Environmental
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OCTOBER 1977

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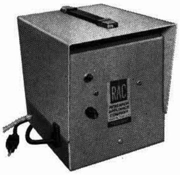

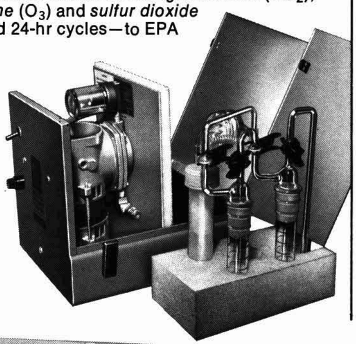

CIRCLE 14

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CIRCLE 15

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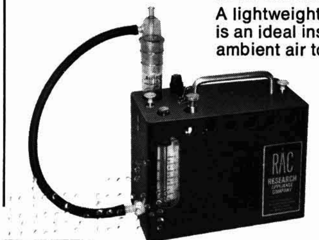

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CIRCLE 18

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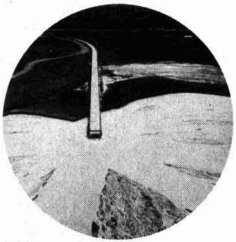
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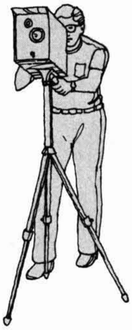
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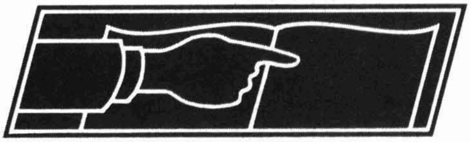
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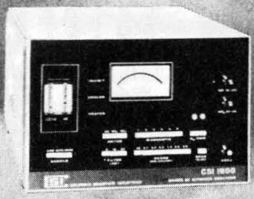

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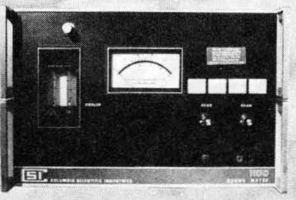

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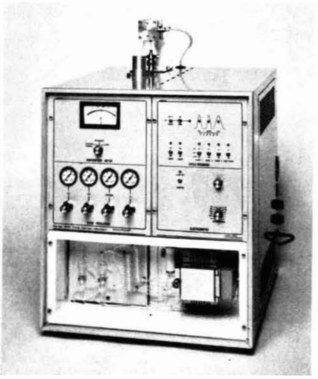

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The search for alternatives

It is easy to be critical of the environmental cleanup strategy the U.S. Congress has imposed upon responsible administrative agencies at the Federal, State, and local levels. This regulatory strategy centers on a standard setting—monitoring—enforcement process coupled with uniform effluent and emission requirements. A July 1977 report by the U.S. General Accounting Office notes that this process (*a*) requires complicated interactions among Congress, administrative agencies, and the courts, (*b*) denies individual citizens free choice of levels of environmental quality, (*c*) requires sound scientific research, and (*d*) relies too heavily on political and administrative simplicity in the form of uniform control requirements.

This strategy is only one of several that might be used, and is undeniably impractical and costly. Alternative economic strategies such as subsidies and tax incentives may help alleviate immediate pollution problems, but are less effective for controlling production than outright charges or waste disposal fees paid by polluters. In the latter case the increased production cost is passed on to the consumer at the marketplace in a more internally consistent manner.

Specific charges for each polluter could be set by permitting dollar values to be determined by the market mechanism. This process has long been advocated by resource economists as an effective alternative strategy for allocating limited resources among competing uses.

At least two factors prevent this process from being useful at this time. First, the general level of environmental degradation that would be acceptable to people of the United States is unknown. Second, a sufficiently powerful central agency would have to be given clear authority to manage the fundamental rights to air and water resource use and thus function as a trustee for the public good. Environmental law is a rapidly changing field and substitute concepts for "property" and "ownership" are evolving but, in general, our legal and social systems do not presently accommodate the role of such a trustee.

It is safe to say that without implementation of the current strategy we would presently have no cleanup. It's tempting to criticize politicians but in a major sense they, more than anyone, have done their jobs. They have listened to the public outcry and responded accordingly. More enlightened strategic responses will require more enlightened research findings, more sophisticated legal concepts, and a more well-defined set of environmental values than present public attitudes indicate.

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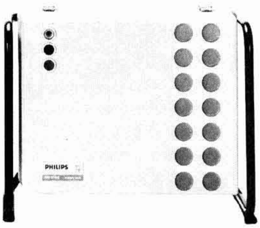

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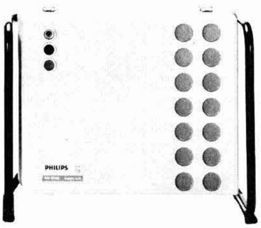

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The Clean Air Act amendments mandate a National Commission of Air Quality that is to deliver its final report to Congress by August 1980. The 11-member commission will consist of 7 public members to be appointed by the President and four congressional members. By March 1, 1978, the commission must report on the implications of meeting or not meeting NO_x standards from mobile sources. By August 7, 1979, the commission must report to Congress on several issues, including: the significant deterioration of air quality; the economic, technological and environmental consequences of achieving or not achieving the goals of the Act; and unregulated air pollutants that cause or may cause a threat to public health and strategies for controlling these pollutants. The commission is authorized to spend $10 million.

The national cost of complying with the federal air and water acts will be nearly $450 billion over the decade 1976–1985, according to the EPA. The cost of meeting the requirements of the Clean Air Act is estimated at $264 billion and for the Water Pollution Control Act Amendments, $183 billion. This amount is equal to about 2% of the GNP summed over the decade. According to another cost analysis, the cost to industry under Carter's dictum that new major air pollution sources use best-available control technology is about $7.5 billion through 1985, with utilities accounting for $3.5 billion.

The EPA has called into question the safety of 123 pesticide ingredients that it has already approved. The reason for this is that the agency has uncovered deficiencies in some of the thousands of health effects tests done by Industrial Bio-Test Laboratories (IBT) between 1970–72. The deficiencies occurred in the way the animal toxicological studies were performed and in discrepancies between the raw data and that reported to the EPA. As a result of these deficiencies, EPA has asked 31 pesticide producers to review and certify the accuracy of all pesticide tests done for them by IBT.

NOAA manager Park

NOAA has a new Ocean Dumping Program, and directing it will be P. Kilho Park, an expert on the chemical aspects of the marine environment. Dr. Park's group will study industrial waste sites in the Gulf of Mexico, off the island of Puerto Rico and off the Atlantic seaboard adjacent to the New York Bight. NOAA is currently studying the ecological effects of marine pollution in the N.Y. Bight. On the subject of ocean dumping, the EPA reports a substantial drop, almost 24%, in the total tonnage dumped annually off the Atlantic and Gulf coasts since the institution of the agency's ocean protection program in 1973. For 1976 alone, the EPA reports a decline of nearly 600 000 tons, which resulted from the denial of 155 dumping permits. Nevertheless, the tonnage dumped in 1976 was substantial: more than 8 million tons.

The Dept. of the Interior is studying sites for the proposed Intermountain Power Project (IPP), a 3000 MW coal-fired plant that will produce electricity for southern Calif., Nevada and southern Utah. The proposed site for the project is now 9 mi from Reef National Park and 50 mi from Canyonland National Park. Interior is gathering environmental (air quality) information to determine whether this proposed site should be moved farther away from the two national parks in south central Utah. Interior Secreatry Cecil D. Andrus has stated that his department will cooperate with Utah in the search for alternative sights, if such are feasible, and he has urged IPP to cooperate in this effort. Andrus is attempting to avoid another Kaiparowits situation.

Regulatory processes to control hazardous materials will be reformed according to a cooperative effort of four federal agencies. The heads of OSHA, EPA, FDA and the Consumer Product Safety Commission cited seven initiatives that could streamline regulatory processes and maximize resources. Among these initiatives are: the development of compatible testing standards and guidelines; development of risk/safety and health assessment methodology; information sharing possibly leading to a national information system on toxic substances; possible cooperative research and regulation development; possible compliance and enforcement cooperation; and possible interagency communication efforts. The agency heads said: "We have agreed to examine, assess and redesign, if necessary, the processes by which we collectively regulate chemicals . . ."

STATES

Seven Michigan companies agreed to pay the state $3.6 million in penalties for missing the July 1 deadline under P.L. 92-500. This sum is believed to be the largest out-of-court settlement reached by any state for failure to meet this deadline. The seven firms are: Abitibi Hardboard ($200 000); Detroit Edison ($120 000); Ford Motor Co. ($1.6 million); Great Lakes Steel ($1.25

million); Harbison Walker (agreed to install a $600 000 cooling tower plus a $5000/day penalty); Hooker Chemical ($75 000); and Pennwalt Chemical ($150 000). In addition to the above companies, U.S. Steel agreed to restore Swan Lake over a 2-y period; the cost of this restoration is estimated at $200 000.

Pascagoula, Miss., has had a taste and odor problem in its drinking water that is believed to have resulted from improper curing of lining material used to coat two of the city's water tanks. The coating material, a bituminous coal tar pitch, had EPA's approval, but this was withdrawn on the advice of the FDA. The larger of the two tanks was properly cured but has never been filled for service, and because it is not in service, the city has a chronic water supply problem. EPA tests of water temporarily pumped into this larger tank have unveiled 14–17 compounds, some chlorinated, at the <10 ppb level. The significance of these compounds is not known because their source is not known; they may not all have come from the lining material.


Texas governor Briscoe

Texas has two new wetlands laws: The Coastal Coordination Act of 1977 and the Coastal Wetlands Acquisition Act. Signed into law by Gov. Dolph Briscoe, the coastal coordination act provides for the protection of coastal wetlands, regulates the discharge of dredged materials and provides for annual studies of problems in coastal natural resource areas. The Texas Natural Resources Council is directed under the law to review the state's coastal programs and to recommend measures to resolve coastal problems. The council must submit a report with recommendations every two years to the governor and the legislature. The acquisition act gives the state General Land Office the authority to designate and certify coastal wetlands and grants the state Parks and Wildlife Dept. the authority to acquire interest in the preserve and manage the coastal wetlands.

An Indian reservation in Montana is the first site in the U.S. to be redesignated a Class I PSD area by the EPA. The Northern Cheyenne Indian reservation in southeast Montana, near Montana Power Co.'s Colstrip mine-mouth power plant, requested the Class I prevention of significant deterioration area designation to preserve their lifestyle and prevent further degradation in air quality.

U.S. Steel will install water pollution control facilities at its Gary, Ind., plant by August 31, 1985. The steel company agreed with Illinois and the Chicago Metropolitan Sanitary District on an $84.7 million clean-up program that will ensure that all process water discharges into Lake Michigan will be eliminated and all process water recycled by the 1985 date.

The District of Columbia will build a sludge-composting facility at its Blue Plains sewage treatment plant, which treats two-thirds of the area's (D.C., Md., and Va.) wastewaters. The District of Columbia received $5.7 million from the EPA toward the construction of the $7.2 million composting plant in the Oxon Cove area of Prince Georges County Maryland. This facility, the largest composting plant in the U.S., will convert sludge, the semisolid residue of the treated sewage, to organic mulch. Eventually a market will be sought for the mulch. Currently the Blue Plains sewage treatment plant produces 700 tons of sludge daily, but this is expected to increase to 2000 tons daily within the next 10 years. Today, the sludge is hauled to upper Montgomery County, Md., for burial.

MONITORING

Switched-on marine photobacterium? Only when no pollutants are present. Under development, under EPA contract, is a combined photobacterium and marine algae that glows brightly in waters that do not contain herbicides, pesticides and heavy metals. In "clean" marine waters, the algae consume carbon dioxide and give off oxygen; the photobacterium then uses this oxygen to emit light. The amount of light reflects the extent of pollution.

The discoverer of sensitive methods for PCB analysis has won the SOCMA Gold Medal for 1977. The medal and a $1000 honorarium were presented to the EPA's Gilman Veith by the Synthetic Organic Chemical Manufacturers Association (SOCMA) last month. Veith's work led to methods that could determine sub-μ/L amounts of polychlorinated biphenyls (PCBs) in natural waters. These methods, in turn, established that PCBs, found in fish, in Lake Michigan, and other waters, came from industrial and domestic effluents. PCB's are now determined by spectrochemical techniques that grew out of Veith's work from the late 1960s to the present.

The EPA has designated a new method for measuring ozone concentrations. The new equivalent method is an automated method, an analyzer that operates on the principle of the chemiluminescence of rhodamine B, an organic dye. The method is Philips PW9771 03 analyzer (Philips Electronic Instruments, Inc., Mahwah, N.J.).

TECHNOLOGY

Oily wastewater treatment is enhanced by ultrasonics, which can reduce operation/maintenance costs by up to 80%. The U.S. Navy Civil Engineering Laboratory (CEL, Port Hueneme, Calif.) developed a portable two-stage, 100-gpm system whose fiberglass coalescing elements are cleaned ultrasonically. This achievement is a "first", according to CEL. First, a gravity separator removes gross oils and heavy suspended solids. Then, a steeply inclined, parallel plate pack removes most other oils and solids by means of cross-flow; these coalescing elements are ultrasonically cleaned and reused. A third stage can be used for further approaches, such as air flotation, active carbon, or a coalescer pack. CEL estimates possible cost reductions from $13/1000 gal to $2.50/1000 gal.

One way to destroy chemical plant odors is by fume incineration of the offending material. That is the way Peabody Engineering (Stamford, Conn.) handled odors from a wastewater treatment plant at Armak Chemical Co. (McCook, Ill.). A 20-ft by 9-ft fume incinerator uses air streams from the biological lagoons as combustion air (18% oxygen). Waste gases from other plant sources are introduced after venturi scrubbing for partial ammonia removal. Then the incinerator, using gas or fuel oil, can handle over 17 000 acfm of the off-gases at about 1500 °F. Waste heat is recovered to provide approximately 15% of plant process stream; this offers a 5-year pollution control system payback.

The use of tall stacks is not always a satisfactory air pollution control measure. This is a conclusion derived from a 5-year study by 11 European members of the Organization for Economic Cooperation and Development (OECD). The study showed that SO_x pollutants from fossil fuel show up thousands of km from

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their points of origin, even when they were emitted from stacks more than 100 m tall. The belief that such tall stacks would so disperse such pollutants that their concentration would be negligible beyond 100 km was found to have little basis in fact. Among events leading to the refutation of this belief has been destructive acid rains and snows, especially in Norway and Sweden, and perhaps, Scotland.


Checking out solar cell voltage

New solar cells that combine liquids and solids may be more economical than all-solid solar cells. These new cells, known as liquid-junction cells, could also be very efficient, according to Bell Labs (Murray Hill, N.J.), their developer. A cell has two electrodes in a water-based solution. One electrode is a semi-conductor. The other can be made of a variety of common metals, or of carbon. Sunlight would cause a current flow between electrodes, much like in an ordinary wet-cell battery. With relatively inexpensively-made polycrystalline cadmium selenide as the semiconductor, light-to-electricity conversion efficiency was 5.1%. Presently, many single-crystal solids are more efficient, but they are also much more costly.

A large reverse osmosis (R/O) water desalination plant is now on stream on New Providence Island in the Bahamas. The plant "sweetens" brackish lake water of 9000–17 000 ppm salinity, about one-half that of seawater. Built and operated by Envirogenics Systems Co. (El Monte, Calif.), the plant has 270 pressure vessels containing 1080 spiral elements with 98% salt rejection. It is operated at 800 psi. Product water is 300 ppm total dissolved solids. The R/O plant is instrumented so that only one man per shift is needed to operate it. It is run under contract to the Bahamian Ministry of Works.

A solution to the problem of dust and sludge can also offer lead and zinc recycling. These fine-particle wastes result from pig iron and steel production, and are normally dumped. However, Lurgi Gesellschaften (Frankfurt, W. Germany) found that the old Waelz Process (rotary kiln) for beneficiating zinc-poor ores could be adapted to the waste dusts and sludges. For example, zinc is volatilized, collected as fine dust, and then reprocessed. Generally, the same holds true for lead. Moreover, iron values, previously lost in the wastes, can be recovered. The concept has been proven at Berzelius Metallhütten GmbH for a long time, and is now amenable to commercialization, according to Lurgi.

INDUSTRY

The first major contract for a solid waste-fired steam plant and recycling installation was let by Hooker Chemicals and Plastics Corp., to Foster Wheeler Corp. (FW, Livingston, N.J.). FW will build the boiler system and supply pollution control equipment for Hooker's plant at Niagara Falls, N.Y. The waste will fire two 1250-psig, 750 °F units, each to produce 300 000 lb/h of steam continuously. FW estimates that the energy saved will be enough to heat 37 000 homes over a 20-year period. Also, solid waste disposal problems of participating communities will be vastly alleviated. The steam units will satisfy all codes and emission requirements, and can use any fuel combination in the boilers.

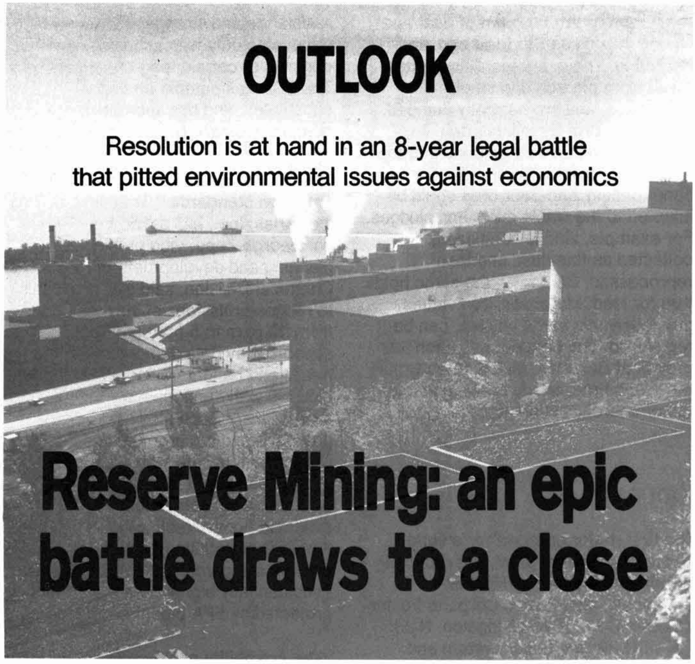

TCA President Ferguson

Substitutes for asbestos, a suspected carcinogen, have been developed by the Tile Council of America (TCA, Mahwah, N.J.). The TCA is a trade association of the ceramic tile industry. Its president, Thomas Ferguson, Jr., said that these substitutes are suitable asbestos replacements not only for the tile industry, but for other industries as well. One substitute is the incorporation of magnesium compounds into hydraulic cements, to give sag resistance and strength previously obtainable only with asbestos. Another consists of certain long-chain polymers. The TCA has patents on these substitutes, and has submitted numerous patent applications.

"Retain the present vinyl chloride emission standards." That is what PPG Industries, Inc., has asked the EPA to do. George Zapp, vice president of planning and development of PPG's Chemical Division, said that proposals to reduce emissions of vinyl chloride from 10 ppm to 5 ppm are "not supported by data demonstrating the needs and benefits," and would burden industry with "unnecessary regulations." Zapp also said that the present standard, promulgated last October 21, is safe with respect to public health, and is the minimum emission level achievable with best available control technology. He noted that PPG is installing equipment to meet present standards, and that its cost is "substantially higher than that originally projected by EPA planning documents."

"The credibility of the national cleanup program may not survive, particularly in states . . . which have conscientiously pursued the national goals," Louis Guy, Jr., of the consulting engineering firm of Patton, Harris, Rust & Guy (Farifax, Va.), said. As one reason, he offered "endless EPA red tape" in the construction grant program. He also scored "the abysmal failure of Congress to authorize funding." Guy noted that states that did the best job of spending federal funds to attain the most cleanup momentum must bring programs to an abrupt halt; only "slowpoke states with unspent money from earlier years can bridge the 1977 funding gap." Citing other faults in funding, Guy said that "the private sector, including my consulting engineering firm, takes it on the chin again."

More economical, less energy consumptive stack gas SO_2 removal was announced by Allied Chemical Corp. (Morristown, N.J.) scientist Kang-Jen Liu and his associates at the 174th national ACS meeting at Chicago, Ill., in late August. "A new engineering principle," based on construction of man-made macromolecules in the form of very specialized membrane films, is the key. SO_2 is removed from stack gas by a basic solution which, when used up, is mostly sodium bisulfite ($NaHSO_3$). At 110 °F, the $NaHSO_3$ is split into basic sodium sulfite and hydroxide solution for reuse as an SO_2 absorber. The other product is sulfurous acid, from which SO_2 can be generated. Operating cost reductions of as much as 43% may be realized.



OUTLOOK

Resolution is at hand in an 8-year legal battle that pitted environmental issues against economics

Reserve Mining: an epic battle draws to a close

The year is 1871. Prospector Peter Mitchell meanders along the Beaver River in a northwesterly direction and notices wild excursions of his compass' needle in the region of Vermilion Lake, Minnesota. There he digs and finds taconite rock, a mixture of mostly silica and magnitite.

That first hole has since been vastly enlarged. It is now the Peter Mitchell Mine, near Babbitt, Minn., the site of Reserve Mining Company's taconite mining operations. That first hole has also erupted into the nation's longest running environmental controversy—a contorted saga played out in state and federal courts for nearly eight years.

Disposal: by gravity

Reserve, a jointly owned company of Republic and Armco Steel Corporations, mines this low-grade iron ore at Babbitt, but it transports the ore 47 miles by rail to Silver Bay on the shores of Lake Superior. There it processes the taconite into higher grade iron-ore pellets that are destined for the nation's steel mills in the East. For every ton of pellets processed, more than two tons of silica waste tailings are formed . . . and disgorged into a delta in the lake.

Reserve's mining operations are successful: The company produces nearly 15% of the domestic ore used by the nation's steelmaking industry. Each day, Reserve produces about 30 000 tons of iron-ore pellets, and discharges 67 000 tons of tailings suspended in 2 million tons of water to Lake Superior. The tailings in this slurry contain trace amounts of several metals, but mostly they contain billions of amphibole silicate—asbestiform—fibers. The heavier fibers sink by the force of gravity to the Great Trough at the bottom, but the lighter, buoyant fibers travel with the prevailing currents to Duluth, Minn., and Superior, Wis., to become part of these cities drinking water.

Fibers similar to those found in Lake Superior are known to cause cancer in humans when inhaled. Whether they induce cancer in humans when ingested is not known with certainty today. Reserve has only been dumping these fibers into the lake for 22 years, not enough time, the experts say, for cancers to become evident.

Dr. Arnold Brown, a noted pathologist and chairman of the department of pathology and anatomy at the Mayo Clinic, testifying as the federal court's expert witness, cited no evidence for an increased incidence of cancer in Silver Bay or Duluth attributable to the inhalation or ingestion of asbestos fibers prevalent in the air and water of these cities. But, he testified, "The fibers should not be present in the drinking water of the people of the North Shore." Further, he continued: "[The] presence of a known human carcinogen [airborne asbestos fibers] . . . is in my view a cause for concern, and if there are means for removing the human carcinogen . . . that should be done."

Conflicting issues

Health—the threat of cancer—is merely one aspect of the Reserve case. Other elements of the dilemma include jobs, profit, public interest and quality of life. The issues evoked during various phases of the case include air and water pollution, land-use practices and conservation of natural resources. But in the end, the most telling factor may be economics.

Reserve applied for the original permits to mine taconite at Babbitt and process the ore at Silver Bay in 1947. The water of Lake Superior was needed to satisfy the huge water requirement of the processing technology then available, and to provide an inexpensive disposal site for the waste tailings.

Reserve was the first major company to seek to develop taconite mining operations in the state, and actually received some encouragement from Minnesota. In fact, the company was granted its permits in November 1947. But the first tailings discharge to the lake did not occur until October 1955. Reserve has been dumping 67 000 tons of tailings daily into the lake since then, for nearly 22 years.

Aside from the matters of air and water pollution, not matters of any great moment back in 1947, Reserve has been a "good citizen." The company has supplied more than 3000 jobs (with a total payroll of $55 million in 1975) to residents of what otherwise would be an economically depressed area. The firm paid nearly $16 million in local and state taxes in 1975, and purchased $45 million worth of materials and supplies in the state that year. Further, the company built homes, schools and churches, and parks and roads in Silver Bay, admittedly to attract workers to that remote area over 20 years ago.

Indeed, closing down Reserve's operations would, in the words of the court, "have a disastrous effect on the economic well-being of families dependent on Reserve for a livelihood." But in 1976 that is precisely what Reserve threatened to do if it was not granted permits to build an on-land disposal basin at Milepost 7, about four miles from its Silver Bay processing plant along its railroad spur.

Once residents of Silver Bay were made aware of the health hazards they were vehement in their desire that Reserve discontinue dumping the tailings into Lake Superior, *but* they also wanted their jobs preserved. The uncertainty of whether Reserve would remain open or not has had its sociological repercussions on Silver Bay residents. One state public interest group has reported increases in the divorce rate and juvenile delinquency as well as an upsurge in alcoholism and drug dependencies.

The legal saga

The legal battles—first focusing on air and water pollution then turning to questions of health—have been circuitous and convoluted. The arguments and counterarguments have taken first a state case, then a federal case and finally a combined case through the state courts up to the state supreme court and, on the federal side, from the U.S. District Court to the U.S. Circuit Court of Appeals and back again. Possibly the only surprising aspect of the case is that it never reached the U.S. Supreme Court.

Among its many interesting twists, the case has witnessed a major company—Reserve—shut down by court order for two days only to be reopened at the order of a federal appeals court; a federal judge—Miles Lord—removed on the grounds of "gross bias" against the firm; the polluting company fined nearly $1 million for violating the state water permit *and* for withholding evidence; and the U.S. Army Corps of Engineers called in to supply filtered drinking water to the citizens of Duluth and other north shore communities.

