatlinburg, Tenn.
Assessing the Effects of Power Plant Induced Mortality on Fish Populations. Oak Ridge National Laboratory, ERDA and the Electric Power Research Institute

Write: W. Van Winkle, Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tenn. 37830

May 3–4 Washington, D.C.
Energy Management in Buildings. New York University–School of Continuing Education

Write: Ms. Heidi E. Kaplan, Information Services Manager, Dept. 14NR, New York Management Center, 360 Lexington Ave., New York, N.Y. 10017

May 5 Houston, Tex.
Water and Wastewater Analyst Association's Annual Conference. Water and Wastewater Analyst Association

Write: Aubrey La Fargue, Box 9968, Houston, Tex. 77015

May 8–12 New York, N.Y.
68th Annual Spring Meeting. American Oil Chemists' Society (AOCS)

Environmental issues will be discussed. *Write:* AOCS, 508 S. Sixth St., Champaign, Ill. 61820

(continued on page 418)

May 8–13 Anaheim, Calif.
97th Annual Conference. American Water Works Association (AWWA)

Theme is "Water and the Environment." *Write:* Jerry Righthouse, Meetings Manager, AWWA, 6666 W. Quincy Ave., Denver, Colo. 80235

May 9–11 Miami Beach, Fla.
Waste Heat Management and Utilization. University of Miami, NASA, EPA and others

Write: Dr. Samuel S. Lee, Chairman, Dept. of Mechanical Engineering, University of Miami, P.O Box 248294, Coral Gables, Fla. 33124

May 10–12 West Lafayette, Ind.
32nd Annual Purdue Industrial Waste Conference. Purdue University

Write: Prof. A. J. Steffen, Room 310, Civil Engineering Building, Purdue University, West Lafayette, Ind. 47907

May 10–13 Ann Arbor, Mich.
20th Conference on Great Lakes Research. International Association for Great Lakes Research

Write: Dr. Andrew Robertson, Coordinator, 20th Conference on Great Lakes Research, GLERL/NOAA, 2300 Washtenaw Ave., Ann Arbor, Mich. 48104

May 17 Indianapolis, Ind.
Toxic Substance and Hazardous Materials Awareness Symposium. Central Indiana Technical Societies

Write: Don Griffin, 1512 Dukane Way, Indianapolis, Ind. 46224

May 17–19 Charleston, W.Va.
23rd Annual ISA Analysis Instrumentation Symposium. Instrument Society of America (ISA)

Environmental topics will be discussed. *Write:* Bill Wagner, Asst. Program Chairman, Union Carbide Corp., Box 8361, S. Charleston, W.Va. 25303

Courses

April 18–22 Cincinnati, Ohio
Legal Aspects of the Occupational Safety & Health Act of 1970. Dept. of Health, Education and Welfare/National Institute for Occupational Safety & Health

Fee: $250. *Write:* Robert A. Taft Laboratories, National Institute for Occupational Safety & Health, Division of Training & Manpower Development, 4676 Columbia Parkway, Cincinnati, Ohio 45226

April 20–22 Washington, D.C.
Occupational Safety & Health Act for Government Agencies, Course No. 338. The George Washington University

Fee: $365. *Write:* Continuing Engineering Education Program, George Washington University, Washington, D.C. 20052

April 21–22 Madison, Wis.
Energy-Industrial Facilities. University of Wisconsin–Extension

Fee: $125. *Write:* Charles E. Dorgan, Program Director, Dept. of Engineering, University of Wisconsin–Extension, 432 North Lake St., Madison, Wis. 53706

April 21–22 New York, N.Y.
Energy Conservation in Industrial Plants. New York University

Fee: $395. *Write:* Ms. Heidi Kaplan, SCENYU REGISTRATIONS, New York Conference Management Center, 360 Lexington Ave., New York, N.Y. 10017