That Reserve's disposal practices wreaked havoc on Lake Superior was documented as early as 1969. That year the Department of the Interior's Taconite Study Group found that the tailings were accelerating the eutrophication of the lake and that they were crossing state boundaries to contribute to interstate pollution. The study group recommended that an on-land disposal facility be constructed within three years.

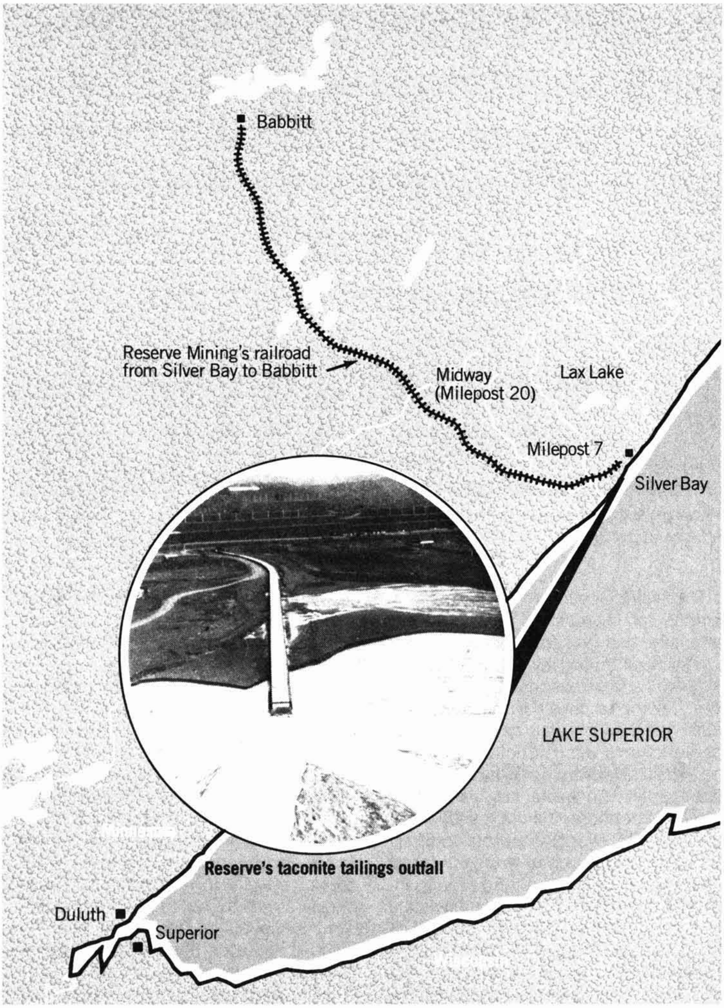
That same year, 1969, the Minnesota Pollution Control Agency (MPCA) promulgated an effluent limitation standard for suspended solids; Reserve's tailings slurry violated this standard. However, the Lake (County) District Court ruled that this regulation was not applicable to Reserve. The state and the MPCA appealed this decision to the state supreme court. The year was 1971.

By now the U.S. EPA had been formed and at its helm was William Ruckelshaus. Ruckelshaus ordered Reserve to develop a water pollution abatement program within six months or face a court challenge. Reserve submitted an unacceptable plan and, in February 1972, the federal government filed suit against the company in U.S. District Court alleging violations of sections of the Refuse Act of 1899, the Federal Pollution Control Act of 1965 and the Common Law of Nuisance.

Federal/state cases joined

In April 1973, U.S. District Court Judge Miles Lord joined the state and federal cases. The list of co-plaintiffs had expanded to include the states of Minnesota, Wisconsin and Michigan and the MPCA; five environmental groups became intervenors.

On April 20, 1974, finding that Reserve's air and water discharges endangered the health of the people of Silver Bay, Duluth and other north shore communities, Lord ordered the processing plant shut down. Two days later, the U.S. 8th Circuit Courts of Appeals stayed (reversed) Lord's order, an action that sent more than 3000 people back to work.



Within another year's time the federal appeals court made its stay permanent. It ordered Reserve to take immediate steps to curb its air pollution and gave the company a "reasonable time" to convert to an on-land tailings disposal system.

Under this order, Reserve submitted a plan to construct a tailings basin near Lax Lake at Milepost 7 along its railroad spur. The Dept. of Natural Resources (DNR) and the MPCA, the state agencies that must permit the site, set up a special permit hearing in June 1975 to review Reserve's application.

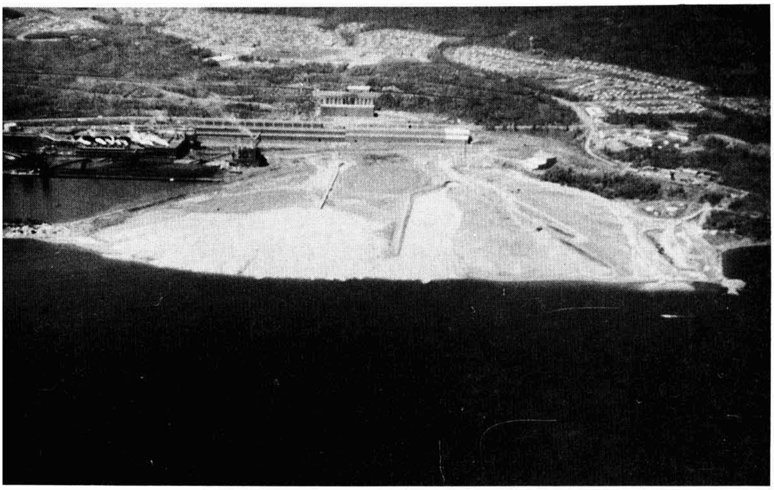
On November 14, 1975, Judge Lord made some injudicious remarks in court. Two months later he was removed from the case to be replaced by the chief federal judge in Minnesota, Edward Devitt.

Eight months later, on July 7, 1976, Judge Devitt, noting that no agreement on an on-land disposal site had been reached, ruled that Reserve must cease discharging its tailings into Lake Superior at midnight July 7, 1977. The federal appeals court later affirmed Devitt's order but inserted the loophole that "upon changed circumstances" (an agreed upon on-land disposal site), the closure order could be modified.

Permits denied

There was no agreement on an on-land site because a month earlier, the DNR and the MPCA, on the recommendations of the special hearing officer, Wayne Olson, refused to grant Reserve permits for the Milepost 7 site, citing instead Milepost 20, a site midway between Babbitt and Silver Bay, as a more desirable site from an environmental standpoint.

Reserve claimed that the Milepost 20 site was economically infeasible and threatened to shut down its Silver Bay operations if Milepost 20 was forced on it. The company took its case to the Lake District Court, which, in January 1977, ruled in its favor.



Water pollution. *Reserve's pelletizing plant at Silver Bay with its tailings slurry outfall to Lake Superior*

The district court said that denial of permits for Milepost 7, even after the company had accepted the stringent conditions imposed by the MPCA, was "unlawful and unreasonable." The agencies' failure to consider the economic consequences as well as the environmental effects was "directly contrary to the decision-making process . . . mandated under Minnesota law," the court ruled. Furthermore, the court stated, use of Milepost 20, which Minnesota could not deliver since it is primarily federal forest land, "would open up a third area to industrial mining uses and is inconsistent with principles of land-use consolidation."

The state agencies appealed the district court's ruling to the Minnesota Supreme Court. On April 8, 1977, the Supreme Court, without opinion, affirmed the lower court's ruling.

On May 26, 1977, Judge Devitt modified his original order to allow Reserve to continue discharging tailings into the lake until April 15, 1980, pending the firm's completion of an on-land disposal basin at Milepost 7, which is expected to take about 34 months. Devitt stipulated that the company had to begin construction on the basin by August 1, with or without state and federal permits.

The on-land disposal plan

Reserve estimates that it will spend in excess of $300 million in the construction of a dam-enclosed basin large enough to contain the pelletizing plant's daily wastes. The construction plans call for the closing off, with dams, of two ends of a valley to form the disposal basin.

As for the tailings themselves, all possible precautions are to be taken to eliminate or reduce fugitive-dust problems. All fine particles are to be submerged under water, and all exposed tailings are to be vegetated. In addition, all access roads and all exposed surfaces of tailings are to be sprayed with water and nonpolluting chemical binders.

The tailings basin is to be operated as a closed system. To assure that it is, Reserve and its parent companies—Armco and Republic Steel—must set up routine air and water monitoring programs.

At the Silver Bay plant itself, Reserve has agreed to install, at an estimated $35 million, emission abatement equipment on the stacks, and to modify certain processing steps to lower emissions. These measures are expected to lower the ambient air levels of amphibole fibers—amosite asbestos fibers that are potentially carcinogenic.

In the latter part of July, the MPCA and DNR issued the necessary permits to Reserve. Since Milepost 7 is also the site of navigable U.S. waters, the U.S. Army Corps of Engineers must also permit the site. The Corps has not yet done so, but the permit is expected to be forthcoming.

The case could now be considered closed except that Reserve has contested some of the conditions stipulated in the MPCA and DNR permits. At press time, Reserve said that the parties were close to settlement on the DNR permit; but still under contestation in the district court in Duluth are the air and water quality standards for fibers stipulated in the MPCA permit.

According to John-Mark Stensvaag, special assistant attorney general, the MPCA permit now states that the ambient air should contain no more fibers than found in the city of St. Paul. Reserve now wants to insert a clause that refers to "a control city such as St. Paul"; such a control city standard will apply, Reserve contends, only if the state proves the necessity for this based on "reasonable medical theory." The MPCA says that it has already proved this point in court. Reserve is also seeking, according to Stensvaag, to enlarge the definition of "fiber" to include fibers that are not necessarily harmful to health.

Reserve had agreed that the tailings basin would be a closed system, which would easily meet the nondegradation water quality standard stipulated in the permit. Now Reserve claims that the MPCA cannot set a water quality standard based on a natural background level of fibers because no medically significant level for fibers in water has yet been established.

At press time, the three-judge panel hearing the case in Duluth had not ruled on the contested matters. Lawyers for both sides would not hazard a guess on when settlement would be reached. Also, still in the balance is the acquisition of the land on which the basin will be built. Reserve must acquire the land from the state, the federal government and one private citizen, a physician who owns a 1200-acre tract at this site. Under a 1945 Minnesota law, the mining company can acquire private land through the process of eminent domain, which Reserve will use if it cannot purchase the land outright.

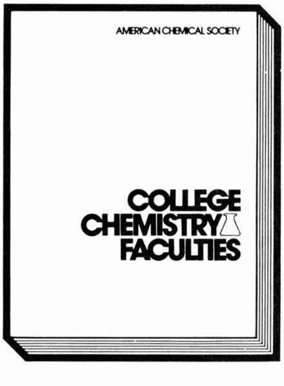
Resolution? maybe . . .

After nearly eight years of litigation, and the expenditure of millions of dollars in legal fees, this epic environmental case appears near legal resolution. However, the asbestiform fiber count in the air of Silver Bay and in the waters of Lake Superior is still excessively high. Reserve can continue to discharge its wastes into the lake until 1980, and the residents of the north shore communities, in the meantime, are forced to drink filtered water. But, the company has agreed to modify its processing plant to lower the ambient air level of these potentially pathogenic fibers, and it has begun preliminary construction of an on-land waste disposal basin.

The people of Silver Bay must surely feel that their public interest has been upheld. They, in this otherwise economically depressed area, still have jobs. And with yearly earnings close to $15 000, real estate taxes averaging only $150 yearly and mortgage payments as low as $60/month, they can continue to live the "good life."

Certainly the issues of an unpolluted environment, health and economics thrashed out in the Reserve case will serve as precedents in legal battles likely to crop up in the future. The solutions worked out in this case may be found not satisfactory in future confrontations. Nevertheless, the approaches to resolution developed here may serve as guideposts in future environmental/economic conflicts, and herein may lie the justification for this eight-year legal marathon.

LRE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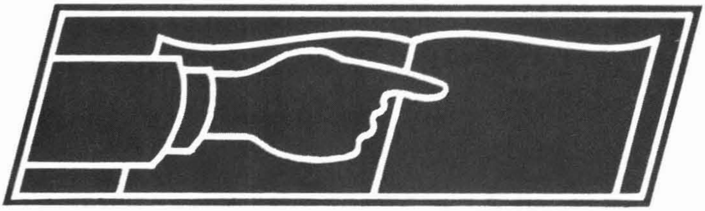
Streamlining the EIS process

Preparing environmental impact statements is often a costly, time-consuming, duplicative task. A noted information systems expert suggests ways to improve it



What have the forthcoming 1980 Winter Olympic Games, electric power stations, and human heart pacemakers in common? Pursuant to the National Environmental Policy Act (NEPA), they, like many other projects and installations, require an environmental impact statement (EIS). "A heart pacemaker, too?" someone asks incredulously. "Yes, if it is plutonium powered," you answer. "Now where would I find an EIS on heart pacemakers?" is the next question you hear. The same question is asked for many other EISs.

Where, indeed? Until very recently, EISs were essentially "fugitive literature." Abstracts and indexes did not exist in reference works such as *Chemical Abstracts, Engineering Index, Environmental Abstracts,* or similar publications. "EISs were not 'findable' like, say, works on bridge building. Once in a while an odd one could turn up, but you can't count on it," Saul Herner, president of Herner and Company (Washington, D.C.), told *ES&T*.

Meets a need

Thus, it was evident that a real need for a way to locate EISs existed, and Herner resolved to meet it. The effort began in 1975 and came to fruition with the first issue in January of this year of *EIS: Key to Environmental Impact Statements,* a monthly publication. Basically, *EIS* provides indexes to subjects involved in the statements it covers, geographical areas affected by proposed actions, and the agency/organization responsible for each statement. Next, abstracts, in readily understandable language, of draft and final EISs are presented, along with descriptive material and a location guide. There is also a monthly editorial, highlighting the contents of each *EIS* issue, and discussing topical environmental items.

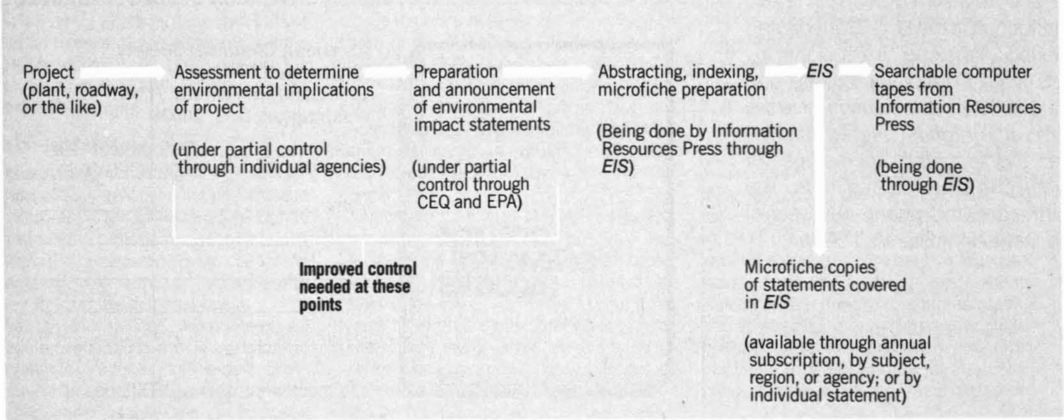
EISs from before this year are not left out of Herner's activities. A division, Information Resources Press (IRP), which publishes *EIS,* is preparing abstracts of all of the approximately 4500 final EISs that appeared since NEPA (1969–1976). These will be available in bound volumes, microfiche, and computer-searchable tapes. As of press time, IRP had about 30 commitments for this past EIS service, as well as approximately 600 subscriptions to *EIS*. The 1969–1976 compilation service will cost a client approximately $10 000; annual subscriptions to *EIS* are $200. Of the 100 employees at Herner, 10 work full time on the compilation service and *EIS*.

Saul Herner gave *ES&T* an example of the benefit that easy location of an EIS might confer. Suppose there is a power plant in northern New Mexico, for which an EIS was written. Now, plans are made to build another one in a nearby geographically and climatologically similar area of southern Colorado. If an assessment and EIS must be done from "scratch," one must figure on the efforts and expenses of some 3–6 man-months of well-paid experts' work; indeed, that is what usually happens.

However, if the New Mexico EIS can be found without a wild agency-to-agency goosechase, some of the information there could well ease and shorten the task of preparing the Colorado EIS. For example, some of the required data for Colorado could be included by reference to like information in the New Mexico statement. This is one of the aims that *EIS* and the service for past EISs is out to accomplish.

Improved control

Streamlining the "findability" and retrievability of EISs is one of IRP's goals; another is to improve control over the EIS process and over the assessment process leading to statement preparation. At present, "control really begins after an EIS



Streamlining the EIS process

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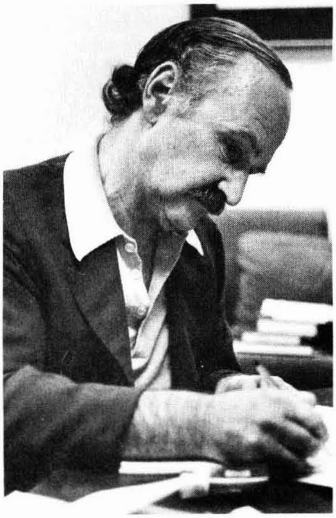
is issued, at which time it is examined by EPA for completeness and adherence to NEPA requirements, and is announced by the Council on Environmental Quality (CEQ) in the *Federal Register,*" Herner told *ES&T*.

Herner believes that EIS management control and public awareness should start at the onset of environmental assessment activity. Thus, for example, if an impact is very negative, that fact should soon be apparent, and the project could be dropped before much money is spent on an EIS and other items. Also, the EIS preparation process could be standardized and improved, especially with respect to cost and time, and elimination of much redundancy of similar statements.



Saul Herner
"More effective controls are needed"

Herner suggests tighter control at the assessment, preparation, and announcement steps, with reasonable allowances for differences between projects or products and agency requirements. Indeed, IRP is planning to work with a U.S. government agency to find ways of establishing and optimizing this control.

The requirement for preparing assessments and EISs is here to stay. But the job can be made more standard, simpler, less time-consuming, less costly, and less duplicative.

Oh yes, about the curious EIS on heart pacemakers—it is described in *EIS,* February 1977, p 57. Or, for more detail, the whole statement, issued July 1976 (Final), can be found at the Office of Nuclear Material Safety and Safeguards, Nuclear Regulatory Commission, Washington, D.C., now a part of the new Department of Energy. It also can be obtained from IRP, which sells microfiche and paper copies of all impact statements it covers. JJ

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CIRCLE 5 ON READER SERVICE CARD

Oil burning can be less "fuelish"

Sometimes its use is unavoidable. In that case, more efficient combustion is desired. Here are some methods than can reduce air pollution, as well

Whether one likes it or not, oil will continue to be a major fuel for the industrial economies of many countries, including this one, for the foreseeable future. Thus, it makes sense to try to find cleaner, more efficient ways of burning it. Indeed, it would be ideal if fuel oil could be made to burn as cleanly as natural gas does. That may be too much to expect, but perhaps one can come close. One approach was devised during the late 1960s by Sonic Development Corp. (Upper Saddle River, N.J.); that technique uses ultrasonics to atomize even very heavy oil. The oil burns with a clear, hot, blue flame, which resembles that of natural gas.

Another method with a touch of *savoir-faire* involves emulsification of fuel oil with water. It was developed by Société Nationale ELF Aquitaine (Courbevoie, France), and is being used at several hundred heating plants and industrial installations in Europe.

It's built to "soot"

The clean burning of fuel oils by emulsification with water is accomplished as follows: Light or heavy fuel oils are emulsified by a proprietary method developed by ELF. Then any mechanical pulverization or atomization burner can receive the emulsion and the necessary air. Regulation of emulsion flow can be automatic or manual. The emulsion is atomized by a pneumatic technique. This emulsion process can be installed in new or existing heaters, ovens, furnaces, or kilns, ELF's Claude Delatronchette told *ES&T*.

The proportion of water in the emulsion varies according to the application. It can reach 60% for furnace applications and 20% for boiler applications. The burning process is suitable for all mechanical atomization burners, and achieves a 90–95% reduction in soot and unburned solids, according to ELF. These lower unburned solids and soot deposits eliminate the need for soot collectors, cut operating costs, and help to produce a constant energy output. The oil flame is more uniform in temperature, more "filling", and more radiating, because of enhanced combustion.

Knocks down NO_x

Instead of 20–30% excess air, which oil burners normally use, the ELF burner concept uses 10% excess air. This use of less excess air leads to a slightly lower flame temperature, and attenuation of temperature gradients in and around the flame. These features, in turn, bring about a reduction in NO_x emissions which, according to ELF, can be 10–50%. For example, when heavy fuel oil is burned in conventional systems, NO_x can be 4200 mL/kg of oil burned, the company estimates. With a heavy oil/water emulsion fuel, NO_x emissions could be 3800 mL/kg. With lighter oils, NO_x emission could be markedly reduced.

Likewise, soot from heavy fuel oil alone could be 140 g/10 h of burning, while unburned solids are 7500 mg/kg of oil burned. With the emulsion, soot is reduced to 5 g/10 h, and unburned solids to 200 mg/kg.

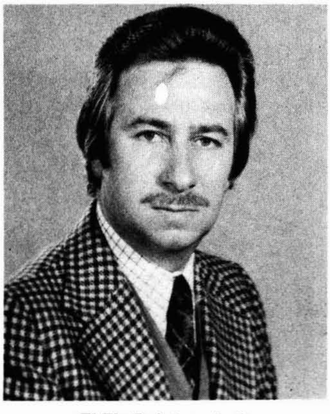
Less SO_3

There will always be some small amounts of residual sulfur, even in low-sulfur, or well-desulfurized oils. When the oil is burned, the sulfur will become SO_2, upon which emulsification can have but little effect. Other means must be used to bring SO_2 within legal or regulatory tolerances, as necessary.

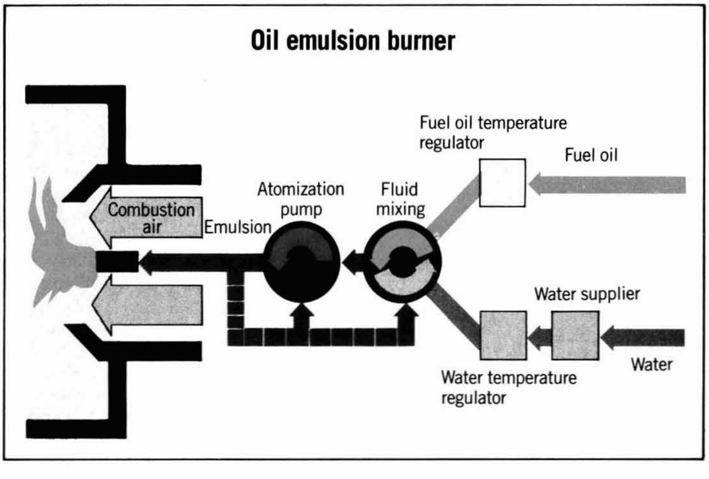
However, with conventional oil burning, some SO_2 will be "upgraded" to SO_3. This SO_3, generally 1–5% of the SO_2 generated, can cause severe flue and stack corrosion. According to ELF, the use of emulsions can reduce SO_2-to-SO_3 conversion by more than 50%, in many cases.

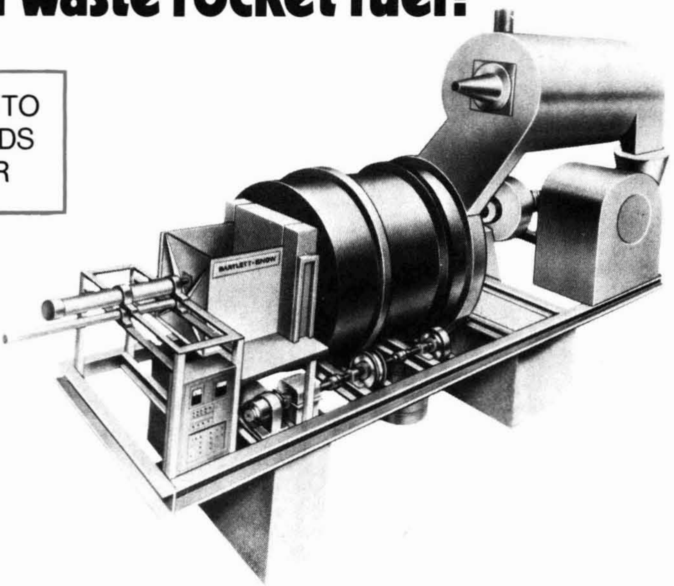
Thus, oil burners can be made to use fuel oils in a cleaner and more efficient manner. An example is the ELF fuel/air/water burner for furnace applications, which emulsifies the oil in the burner. Atomization by ultrasonics is another technique, and there might be more approaches extant, or under development. Be that as it may, oil will be needed in the economics of most countries and economic sectors for many years to come. For this reason, the optimization of its combustion efficiency serves the causes of fuel conservation and pollution abatement well.

JJ



ELF's Delatronchette
clean fuel oil use with savings

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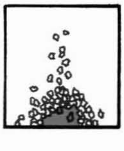
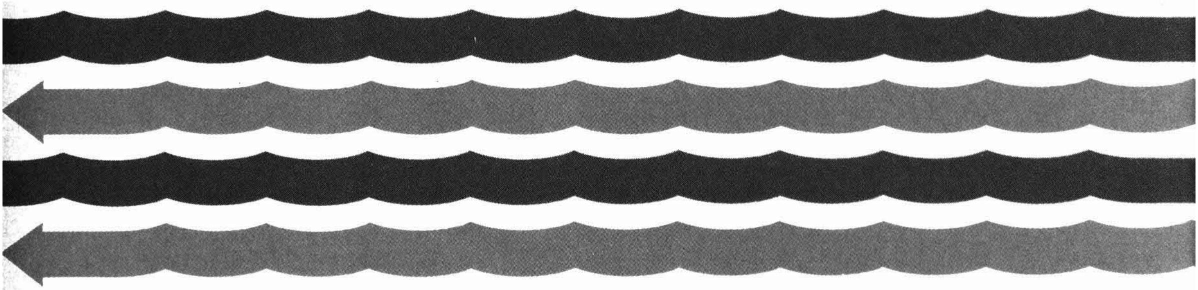


FEATURE

Converting wastes to raw materials

By redesigning processes to recover wastes, Philips, an international company, has reduced the discharge of pollutants to the environment and achieved economic benefits

J. J. A. Ploos van Amstel and J. Lee-Frampton
N. V. Philips' Gloeilampenfabrieken
Eindhoven, The Netherlands



Because of its international structure, Philips' efforts to minimize pollution from its own production processes cannot be restricted to meet only local or national regulations. Therefore, the company has established a system of international cooperation to ensure that its antipollution measures and procedures are fully implemented and coordinated throughout the company.

Tests and intensive research have led to a wide variety of antipollution measures; for example, redesigning certain production processes and equipment to reduce pollution is accorded much attention throughout the company. The overall aims are to prevent pollution whenever possible, and to minimize waste products. This involves policy bodies, steering groups and supervisory boards extending as far as Philips' national organizations, product divisions, plants and departments. In addition, there is very close liaison with local, regional, national and supranational authorities concerning standards and specifications.

The data collected from these sources are analyzed by a team based in Eindhoven, The Netherlands, charged with the responsibility of integrating Philips' total environmental policy. The team, known as the Pollution Control Office (PCO), a department of the building design and plant engineering division, is headed by Ploos van Amstel. The PCO acts as a consultant to Philips' plants to reduce pollution from these plants as low as possible, and certainly within legally imposed limits. This office also encourages the development of processes and products that are harmless to the environment. Finally, the PCO supervises the implementation of all antipollution measures it imposes.

Putting the policy to work

In the past, measures taken by Philips were chiefly directed at solving existing environmental problems. It was typical of those times that the product and the process were accepted, while the consequences to the environment were simply dealt with by purification techniques which, in turn, often created environmental problems of their own.

Experience showed that it was frequently possible to obviate environmental problems by making slight modifications to the product and/or process. For instance, a large waste-burning incinerator at Maarheeze (near Eindhoven) was shut down only two years after its start-up because the company had learned to do without it, simply by redesigning the polluting elements of the processes involved. In practice, of course, it is not possible to prevent all environmental problems. Compromises among technical, economic and ecological factors are often necessary to bring about an optimum solution.

Water pollution

Almost every industrial process uses water and yet it is now becoming apparent that water is by no means a limitless resource. Already the scarcity of good-quality groundwater and the increasingly high costs involved, especially where wastage is concerned, has forced the company to economize. The Water Economy Committee (WEC) at Philips' headquarters at Eindhoven has been systematically studying ways to reduce wastage.

The WEC found that four factory sites in Eindhoven, with a total annual water consumption of 12–13 million m^3, use 60–70% of the water for cooling purposes. Needless to say, the committee first directed its attention to the main water consumers such as the boiler houses and engine rooms. And, in the meantime, compressors and vacuum pumps have been fitted with thermostatic control valves to regulate the intake of water, the maximum permissible cooling-water temperature being set in advance. The committee is convinced that water economy can be achieved in most instances simply by fitting inexpensive control valves. Only when huge quantities are involved, or where the installations are complex, are cooling towers or water-cooled refrigerators ever necessary. Machines do not require a constant supply of cooling water and, simply by installing relatively inexpensive on/off valves in the cooling-water supply, the water otherwise consumed during the nonoperational period can be saved.

Generally, the cooling-water temperature can rise to some 40 °C without causing harm to machinery; yet, in the past, it was the practice to drain off this water as soon as its temperature had increased by about 2 °C. The new arrangements have already led to a saving of about 3 200 000 m^3 water per year in the Eindhoven area. Figure 1 gives an idea of the costs involved. Figure 2 graphically depicts the reduction in groundwater usage.

Even simple modifications and/or redesign have led to important savings of raw materials that otherwise would have been discarded as waste products. The costs of the new approach often proved less than those of the original, with the result that production costs were reduced in a significant number of instances.

Plant modification/redesign

Below are several examples of process changes that have resulted in savings of water and chemicals.

Etching incandescent lamp filaments

With the help of small and almost completely closed etching cabinets, it is possible to use much smaller absorption towers for the removal of the nitrous gases generated during etching. The quality of the filaments produced by this new method is the same as with the old one. Total investments required in the new system are 20% of those necessary for a conventional system with a conventional pollution abatement system.

Washing black-and-white television tubes and screens of color television tubes

This is done with diluted hydrofluoric acid that dissolves a thin film of glass on the inside of the tube. This dissolved glass is converted into compounds that are only partly soluble in the acid; the nonsoluble compounds crystallize out as a granular product. Because of the harmful effect of these solid compounds on the washing process, the saturated solution is drained off.

It was found that the precipitate can be removed from the bath quite simply by filtration. Accordingly, the baths need no longer be drained off, and all that is necessary is to keep them at the appropriate concentration by the addition of concentrated hydrofluoric acid. This modification of the process has reduced the consumption of hydrofluoric acid by half.

Washing color-TV tube cones

In the past, this was also done with dilute hydrofluoric acid. At present, a soda solution is used for washing. The effect of this process modification is that the process has become cheaper, safer and environmentally acceptable.

Washing silver-cupped lamp envelopes

For this, a dilute mixture of hydrofluoric acid and hydrochloric acid was used in the past. The hydrochloric acid was added to increase the solubility of silicofluorides, so that the use of the etching bath could be prolonged. The introduction of a system of filtering (as described already with respect to the washing of TV tubes and screens) extends the life of the bath considerably. The savings: 100% hydrochloric acid and 70% hydrofluoric acid. Subsequent experimentation obviated the need for hydrofluoric acid in the washing process.

Etching silicon wafers for transistors

This takes place in a mixture of nitric acid and hydrofluoric acid. The solutions are drained off after one use. It was soon discovered that a bath could be used four to ten times, depending on the type, without any change in the electrical properties of the product. Furthermore the spent etching agent does not have to be drawn off, but can be sold to the stainless steel industry. All these and other process modifications have led to a reduction in the consumption of hydrofluoric acid by about 75%.

Etching of printed wiring panels

The technology used to the present day is based on a phenolic paper laminate coated with a copper film. In principle, all this copper is etched away with the exception of the pattern of conductors. In the past, very diverse etching agents were used for this: chromic acid; ferric chloride; ammonium persulfate; sodium chlorite; or cupric chloride. The result was a wide range of specific waste materials, often with the possibility of poor recovery of copper. After many years of research and pilot

FIGURE 1

Cost of water used at the Eindhoven plants

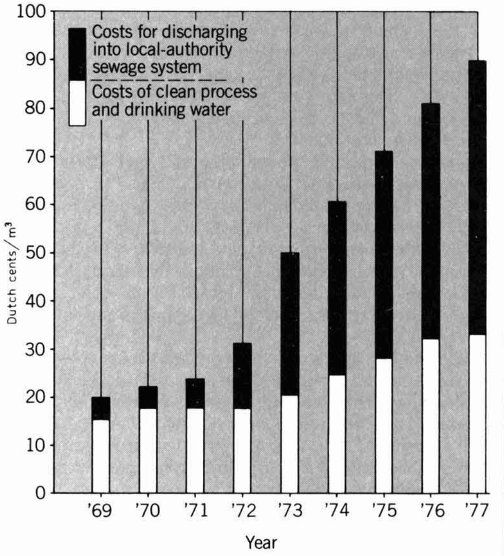


FIGURE 2

Reduction of ground water usage (Eindhoven plants)

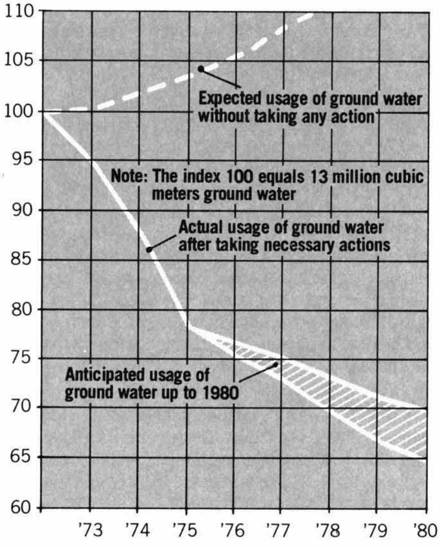
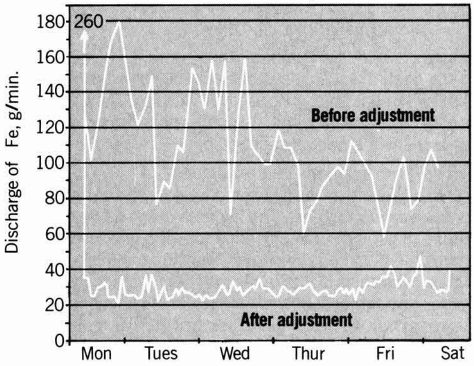


FIGURE 3

Adjustment of process equipment leads to a decrease in iron discharge



production, many print departments (within Philips) have mainly adopted cupric chloride as an etching agent, which allow the economical recovery of copper from the spent etching baths. This eliminates pollution problems. Meanwhile, work is proceeding on a new technology, a process in which copper is deposited out only where conductors are desired.

Recovering metals from rinsing water

Since some metals have been found to be substances that may be particularly dangerous to health, it is vital to prevent their discharge to the environment. That this can be achieved by process modification is shown by the following example in which the discharge of metals with the flushing water is reduced to a minimum, and there is increased efficiency in the use of copper, silver, tin and zinc.

After components have been copper-plated by electrodeposition of the metal, they are passed through a series of rinsing procedures to remove the bath liquid still adhering to them. Most of that liquid will be removed by the first rinsing and the "pollution" there will be relatively high. Instead of discharging this water to sewers as was formerly the case, the rinsing basin is now linked to a closed recirculation system in which the copper is removed from the rinsing water electrolytically. The system is designed to ensure that the quality of the rinsing water remains as high as possible. The plates on which the recovered copper is deposited are re-used in the actual copper-plating bath, so that copper, too, is partly recycled.

Recovery of phosphors in the manufacture of color-TV tubes

At a particular phase in this process, the screens are covered with a phosphor suspension, which is then made to adhere to the glass in a particular pattern by means of ultraviolet light.

The non-radiated surface area (approx. two-thirds) is then rinsed with water. In the original process setup, the rinsing water and the suspension were discharged to sewers. It later proved possible to separate the suspension from the rinsing water by centrifugation, and to make it (the suspension) suitable for re-use by passing it through a regeneration process.

This modification has already been introduced for red and green phosphors and arrangements are now being made for the blue phosphor.

Phosphate discharge down by 90%

Wastewater containing phosphate is discharged in the preparation of fluorescent powders for fluorescent lamps. The phosphate was formerly removed in a purification process in which lime was used. This prevented the eutrophication of the water by the phosphates, but it meant that the phosphates had to be removed in the solid state (by precipitation).

In the meantime a much better solution has been found. The process now includes a post-reaction phase in which 90% of the formerly discharged phosphates are converted into fluorescent powder, with the result that the phosphate discharge has been decreased by the same amount. At the same time the efficiency of the process has increased by 10%.

Masks for color TV tubes

Figure 3 shows the advantage of careful adjustment to process equipment. In this particular example, the process relates to the discharge of iron during the etching of TV masks, and shows how the process drastically improves from a "peak-to-valley" situation prior to adjustment to an almost completely smooth one after adjustment (nearly 80% improvement).

Regeneration of solvents

Efforts to promote process efficiency via solvent regeneration are, of course, not new, but people have been insufficiently aware of the possibilities that exist for regeneration. Since 1971, the increasing shortages of raw materials, the resultant steep increase in prices, and concern for the environment have been additional reasons for favor of regeneration of solvents on a larger scale.

Before 1971, only four solvents were regenerated in the Dutch plants. They included trichloroethylene and perchloroethylene. Now there are many, including freons and alcohols, and the quantities regenerated are increasing all the time.

Regeneration also reduces costs. Re-use means that far smaller quantities of solvents are brought in, while the costs of transport and destruction by incineration also disappear. Also, it has been found that a regenerated agent used for one process, can also be used as a raw or auxiliary material in another process.

The cost of regeneration is almost always lower than the sum of the additional purchases and transport and incineration costs, but the actual relation will depend on the market situation. Between 1968 and 1971, the various Philips' establishments in The Netherlands (except the Pharmaceutical-Chemical Product Division, which has its own facilities) submitted 300 000 L of solvents per year for regeneration. The corresponding figure in 1972 was 450 000 L; in 1973, 700 000 L; and in 1974, 1.3 million L.

Reversing a management decision

Late in 1970, one of the plants of the Pharmaceutical-Chemical Products Division was faced with serious complaints about the smell resulting from the discharge of waste to surface water in the neighborhood. Although there had been no change within the plant, and the wastewater discharges were still the same, they appeared to be at least partly the cause of the smell. Later, the explanation was found to be that the dock into which the waste was discharged was being deepened. This led to a lack of oxygen and to fermentation processes in the deeper water, which meant that malodorous gases were being released. Under the pressure of public opinion, Philips decided to build a biological purification system.

The plan was divided into two phases. Phase 1 was the reduction of wastewater discharge from 6600 tons COD/y to 3300; and Phase 2 will be the reduction of wastewater discharge from 3300 to not more than 500 tons COD/y.

An initial inventory soon enabled a distinction to be drawn between the large quantities of chlorides that were discharged with the cooling water, and the organic substances that were used in the processes or were left behind as residues after them.

The large quantities of chloride originated in the spring water used. So, in cases where the temperature of the cooling water did not need to be high, use was made of river water. Also, since the capital costs involved in a purification plant depend partly on the amount of wastewater to be treated, a study was made of the feasibility of recirculating the cooling water. This proved to be a definite possibility.

The second inventory took more time and was more difficult. Department after department and process after process was examined. Almost all the processes are chemical, and a certain degree of recirculation of solvents is built in. Nevertheless, the analysis of the data yielded greater insight into the processes and into the possibilities for recirculation and regeneration. The processes were consequently modified in that direction.

These activities also led to the conclusion that more attention would have to be paid to the use and misuse of chemicals, particularly those previously used for other processes. This has led to unexpected savings.

The effect of process modifications, already referred to, soon became apparent. By the end of 1973, pollution had been reduced to 2400 tons COD/y. This result was achieved by analyzing the volume, the COD content and the pH for every process layout, and adapting the processes on the basis of that knowledge.

For example, in the production of an ester, an intermediate step in the synthesis of vitamins, the first layer was drawn off for regeneration of acetone. The other layers were discharged to the sewage system. Analysis showed that the first layer contained much less acetone than had been assumed, and that the second and third layers contained far more than anyone realized. Fractionating the second and third layers yielded a reduction of 300–400 tons COD/y.

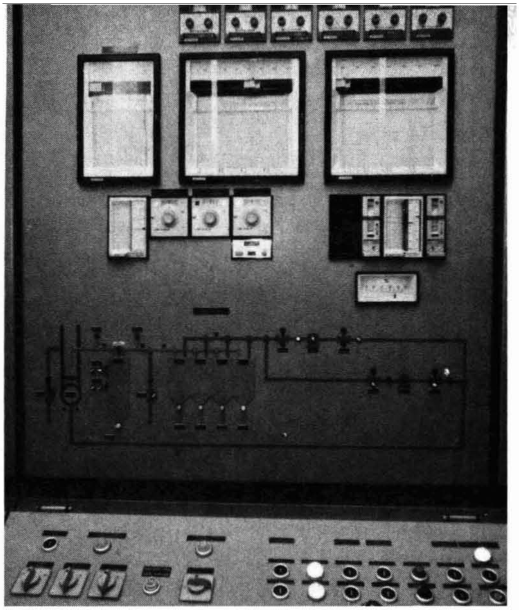
In similar processes, no attempt was made to recover chemicals because of an assumed economic disadvantage. That situation has now been changed because it had been found that when effluent charges are taken into account they swing the balance in favor of recovery.

In the course of making the inventory of a similar process, one process layer was found to be a condensation product of acetone and an aldehyde, of no use in the particular process. Modifying the pH of the process resulted in the condensation product breaking down into constituents that could be used again in the same process without side effect on either the product or the process.

Economic aspects, management decisions

In a number of cases, process modification was found to yield immediate financial advantage even when the costs in the old situation were compared directly to those in the new. On the other hand, a number of processes have proved slightly more costly in the new situation, but they are still more financially attractive in relation to the capital costs involved in wastewater treatment and/or effluent charges.

After consultation with the authorities and public advocacy groups, the developments reported here with their favorable effects on the environment, led to cancellation of Phase 1 by the management. The COD content of 2400 tpy achieved by process adaptation is in fact much lower than that planned after the completion of Phase 1.



Instrumentation. *Monitors industrial wastes*

It was also decided to use the planned interval of 2.5 y between Phases 1 and 2 for further investigation. Furthermore, the management has become convinced that even if the capital investment and annual cost are ignored, process modification is preferable to purification because:

- no sludge, which is difficult to dispose of, will be formed
- no filtering arrangements are necessary
- no unpleasant odors are created
- less space is needed
- there are also possibilities for tackling the problem of salt reduction.

After further study, Phase 2 may prove unnecessary; this should soon be established. If Phase 2 is unnecessary, a small treatment plant capable of dealing with about 300 tpy will be adequate to handle the remaining wastewater COD load, thus proving that careful investigation and modification of existing

TABLE 1

Environmental aspects of developing a new product

Function/job	Sphere of influence	Environmental aspects
Market research	Product specification; series size.	Noise regulations, power consumption, water consumption, service life, dangerous substances.
Research	Technology-manufr. techn.; materials; product functions.	Harmfulness, scarcity, processibility of waste.
Development	Product specification; choice of material; of procedure; of process; of concept; life.	Best available, with respect to environmental matters; value of by-products.
Purchasing	Choice of supplier; choice of material.	Scarcity, risks/packaging.
Engineering	Use of materials, minimizing of losses; choice of progress; integral prod. equipment; recirculation systems.	Process residues, rejects, waste.
Sales	Group replacement, obligation to take back.	Self-destruction, expert processing.
Production	Discipline quality; control of processing and production machinery; maintenance; control of waste flows.	Waste products, dangers, separating various types of waste.
Dispatch		Transport, packaging.

processes can eliminate the necessity of building new plants or redesigning new processes.

Monitoring industrial wastes

In essence, Philips adopts a three-part approach to its in-house environmental control. First, it tries to prevent pollution by modifying or designing processes to give zero pollution; second, where this cannot be achieved, the company attempts to minimize its pollution and contain it in-plant (by recycling, this pollution is lowered to acceptable levels); and, third, all waste products are purified and the ensuing pollution, if any, is kept to minimal levels.

The waste products from all Philips plants in The Netherlands, for instance, are sent to the chemical wastes center in Eindhoven where they are stored in specially-labeled containers. Here, the wastes are carefully monitored (pH, redox, temperature and heavy metals) by using Philips' monitoring and analytical instrumentation developed by the company's Science & Industry Division. Where necessary, chemical wastes are neutralized prior to their disposal or recycling treatment.

Environmental aspects of developing new products, processes

It is vitally important, when developing products and processes, to forecast the environmental consequences as accurately as possible, to control them and, as far as possible, to prevent them.

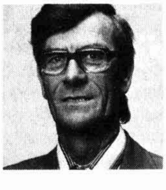
The incorporation of environmental responsibility in corporate management is closely related to the industrial activity. The creation of new products and processes is an operation consisting of a number of successive phases; at every state, different jobs and functions are involved, each with its own sphere of influence. Table 1 gives a picture of the environmental aspects of creating new products.

Aspects such as quality requirements, resistance to tropical conditions, visual requirements in relation to the function of the product, preservation during temporary storage and packaging can also have consequences for the environment, and must be considered.

The result is that the problems caused by waste are dealt with in a variety of ways, depending frequently on local circumstances. Because of the need to meet particular qualitative and quantitative requirements of environmental legislation, problems will have to be solved within the confines of the individual plant, and a basic approach will have to be adopted.

Re-use, regeneration to raw or auxiliary materials and the supply of regenerated substances as raw materials are some examples of how wastes can have a certain *residual value,* thereby making them by-products in the accepted sense of the word. The costs, and the method of disposing of those wastes that cannot be put to further use, also affect the choice of raw and auxiliary materials. The preparation of a materials "balance sheet" for raw and auxiliary materials helps increase one's knowledge of the environmental consequences of a new process, or the start-up of a new product production.

J. J. A. Ploos van Amstel *directs Philips' Pollution Control Office. Dr. Ploos van Amstel joined Philips in 1970 as a process engineer concerned with environmental protection.*



Jon Lee-Frampton *is in the Science & Industry Division Press Office of Philips Eindhoven. Before coming to Philips, Lee-Frampton was a journalist on London's Fleet Street.*

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The first use of remote sensing began around the century with the training of observers to compare black plumes to a series of charts of graduated shades of blackness (Ringelmann method). The technique was altered and extended to plumes other than black ones in 1948 with the training of observers to evaluate the degree to which the plume obscures light (opacity method). The EPA now uses the opacity method and has established opacity standards for particulate emissions.

Instrumental remote-sensing methods have been used for air pollution measurements for over a decade. Various techniques such as longpath, high-resolution infrared spectroscopy have been used on a research basis to identify and measure the concentration of various pollutants in the atmosphere. In recent years the development of a number of electro-optical techniques for remote measurement of the concentration of pollutants emitted by stationary sources has been moderately rapid. Most of these techniques have evolved from laboratory methods that have been in use for many years.

For stationary source applications, it is likely that remote sensing will find its greatest use in enforcement and surveillance activities. It is also possible that at a large industrial complex, where there are many pollutant sources within a single plant boundary, the use of remote sensors for continuous monitoring would be practical. The particular advantage of a remote sensor over a contact sensor in these applications is its ability to monitor a number of different sources sequentially in a relatively short time. In enforcement activities, where a single remote sensor could be used to monitor several sources per day, it is estimated that operational costs would be one-tenth the cost of contact sensors, although the initial cost of the remote sensor would probably be significantly more than that of the contact sensor. Other advantages of remote sensors for enforcement purposes are that they can monitor emissions on an unannounced and non-interfering basis from off the source property, and most of the sensors can operate at night as well as during the day.

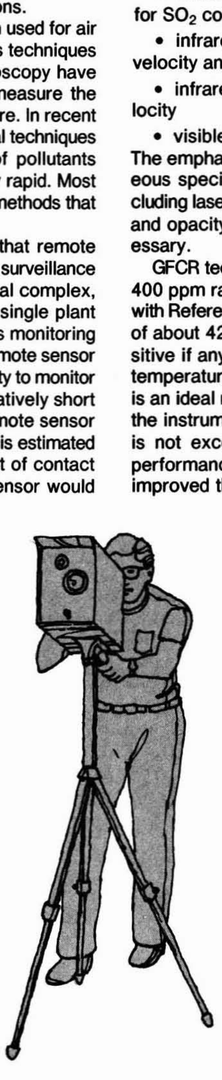
A variety of programs have been conducted within EPA over the past several years to evaluate the capability of various ground-based remote-sensing techniques for measuring the SO_2 concentration, velocity, and opacity of effluents from coal-burning power plants.

Measurement programs

Several techniques have been developed that can measure the concentration and velocity of gaseous species and particulate opacity. The velocity measurement is needed so that a mass emission rate may be determined. In order to evaluate the accuracy, utility, and state of development of some of these techniques, a series of measurements have been conducted at coal-burning power plants, and the results of the remote measurements were compared with the results of instack measurements made using the EPA Reference Methods. The techniques studied in these programs are:

- infrared gas-filter correlation radiometry (GFCR), for SO_2 concentration
- Fourier-transform infrared spectroscopy (FTIS), for SO_2 concentration
- ultraviolet matched-filter correlation spectroscopy (MFCS), for SO_2 concentration
- infrared and ultraviolet television (IRTV and UVTV), for velocity and SO_2 concentration
- infrared laser-Doppler velocimetry (LDV), for plume velocity
- visible laser radar (lidar), for plume opacity.

The emphasis in the work described on measurements of gaseous species concentrations has been on techniques not including lasers because of overall practicality. For remote velocity and opacity measurements, techniques using lasers are necessary.



GFCR technique is able to measure SO_2 concentrations in the 400 ppm range with an accuracy of about 25% (as compared with Reference Method 6) for a plume 2-m thick at a temperature of about 425 °K. The present instrument does become insensitive if any of the parameters—pathlength, concentration, or temperature—drop much below the above values. The GFCR is an ideal remote sensor in that one person is able to operate the instrument and reduce the data, and the instrument's cost is not excessive (about $25 000). Furthermore, the overall performance of the instrument can probably be significantly improved through the use of cooled detectors, more efficient optics, and better calibration procedures. The technique is readily adaptable to other gases such as CO, HF, and HCl.

FTIS is probably capable of yielding greater accuracy than the GFCR if a reliable plume temperature can be determined. However, instrument cost, complexity of data reduction and complexity of operation are much greater for the FTIS than for the GFCR. Since most pollutant monitoring is done on a single pollutant basis, the GFCR must rate well ahead of the FTIS in overall practicality for enforcement needs. If cases arise where multipollutant monitoring becomes important, the FTIS could become more practical.

For general research studies to characterize gaseous pollutants emitted by various types of sources and to determine optimum spectral regions for the operation of specialized instruments (for example, the GFCR), an FTIS system will remain the most suitable spectroscopic method. This type of research activity is being conducted at EPA; the grating spectrometer used in the past has been replaced by an FTIS coupled to telescopic optics. The system is mounted in a van, and in conjunction with a remotely located light source, can make longpath (about 2 km) absorption measurements at a spectral resolution of 0.125 cm^{-1}. Single-ended measurements of emission spectra from warm plume are also made.