April 25–26 Madison, Wis.
Heat Pumps. University of Wisconsin–Extension

Fee: $125. *Write:* Charles E. Dorgan, Program Director, Dept. of Engineering, University of Wisconsin–Extension, 432 N. Lake St., Madison, Wis. 53706

April 25–27 Washington, D.C.
Energy Conservation Opportunities and Guidelines for Existing Buildings. George Washington University

Fee: $365. *Write:* Continuing Engineering Education Program, George Washington University, Washington, D.C. 20052

April 25–28 Boston, Mass.
Source Sampling for Particulate Pollutants, Course No. 450. Air Pollution Training Institute

Fee: $140. *Write:* Registrar, Air Pollution Training Institute, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

April 28–30 San Antonio, Tex.
Fourth National Noise Symposium. University of Texas at San Antonio

Fee: $200. *Write:* George D. Vaughan, Director, Continuing Education Service, University of Texas Health Science Center at San Antonio, 7703 Floyd Curl Drive, San Antonio, Tex. 78284

May 5–6 Chicago, Ill.
Environmental Law Course. Government Institutes, Inc.

Fee: $295. *Write:* Nancy McNerney, Government Institutes, Inc., 4733 Bethesda Ave., N.W., Washington, D.C. 20014

May 9–10 Madison, Wis.
Energy—Commercial Buildings. University of Wisconsin–Extension

Fee: $125. *Write:* Charles E. Dorgan, Program Director, Dept. of Engineering, University of Wisconsin–Extension, 432 N. Lake St., Madison, Wis. 53706

(continued on page 421)

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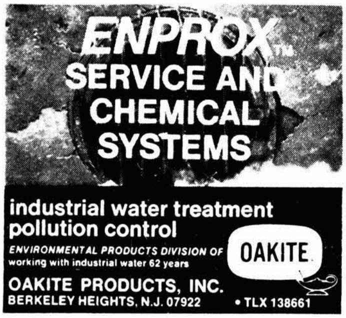

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Application of Air Quality Simulation Modeling for Impact Assessments and Impact of Point Source Emissions on the Air Environment. University of California–Davis

Fee: $375. *Write:* University of California–Davis, University Extension, Davis, Calif. 95616

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Performing and Observing Source Sampling. Ecology Audits, Inc.

Fee: $200. *Write:* Billy J. Mullins, Jr., Vice President & General Manager, Ecology Audits, Inc., 11061 Shady Trail, Dallas, Tex. 75229

May 14–15 and 21–22 Pittsburgh, Pa.
New Concepts of Occupational Medicine Under OSHA. Industrial Health Foundation.

The course, to be conducted on two consecutive weekends, is designed for physicians in industry. Fee: $325 (member); $385 (nonmember). *Write:* Dr. Daniel C. Braun, President, Industrial Health Foundation, 5231 Centre Ave., Pittsburgh, Pa. 15232

Call for Papers

May 1 deadline
Alternatives for Cadmium Electroplating in Metal Finishing. Dept. of Commerce/National Bureau of Standards, EPA and others

Conference will be held October 3–6 at Gaithersburg, Md. *Write:* Edward J. Dyckman, Defense Industrial Resources Support Office, Dwyer Building, Cameron Station, Alexandria, Va. 22314

May 15 deadline
Fourth Joint Conference on Sensing of Environmental Pollutants. American Chemical Society, EPA and others

Conference will be held November 6–11 at New Orleans, La. *Write:* Dr. V. E. Derr, Program Chairman, 4th Joint Conference on Sensing of Environmental Pollutants, National Oceanic and Atmospheric Administration, ERL-WPL, R 45.3, Boulder, Colo. 80302

May 15 deadline
ASTM Symposium on Aquatic Toxicology. Committee E-35 on Pesticides and its Subcommittee on Safety to Man and Environment/American Society for Testing and Materials (ASTM).