MFCS (Barringer COSPEC) was shown to be able to measure SO_2 mass emission rates with an accuracy of about 25%. Much of this error is attributable to wind-velocity measurement errors. Another system, the UVTV system, was found to be able to measure SO_2 concentrations with an accuracy of about 25% for relatively clean plumes. Further work is necessary to determine the practicality of an IR or UVTV velocity measurement. Both the MFCS and UVTV systems are restricted to daylight operation. The LDV technique was shown to be well suited for remote stack-exit velocity measurements, and to have the potential of measuring a particulate mass emission rate.

The accuracy of the lidar system, as determined by use of calibrated screens, was within 3% opacity for screen opacities under 50%. At the coal-fired power plant study, good correlation was obtained between lidar and instack measurement of plume opacity, although the lidar measurements were consistently higher than the instack measurement. This difference, probably owing to a velocity cone at the top of the stack studied, would probably be much less if the instack measurements of opacity had been made at the stack exit.

The experience gained in conducting the evaluations described above has led to the formulation of some general procedures, that, though they may seem obvious, are considered necessary for reliable evaluations:

- Data obtained by the remote and instack methods should not be compared until the measurements are complete to preclude any unintentional bias.
- Instack measurements should be conducted using a continuous monitor in addition to the Reference Method because the remote instrument is also continuous.
- Calibration of all instruments must be thorough and careful.
- Any changes that occur between the instack measurement point and the stack exit must be determined.

Two operational modes of remote sensing considered most applicable to stationary source measurements are depicted in Figure 1. These modes include both the active mode, which involves the use of a controlled light source, and the passive mode where the plume itself or sunlight scattered by the atmosphere serves as the light source. All of the active systems envisioned for stack-exit measurements use laser sources. The active longpath systems use both laser and continuum light sources. The general characteristics of selected remote-sensing techniques are summarized in Table 1.

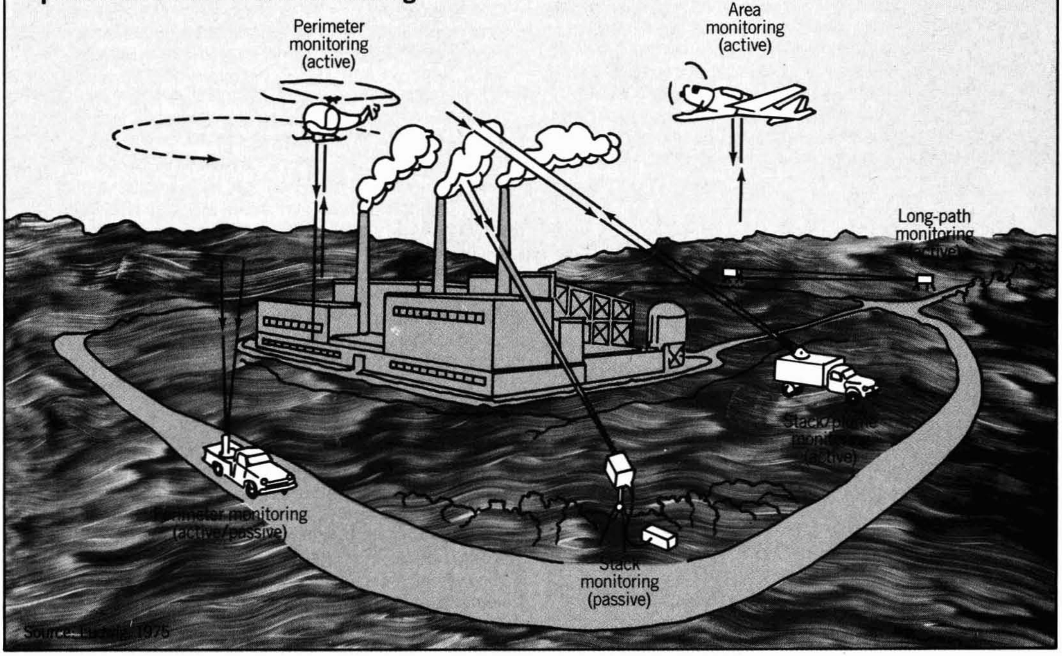
Measurement sites

Figure 2 shows various measurement locations for validation of remote sensors. Measurements at "A" characterize the flue gas at conventional sampling locations. While the EPA Reference Method should serve as the primary standard, the use of an additional method such as a cross-stack or extractive continuous monitor is recommended. If these two methods agree, then there is increased confidence in the instack data. Measurements at "B" characterize flue gases as they exit the stack. A continuous monitor similar to that used at "A" is used for these measurements. Comparison of the results obtained at "A" and "B" will reveal any changes in flue-gas characteristics that may occur while the gases traverse the stack.

The various remote-sensing methods under study can be evaluated first at location "C" and the results compared directly with those obtained at "B." These results furnish the required validation data for stack-exit measurements. As a simplification, if it is possible to show that no changes in flue-gas characteristics occur between "A" and "B," then measurements at "A" are sufficient. Some of the remote-sensing techniques that are under development can be used at "D" for plume tracking, modeling and reaction studies.

The measurements indicated by "E" are made by an "uplooking" instrument that is moved along a path that encircles a stack (or an extended area source). This measurement yields

FIGURE 1.
Operational modes of remote sensing



Source: Ludwig, 1975

TABLE 1

Summary of selected remote-sensing techniques

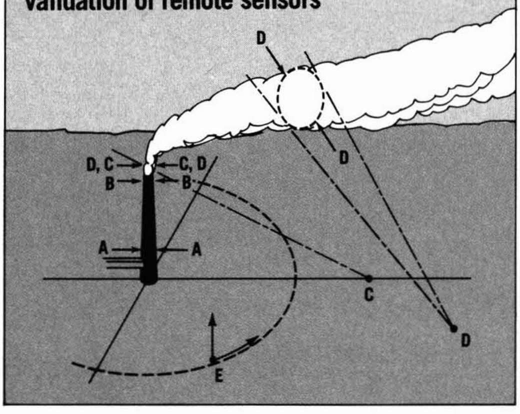
Technique or instrument	Spectral region	Species or parameter	Mode	Comment
Active techniques				
Differential absorption	VIS, UV, IR	Many gases	Stack, area, or perimeter	Preliminary field testing under way. Complicated and expensive but with excellent potential; 3 dimensional
Lidar	VIS	Opacity	Stack or area	Operational day or night for stacks. Area use being developed
LDV	IR	Velocity	Stack or perimeter	Operational day or night for stacks. Has potential as mass monitor
Long-path absorption	VIS, UV, IR	Many gases	Area or perimeter	Can use laser, dispersive or GFCR systems, ppb levels, double-ended
Raman	VIS, UV	Many gases	Stack	May not have enough sensitivity
Fabry-Perot Raman	VIS, UV	Some gases	Stack	Lab tested only, has increased sensitivity over plain Raman
Fluorescence	VIS, UV	Many gases	Stack	Lacks sensitivity and specificity
Passive techniques				
Matched filter correlation	VIS, UV	NO_2, SO_2	Stack or perimeter	Commercially available, day time operation only
Gas-filter correlation	IR	SO_2	Stack or perimeter	Stack instrument field tested. Area instrument under development. Day or night use. Potential for many gases
Photography	VIS	Opacity	Stack	Needs further development
Vidicon	UV, IR	SO_2 and velocity	Stack	Needs continued development and evaluation
Heterodyne radiometer	IR	Many gases	Stack or area	Lab tested only, field testing planned
Spectrometer	IR	Many gases	Stack	Requires high resolution grating or interferometer instrument for sensitivity and temperature data

the pollutant optical depth (product of concentration and pathlength) in a vertical column surrounding the stack. These data, coupled with the local wind velocity, allow calculation of a mass emission rate. This type of perimeter measurement is especially applicable to extended area sources, but the validation is most accurately done on a single isolated stack.

Most of the measurements described in the article were conducted at the River Bend Steam Plant of Duke Power Company near Charlotte, N.C. At this four-unit, 600 MW, coal-burning power plant, the EPA Emissions Measurement and Characterization Division, with the cooperation of Duke Power Company, conducts many of its instrumentation test and evaluation programs. One stack at this plant is fitted with a number of ports to allow attachment of various cross-stack and extractive monitoring systems. The semipermanent equipment includes a Lear-Seigler Model RM-4 transmissometer to measure opacity and a Du Pont Model 460-1 continuous extractive analyzer for SO_2 and NO_x.

The remote measurement site at Duke Power is about 400 m slant range from the top of the instrument stack; the line-of-sight is about 8° above the horizontal. Most of the remote measurements are made from this site, but other sites are also used. The ports on the instrument stack are between 1–3 m above the plant roof level. There is a ladder to the top of the stack to permit "B"-type measurements. A small building has been assembled on the plant roof near the instrumented stack to house instrument recorders and to serve as a site laboratory. When plant operating conditions permit, the generating load can be varied to change the effluent exit velocity and selected precipitator selections can be shut off to increase plume opacity. In this way the effect of these known changes on the operation of the remote instruments is determined.

FIGURE 2.
Measurement locations for validation of remote sensors



Measurements

The **GFCR instrument** was developed for EPA by Science Applications, Inc. The instrument's operating principles are indicated in the simplified schematic (Figure 3). Plume radiation traverses the two pairs of optical channels and is focused onto an infrared detector after being spectrally filtered and optically chopped at a carrier frequency of 800 hz (ω_3). The filter is centered at 2500 cm^{-1} and has a bandwidth of about 25 cm^{-1}. This particular configuration is optimized for SO_2 concentration measurements.

In a single channel radiation from plume species other than SO_2 (or atmospheric species) is modulated by the two cells in an identical manner at 40 hz (ω_1) and produces no ac signal at the detector. Plume SO_2 radiation is attenuated by the SO_2 in correlation cell 1, but not by the N_2 in cell 2; thus an ac signal will be produced by the detector that depends on the plume and correlation cell SO_2 concentrations and temperatures. In the other channel the correlation cell contains a different amount of SO_2 and thus will produce a different signal at 100 hz (ω_2) at the detector, owing to plume SO_2. These signals are separated, amplified, and their ratio calculated. This calculated signal is a function of plume SO_2 concentration, and the instrument is calibrated by determining this ratio as a function of known SO_2 concentrations in a heated cell. The ratio technique has the advantage of essentially eliminating the temperature dependence of the resulting signal.

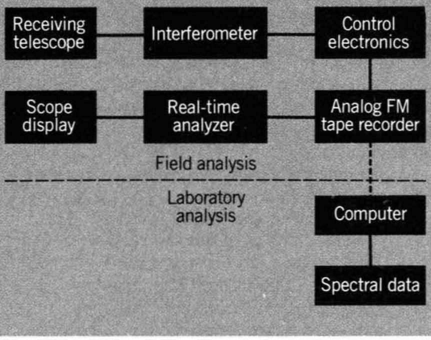
Preliminary data were obtained with the GFCR in the fall of 1974, along with comparison data from EPA Reference Method No. 6 and the Du Pont extractive analyzer. The GFCR results were within about 25% of the Reference Method results.

Since the completion of the measurements described above, one problem has occurred with this GFCR instrument: the correlation cells containing SO_2 have shown a tendency to leak over long periods of time (several months). It has not yet been determined whether the leaks result from interaction of the SO_2 with the sealant that bonds the sapphire cell windows to their quartz body or possibly just failure of the sealant. This is not now felt to be a major problem, since cells of more recent design have shown much greater stability. The first model of this instrument lacked sensitivity; a new model is now being evaluated. This new model uses telescopic optics and liquid nitrogen-cooled detectors to increase sensitivity by about two orders of magnitude.

The use of **FTIS** in laboratory emission or absorption spectroscopy is a well-established technique. A block diagram of the system used for remote-sensing measurements is shown in Figure 4. The interferograms produced in the field by the interferometer were processed by a real-time analyzer to ensure that the entire system was operating properly. Tape recorded interferograms were later processed on a large computer to produce high-resolution spectra for analysis. In addition to recording spectra of plume emission, calibration spectra of blackbody radiation, the sky background, and the atmospheric attenuation between the plume and the FTIS were also obtained. (The EPA-owned FTIS system allows complete data processing in the field.)

The principal problem in calculating a species concentration from its emission spectrum is that the temperature must also be determined from that spectrum to be a truly remote technique. This is a difficult calculation since an error of just 5% in the temperature will lead to an error of 10–20% in SO_2 concentration for the 4 μm band at 400 °K. This situation essentially prohibits the use of any simple data analysis technique.

FIGURE 4
The FTIS system: a block diagram

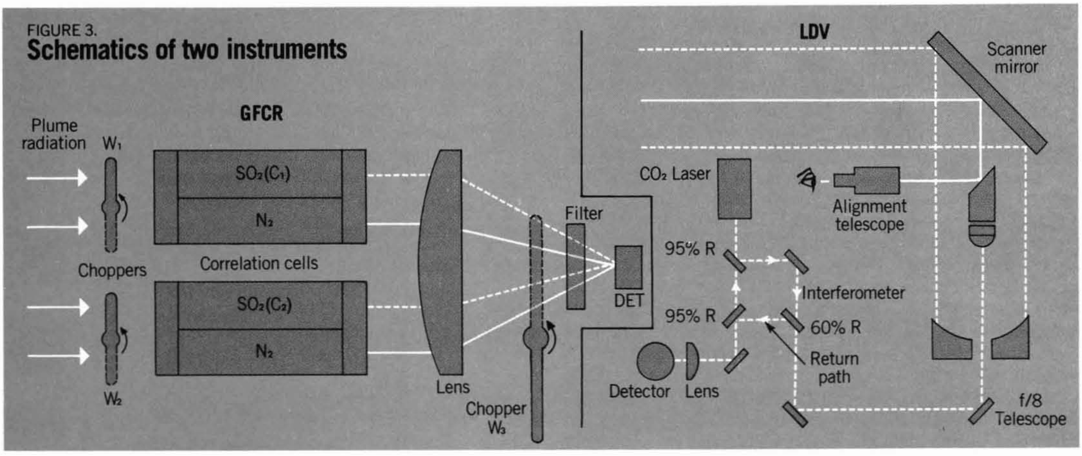


The details of the FTIS measurements were previously reported (see Tanabe, L. H., Report on EPA Contract 68-02-1804, 1975). In the preliminary calculation of SO_2 concentration, the temperature was determined by measuring the separation between the P and R branches of the SO_2 band. This method gave results in considerable error. A second temperature measurement was based on the strength of CO_2 radiation from the plume and a knowledge of the CO_2 concentration in the plume. This method gave much better results; however, a number of assumptions were made, and it is not certain that the results could have been obtained without a prior knowledge of the plume characteristics.

Considerable work has been done toward the goal of analyzing plumes remotely by using an FTIS. There is no question that the FTIS is the most suitable instrument for obtaining high-resolution spectra of stack emissions for species identification purposes. In previously reported work (see Additional reading, Prengle et al., 1973), a temperature measurement determination was based on the total energy content in the central burst of the interferogram. The method was shown to work reasonably well on particulate-free plumes, but no measurements were made on plumes containing appreciable amounts of particulates.

The first instrument developed especially for remote sensing of SO_2 emissions from power plant plumes was the **correlation spectrometer (COSPEC)** developed by Barringer Research. This instrument measures the ultraviolet attenuation of SO_2 in plumes; scattered sunlight serves as the source of UV radiation. The

FIGURE 3.
Schematics of two instruments



instrument uses a small grating monochromator to produce an SO_2 spectrum at the exit slit, where a mask (the "matched filter") matched to the structure of the SO_2 bands in the 0.31 μm region alternatively transmits peaks and valleys in the SO_2 spectrum to a detector.

The COSPEC instrument is used most effectively in an "uplooking" perimeter mode. In this mode, the SO_2 optical depth is measured in a vertical column surrounding the source in question. By also measuring the local wind velocity, the SO_2 mass emission rate from the source may be calculated.

An evaluation of this type of measurement is most accurately done where there is a single stack serving as the source. This situation does not exist at the Duke Power Plant site, and a site was selected in the Southwest where a coal-burning plant was operating with a single stack. From measurements taken there, it was found that the COSPEC and instack mass-emission rate measurements agreed to within ±25%. The wind velocity measurements were considered to be a major source of error in these measurements. (Wind velocity was determined by tracking a pilot balloon with a theodolite.)

During August, 1975, a **UVTV** system developed by Dr. Reginald Exton of NASA/Langley Research Center and an **IRTV** system developed by Mr. Edward Cross of Aerospace Corporation were both operated at the Duke Power Plant site. The UVTV produces a visible picture showing the attenuation of scattered solar UV energy by plume constituents; the plume appears darker than the bright sky background. The IRTV produces a visible picture of the infrared radiation from warm plume constituents; the plume appears brighter than the cool sky background.

The UVTV was shown to be able to measure SO_2 concentrations with an accuracy of ±25% if the plume is relatively clean (opacity <20%). The data are obtained by filtering the camera first at 0.34 μm, where particulate opacity is measured, and then at 0.31 μm, where particulate opacity plus SO_2 opacity is measured. From these two measurements, the SO_2 attenuation can be determined and the concentrations calculated. Calibration is obtained by sighting the TV camera through cells that contain known amounts of SO_2. The IRTV is not able to measure SO_2 concentration because of a lack of spectral resolution and knowledge of the plume temperature.

It was anticipated that both systems would be able to measure the plume velocity, with the IR system having the advantage of being able to operate at night. The velocity was calculated by measuring the time required for gradients in the plume to travel a known distance, by using successive frames from the videotaped TV picture. The velocity determined in this manner was about a factor of two less than that determined from instack measurements. The assumed explanation for this is that the observed gradients are caused by the mixing of ambient air with the edges of the plume. Such a situation would be expected to produce a velocity somewhere between that of an ambient air and the true plume velocity. It was observed that the TV velocity did track the instack velocity in a regular manner during periods of velocity change, and thus it may be possible to demonstrate a consistent empirical relationship. Work in this area is continuing.

Since emission standards for stationary sources are generally based on a mass-emission rate, it is necessary to measure effluent velocity as well as concentration by remote methods to take full advantage of remote-sensing techniques. The **LDV** (Figure 3) technique has been in use for about 10 years to make non-contact velocity measurements in experiments concerning wind tunnels, clear-air turbulence, wake vortices and atmospheric winds. The principle of operation is simple. A CO_2 laser beam is propagated through the atmosphere and brought to focus at the desired range. Aerosols in the atmosphere scatter a fraction of the laser energy back toward a receiving telescope. Since the aerosol particles are in motion, backscattered energy will be shifted in frequency from the outgoing laser beam because of the Doppler effect. The shift in frequency depends on the laser wavelength and the velocity component along the laser beam. The backscattered energy and a fraction of the outgoing laser beam fall on the same detector, and the difference in frequency is detected by conventional heterodyne techniques.

In order to determine the feasibility of remotely measuring stack effluent velocity by LDV, a program was undertaken using an existing LDV system at the Duke Power Plant site. Measurements were conducted in August 1974 and January 1975, and the results have been described in detail by Miller and Sonnenschein (1975) (see Additional reading). Although the primary aim of the program was to demonstrate the feasibility of the remote velocity measurements, a secondary aim was to determine what, if any, relationship exists between the intensity of the backscattered signal and the attenuation coefficient of the plume (as determined from the opacity of the plume). It was shown that a reasonably linear relationship exists between plume attenuation coefficient and mass density for a given type of particulate source. Thus, the LDV measurement, utilizing a single instrument, has the potential to give a mass-emission rate for particulates.

Analysis of the velocity measurements found the LDV values within 14% of the instack values obtained by using EPA Reference Method 2. Since Reference Method 2 is considered accurate to ±20%, the agreement is about as good as might be expected. Although only two sets of data relating backscatter signal strength to plume attenuation coefficient were obtained, there is certainly good indication that a linear relationship exists. This relationship, if verified by additional measurements on a variety of sources, would allow a single LDV instrument to be used to measure a particle mass-emission rate when calibrated for a particular type of source.

The **lidar** technique for remote measurement of plume opacity was first demonstrated by Evans (1967) (see Additional reading) who used lidar equipment designed for atmospheric studies. He showed that the opacity and transmittance of a plume could be determined by aiming the laser beam through the plume and comparing the relative backscatter intensity of the beam by the atmosphere in front of and behind the plume. In 1972, a van-mounted lidar designed for plume opacity measurements was developed for EPA by General Electric Company. This system is shown in operating configuration at the Duke Power Plant site in Figure 5. The operating characteristics of the system are given in Table 2.

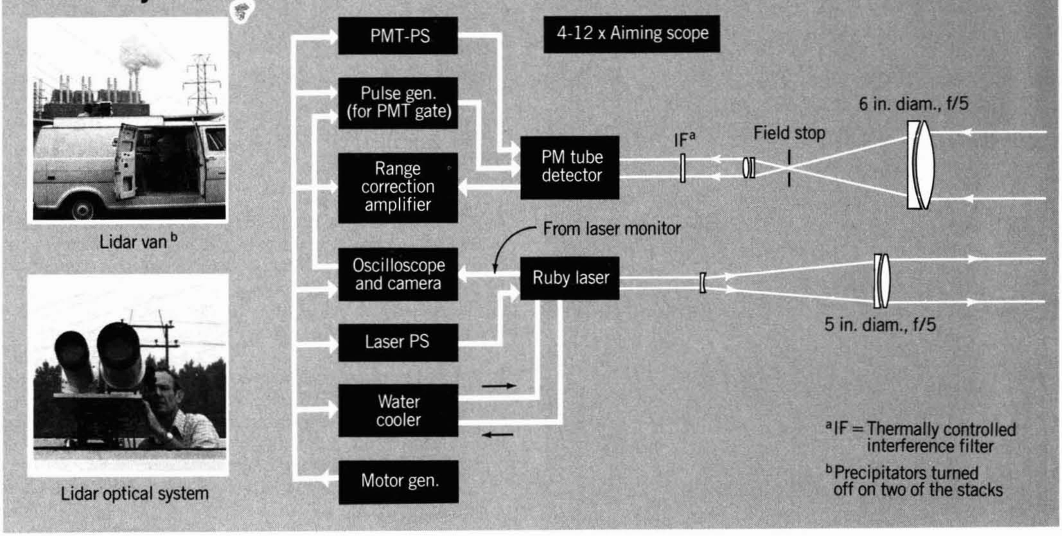
The accuracy of the lidar was determined by using neutral density screen targets of known opacity. The opacity of 1-m diameter screens was determined by laboratory transmis-

TABLE 2

Mobile lidar systems characteristics

Component	Characteristic
Transmitter	
Laser	Rotating prism, Q-switched ruby
Wavelength	694.3 nm
Pulse width (FWHH)	<30 nanoseconds
Maximum output	1.0 joule
Repetition rate	3 pulses per minute
Cooling	Deionized water
Objective lens	12.7 cm, f/5
Beam divergence	~0.5 miliradian full angle
Receiver	
Objective lens	15.25 cm, f/5
Field-of-view	4 miliradian full angle
Bandpass (FWHH)	1.2 nm
Photomultiplier	IT&T F4084 (modified S-20)
Off-gating	≥60 dB
Response	~100 nanoseconds

FIGURE 5.
The lidar system at Duke Power



[a] IF = Thermally controlled interference filter

[b] Precipitators turned off on two of the stacks

someters, which were in turn calibrated by using Kodak Wratten neutral density filters. The lidar opacity measurements of the calibrated targets were made at a distance of 200 m. The results indicated that the lidar is accurate to within 3% opacity for opacities less than 50%. At higher opacities the results showed maximum error of about −15% opacity for a targeted opacity of 100%. This decline in accuracy for opacities is of little concern since no opacity standards for emission sources are above 50% opacity.

A series of measurements were made at the Duke Power Plant site over several years at a range of 400 m to compare the lidar results with those of the instack transmissometer. The comparison showed a high degree of correlation (coefficient 0.993) between the remote lidar measurement and the instack measurement of opacity. However, the remote measurements were higher than the instack measurement by about 3% at the 3% instack opacity level and by about 8% at the 30% opacity level. Interestingly, the correlation would have been almost exact if no adjustment had been made for the stack diameter change at the top of the stack. This discrepancy demonstrates the need for making stack-exit measurements by using instack instrumentation at the stack exist as previously discussed.

Planned activities

The type of measurement that can be made with the MFCS (the "uplooking" perimeter measurement to yield mass-emission rates) has excellent potential for monitoring emissions from extended area sources, where no single stack is generally involved. For this reason the measurement concept is being extended to the infrared spectrum with the development of an "uplooking" GFCR instrument for SO_2 in a plume against the cold sky background. This type of instrument, first described in 1975, has the advantage (over the MFCS instrument) of being able to operate at night and of being applicable to a greater number of pollutants. A comparison of both the "uplooking" GFCR and the MFCS against the Reference Methods at an isolated stack was conducted during the summer of 1976. An LDV system, piballs, and a tethered balloon were used to measure the local wind velocity. The analyses of these data has not yet been completed.

Evaluations of the lidar system are still under way; comparisons are being made with both trained observer and instack transmissometer measurements. Work is being conducted by SRI International to develop a small portable lidar for remote plume opacity measurements that would cost approximately $20 000.

The continued cooperation of Duke Power Co. is gratefully acknowledged. Dr. H. M. Barnes, Mr. K. Foster, Mr. R. Rollins, and Mr. N. White, all of EPA, contributed significantly to various phases of the evaluation programs. Appreciation is also expressed to the contractors participating in the development and evaluations of the remote-sensing instruments, and to NASA for assistance in funding and technical areas in the LDV programs.

Additional reading

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William D. Conner *is a research physicist within the emissions measurement and characterization division of EPA's Environmental Research Laboratory. Mr. Conner has developed some of the fundamental concepts in remote and in situ measurement of particulate matter opacity.*

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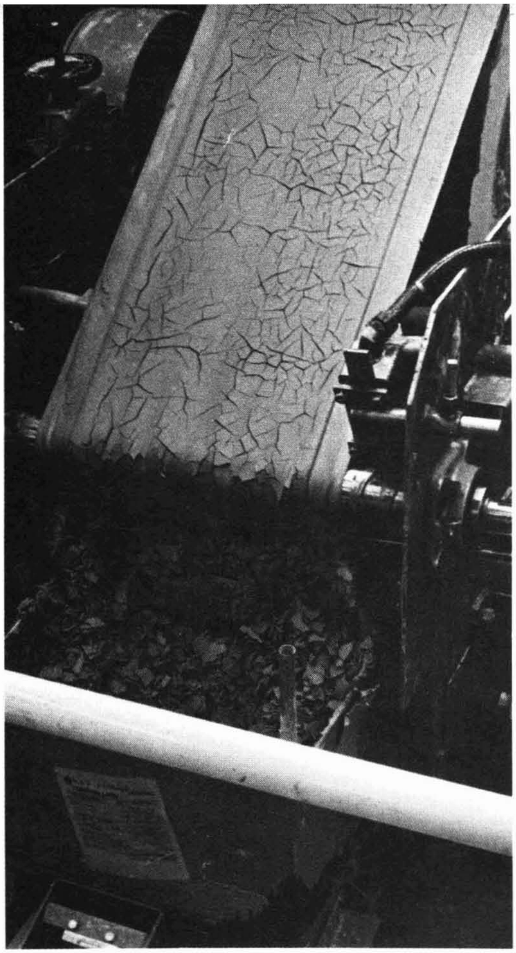

Municipal sludge disposal economics

Different sewage sludge disposal techniques vary in cost and energy recovery possibilities. Here is a look at some of them

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Costs for disposal of sludges from a municipal wastewater treatment plant normally represent at least 25% of the total plant operating cost. The most popular ultimate disposal options and rough estimates of the extent of use are as follows:

	Percent of sludge	*Amount (dry solids, tons/day)*
Landfill	25–30	>4000
Land application	25–30	>4000
Incineration	25–30	>4000
Ocean dumping	15	2500
Total		>14 500

Sludge handling options considered are shown schematically in Figure 1. Option 1 includes two possible sludge dewatering processes prior to incineration: vacuum filtration to produce a 20% solids cake (Option 1a), or filter press dewatering to produce a 40% solids cake (Option 1b). Option 2 substitutes thermal conditioning of the sludge for the chemical conditioning of Option 1a.

Option 3 involves essentially complete oxidation of the sludge while in the liquid phase. Option 4 includes two possibilities prior to land application or landfill disposal: aerobic digestion (Option 4a) or anaerobic digestion (Option 4b). Option 5 produces a dry (<5% moisture) fertilizer product for sale.

Estimates of both capital investment and operating costs (with common bases), as well as detailed energy-use comparisons have been prepared. Relative costs, not the absolute magnitudes of the costs, are important in this analysis.

Thermal processing

Thermal processes for improving sludge dewaterability and ultimate disposal have been selected by an increasing number of municipalities in the last 15 years (*ES&T,* November 1976, p 1080). The total number of sludge incinerators increased from 75 in 1960 to slightly over 200 in 1970. Since 1970, another 200 units have been installed or are now under construction. The EPA has predicted that the average number of incinerators installed annually through the 1970s will be approximately 70; however, the actual annual rate of installation appears to be closer to half of this projection.

Prior to 1973, municipal sludge incinerators were not designed with energy as the foremost consideration. Therefore, most incinerators of the pre-1973 period burned sludge with a 15–30% solids content, which required significant fuel usage. Thus, it is important to produce a sludge with a high solids content. A reasonable objective is a 35–40 wt % solids cake with a ≥60% volatile solids content. it should be borne in mind that fuel requirements increase as the volatiles content decreases.

Although incinerators always require some fuel because of startup, the process is not necessarily a net consumer of energy. Indeed, as the feed solids content is raised above 35% solids, incineration becomes a net producer of energy. Incineration produces more steam and uses more fuel when sludge solids content is lower; however, since fossil fuel is a more valuable energy form than steam, which may or may not be usable or marketable, one should minimize fuel usage, not maximize steam production.

Presently, at least two dewatering techniques produce a sludge with a solids content of about 40% (and ≥60% volatiles content), thus minimizing fuel usage. These techniques involve:

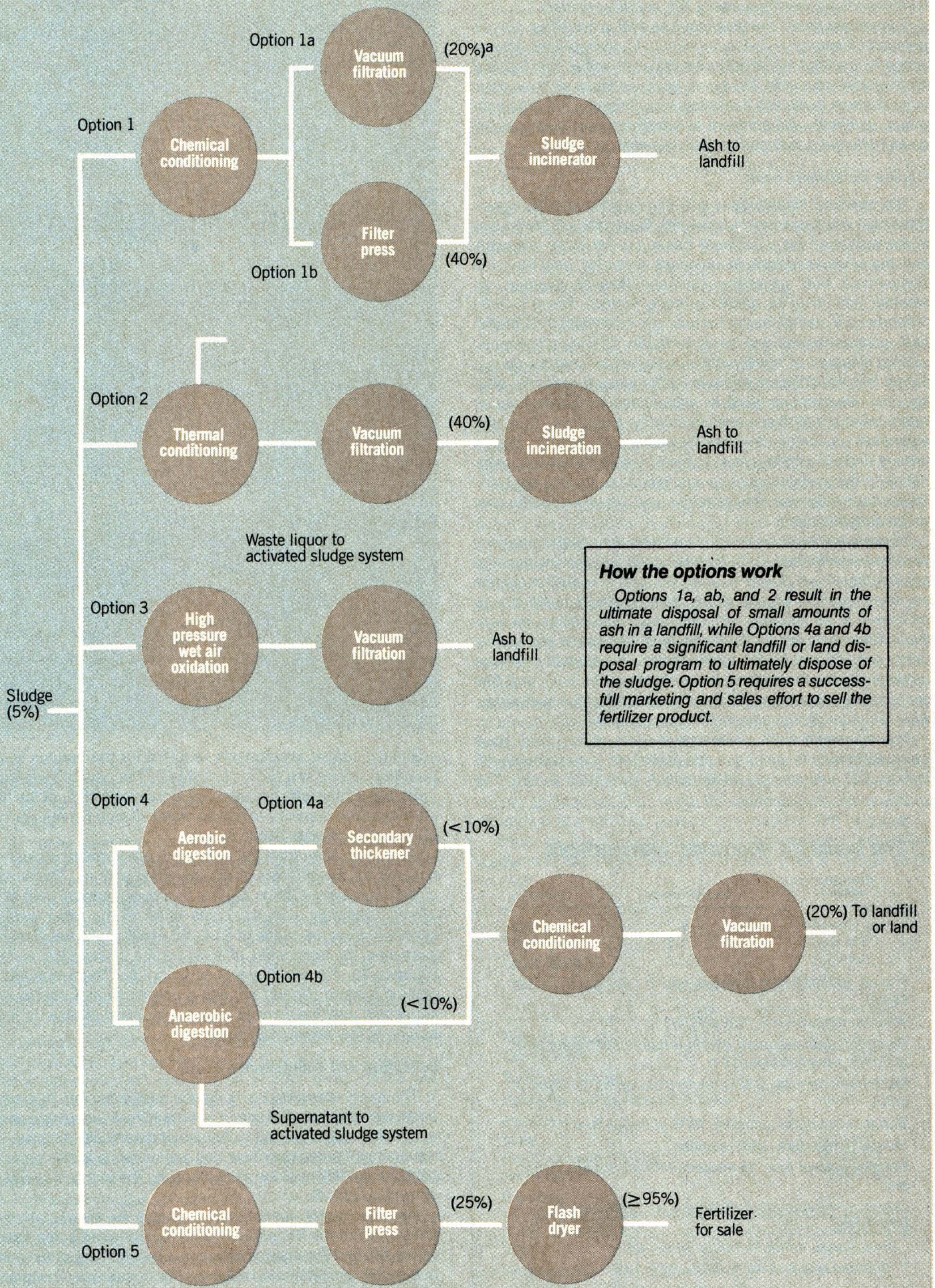
- pressure filtration after chemical conditioning (Figure 1, Option 1b)
- low temperature thermal conditioning followed by vacuum filtration (Option 2).

Approximately 30 new sludge incinerators using these dewatering techniques are in various stages of planning, design, construction, and operation. These same techniques could also be used to retrofit pre-1973 incinerators to improve their net energy balance dramatically.

While both of the above-mentioned techniques markedly improve the heat balance around the incinerator itself, increased

FIGURE 1

Sludge handling options



How the options work

Options 1a, ab, and 2 result in the ultimate disposal of small amounts of ash in a landfill, while Options 4a and 4b require a significant landfill or land disposal program to ultimately dispose of the sludge. Option 5 requires a successfull marketing and sales effort to sell the fertilizer product.

[a] Indicates weight % solids in sludge

energy usage can occur in other process areas of the plant. For example, thermal conditioning processes use electric power and steam, as well as produce a heat treatment liquor that requires a larger base plant to handle the added BOD load. This increases the power required in the aeration system.

To evaluate these two processes as well as the other options in terms of energy use, it is necessary to compare the energy usage for the total municipal treatment plant, rather than just that for the incinerator units. Moreover, because these systems differ in investment costs and operating requirements, it is also necessary to identify and compare all significant cost components, so as to derive a true comparison between systems.

Capital investment costs

The absolute magnitude of non-site-specific capital investment cost estimates may vary widely, depending on the source of the published data. Common bases are generally not used, and the wide variations in reported costs for facilities with comparable flow capacities (average flow or average dry weather flow) may be related to many factors. These include differences in design bases for average or maximum contaminant concentrations and peak hydraulic flow requirements; various degrees of conservativism related to process design safety factors; different allowances for excess capacity; site-specific requirements such as pilings; and variations in labor rates, labor productivity, and contracting practices. Thus, the estimates presented here are based on very specific design criteria and assumptions, and this is why only the relative magnitude of the investment costs are important for this analysis. These cost estimates should not be used for site-specific cost estimating purposes.

To compare the economies of scale for the options, analyses have been performed for three plant capacities having average dry weather flows (ADWF)—10, 100, and 500 million gallons per day (mgd). The population served by these three plants was estimated to be 100 000, 667 000, and 3.333 million, respectively, based on a per capita discharge of 100 gpd for the smaller plant, and 150 gpd for the larger plants. The amount of sludge produced by the three plants is, respectively, 11.5, 77, and 384 dry tons/day, based on 0.23 lb of sludge solids per capita/day. Specific plant design parameters are listed in Table 1.

The estimated capital investment costs of the three base plants (prepared on a unit process basis) are approximately $5 million, $27 million, and $108 million (mid-1975 costs). The additional capital investments required for the various sludge handling options are shown in Table 2. The capital investment costs associated with the assumed increase of 25% of the base plant aeration capacity to handle waste sludge liquors were included under sludge handling costs.

TABLE 1

The basis for economic comparisons

Plant size, ADWF[a]	(PDWF/ADWF)	PDWF[b]
10 mgd	2	20 mgd
100 mgd	1.5	150 mgd
500 mgd	≤1.5	750 mgd

Primary sedimentation, overflow rate = 1000 gal/day/ft^2 at PDWF

Aeration retention time, 6 h at PDWF

Secondary sedimentation, overflow rate = 1000 gal/day/ft^2 at PDWF; retention time ≥2 h

Mechanical aeration, 2 lb O_2 transferred/hp-h (1 lb O_2/lb BOD)

Sludge recirculation pumping, 75% of design flow

Sludge storage tank, 24-h retention

Chlorine contact tank, 15 minutes; chlorine dosage, 5 mg/liter

Chemical requirements (added on a dry solids basis) for dewatering

Raw sludge, 2.5 wt % $FeCl_3$, 10% CaO

Digested sludge, 4 wt % $FeCl_3$, 12% CaO

[a] ADWF = average dry weather flow.
[b] PDWF = peak dry weather flow.

TABLE 2

Sludge handling options: their capital costs (millions of dollars) . . .

Sludge option	Plant size 10 mgd	100 mgd	500 mgd
1a	1.9	6.2	23.7
1b	1.8	5.3	21.3
2	2.3	8.4	28.7
3	2.3	9.3	31.4
4a	1.3	5.0	23.1
4b	2.1	9.5	44.5
5	2.1	5.0	24.0
Base plant	5.1	26.7	107.8

the electric power they would use (10^6 kWh/y)

Sludge option	Plant size 10 mgd	100 mgd	500 mgd
1a[a]	0.55	3.4	16.3
1b[a]	0.42	2.8	13.9
2[a]	1.45	9.6	46.8
3	3.20	21.1	104.7
4a	2.54	16.7	83.5
4b	1.05	6.2	31.0
5	1.26	8.5	42.2
Base plant	3.23	24.9	124.7

their gas or oil usage/production (10^9 Btu/y) . .

Sludge option	Plant size 10 mgd	100 mgd	500 mgd
1a[b]	~100 (~60)[c]	~700 (~400)	~3800 (~2000)
1b[b]	7.2 (25.1)	48.4 (168)	241 (837)
2[b]	1.2 (8.0)	8.3 (55.0)	41.4 (300)
3	6.3	42.2	210
4a	←	none	→
4b	11.0 (21.9)	74.5 (149)	366 (732)
5	50.4	336	1682

As can be seen from Table 2, there are variable economies of scale for the different sludge-handling options. The aerobic digestion system (Option 4a) has the lowest capital cost at the 10-mgd capacity, with the costs of all of the other systems varying in a narrow range of $1.8–$2.3 million. As the plant size increases, the economies of scale for the incineration systems (Options 1a, 1b, and 2) are quite favorable. The anaerobic digestion system (Option 4b) has a poorer capital cost-scaling factor and may become an expensive option relative to incineration at the larger plant sizes.

Operating and maintenance costs

The direct operating costs can be subdivided into four areas: costs deriving from the use of energy (direct fuel usage and/or electricity); costs relating to the use of chemicals, supplies, and replacement parts; operating and maintenance labor costs; and costs for landfilling of the sludge or ash. The unit cost bases are shown in Table 3.

Besides capital costs, Table 2 shows the electrical power consumption, the Btu equivalent of fuel required in the form of gas or oil, and the energy values (in parentheses) of the steam or digester gas produced by the particular process. The quantity of digester gas produced is assumed to be 600 Btu per capita/day. The quantity of steam produced by the incineration process was calculated based on the enthalpy differences between stack

. . . and their operating costs

Base plant only (without sludge disposal) Sludge[d] options	10 mgd	500 mgd
	19¢/1000 gal	8¢/1000 gal
1a	\$98–\$130/ton[e]	\$61–\$92/ton
1b	\$61–\$80/ton	\$25–\$44/ton
2	\$79–\$88/ton	\$30–\$36/ton
3	[f]	[f]
4a	\$73–\$88/ton	\$47–\$70/ton
4b	\$72–\$98/ton	\$44–\$70/ton
5	\$78–\$118/ton	\$41–\$81/ton
Base plant & option 1b	26¢–28¢/1000 gal	10¢–11¢/1000 gal
Base plant & option 2	28¢–29¢/1000 gal	10¢–11¢/1000 gal
Base plant & option 4b	27¢–30¢/1000 gal	11¢–13¢/1000 gal

[a] An increment of 0.13, 1.0, and 4.1 × 10^6 kWh/y should be added at the 10, 100, and 500 mgd levels, respectively, to account for the power used on the air pollution control equipment in the incinerator options.

[b] These oil usage numbers are based on a 1400 °F exhaust and will be lower for the incinerators operating at the 1100–1200 °F exhaust temperature range.

[c] Production or credit values are shown in parentheses.

[d] Range of sludge handling costs calculated assuming from no credit to \$2 per million Btu credit for recovered energy (steam or digester gas) for Options 1a, 1b, 2, and 4b. For Option 5, the credit for sale of fertilizer at plant gate varied from nothing to \$40/ton. Possible variation in hauling costs were considered for Options 4a and 4b. Variations in chemical usage were considered for options 1b, 4a, and 4b.

[e] Dollars per dry ton of initial sludge solids.

[f] Insufficient data were available for preparation of total operating cost estimate.

Sludge option key
1a = Chemical conditioning + vacuum filtration + incineration
1b = Chemical conditioning + filter press + incineration
2 = Thermal conditioning + vacuum filtration + incineration
3 = High pressure/temperature wet air oxidation
4a = Aerobic digestion
4b = Anaerobic digestion
5 = Flash drying/fertilizer production

gases at 1400 °F and at 500 °F. The additional electrical power required for aerobic treatment of return sludge liquors in Options 2, 3, and 4b has been charged against the sludge handling system costs.

As can be seen from Table 2, the incinerator options, 1a and 1b, which start with chemical conditioning of the sludge, consume substantially less electrical power at all treatment plant sizes. The incinerator option, Option 2, based on thermal conditioning of the sludge, uses considerably more electricity than do the first two incinerator options, but also consumes less fuel, which partially compensates for the electric power demand difference. In this analysis, anaerobic digestion is the third lowest user of electricity for all plant sizes (assuming that pumps, gas blowers, and aeration equipment are all electrically driven).

Anaerobic and aerobic digestion require no direct external fossil-fuel input. The relative use of fuel among all the other options stays relatively constant for all plant sizes. Of the fuel-requiring systems, Option 2, based on thermal conditioning, has the lowest absolute requirement for an outside source of fuel. Moreover, both incinerator options, based on the combustion of approximately 40% sludge cake (Options 1b and 2), can produce a significant amount of steam that may be used for driving the incinerator scrubber fan, for heat treatment, or for space heating. Excess steam also may be sold for off-site use, but this is very site-dependent.

The anaerobic digestion process can be a significant net producer of fuel gas, a more valuable form of energy than steam. The absolute quantity of this gas is dependent, however, upon the extent of volatile solids conversion and the amount of gas required to heat the digester, which, in turn, is directly related to the ambient temperature and digester design. Thus, comparably designed and operated digesters can show a much greater net heat output in a warm climate than in a cold climate.

Because of the different energy forms used and produced, it is extremely difficult to make a meaningful comparison of net energy usage for the total treatment plant, including the sludge disposal options. However, if one assumes that 1 kWh of electric power is equivalent to 8500 to 9000 Btu of fuel fired, equates the energy in steam to the enthalpy value, and the energy in digester gas to its fuel value, Option 2 could be equivalent to Option 4b. Anaerobic digestion in many cases will be somewhat more favorable, but the more meaningful comparison is to look at operating costs and the sensitivity of these costs to fuel and power cost increases.

As indicated in Table 2, the two incinerator options producing the 40% sludge solids (Options 1b and 2) could have the lowest operating costs for treatment plants ranging in capacity from 10–500 mgd. The cost competitiveness of these incinerator options is likely to increase with plant size.

Sensitivity analysis

Sludge handling costs may be significantly affected by changes in chemical usage, hauling costs, and energy credits. With a 10-mgd plant capacity, changes in the initial cost factors in the direction most favorable to anaerobic digestion indicate that under the most favorable conditions, the plant with anaerobic digestion could have a total operating cost of 2–8— lower than a plant with incinerators. This is outlined in Table 4.

In this non-site-specific type of analysis, these small differences are of questionable significance, because site-specific factors may produce much larger cost differentials between options. Indeed, it appears that at all plant sizes of 10–500 mgd, incineration could be economically competitive now and in the future, even with fuel prices at twice the current levels. Therefore, incineration should be included in all future sludge management studies for large plants (>10 mgd).

The last thermal processing option (Option 5) is particularly sensitive to the market price of the final fertilizer product. The net cost to the municipality drops by \$10/ton for every \$10/ton increase in the price of the product. However, a price of \$40/ton of product would be required to yield a total cost to the municipality comparable to that for the two low-cost incinerator options (Option 1b and 2). The concentration of the sludge solids going to the dryer would have to be increased from the currently assumed 25% to 40% to make this option competitive with incineration at a fertilizer product sale price of \$30.

Thus, for the 10-mgd plant size, incineration of municipal sludge that has been treated to produce a 40% sludge solids

TABLE 3
Unit costs

	Plant size (ADWF)		
	10 mgd	100 mgd	500 mgd
Electric power cost (¢/kWh)	2	1.5	1.5
Fuel \$2/10^6 Btu			
Operating and maintenance/labor	\$6/h		
Chemicals			
Lime	\$25/ton		
Ferric chloride ($FeCl_3$)	\$134/ton		
Polymers	\$1000/ton		

Supplies

All maintenance and operating supply costs were adjusted to a mid-1975 Whole Price Index for Industrial Commodities of 170.

Hauling costs \$0.1–0.2/ton/mile: 15–30 miles
\$3/ton of slurry or dry ash

Landfill disposal \$1/ton of slurry or dry ash

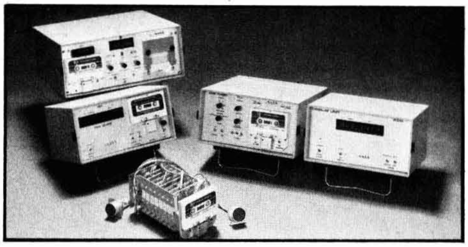


TABLE 4

Operating cost sensitivities

Possible changes considered	Percentage change in total operating costs for three options[a] (%)		
	1b	2	4b
Power costs doubled	+0.75	+2.75	+1.9
Chemical usage halved	−3.00	0	−2.8
Fuel costs doubled	+1.3	+0.1	—
Hauling costs halved	Neg.	Neg.	−3.1
No heat recovery by steam generation at credit of $\$1/10^6$ Btu[b]	+2.5	+1.1	—
Recovered gas value increased from $\$1/10^6$ Btu to $\$2/10^6$ Btu	—	—	−2.0[c]
Total change in plant operating costs	+1.55	+3.95	−6.0
Initial relative total plant operating costs	1.00	1.04	1.07
Changed relative total plant operating costs	1.02	1.08	1.0

[a] 10 mgd, average dry weather flow.
[b] Except for Option 2 for heat treatment use.
[c] For Option 4b assume value of recovered gas is doubled.

content (≥60% volatiles) is competitive with a wide variety of other sludge handling techniques. This assessment is based on a comparison of capital and O&M costs, as well as on an analysis of fuel and electrical power consumption. As the plant size increases, incineration may provide lower capital and operating costs. Moreover, the thermal processing solution eliminates major management and institutional questions involving the final disposition of large quantities of sludge that must ultimately be disposed of on, or in the land.

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CURRENT RESEARCH

Particulate and Smoke Emission from a Light Duty Diesel Engine

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■ Particulate and smoke emissions were studied in the exhaust of a Mercedes Benz type OM 616 diesel engine. The weight and size distribution of the particulate matter emitted and the intensity of the smoke were measured at different engine loads and at various constant speeds in the range 35–96 km h^{-1}. The level of the particulates emitted during a simulated seven-mode Federal Test Procedure was also determined. The results showed that both the particulate and smoke emissions were highly dependent on engine speed and load. The particulate matter collected was analyzed for its chemical composition, showing that 60–75 wt % of the particulate matter was organic compounds.

In recent years a considerable amount of work has been directed toward the study of particulate emission from diesel engines, but most of the previous work dealt with the emission of visible smoke from heavy and medium duty engines. Only a few investigators studied emissions from light duty diesel engines, with the main emphasis on the measurements of smoke, odor, sulfate, and gaseous emissions (*1–9*). Less attention has been paid to particulate emission; the previous investigations focused on the amount of particulate matter emitted under various driving cycles (*6–8*). Data showing the direct effects of engine speed and load on particle mass emission, size distribution, and smoke emission have not yet been reported. The objective of this investigation was to study the physical and chemical characteristics of the particles emitted from a light duty diesel engine and to evaluate the effects of speed and load on the amount and size distribution of the emitted particulate matter and on the smoke emission.

Experimental

Apparatus. The engine was a four cylinder in-line 1976 Mercedes Benz type OM 616 diesel engine (standard engine in the Mercedes Benz Model 240 D car), mounted on an eddy current dynometer. American Oil Co. number 2 diesel fuel was used throughout the experiments. The physical and chemical properties of the fuel are given by Laresgoiti and Springer (*10*).

The exhaust system consisted of the standard exhaust manifold supplied with the engine, a 30-cm-diam, 60-cm-long surge tank, a 4.3-m-long, 50-mm-diam (2 in.) black iron pipe (simulated exhaust system), and a 25-mm-diam sharp-edged orifice (orifice A, Figure 1). The surge tank was added to reduce the pressure and flow fluctuations in the exhaust (*11*).

Descriptions of the sampling system and procedures were given in detail in refs. *10–14* and will not be repeated here. Only a brief summary is provided to facilitate the understanding of the results.

The sampling probes were made of 316 stainless steel tubes with dimensions 3.98-mm-i.d., 1.18-mm wall thickness or 2.66-mm-i.d., 1.16-mm wall thickness. The probes were located in the center of the exhaust pipe facing the direction of flow.

Particulate matter was collected on Gelman 47-mm-diam type A glass fiber filters placed in a modified Gelman 2220 filter holder. The entire filter unit was surrounded with beaded heaters and Kaowool insulation (Figure 2a).

The flow rate through the probe was adjusted to the proper value for isokinetic sampling. At steady operating speeds the flow rate of the sample was measured by a wet test meter installed after the filter. The flow rate was adjusted by a bleed valve compensating for the increase in filter resistance with time. Under cyclic operating conditions the flow rate through the probe was modified and adjusted continuously with the control system described by Laresgoiti and Springer (*10*). Two high-vacuum pumps provided the flow through the sampling train.

The particle size distribution was measured with a Model 225 Royco particle counter. The exhaust sample was drawn from the exhaust system through a 2.66-mm-diam (1.16-mm wall thickness) stainless steel sampling probe (Figure 2c). At each steady engine speed, the flow rate through the probe was measured with a 2.77-mm-diam sharp-edged orifice (orifice B, Figure 2c) and controlled by a stainless steel metering valve (valve B, Figure 2c). To prevent condensation in the sampling line, the probe, orifice, and metering valve were wrapped with heating tape and Kaowool insulation.

The sample was diluted with filtered ambient air. The sample gas–air mixture was then fed through a 11.4-L dilution chamber to reduce the temperature of the sample below 49 °C and the particle concentration below 120 particles/cc. These values were dictated by the specifications of the Royco counter. The dilution air flow rate was adjusted by a bleed valve (valve C, Figure 2c) and measured with a sharp-edged orifice (orifice C, Figure 2c).