Conference will be held October 31–November 1 at Cleveland, Ohio. *Write:* Leif L. Marking, Fish Control Laboratory, P.O. Box 862, La Crosse, Wis. 54601

CLASSIFIED SECTION

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ENVIRONMENTAL MANAGERS

Immediate openings for senior managers experienced in process/control technology, environmental planning or marketing of professional services, to be involved in definition and solution of environmental, resource and energy-related problems or development of new business therein. 8–10 years' project management or marketing experience, with strong consulting background. Send resume, including salary history and present requirements to: **Marilyn J. Kay, Personnel Director**

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ADMINISTRATIVE OFFICER 1 AIR QUALITY MONITORING

Wisconsin Department of Natural Resources, Milwaukee. Starting pay between $1489 and $1654 per month. Duties: Direct and coordinate air quality monitoring program for SE Wisconsin. Supervise three units in repair, maintenance, operation, data collection, and quality assurance for multi-station monitoring network. QUALIFICATIONS: BS in chemistry, chemical engineering, or atmospheric science and 5 years progressively responsible experience in analytical chemistry and instrumental analysis. Experience should include work with and understanding of data quality assurance. At least two of the five years shall have included supervisory experience. Experience in continuous air quality monitoring and current EPA approved air monitoring methods and electronic data acquisition and verification is highly desirable. *Apply by April 29.* State application forms available from **Mrs. Ruth Anderson (608-266-1407), Department of Natural Resources, Box 7921, Madison, WI 53707.**

Environmental Chemist: 2 year General and Technical College has a projected opening in the area of Chemical Water and Air Analysis. Beginning September 1, 1977. Present Environmental Control Program has strong cooperation with the E.P.A. and other Governmental and Industrial agencies. Academic position at the Instructor or Assistant Professor level requires a minimum of an M.S. or higher degree. Teaching experience on the freshman and sophomore level is also highly desirable. Salary commensurate with background, degree and experience. Send complete curriculum vita to: **Prof. N. L. Reuter, Chairman, Chemistry Department, Raymond Walters College, 9555 Plainfield Road, Cincinnati, Ohio 45236.** (Equal Opportunity/Affirmative Action Employer.)

Applications accepted for 14 days after publication date.

ENVIRONMENTAL ENGINEERS

We have many position openings in U.S. for professionals experienced in the design, application and/or sale of air, water or waste pollution control equipment, chemicals and systems. Client companies pay fees. Send resume & salary history in confidence to Roger M. Hoffman.

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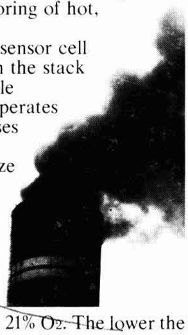
It helps your
cranes keep their sea legs.

MSA INSTRUMENTS in the NEWS

COMBUSTION CONTROL• HEALTH & SAFETY • ENVIRONMENTAL• PROCESS

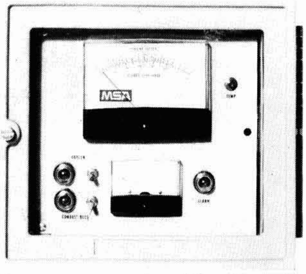
On-stack oxygen analyzer saves fuel while measuring emissions.

MSA's new Model 803 Oxygen Analyzer was designed to solve many of the practical operating problems that you face in accurate monitoring of hot, dirty flue gases.



The Model 803 sensor cell mounts directly on the stack for shortest possible sampling line. It operates hot to keep all gases above their dew points and minimize plugging. The stabilized fuel cell sensor measures oxygen—not an effect of oxygen—so it produces a high-level signal. It analyzes 0.1% to 21% O2. The lower the oxygen concentration, the better the readability on its logarithmic scale.

Users of the Model 803 Oxygen Analyzer have commented on its fast response to changes in furnace operating conditions. And its close matchup between oxygen readings and theoretical calculation of O_2 content gave them fuel savings that paid for the analyzer quickly.



One operator of a 120-million Btu heater fired with fuel oil had a history of plugging troubles with other analyzers until he tested a Model 803. Now he reports, "This was the first analyzer installed that successfully worked when we merely followed instructions."