A portion of the diluted exhaust sample was drawn into the Royco counter through a 9.5-mm-i.d., 3-m-long tygon tube. The flow rate through the Royco counter (measured with a

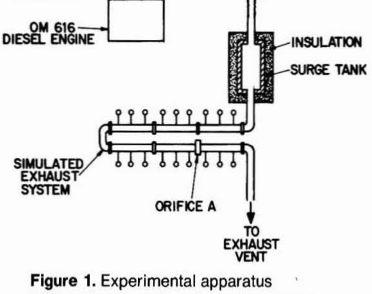

Figure 1. Experimental apparatus
Circles: thermocouple and sampling locations

Kontes metering tube) ranged from 850 to 1400 cc min^{-1}. This was about 2% of the sample gas–air mixture flow rate. The particle sizes were recorded in five size ranges yielding the number of particles of diameters greater than 0.3, 0.7, 1.4, 3.0, and 5.0 μm.

At selected conditions particle size distributions were also measured with a Model 50-000 high-temperature Andersen stack sampler. The sampler was connected to a 3.98-mm-i.d. (1.18-mm wall thickness) stainless steel probe. A Gelman type A 142-mm-diam glass fiber filter housed in a steel holder was mounted directly behind the sampler (Figure 2b). The sample unit was surrounded with beaded heaters and enclosed in Kaowool insulation, keeping the sampling system temperature above 38 °C to prevent condensation of the exhaust gas. The flow rate through the Andersen sampler was adjusted with the vacuum pump bleed valve to ensure isokinetic sampling at the probe inlet. When the Andersen sampler was being used, the exhaust sample was not diluted with ambient air. The intensity of the smoke was measured with a Bosch smoke meter.

Test Procedures. Before any data were taken, the engine was operated at 1800 rpm and 18 hp for 30 h to break in the engine and to condition the exhaust system. Before each new steady state speed test, the engine was operated for 4 h at the conditions of the test. Before each cyclic test the engine was run 10 complete cycles. With these procedures during the actual tests, changes were not observed in any of the measured parameters, at least within the scatter of the data.

To determine the total weight of the emitted particulate matter, the filters were placed in an air-tight container containing $CaCl_2$ as a desiccant for 24 h after each test. The filters were then weighed and prepared for chemical analysis. The sulfate content of the particulates was examined by the Barium-Thorin titrimetric procedure (*10*). Blank filters (i.e., before particulates were collected on them) were tested for sulfate content. The results did not show any sulfate.

In addition, the particulate matter collected was analyzed for organic solubles by extracting (for 3 h) the organic solubles from the particulate sample by the soxhlet technique. The solvent (benzene) was then evaporated and the remnant weighed, giving the weight of the organic solubles. After weighing the extracted organic solubles, all the samples were combined. The samples were then analyzed by infrared absorption to determine the most common types of molecular groups present in the exhausted organic matter.

The total particulate matter collected on the filters was subjected to electron microprobe analysis to determine the metals present in the sample.

To study the possible formation of particulate matter in the exhaust system, samples were collected on filters (Figure 2a) along the entire length of the exhaust system at steady engine

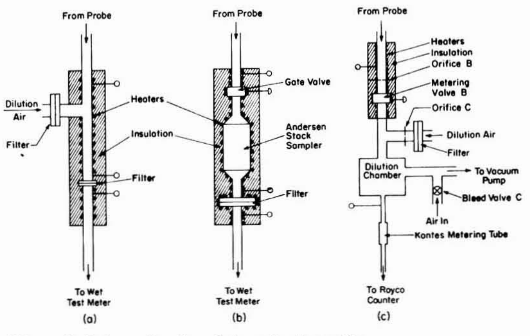

Figure 2. Schematic of particle collection units

(a) Unit housing filter for collecting total particulate matter; (b) unit housing Andersen sampler for particle size measurements; (c) unit used in conjunction with Royco particle size analyzer. Open circles: thermocouple locations

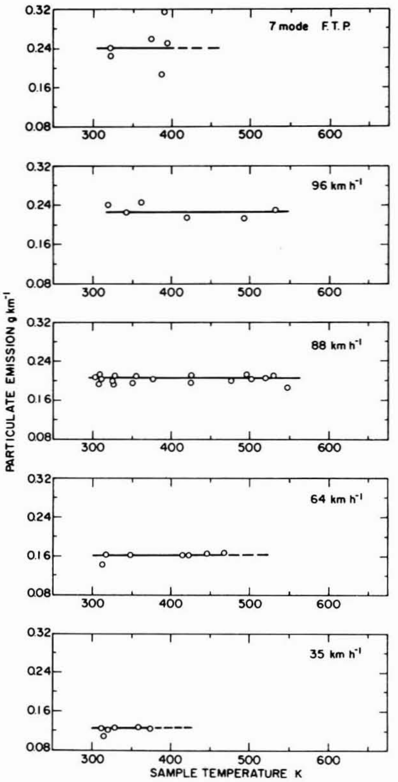

Figure 3. Particulate emission vs. sample gas temperature during simulated seven-mode Federal Test Procedure, and 35, 64, 88, and 96 km h^{-1} cruise conditions. (— - - -) Fit to data

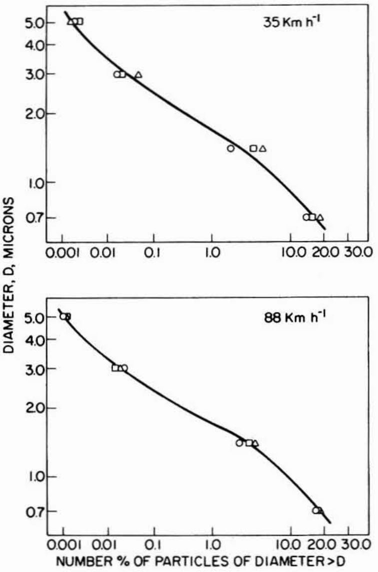

Figure 4. Influence of sample probe location on measured particle size distribution

Sample probe distance from surge tank: ○ 0.7 m, □ 3.0 m, and △ 4.0 m. Dilution ration 8:1. Steady engine speed, cruise conditions speeds and loads corresponding to a 1976 240 D Mercedes Benz diesel car cruising at 35, 64, 88, and 96 km h^{-1}, and under a simulated seven-mode Federal Test Procedure. The results are presented in Figure 3. The horizontal axis in this figure is the sample temperature which corresponds to different sampling points along the exhaust system. The data in Figure 3 suggest that no significant amount of particulates forms in the exhaust within the temperature ranges achieved in these tests (300–550 K). This implies that most particulate matter forms either in the combustion chamber or in the exhaust manifold. Particulate formation due to condensation in the exhaust pipe was insignificant.

Between 300 and 350 K, particulate matter was collected on the filters both by diluting the sample with ambient air (dilution ratio 8:1) and without dilution. The mass of the collected particles was the same with and without dilution. Since sample temperature and dilution did not affect the mass emission, all subsequent samples used for determining mass emission and chemical composition were taken without dilution at a point where the sample temperature was about 300 K (about 3 m from the surge tank). It is noted that dilution was unnecessary even at sample temperatures as low as 300 K because water condensation on the filter was not a problem. Water condensation did not occur because the air–fuel ratio in the diesel engine was high (ranging from 25:1 to 40:1). This is in contrast with the operation of the spark ignition engine where the air–fuel ratios were much lower (~15:1), resulting in water condensation on the filter at temperatures below ~300 K (*10*).

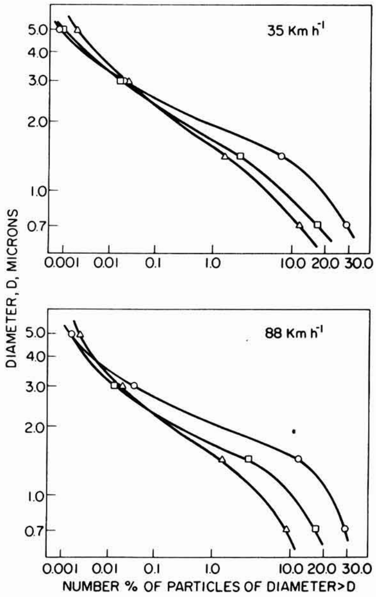

Figure 5. Effect of dilution ratio on measured particle size distribution

Dilution ratios: O 4:1, □ 8:1, and △ 12:1. Probe location 3 m from surge tank. Steady engine speed, cruise conditions

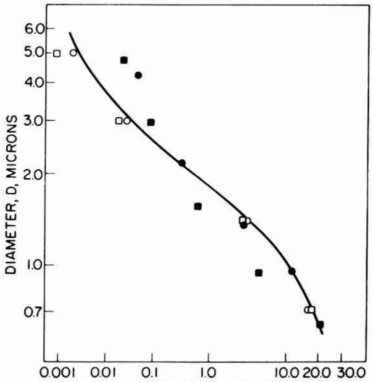

Figure 6. Comparison of particle size distribution measured by Royco counter (dilution ratio 8:1) and Andersen sampler

Royco data at O 35 km h^{-1} and □ 88 km h^{-1} cruise conditions. Andersen data at ● 35 km h^{-1} and ■ 88 km h^{-1} cruise conditions. Symbols: average of data taken at three sample locations: 0.7, 3.0, and 4.0 m from surge tank

Both the position of the sampling probe and dilution ratio may affect the measured size distribution. To evaluate the influence of sample probe location, size distributions were measured at three points along the simulated exhaust system: 0.7, 3.0, and 4.0 m from the surge tank (Figure 1). The measurements were performed at steady engine speeds and loads corresponding to 35 and 88 km h^{-1} cruise conditions. The ratio of the total volume flow of sample gas–air mixture to the volume flow of the sample gas flowing through the sampling probe (defined as the "dilution ratio") was held constant at 8:1. The results given in Figure 4 indicate that the sampling location does not affect significantly the measured particle size distribution. For this reason, all subsequent particle size distribution measurements were made 3 m from the surge tank.

The particle size distribution was also measured at the three dilution ratios: 4:1, 8:1, and 12:1. Engine speed and load were again set corresponding to 35 and 88 km h^{-1} cruise conditions. Results of the measurements indicate that the particle size distribution depends somewhat on the dilution ratio (Figure 5). As the dilution ratio increases, the percentage of the smaller particles also increases. Since the coagulation rate is proportional to the square of the concentration of particles in a given size range (*15*), an increase in dilution ratio decreases the particle concentration and hence decreases the coagulation rate. A lower coagulation rate results in a larger percentage of smaller particles.

The accuracy of the results given by the Royco counter could be assessed by measuring the size distribution by another instrument such as the Andersen stack sampler. Unfortunately, the Royco counter provides the number distribution while the Andersen sampler yields mass distribution. A direct conversion from one distribution to the other requires a knowledge of the shape of the particles, the mass distribution of the particles on the backup filter, and the density of the particles. All these parameters are unknown, preventing an exact comparison between the two instruments. A rough comparison could be made, however, by assuming that all particles are spherical, by estimating the distribution on the backup filter by "matching" the results of the Andersen sampler and the Royco counter at one data point, and by taking the particle density to be 1 g cm^{-3}. A comparison of the size distributions was made on the basis of these simplifying assumptions (Figure 6). There is reasonably good agreement between the data given by the two instruments, lending some confidence to the size distribution measured with the Royco counter. Additional details of the apparatus and test procedures are given in ref. *10*.

Results

The results presented in Figure 3 are cross-plotted in Figure 7 to evaluate the dependence of the particulate emission on speed. Figure 7 indicates the mass of particulate matter emitted at various steady engine speeds corresponding to road load conditions. The emission increases significantly with speed. It is interesting to observe that at corresponding speeds, the mass of particulate matter emitted by the diesel engine is about 10 times higher than the mass emitted from the 350 CID Chevrolet engine operating on unleaded fuel [with or without catalyst (*13*)], and about five times higher than the mass emitted by the same Chevrolet engine operating on leaded fuel [without catalyst (*12*)].

The change in particulate concentration in the exhaust with load and engine speed (rpm) is shown in Figure 8. The amount of particulate matter emitted is governed by the combustion chamber geometry, the position and geometry of the fuel jet spray, the combustion chamber temperature, the time available for combustion, and the amount of fuel injected per stroke. In this work changes in the geometries of the combustion chamber and of the fuel jet spray were not considered since they were fixed for the engine. Thus, the amount of particulate matter emitted was mostly governed by the combustion chamber temperature, the combustion time, and the mixture composition. High combustion chamber temperature, long combustion time (i.e., low rpm), and lean mixtures result in lower particulate emission, while lower combustion chamber temperatures, shorter combustion times, and richer mixtures lead to higher emissions. The combination of these factors may explain the behavior of the particulate emission presented in Figure 8. Above 1500 rpm the particulate concentration decreases with load up to about 75% of full load. Above 75% of full load the particulate concentration increases with load. At a fixed rpm the time available for combustion remains constant. However, an increase in load results in higher combustion chamber temperatures and richer mixtures. Up to 75% of full load the combustion temperature is sufficiently high to assure efficient combustion and relatively low emission rates. Above 75% of full load the mixture becomes too rich to achieve complete combustion at the prevailing combustion chamber temperature. Hence above 75% of full load the amount of unburned combustion products and, correspondingly, the particulate emission increases.

As the engine speed decreases the time available for combustion increases while the combustion chamber temperature decreases. At lower speeds (below about 1500 rpm), the increase in combustion temperature due to the increase in load is insufficient to compensate for the larger amounts of fuel necessary to produce the higher loads—hence an increase in particulate emission with load.

At constant load (Figure 9) the particulate emission initially decreases with speed, reaches a minimum between 2000 and 3000 rpm, and then increases. In the lower rpm ranges the combustion chamber temperature increase is sufficient to compensate for the smaller time available for combustion (higher rpm), resulting in improved combustion and decreased particulate emission. At higher speeds (about 2000 rpm) the opposite happens, i.e., the increase in temperature is insufficient to compensate for the decrease in combustion time yielding increased emissions. At very low loads (near zero load) the temperature may be very low in the combustion chamber, causing the particulate emission to increase with speed at all speeds.

The mass of particulates emitted per unit mass of fuel burned as a function of speed and load is shown in Figures 10 and 11. These results show a trend similar to those in Figures 8 and 9. The slight difference in the trend in the data is due to the fact that the fuel consumption is not a constant but varies both with speed and load (Figure 12).

The amount of smoke emitted (expressed in Bosch units) as a function of load and speed is shown in Figures 13 and 14. As expected, the smoke varies with speed and load in the same manner as the mass of emitted particulate matter.

The results of the chemical analysis of the particulate

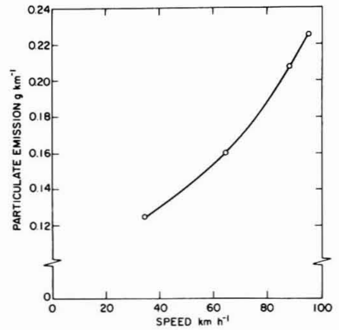

Figure 7. Particulate emission vs. steady engine speed

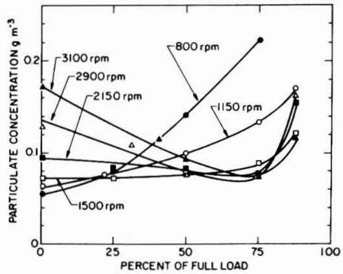

Figure 8. Exhaust particulate concentration as a function of engine load and speed

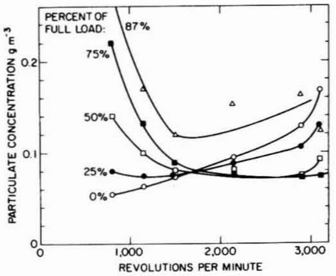

Figure 9. Exhaust particulate concentration as a function of engine speed and load

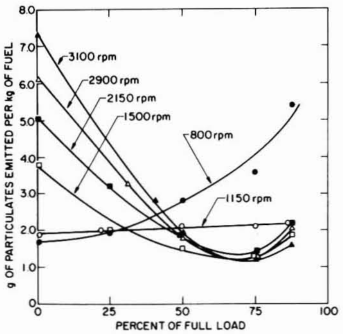

Figure 10. Particulate emission per unit mass of fuel consumed as a function of engine load and speed

matter emitted at steady speeds are shown in Table I. Neither sulfates nor metals could be observed in the particulate samples. This implies that the particulate matter contained less than 1 wt % of sulfates and metals. The observation regarding the absence of metals in the sample is in agreement with that found by Braddock and Gabele (*7*). The observed sulfate content is somewhat lower than those (2–3%) reported previously (*5–9*). However, in all previous investigations the sample was diluted and, hence cooled, before it was collected and analyzed. In the present study the sample used in the chemical analyses was taken directly from the exhaust stream and was maintained at the exhaust gas temperature. The difference in sample temperature may account for the difference in the sulfate content.

The major portion of the particulate matter was organic solubles. The mass percent of organic solubles varied from 75% at 35 km h^{-1} to 60% at 96 km h^{-1}. An attempt was made to identify by infrared spectra the structure of the organic solubles. Since benzene was used as solvent, it was possible to detect the presence of alkyl groups only. The presence of aromatics and other groups could not be detected because their absorption peaks were blocked by the absorption peaks of the solvent.

Particle size distributions were measured at 24 engine operating conditions. The speeds investigated were 800, 1150, 1500, 2100, 2880, and 3100 rpm. At each steady rpm, the load was adjusted to approximately 0, 25, 50, and 75% of full load. The size distribution is reported in terms of the number of particles in a given size range, as provided directly by the Royco counter. The data were not converted to mass distri-

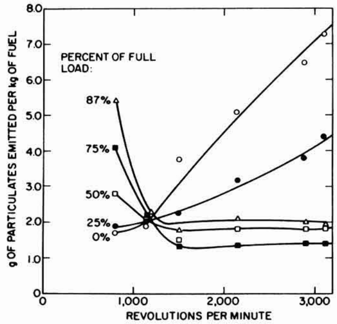

Figure 11. Particulate emission per unit mass of fuel used as a function of engine speed and load

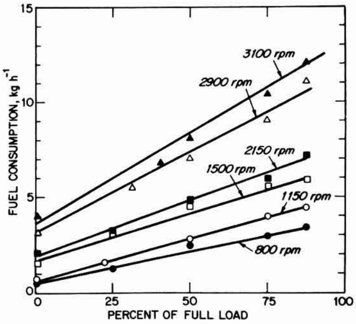

Figure 12. Fuel consumption as a function of engine speed and load

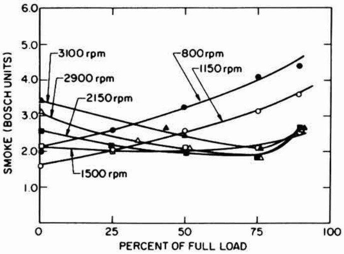

Figure 13. Smoke emission as a function of engine load and speed

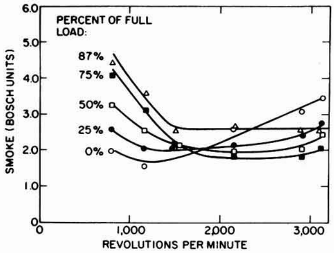

Figure 14. Smoke emission as a function of engine speed and load

Table I. Chemical Analysis

Equiv road load, km h^{-1}	Wt % organic solubles[a]	Sulfate content[b]	Metal content[c]
35	75	Not observed	Not observed
64	65	Not observed	Not observed
88	70	Not observed	Not observed
96	60	Not observed	Not observed

[a] Soxhlet extraction. [b] Barium-Thorin titrimetric procedure. Lowest sulfate weight observable was ~10 μg. This is less than 1% of the total sample weight. [c] Electron microprobe. Weight of metal content was less than 1% of the total sample weight.

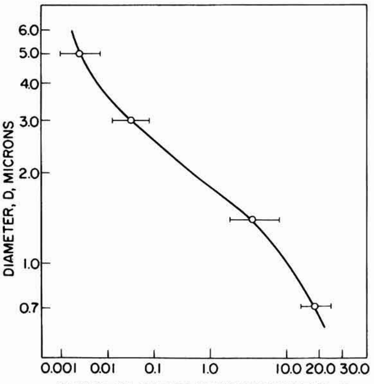

Figure 15. Particle size distribution

Circles: average of 24 data points for speeds ranging from 800 to 3100 rpm and for loads ranging from 0 to 75% of full load. Bars: data scatter bution since, as noted earlier, the shape and density of the particles were unknown. The results do not show any significant systematic variation in size distribution, either with speed or with load. The changes in the size distributions with speed and load were within the scatter of the data. The measured size distribution is shown in Figure 15. Each circle represents an average of the 24 tests, the bars indicating the data scatter. About 90% of the particles were smaller than 1 μm, and 99% of the particles were smaller than 2 μm.

The foregoing results indicate the trend in particulate and smoke emissions at steady speeds and under a simulated driving cycle. This must be borne in mind when applying the results to emissions from an automobile under actual driving conditions.

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Analysis of Ozone at Low Concentrations with Boric Acid Buffered KI

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■ Ozone analyses with a modified potassium iodide absorbent (BKI: 0.1 M H_3BO_3/1% KI) give consistent agreement with UV photometry over the concentration range 0.1–3.5 ppm. The colorimetric iodine response with this BKI solution is both precise and stable. Trace reducing contaminants (ozone demand) in the potassium iodide reagents are a major problem in the work at 0.1 ppm. Iodometric analyses with NBKI (0.1 M Na_2HPO_4/0.1 M KH_2PO_4/1% KI) give results that increase with time and are 15–30% larger than those obtained by UV or BKI. These data are explained by the formation of a second product, P, in addition to iodine, when ozone is absorbed in NBKI and certain other buffered KI solutions; P slowly liberates additional iodine. At room temperature the kinetic rate of H_2O_2 + NBKI agrees with that of P + NBKI. Since other potential products have been excluded on this basis, P is tentatively identified as H_2O_2.

The absorption of ozone in a neutral buffered potassium iodide solution (NBKI: 1% KI, 0.1 M KH_2PO_4, 0.1 M Na_2HPO_4) is the basis of a reference technique adopted by the Environmental Protection Agency in 1971 (*1*). This method is based on the original work of Saltzman and Gilbert (*2*) as incorporated into the Public Health Service Methods (*3*). The discrepancy between numerous investigations into the stoichiometry of iodometric analyses at all concentration levels has already been mentioned (*4*). The most recent investigations (*5–11*) appear to show that the absorption of low concentrations of ozone (LC, 0.1–1 ppm) in NBKI produces iodine in excess of that given by the stoichiometric equation:

$$O_3 + 2I^- + 2H^+ = I_2 + H_2O + O_2 \qquad (1)$$

In addition there is evidence that the overall result is affected by the humidity of the gas stream (*6, 9*).

I have compared the stoichiometry of NBKI and other iodometric procedures against each other and against ultraviolet photometric absorption (253.7 nm) by use of a modified Dasibi ozone monitor at concentrations ranging from LC to high concentration ($100–10^4$ ppm ozone). In this paper I present evidence that at LC, a new reagent, boric acid buffered potassium iodide (BKI: 1% KI, 0.1 M H_3BO_4) produces iodine quantitatively according to Equation 1, and that NBKI yields 15–30% more iodine than predicted by Equation 1. A mechanism is presented which quantitatively accounts for a major source of variability in NBKI analyses. Results with certain other reagents are also given. The experiments at high concentration will be reported elsewhere.

Experimental

The apparatus is shown in Figure 1. Air or O_2 passes through an ozone generator (*12*), and the ozonized stream is sampled by a modified Model 1003-AH Dasibi ozone meter (SN 1308). Components in contact with ozone were composed of Teflon, Kynar, and Pyrex.

A second sample (point "1" in the figure) could be diverted into two Ace Glass No. 7531-10 midget impingers. The same two impingers were used in all runs reported here. After each run the impingers were washed with water that had been distilled, ion-exchanged, and redistilled twice more in a glass still (DW). They were then vacuum dried in-situ. Ten milliliters of absorbing solution were generally used in both impingers, although in some experiments the volume of absorbent in the first impinger was varied. Close to the end of this

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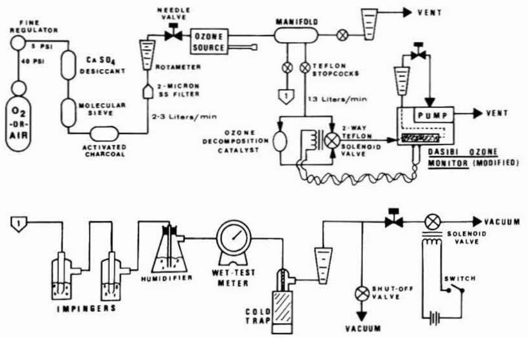

Figure 1. Apparatus

work, the humidifier was removed since gas emerging from the impingers was already close to saturation. The "shut-off" valve was normally closed, and the needle valve downstream of the impingers was adjusted for the desired flow rate (usually 0.5 L/min) under operating conditions.

After the impingers were filled and installed, the stopcock leading to point 1 was opened; gas flow started when the solenoid was opened. At the end of a fixed time (usually 10 min), the solenoid was closed and the impingers were removed for analysis.

Photometric Apparatus and Methods

The Dasibi meter has already been described (*13, 14*). For the present experiments, the solenoid valve was removed from the instrument to an external position and was reconnected via a channeled Teflon block in the original mounting. Other workers (*15, 16*) have reported that this improves stability and precision. Paur and Beard (*16*) suggested that a separate unozonated reference stream be employed in lieu of the catalyst. Although the catalyst was routinely used in this investigation, these measurements were compared with those made with a separate reference stream; there was no detectable difference.

The concentrations of ozone in the Dasibi photometer are given by a form of Beer's law (*13, 14, 17*)

$$[\mathrm{O}_3]_{\mathrm{ppm}} = \frac{10^6}{\alpha_0 L}\frac{p_0}{p}\frac{T}{T_0}\ln\frac{I_0}{I_0 - R} \tag{2}$$

which was used to compute instrumental ozone readings. The temperature of gas emerging from the photometer cell, T, was 41 ± 1 °C as measured with a thermocouple at the exit port of the cell in the Dasibi; the instrumental reading, R, was averaged over each run. p was taken as the local barometric pressure plus 2.2 torr, the differential between the manifold and atmosphere, while α_0 was taken as 134 $\mathrm{cm}^{-1}\ \mathrm{atm}^{-1}$ (*18, 19*). The unmodified Dasibi employed a small rotameter with an *upstream* needle valve, and its reading was erroneously high; it was replaced with a more accurate flow meter and *downstream* metering valve to assure sufficient flow to purge the photometer cell (~1.1 L/min) between sampling cycles (*14, 17*).

Paur (*16, 20*) has found that different Dasibi instruments agree within 1% when they are in good working order. After completing this work, the present Dasibi was compared with another Dasibi instrument that was within 2% of gas-phase titration and a 3-m UV photometer (*5, 6, 16, 21*). At a nominal ozone concentration of 0.250 ppm, the present Dasibi read 1.6 ± 0.6% less than the calibrated instrument; on the basis of this evidence, it is assumed that the absolute accuracy of the present UV measurements is better than 4%.

Reagents and Chemical Analysis

Preliminary experiments indicated that trace contaminants in the water used to make up solutions might be a factor in potassium iodide analyses. This possibility was investigated by using different sources of water: distilled water from the laboratory tap (TW), TW that was subsequently ion exchanged (IW), and DW. In general, using these different sources of water had no significant effect at 1.0 and 0.5 ppm. There was evidence of a small effect at 0.1 ppm (see Table II and Results at 0.1 ppm—section below).

Several workers have reported that various brands or grades of potassium iodide contain traces of a reducing agent (*8–10, 22–24*). Some state or imply that this is intentionally added to reagent grade KI (*9, 10*) whereas "KI meeting USP specifications usually contains little or no reducing agent . . ." (*10*). However, they offer no evidence for this assertion. While some of these reports (*22*) have implied that this additive (or impurity) will reduce both iodine and ozone ("iodine demand"), others only acknowledge that ozone is reduced ("ozone demand"). This is a significant distinction since the colorimetric step is quantitatively calibrated by adding *iodine* to the absorbant solutions, whereas it is ozone that is actually collected and analyzed. Although it now appears that there was a significant ozone demand during the experiments at 0.1 ppm (see below), it was not recognized at the time many of the experiments were conducted. The effect was negligible at the higher concentrations studied.

Four different sources of KI were used in the experiments (see Table II), and two different lots of Fisher ACS grade buffer chemicals were used to prepare the NBKI. Fisher Lot 721474 ACS grade boric acid crystals were used to prepare all of the BKI solutions, except for three runs using "Batch 12" as noted in Table II. These variations in the source of buffer chemicals had no noticeable effect. Replicate experiments were run with both air and oxygen; however, there was no detectable difference between ozone analyses in these two gases so that the combined data are considered jointly.

All solutions were stored in glass-stoppered bottles which were kept in a dark cabinet. Absorbing reagent was always removed from the stock solutions in the dark.

The concentration of iodine in the absorbent solutions was determined by filling 1 cm^2 glass-stoppered matched cuvettes liquid-full and measuring the 352-nm absorbance of I_3^- with a Bausch and Lomb Model 710 spectrophotometer. The cuvettes were always prerinsed with sample.

Beer's law curves were run initially and again after an interval of 1½ months. Iodine solutions were prepared as prescribed in the *Federal Register* (*1*) with NBKI and BKI stock solutions. The solutions were titrated against commercial 0.1 N (±0.1%) sodium thiosulfate solution; this titer was confirmed by standardization against 0.1 N KIO_3 solution. The absorbances of the diluted iodine stock solutions were stable during these calibrations (10–25 min) while the solutions were kept in stoppered volumetric flasks or in the (liquid-full) glass-stoppered cuvettes.

Both Beer's law calibrations were in excellent agreement, even though they were each performed using different sources of KI (I and later both II and III). The plot of absorbance vs. I_3^- passed through the origin and thus showed no evidence of iodine demand. However, the absorbent solutions were about 2–3 weeks old at the time they were used in these calibrations, and "fresh" solutions at 0.1 ppm did show evidence of iodine demand (see below).

Comparison of NBKI with UV and BKI

When NBKI was the absorbent at 0.35, 0.5, and 1.0 ppm ozone, the quantity of iodine in the first impinger continuously increased with time even after the absorption of ozone was stopped. At the concentration of 0.1 ppm, on the other hand, there did not appear to be any substantial liberation of iodine after the absorption was complete; the 0.1 ppm results are discussed separately. In the second impinger there was little iodine during all runs (about 5% of impinger 1), and there never was any sign of post-absorption color development. Initial NBKI ozone analyses (2 min after ozone collection had ceased or 12 min after the start of each 10-min run) are compared with UV and BKI in the first three rows of Table I. When the triiodide absorbances (or equivalent iodine concentrations) are plotted on the reduced coordinates of Figure 2, it becomes evident that the additional iodine produced after absorption can be explained as the product of a first order reaction between a second substance, P, and NBKI:

$$\mathrm{P} + \mathrm{NBKI} = \mathrm{I_2} + \mathrm{Products} \tag{3}$$

P is formed when ozone is absorbed in NBKI (see the By-Product Formation section below). These observations are generally consistent with the original work of Saltzman and Gilbert (*2*). It follows that any ozone measurement procedure using NBKI must, at least, specify the precise time at which the "developed" iodine is to be measured.

BKI, however, yielded precise analyses that were stable with time (less than 0.5% change) under all conditions studied. The BKI measurements were also very repeatable (better than 1% on successive runs). For this reason, BKI analyses were regularly alternated with the experiments employing other absorbents. Since daily variability in flow and chemical factors affected the alternate BKI and NBKI runs in the same way, the ratios of NBKI to BKI should be more accurate than that of NBKI to UV data.

Comparison of BKI with UV

The average ratio of BKI to UV measurements (BKI/UV) for all data under standard conditions (10 cc in impinger 1, 0.5 L/min, 10 min) was 0.999 ± 0.007 SE ($n = 37$) at 1.0 ppm (see Table I). If the UV Dasibi measurements utilizing Equation 2 are regarded to have an absolute accuracy of ±4%, the BKI analyses are clearly consistent with the 1:1 ozone-to-iodine stoichiometry of Equation 1.

Figure 3 shows these averages (diamond points and error bars represent 1 SD) along with BKI/UV when the gas flow rate, volume of absorbent in the first impinger, and bubbler type (Ace No. 7532-10 frit vs. standard 7531-10) were varied. The coordinate, ozone absorbed per volume of absorbent, provides a convenient scale for displaying the results of these analyses and reveals a tendency for BKI/UV to decrease with a decrease in this ratio; the magnitude of this effect is consistent with the proposed presence of a trace contaminant in the potassium iodide reagents as discussed below. It is apparent from the figure that BKI analyses were not affected by the use of a frit-type absorber rather than an impinger. However, the use of a frit was not advantageous since it did not prove to be a more efficient absorber and it required a larger pressure differential. Figure 3 also shows that variations in absorbent volume (5–25 mL in impinger 1), sample flow rate (0.25–1 L/min), and sampling time (5–20 min) did not affect the 1:1 BKI/UV.

Results at 0.1 ppm

BKI and NBKI results at 0.1 ppm are presented in Table II. These data are not as precise as those at the higher concentrations, and the average BKI/UV ratio at this concentration, BKI/UV = 0.877, is significantly below 1.0. Part of this low bias and scatter can be attributed to reduced experimental precision, and part of it is consistent with the presence of reducing contaminants in the potassium iodide reagents (ozone demand).

The experimental uncertainty at 0.1 ppm ozone is estimated to be ~(±)5–6%, but some of this may have appeared as systematic bias. The major sources of error include about 3% due to the finite precision of digital outputs from the Dasibi and spectrophotometer and imprecision in correcting for the absorbance of reagent blanks (*17*).

Table II presents six groups of 0.1 ppm data (A–F), each of which were taken sequentially during a single session. Since changes in ozone concentration, flow rate, pressures, and other parameters were minimal during each individual session, systematic intragroup differences are significant even though they may be less than the intergroup variability. Twelve distinct absorbent solutions, prepared at different times, were used in these experiments as noted under "Absorbent Batch". The KI source is also listed with the age of each solution at the time a datum was taken (see the Reagents and Chemical Analysis section). The same buffer chemicals were used throughout, except for the change in solution 12 as noted.

These data suggest that "ozone demand" is responsible for the low BKI/UV at 0.1 ppm. Fresh solutions of BKI prepared from Lots II, III, and IV (see Groups D, E, and F) consistently gave lower analyses than like solutions which had aged. A portion of the reducing contaminant is apparently consumed by slow reactions involving oxygen. The data for TW also seem low. Fresh solutions of BKI prepared from Lot II resulted in

Table I. Summary of Average Analysis Rations (2 Min After Absorption)

Buffer	ppm O_3	Ratio to UV	Ratio to BKI	$\Delta O_{3,\infty}/UV$
NBKI	1.0	1.18 ± 0.008[a] $n = 25$	1.17 ± 0.007 $n = 8$	0.137 ± 0.002 $n = 25$
NBKI	0.6	1.20 ± 0.01 $n = 8$	1.15 ± 0.007 $n = 5$	0.139 ± 0.003 $n = 9$
NBKI	0.35	1.18 $n = 1$	1.20 $n = 1$	0.126 ± 0.006 $n = 4$
BKI	1.0	1.021 ± 0.003 $n = 37$	. . .	. . .
BKI	0.6	1.000 ± 0.007 $n = 27$	. . .	. . .
BKI	3.5	0.993 ± 0.012 $n = 2$	. . .	. . .
0.01 M NBKI (0.01 M Na_2HPO_4/ 0.01 M KH_2PO_4)	1.0	1.04 ± 0.009 $n = 2$	1.007 ± 0.023 $n = 2$	0.024 $n = 1$
0.01 M KH_2PO_4	1.0	1.03 ± 0.0075 $n = 4$	0.989 ± 0.013 $n = 4$	0.0264 ± 0.0015 $n = 3$
0.1 M KH_2PO_4	1.0	1.22 $n = 1$	1.18 $n = 1$	0.138 $n = 1$
10^{-4} N H_2SO_4 (pH = 4)	1.0	1.01 $n = 1$	1.01 $n = 1$	≈0
0.1 M $(NH_4)_2SO_4$	1.0	1.07 $n = 1$	1.04 $n = 1$	0.057 $n = 1$
0.05 M Na acetate/ 0.05 M acetic acid	1.0	1.19 $n = 1$	1.17 $n = 1$	0.131 $n = 1$
0.1 M Pthallic acid	1.0	1.23 $n = 1$	1.19 $n = 1$	0.167 $n = 1$

[a] Deviations represent ±1 standard error.

the lowest analyses of all (points 11, 16, 22); they lie approximately 10% below 0.1 ppm data which corresponds to about 5×10^{-6} iodide equivalents of reducing impurity per mole of KI (3×10^{-8} equiv/g). If fresh solutions and those prepared from II and TW are excluded, the average BKI/UV at 0.1 ppm increases to 0.961 ± 0.01 SE (7 points). When the sampling time was doubled (compare points 19 and 20, 22 and 24), the analyses also increased as would be expected if a reducing contaminant was initially consumed by ozone.

The USP grade KI (Lot II) displayed the largest interference from reducing contaminant; thus, the present data are not in concert with previous reports that USP grade KI is better for ozone analyses than the reagent grade (*9, 22, 23, 24*). Furthermore, according to the manufacturer of KI Lots I and II, no reductant or other material is ever intentionally added either during the production or the bulk chemical or in subsequent processing and packaging of the final product (*25*).

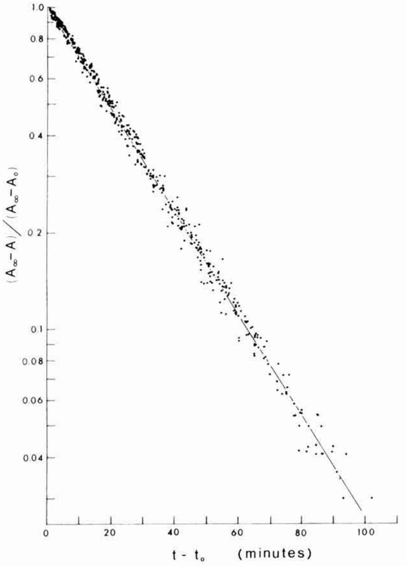

Figure 2. Reduced absorbance vs. time after ozone collection
A_∞ is final limiting value of absorbance and A_0, initial absorbance, t_0 minutes after collection. Solid line: least-squares statistical rate constant (see text)

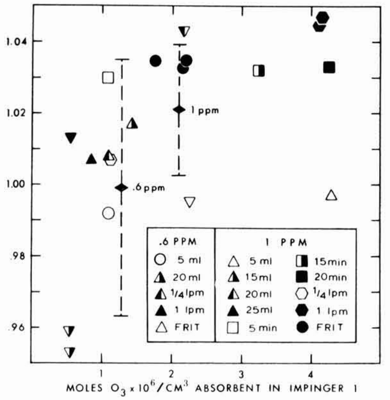

Figure 3. Ratio of BKI to UV analyses at 0.6 and 1.0 ppm for various conditions
Diamond points and standard deviation error bars: mean values for all BKI data at 0.6 ppm, 1.0 ppm, and standard conditions (see text)

There is no significant difference between NBKI and BKI analyses in Groups A and B of Table II. Neither absorbent exhibited a significant increase in absorbance after collection was complete. This agreement is consistent with Jaffe's report (*26*) that NBKI/UV ≥ 1 and approaches unity as $[O_3] \rightarrow 0$. Alternatively, experimental error or hidden variables such as trace impurities could have masked intrinsic differences at this concentration level (see also By-Product Formation below).

There was evidence (*17*) that fresh reagent II had "iodine demand" as well as "ozone demand", whereas aged II and the other reagents only had ozone demand. Hodgeson et al. (*8*) have also reported KI reagents in which there may be a loss of ozone without the consumption of iodine, as well as some in which there is a loss of both O_3 and I_2 so that Beer's law calibrations show a negative intercept.

Unfortunately, these data do not adequately resolve the questions of iodine and ozone demand, nor do they identify or quantify the impurities. I believe that the addition of hydrogen peroxide, which has been used to treat iodine demand (*22*), should be investigated as a possible means to deactivate the reducing impurities; a measured amount could be routinely added, and the fresh absorbent could then be set aside for several hours to allow

$$H_2O_2 + 2I^- = I_2 + 2OH^- \qquad (4)$$

it to go to completion. If the present levels of ozone demand are typical, only a small iodine blank would be produced when "sufficient" H_2O_2 is added to reagent with no initial ozone demand.

By-Product Formation with NBKI and Other Absorbents

As noted, absorption of ozone in NBKI and several other 1% KI reagents at 0.35 ppm and above resulted in the formation of a second substance, P, in addition to iodine; P continuously reacts with the absorbent to liberate additional iodine. This conclusion is supported by the following experimental observations: Iodine is continuously formed in impinger 1 after the collection of ozone is stopped; and the rate of iodine formation agrees with the first order rate law:

$$dP/dt = -kP \qquad (5)$$

where $k \approx 0.0365$ min^{-1} for NBKI and the other P-forming absorbents tested. The value of k was independent of ozone concentration and was insensitive to solution pH and the kind of buffer used; the quantity of P present immediately after absorption is a function of the absorbent and is proportional to ozone concentration.

If Equation 5 is integrated, the 352-nm absorbance of KI_3^- after ozone collection in NBKI solutions (proportional to iodine concentration) may be written as

$$\ln \frac{[P]}{[P_0]} = \ln \frac{A_\infty - A}{A_\infty - A_0} = -k(t - t_0) \qquad (6)$$

where A_0 is the absorbance at the time of the initial observation, t_0 (2 min after the collection of ozone has ceased), P_0 is the concentration of P at t_0, and A_∞ is the final absorbance ($t \rightarrow \infty$). Table I gives $[A_\infty - A_0]$ expressed as an equivalent increment in analyzed ozone concentration, $\Delta O_{3,\infty}$.

k and A_∞ were selected to minimize the RMS deviation between each set of data points and Equation 6. The average of the k values determined in this way, $k = 0.0365$ min^{-1}, was then used to recompute each A_∞. The computation yielded high correlation ratios (0.99–0.999) within each individual data set and for the $[A_\infty - A]/[A_\infty - A_0]$ vs. $(t - t_0)$ data merged from all the individual runs (Figure 2).

Table II. Results at 0.1 ppm

No.	Buffer	KI lot	Batch	Ratio to UV	Water	Age	Other	Notes
				Group A				
1	BKI	I	2	1.01	DW	1 day		1. 0.5 mL of Run 14 added to each impinger
2	NBKI	I	1	0.982	DW	3 weeks		
				Group B				2. O_3 absorbed 20 min
3	NBKI	I	1	0.924	DW	3 weeks		3. Absorbent had 2×10^{-4} mol/L I_2 added
4	NBKI	I	1	0.925	DW	3 weeks		
5	NBKI	I	3	0.876	TW	1 week		4. Batch 12 prepared with Merck Lot 62716 AR boric acid
6	BKI	I	2	0.952	DW	1.5 day		
7	BKI	I	2	0.950	DW	1.5 day		
8	BKI	I	2	0.940	DW	1.5 day		
				Group C				
9	BKI	I	2	0.978	DW	2 days		
10	BKI	I	4	0.875	TW	3 days		
				Group D				
11	BKI	II	5	0.842	IW	3 hrs		
12	BKI	IV	6	0.941	IW	1 day		
				Group E				KI Lots
13	BKI	III	7	0.958	DW	5 days		I. Fisher certified ACS grade, Catalog P410, Lot 723519
14	BKI	II	5	0.836	IW	0.5 day		
15	BKI	II	5	0.915	IW	0.5 day	Note 1	
16	BKI	II	8	0.815	DW	Fresh		
				Group F				II. Fisher laboratory grade, Catalog P411, Lot 745906 (USP)
17	BKI	IV	9	0.899	DW	Fresh		
18	BKI	II	8	0.810	DW	5 h		III. Ventron Corp. (ALFA) optronic grade, Catalog 87627, Lot 042172
19	BKI	III	11	0.937	DW	Fresh		
20	BKI	III	11	0.952	DW	1 h	Note 2	
21	BKI	II	5	0.799	IW	1.5 days		
22	BKI	II	12	0.726	DW	Fresh	Note 4	IV. Mallinckrodt analytical reagent grade, Catalog 1123, Lot BCN
23	BKI	II	12	0.797	DW	0.5 h	Notes 3, 4	
24	BKI	II	12	0.816	DW	1 h	Notes 2, 4	
								Average ratio to UV
	All BKI Lot I except 5 (TW):							0.962 ± 0.032 SE ($n = 5$)
	All BKI points:							0.877 ± 0.076 SE ($n = 21$)

As noted, ΔO_3/UV was practically independent of $[O_3]$, and this is shown in Table I. These values, together with the NBKI/UV ratio (2 min after absorption) may be used to calculate NBKI/UV at later times:

$$\frac{\text{NBKI}}{\text{UV}} = \frac{\text{NBKI}}{\text{UV}}\bigg|_{2\text{ min}} + \frac{\Delta O_{3,\infty}}{\text{UV}}\left[1 - e^{-k(t-t_0)}\right] \qquad (7)$$

The ratios for other buffers are also given in Table I. Although the quantity of P ($\Delta O_{3,\infty}$) is generally different from that obtained in NBKI, the decay rates were consistent with Equation 5 and were insensitive to pH (since pH varies from buffer to buffer). Thus, it appears that the same by-product is produced when ozone is absorbed in a number of different buffers.

Table II also shows that as the concentration of *buffer* is lowered, the ratio of iodide analysis to UV (2 min after absorption) approaches unity, and P becomes negligible. When the pH of a solution of unbuffered KI was adjusted to 4 with dilute acid (H_2SO_4), there was also no evidence of P formation; when boric acid and KH_2PO_4 are combined, approximately as much P is formed as when KH_2PO_4 is used alone. Therefore, it is tentatively concluded that certain buffer anions catalyze the formation of P; $[P]/[I_3^-]$ initially produced appears to decrease with buffer concentration; and the absence of P in BKI is due to a lack of P producing activity in BKI rather than a P-inhibitory effect.

In an attempt to identify P, I considered a number of compounds that could react with aqueous KI to yield iodine. It seems unlikely that P incorporates the phosphate buffer since P (or something that had very similar reaction characteristics) was produced in other buffers as well. Of the possibilities for P that were considered, IO_4^-, IO_3^-, IO^-, and H_2O_2, only H_2O_2 reacted with KI at a rate similar to P.

Figure 4 presents data on the rate of iodine formation for a dilute solution (~5×10^{-5}%) of H_2O_2 in NBKI. These data were taken in a second laboratory at ~23 °C (vs. 20.5 °C during the ozone work), and a different source of water was used to make the solution. "A_∞" was determined under the constraint $k = 0.0365$ min^{-1}. As shown, these data lie within a 99% confidence band defined by a linear regression of all NBKI "decay" experiments; therefore, P is tentatively identified as hydrogen peroxide (*17*).

As noted, $[P]/[O_3]$ was constant in NBKI (~0.13–0.14) for fixed absorption conditions and ozone concentrations of 1.0, 0.6, and 0.35 ppm; this suggests that the ratio might hold constant at 0.1 ppm as well. However, at 0.1 ppm the predicted increase in absorbance is very small and may have been masked by experimental error.

Conclusions

Iodometric analyses with a 0.1 M boric acid buffered KI reagent are precise and agree with UV photometry between

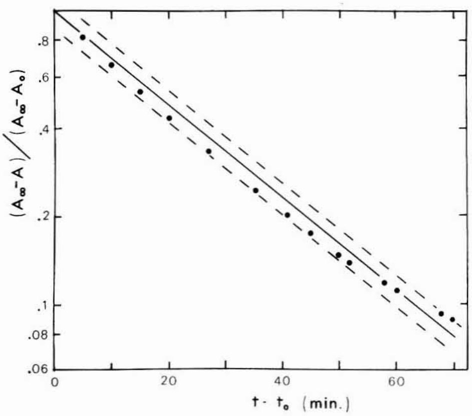

Figure 4. Reduced absorbance vs. time for H_2O_2 in NBKI (points). Solid line: least-squares rate for P in NBKI. Dashed lines: SD for data at 95% confidence level

0.35 and 3.5 ppm. It appears that good agreement can also be obtained at 0.1 ppm, providing the KI is free of reducing contaminants.

NBKI analyses in dry air or oxygen are high by a factor of 1.15–1.20 when colorimetry is performed 2 min after the completion of a 10-min absorption. This error continuously increases with time between absorption and analysis. The absorption of ozone into NBKI and certain other buffered reagents results in the formation of a second product, P, in addition to iodine. P reacts with NBKI to form iodine with a pseudo-first order rate constant of approximately 0.0365 min^{-1} at 20.5 °C; the amount of P is proportional to ozone concentration. There is evidence that P is hydrogen peroxide.

P was not detected in 1% KI solutions containing 0.1 M boric acid (BKI), very dilute solutions of the various buffers, or when the pH of unbuffered KI is preadjusted to 4 with dilute H_2SO_4.

Some of the disagreement between previous investigations with NBKI may be explained by variations in $[P]/[O_3]$ due to differences in sample flow rate, collection time, the interval before spectrophotometric analysis, and by the trace contaminants present in some KI sources.

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Nomenclature

A = absorbance of I_3^- in solution
k = reaction rate constant, min^{-1}
I_0 = integrated light intensity in photometer
L = length of photometer cell, 71 cm
p = pressure in photometer cell, torr
R = reading displayed on photometer
t = time, min
T = temperature of photometer cell, K
α_0 = absorption coefficient at p = 760 torr, T_0 = 273 K, $\mathrm{atm}^{-1}\,\mathrm{cm}^{-1}$

Subscripts

0 = reference or initial condition
∞ = final condition

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Determination of Trace Element Contamination of Sediments by Multielement Analysis of Clay-Size Fraction

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■ Samples of total sediments and the clay-size fraction are analyzed for more than 20 elements to evaluate the use of trace element concentrations in the fine fraction to determine if the sediments have received anthropogenic inputs of elements. The samples are from Lake Superior and the harbor of Duluth, Minn., and Superior, Wis. The concentrations of trace elements in the samples of total sediments vary by more than a factor of two over the study area, and they are not related in a simple fashion to sample location. The ability to detect contaminated sediments is not improved when the values of concentrations are corrected for the effects of dilution by quartz. In contrast, the concentrations of trace elements in the clay-size fraction vary less than 15% from their mean values from site to site except for some areas that have high concentrations of Cr, Cu, Zn, Hg, and As. The high concentrations of these elements result from anthropogenic inputs.

Restricted disposal of sediments containing unacceptable materials is required by current regulations of the Environmental Protection Agency (EPA) during dredging operations for waterway maintenance (*1, 2*). Placement on land or placement within enclosed dikes are accepted procedures for the disposal of dredged material classified as polluted (i.e., environmentally unacceptable), but these methods are considerably more expensive than dumping the material into waterways, as is permitted for material classified as not polluted. Unrestricted disposal of sediments containing excessive amounts of toxic materials results in undesirable conditions that expose the biota to their effects. The long-term effects of benthic organisms inhabiting and ingesting contaminated sediments are of special concern (*3, 4*).

The EPA recommends the use of the elutriate test for predicting the effects of dredged material on water quality due to the release of contaminants from the sediment (*1, 2*). However, no simple procedures are available to determine the magnitude of anthropogenic contamination of sediments. This is especially so for potentially toxic trace elements. Suitable methods to diagnose the status of trace element contamination of sediments are needed to study the effects of dredged material on benthic and other organisms and to determine its environmental acceptability.

Because all naturally occurring elements are present at some concentrations in all natural materials, a procedure to determine the status of trace element pollution of sediments must distinguish anthropogenic inputs of these elements. One common approach is to measure the concentrations of each element in samples of total sediment. The results obtained by this approach are often ambiguous because the effects of pollution on the concentrations of trace elements in samples of total sediments are difficult or impossible to separate from natural variations in trace element concentrations that result from spatial and temporal differences in the proportions of the various components of sediments, such as mineral species, metal oxides, and organic matter.