Another company, operating several marine-style 20,000-lb steam boilers, liked the demonstration of the 803 so well that they kept the demonstration model and ordered another for full evaluations.

If you need a dependable, accurate oxygen analyzer that stays out of trouble and saves you fuel, get details on the Model 803.

Circle No. 18

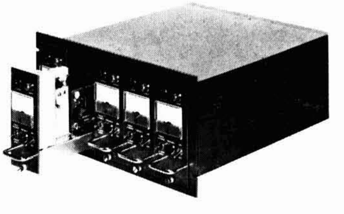
Make sure/check MSA

Factory cuts fuel bill for dryer in half by monitoring combustible solvents.

The printing and dyeing operation in a fabric finishing plant involved the removal of mineral spirits from the cloth in a gas-heated dryer. Insurance regulations called for control of solvent vapor below 15% LEL. To achieve this level, the operator was forced to change air in the dryer as often as four times a minute—wasting fuel and heat.

An MSA instrument specialist studied the problem, came up with a two-point combustible gas analyzer system with sensors mounted in strategic monitoring points. The MSA instrument system monitors and measures the concentrations of combustible vapors so accurately that the dryer can be operated safely at much higher solvent concentrations. That translates directly to fuel savings.

The analyzer was set up to provide an audible alarm at 20% LEL; if the vapor concentration reaches 25% LEL, it automatically shuts off the gas, starts the fan, and increases the amount of makeup air to reduce vapor concentration. Result: The plant is a safer place to work. The insurance firm has since increased the allowable top limit to 30% LEL. The company saved half of its annual fuel bill for operating the dryers, and savings have already paid for the MSA instrument system. The plant is planning a similar installation in its finishing department.

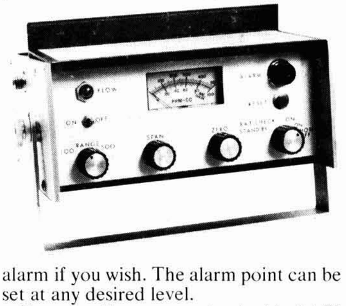


Circle No. 19

New carbon monoxide indicator joins the MSA portable instrument line.

MSA now offers a battery-operated CO indicator that will work a full shift between charges. The Portable Carbon Monoxide Indicator, Model 70, provides over eight hours of detection of airborne CO in the 0-100 parts per million (ppm) range or 0-500 ppm range.

The Model 70 helps you keep track of "the silent killer" in garages, loading docks, coke plants, open-hearth furnaces, manufacturing plants, refineries and similar locations. When CO concentrations reach preset TLV levels, the instrument provides a visual alarm, plus an audible alarm if you wish. The alarm point can be set at any desired level.



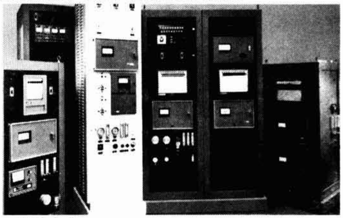
For compliance records, the Model 70 CO Indicator is calibrated for use with a 1-volt recorder, or it can be adapted easily to other recorders.

Recharging is by 115-volt ac source or from a 12-volt battery. Maintenance on this solid-state unit is simple. A calibration check kit is available for reproducible testing and certification.

Ask your MSA instrument specialist for more details or write for literature.

Circle No. 20

Questions about OSHA limits on hazards?



MSA has some answers.

Your workplace atmosphere must meet OSHA regulations on over 500 gas, vapor and dust hazards whose TLVs (Threshold Limit Values) have been determined.

MSA has the spot and continuous monitoring instruments to help you detect most of the hazards on the official list.

One way to start on your hazardous-atmosphere monitoring problems is to discuss them with an MSA field representative.

Circle No. 21

Call us (we're in the Yellow Pages). Or circle the appropriate Reader Service Number. MSA Instrument Division, 600 Penn Center Boulevard, Pittsburgh, PA 15235.