Attempts to minimize these effects have concentrated on analyzing the samples for each such component and then correcting the concentrations of trace elements to reflect the effects of each component (*5–8*). Studies of this type have generally shown that concentrations of trace elements correlate highly with the concentrations of clay and silt-sized material in the sediments. This is especially important in studies involving trace elements because major components of the fine fraction are clay minerals, hydrous oxides of Al and Fe, and organic matter. These materials are thought to be important scavengers of elements contributed by anthropogenic sources because of their capacity to sorb and desorb metal ions. We report here a procedure that uses results obtained by multielement analysis of the less than 2-μm fraction (clay-size fraction) of sediments to determine if they have received anthropogenic inputs of elements.

Experimental

The samples of sediment were collected from Lake Superior and the harbor of Duluth, Minn., and Superior, Wis., from 1973 through 1975 with a 23 × 23 cm Ponar dredge. All nonferrous parts of the dredge were replaced with aluminum or stainless steel to minimize possible contamination. The samples were sealed into heavy plastic bags on board ship, mixed thoroughly in the plastic bags after the samples arrived in our laboratories, and a portion was transferred to borosilicate bottles and stored at 4 °C until analysis. A core sample of lake sediment was collected with a piston corer at a water depth of 40 m. Samples of lacustrine sediments were collected from interior portions of the faces of "red clay" cliffs along the Wisconsin shore of Lake Superior. The results of grain size analyses and a description of the samples are given elsewhere (*3, 9*).

Samples of the clay-size fraction were separated by a gravity settling technique based on Stokes' law. Approximately 30 g, on a dry weight basis, of field wet sediment were mixed with 900 mL of distilled-deionized water for 1 h in a 1-L polyethylene bottle. After the mixture stood undisturbed for 433 min at 24 °C, a sample was withdrawn by pipet at a depth of 10 cm below the water surface (*10*). Depending upon the amount of clay-size material in the sample, the size of the aliquot withdrawn varied from 15 to 50 mL to give about 70 mg of clay-size material for analysis. The sample was then collected on a 0.45-μm Millipore filter and dried at 60 °C in preparation for analysis. Samples of total sediments were dried at 60 °C and ground to pass a 100-mesh plastic sieve before analysis.

All analyses of the sediments were by our procedures of instrumental and radiochemical neutron activation, which are based on those of Allen et al. (*11*), Henzler et al. (*12*), Denechaud et al. (*13*), and Gordon et al. (*14*). The samples of the clay-size fraction generally curled away from the filter during drying, and no blank correction due to the filter paper was needed. Six of the samples were analyzed by x-ray diffraction using the techniques described by Jackson (*10*). Concentrations of quartz were measured in eight of the samples of total sediments by procedures using a $Na_2S_2O_7$ fusion and H_2SiF_6 dissolution (*10*). The concentrations of elements in the filtered aqueous phase were determined by atomic absorption and neutron activation analysis.

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Results and Discussion

Separation of Clay-Size Fraction. The detection of trace element contamination of sediments is based on intersample comparisons of trace element concentrations in the clay-size fraction. This procedure has the advantage of minimizing the effects of systematic bias introduced by the sampling and analysis techniques, but if it is to be used to its maximum advantage, potential variations of the trace element concentrations in the clay-size material resulting from the possible effects of leaching or size fractionation of particles during the separation of the clay-size fraction must be negligible.

Potential losses of elements from the sediment as soluble species or as very small particles not collected by the filter during the separation of the clay-size fraction will tend to lower the measured concentration of each element. Analysis of the filtrate shows that such losses of elements are critically dependent on the care used during filtering (*15*). In those cases where significant losses did occur, very insoluble elements such as the rare earths (*16*) and Sc were also present at concentrations up to 10 ppb in the aqueous phase (*15*). This suggests that such losses are due to colloidal particles passing through the filter. Losses of all elements are insignificant if the application of suction to the filter apparatus is delayed for several minutes after the transfer of the suspension and if it is then applied with gradually increasing intensity. If one then assumes the extreme case that all of each element found in the aqueous phase was derived solely from the clay-size fraction, the total loss of Hg for samples filtered carefully ranged up to 10% of the amount found in the clay-size fraction, while those for the other elements did not exceed 5% and were generally less than about 3%. Lee et al. (*17*) also report only small amounts of most elements are released to the aqueous phase in mixtures of sediment and water.

Changes in the concentrations of trace elements in the clay-size fraction may also result from possible size fractionation of the clay-size particles during their separation because of differences in their size and density. The conditions described assume that the particles have an equivalent spherical diameter of 2 μm and a density of 2.65 g/cm^3. These values can only approximate the correct parameters for the fine particles of sediments. This is unavoidable, but the effects on the final results are negligible as shown by their uniformity. Also, such potential effects are minimized here because the procedure used to separate the clay-size fraction is the same for all of the samples. Separation and collection of a portion of the total content of clay-size material in the sample, as were done in this study, are much faster and easier than repetitive separations needed to collect all of the clay-size fraction. Analysis of samples collected by each procedure shows that the concentrations of trace elements in such samples are identical within their analytical uncertainties (*15*). This shows that analysis of a subsample of the total clay-size material yields results representative of the total fraction of such material in the sample. This also suggests that natural processes that suspend and transport clay-size material have little effect on its composition.

Graphical Representation of Results. Comparison diagrams displaying the ratio of the concentration of each element in the sample to a standard value are useful to discern patterns of trace element concentrations. Such diagrams (Figure 1) are made by plotting the concentration ratios as a function of the elements studied. While the values used for the standard of comparison are arbitrary, we have found it advantageous to use the average concentration of each element in the samples from the prehistoric (13–33 cm) portion of the sediment core (Table I). Differences in trace element concentrations between samples can then be readily identified by comparing individual diagrams.

Detecting Sediments Polluted with Trace Elements. The values of trace element concentrations in the 24 samples of total sediment and clay-size fraction are summarized in a comparison diagram (Figure 1). Each bar in Figure 1 represents the range of concentrations found for each element in the total sediment or clay-size fraction. (The data for all of the samples are available as Table III which has been deposited with the ACS Microfilm Depository Service.) Comparison of the results given in the two parts of Figure 1 shows that the ranges of concentrations of almost all elements in the clay-size fraction are considerably smaller, up to a factor of 12 for Cs, than those for the total sediments. It is evident that the sample-to-sample variations characteristic of the results obtained by analysis of samples of total sediment (*6–8*) are greatly reduced when samples of the clay-size fraction are analyzed. Exceptions to this trend are the elements commonly used by man, such as As, Cr, Cu, Hg, Na, Sb, and Zn, whose ranges of concentrations are extended to higher values in the clay-size fraction. This suggests that the high concentrations found for these elements in the clay-size fraction may result from some of the samples having received anthropogenic inputs. The almost constant concentrations of the other elements (the rare earths, Ba, Co, Cs, Fe, Ga, Hf, Rb, Sc, and Th) in the clay-size fraction show that its composition is the same throughout the study area.

This evidence for the uniformity in composition is especially significant when the diversity of the geochemical properties of these elements and the size of the study area (about 300 km^2) are considered. Such uniformity of trace element concentrations might be expected from the observation that isolating the clay-size fraction by dispersion of the sediment in water has an insignificant effect on its composition and that the clay-size fraction is readily transported by water.

The uniform composition of the clay-size fraction throughout the study area is a great advantage in detecting sediments contaminated with trace elements, as illustrated by the following example. The concentrations of trace elements in the clay-size fraction and total sediment of two of the samples are given in Table I. Figure 2 is a comparison diagram for these samples. Sample H-9 is from a remote area of the

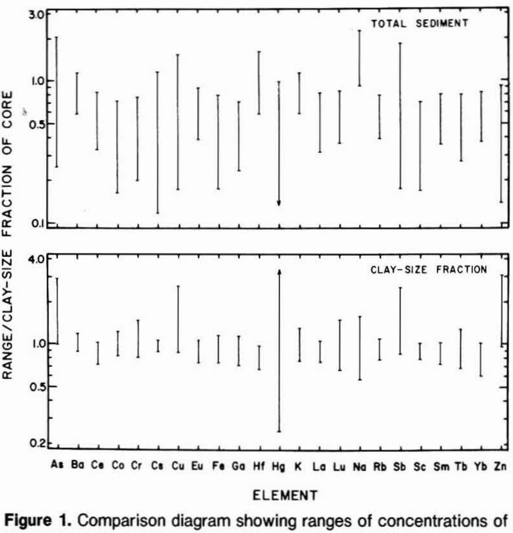

Figure 1. Comparison diagram showing ranges of concentrations of trace elements in all samples of total sediment and clay-size fraction

Each bar represents range of concentrations of element divided by corresponding concentration of that element in prehistoric portions of sediment core (Table I) harbor that is not used by ships and does not directly receive any industrial effluents. It supports a diverse population of aquatic organisms characteristic of natural areas (*18*). This area is expected to be polluted less than any other portion of the harbor. In contrast, sample H-2 is from a heavily used shipping lane near the outfall of a sewage treatment plant, an area likely to receive anthropogenic inputs of elements. Recognizing which elements, if any, in either sample might be affected by anthropogenic inputs is nearly impossible by inspection of the results obtained for the samples of total sediments (Figure 2). The sample suspected of being contaminated, H-2, has lower concentrations of all elements except Na, K, and Hg. However, inspection of the results for the clay-size fraction of these samples (Figure 2) shows clearly that the samples have similar compositions except that sample H-2 has anomalously high concentrations of As, Cu, Hg, Sb, Zn, and maybe Cr. Anthropogenic inputs must be considered as one source of these enrichments.

Diagrams similar to those in Figure 2 can be made from the results for the other samples. They are similar in nature to those in Figure 2, except that none of the other samples has as many elements enriched as greatly as those of sample H-2. Most of the samples from the open lake show little or no enrichment of the elements studied.

Background Concentrations. The use of trace element concentrations in the clay-size fraction to detect contaminated sediments eliminates the problems associated with sample-to-sample variations characteristic of total sediments. This simplifies the problem to one of showing that any anomalous concentrations of trace elements in the clay-size fraction are the results of anthropogenic inputs and not those of natural geochemical processes. This requires a determination of the range of background concentrations of each element in the clay-size fraction.

The surface enrichment of Mn, Fe, and other elements associated with their hydrous oxides that often occur as a result of sediment diagenesis is one process that can produce high concentrations of trace elements. This process is probably of little consequence to the dredging operation because the surface few centimeters of the sediment contribute only a small portion to the total volume of dredged sediment. It might be important for the interpretation of the results for the samples from Lake Superior because the Ponar dredge used to collect the sediment seldom samples deeper than 15 cm. The effects of diagenesis on the samples from the harbor should be small because most of the harbor samples are collected from areas that are dredged every 1–2 years and are frequently disturbed by strong currents from maneuvering ships.

The concentrations of selected elements in the clay-size fraction at various depths in a core sample of sediment from Lake Superior are shown in Figure 3. Sediment deeper than 3 cm is estimated to have been deposited more than 100 years ago (*19*). The elements As, Cu, Mn, and Zn have higher concentrations in the near surface samples with Mn showing the greatest enrichment. All of the other elements show no surface enrichment and have concentration profiles that resemble those of Cr, Sc, and Co in Figure 3. Tentative upper limits to

Table I. Concentrations of Trace Elements in ppm in Samples of Sediment

	Sample H2		Sample H9			Av value for 13–33-cm portion of sediment core (clay-size fraction)[b]
	Total sediment[a]	Clay-size fraction	Total sediment	Clay-size fraction	Quartz	
As	5.4 ± 0.5	21	6	10	0.58	12 ± 1
Ba	430 ± 20	520	440	437	19	460 ± 40
Ce	29.6 ± 0.5	100	63.4	77.3	6.2	96 ± 4
Co	7.92 ± 0.08	25.5	12.7	21.7	0.09	25 ± 1
Cr	51 ± 1	185	73	111	1.9	124 ± 1
Cs	1.8 ± 0.1	6.2	2.9	5.7	0.20	6.3 ± 0.2
Cu	19.3 ± 0.2	172	35.9	57.6	0.74	65.9 ± 0.2
Eu	0.81 ± 0.01	1.62	1.07	1.18	0.063	1.50 ± 0.06
Fe	21300 ± 200	75700	31300	52400	233	70500 ± 700
Ga	8.2 ± 0.1	26.5	13.9	28.4	1.07	. . .
Hf	4.5 ± 0.1	5.0	5.7	4.5	0.90	5.4 ± 0.1
Hg	0.14 ± 0.02	0.99	0.05	0.074	. . .	0.3 ± 0.2
K	22500 ± 500	18100	18300	23000	1160	23700 ± 1600
La	18.9 ± 0.3	45	28.9	38.4	2.59	47 ± 2
Lu	0.287 ± 0.008	0.92	0.46	0.49	0.047	0.61 ± 0.01
Mn	. . .	. . .	. . .	. . .	5.6	710 ± 60
Na	8920 ± 30	6290	7380	4870	698	5300 ± 400
Nd	. . .	. . .	. . .	. . .	. . .	45 ± 6
Rb	63 ± 2	108	76	110	4.0	115 ± 8
Sb	. . .	. . .	. . .	. . .	. . .	1.3 ± 0.1
Sc	6.06 ± 0.02	20.8	10.6	17.7	0.268	20.3 ± 0.3
Sm	3.78 ± 0.02	8.23	5.3	6.5	0.522	8.5 ± 0.2
Tb	0.45 ± 0.02	1.1	0.73	0.93	0.078	1.18 ± 0.02
Th	. . .	. . .	. . .	. . .	1.28	18.5 ± 0.3
U	. . .	. . .	. . .	. . .	0.45	. . .
Yb	1.96 ± 0.08	3.4	3.1	3.2	0.31	4.0 ± 0.1
Zn	64 ± 3	530	91	166	1.0	172 ± 14

[a] The uncertainty associated with each value represents 1 standard deviation based on counting statistics. When converted to percent, these values also apply to the results for the other samples. An additional uncertainty of about 1% applies to the values for each sample. [b] Uncertainties are 1 standard deviation from the mean value of the five samples of core.

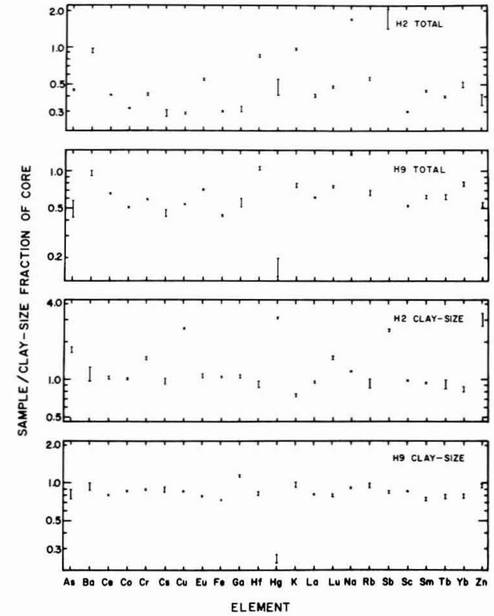

Figure 2. Comparison diagram showing ratios of concentrations of elements in clay-size fraction and total sediment of two samples from Duluth-Superior harbor

Error bar represents 1 standard deviation

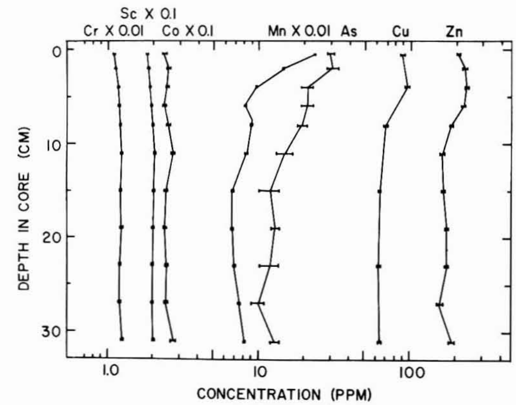

Figure 3. Concentrations of some elements in clay-size fraction of sediment core as a function of depth

the background concentrations of trace elements can then be determined for the clay-size fraction in the study area (Table II), if one assumes that the observed enrichment is the result of diagenesis and not anthropogenic inputs.

A second approach to determine background values assumes that most of the samples analyzed have not received anthropogenic inputs of elements, such as the samples from Lake Superior, or are not seriously affected by the effects of diagenesis, such as most of those from the harbor. For this situation, the lowest and/or modal value of concentration of each element in the clay-size fraction will approximate the background values (column 3 of Table II).

A third approach is to consider the concentrations of each element in the important sources of sediment. For the Duluth-Superior area, much of the sediment is derived from the deposits of lacustrine "red clay" along the Wisconsin shore (*20*). The average concentrations of each element in the clay-size fraction from three samples of red clay are given in column 4 of Table II. Other sources of sediment might also be significant, and their contributions may be best considered by using the average concentration of each element in the clay-size fraction of the prehistoric portion of the sediment core (column 2 of Table II) as a fourth approximation to the background values.

The general agreement of the values derived from all four approaches allows a single value to be recommended as the current, best approximation of the background concentration of each element (column 5 of Table II). The tentative maximum values, especially for Zn, Cu, and As, also need to be considered if the method used to collect the sediment yields samples sensitive to the effects of diagenesis.

The recommended values in Table II can be used to prepare maps showing the spatial distribution of each element in the study area. Figure 4 is such a map showing the locations of the sample sites and the ratios of the concentration of Zn in the clay-size fraction to a background value of 180 ppm. Most of the samples have about the same concentration ratio for Zn except those from the northern part of the harbor and the old disposal sites for dredged material which are enriched in Zn. Similar maps for the other elements show that the relative distributions of Cu and Hg are about the same as those of Zn. Most of the other elements have ratios that are near one throughout the entire study area except for As, Sb, Co, and Cr which are most enriched in samples H-2 and H-3.

It is instructive to consider why the trace element concentrations in the clay-size fraction are much more uniform compared to those for samples of total sediments. This is apparently a result of the weathering and transport properties of the mineral and other components of sediments. Comparison of the element concentrations in quartz, the most abundant mineral in these sediments, to those in the samples of total sediment or clay-size fraction (Table I) shows that quartz has very low concentrations of all trace elements except Hf, Th, and U. (These elements are associated with zircon which is also isolated by the procedure used to separate quartz.) While it is generally known that sediment samples containing high concentrations of quartz tend to have low concentrations of most trace elements, correcting the concentrations of trace elements in samples of total sediments for the effects of dilution by quartz does not reduce the sample-to-sample variations of trace element concentrations. Comparison diagrams made from the corrected values (not shown) show that the ratios of most elements are greater than one and have as great a range as do the uncorrected values. This indicates that other minerals containing high concentrations of trace elements must also occur in the silt and larger size fractions of the samples.

For example, the results of x-ray diffraction analysis show that zircon, magnetite and ilmenite are present in the samples of total sediment. All of these minerals have high concentrations of some trace elements (*21*). Local variations of the concentrations of these minerals, quartz, and the clay-size fraction produced by the differential transport by water of particles having different sizes and densities will result in temporal and spatial variations of trace element concentrations in samples of total sediments that are independent of anthropogenic inputs. In contrast, the clay-size fraction generally has low concentrations of quartz and other minerals that tend to concentrate in the sand and silt size fractions of sediments. This occurs because when grains of the above minerals are reduced to a size of several micrometers, they are more susceptible to dissolution than are similar size particles of clay minerals and oxides of Al and Fe (*22*). In addition,

Table II. Concentrations of Trace Elements in ppm in Samples of Clay-Size Fractions Used to Determine Maximum and Recommended Values of Background Concentrations

Element	Max concn in sediment core	Av value in 13–33-cm portion of sediment core	Modal value from all samples	Av value from "red clay"	Recommended single value
As	31	12	16	12	14
Co	28	25	25	20	25
Cr	125	124	120	100	120
Cu	94	66	75	68	70
Hg	0.56	0.3	0.4	. . .	0.4
Sb	1.9	1.3	1.3	. . .	1.3
Zn	233	172	190	134	180

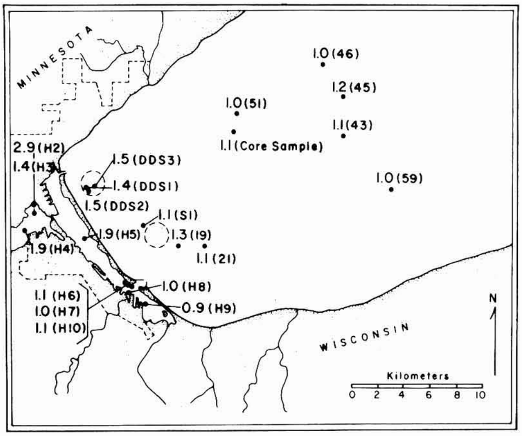

Figure 4. Spatial distribution of zinc shown as ratio of concentration of zinc in clay-size fraction divided by background value of 180 ppm
Symbols in parentheses identify each sample. Circles shown by dashed lines indicate old disposal sites for sediments dredged from harbor

particles of the clay-size fraction are transported and mixed more efficiently by water. The combined effects of both processes result in the clay-size fraction having almost uniform mineral and therefore chemical compositions over much larger areas than are found for samples of larger particles. The content of organic matter in these samples is uniformly low, but this may also be important in other sediments.

Uniform background concentrations of trace elements in the clay-size fractions of sediments over large areas plus its ability to scavenge elements make the clay-size fraction the best portion of the sediment to analyze for monitoring anthropogenic inputs of elements. An intensive program of sampling and analysis using the approach outlined here will identify in detail which areas of sediment are enriched in trace elements due to anthropogenic inputs more clearly than an approach based on the analysis of total sediments. The environmental acceptability of such sediments can then be determined by appropriate bioassay and sediment preference tests before they are dredged.

Acknowledgment

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Supplementary Material Available. *Table III (15 pages), which contains the data for all 24 samples of total sediment and clay-size fraction, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Operations Office, Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number ES&T-77-984.*

Polynuclear Aromatic Hydrocarbons in Marine Tissues

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■ Shell and fin fish contain benzo(a)pyrene and other polynuclear aromatic hydrocarbons at the parts per billion level or below. The presence of pyrene at a much higher relative concentration than its methyl isomers indicates the hydrocarbons are from a combustion source.

A National Academy of Sciences workshop on oil pollution (*1*) found that the principal concern to public health is the danger of eating oil-contaminated marine tissues. Since petroleum contains small concentrations of potentially carcinogenic aromatics (*2*), it has been considered as one of many possible sources of such contamination.

In response to this concern, the American Petroleum Institute conducted a study of polynuclear aromatic hydrocarbons (PAH) in marine animal tissue. This included the measurement of typical polynuclears, such as benzo(a)pyrene (BaP), in the edible portions of shell and fin fish. Concentrations were observed on a wet weight basis.

Method of Analysis

Carbon-14 labeled benz(a)anthracene (BaA) and BaP were employed as internal standards in the method of analysis. After adding these standards to the starting sample, a modification of the method of Howard et al. (*3*) was used to prepare a PAH concentration that was in turn analyzed by a combined GC/UV procedure (*4*).

A weighed sample of approximately 450 g is placed into 300-mL of redistilled ethanol and 15 g of KOH. The spike solution of carbon-14 BaA and BaP is added, and the mixture digested for 2 h. The resulting solution is transferred to a 2-L separatory funnel with two 125-mL water and two 100-mL ethanol washes. The PAH's are then extracted with 150-, 100-, and 100-mL portions of isooctane. Each of the three isooctane extracts is washed with four 250-mL portions of warm water. The isooctane washed extracts are combined and reduced on a steam bath under N_2 to ~25–30 g. An equivalent weight of isooctane is added, and the resulting solution extracted with five 100-g portions of 10:1 dimethyl sulfoxide:H_3PO_4 (DMSO). Then 720 mL of water is added to the combined DMSO extracts, and this solution is back extracted with three 100-mL portions of isooctane. Each isooctane portion is washed with three 250-mL portions of water. The isooctane solutions are combined and reduced to ~10 mL on a steam bath under N_2. A 1-mL sample may be removed at this point for counting.

The isooctane solution is eluted through a long narrow (6 mm × 90 cm) column of 2% deactivated alumina. The solvent elution procedure is as follows: 5 mL prewash of cyclohexane, 10 mL sample, 30 mL of 10% benzene/90% cyclohexane, 30 mL 20% benzene/80% cyclohexane, 30 mL benzene, and 30 mL 50% benzene/50% methanol. Ten-milliliter fractions are collected throughout the separation. One-milliliter samples are taken for counting, and the fractions combined according to the counting data. The combined fractions are reduced on a steam bath under N_2 after adding 5 μL of *n*-hexadecane to prevent going to dryness. An aliquot of this concentrate is then injected into a gas chromatograph where the GC peaks are trapped, and the UV absorption spectra of selected trapped peaks are then measured. These spectra provide a quantitative measure of individual PAH's in the aliquot. Quantitation on a total sample basis is calculated from the observed recovery of the ^{14}C labeled standards, BaA and BaP.

The precision and accuracy of the method were evaluated by analyzing known blends containing phenanthrene, 2-me-phenanthrene, 1-me-phenanthrene, fluoranthene, pyrene, BaA, chrysene, triphenylene, BaP, BeP, perylene and B(g,h,i)P, at concentrations of 1 and 6 ppb. Individual compounds were measured within 2-sigma limits of 1 and 2 ppb, respectively. Later in this manuscript, the concentration ratio of methylpyrene to pyrene is shown to be of special significance in the interpretation of the findings of this study. For this reason, special commentary is warranted with regard to the ability of the method to handle the methyl-substituted isomers. Two cross-checks on this were available for most of the samples. Gas chromatograms, for example, provide such a cross-check as illustrated in Figure 1 for the Long Island Sound oysters. The concentration of methylpyrene is much lower than that of pyrene which agrees with the UV measurement listed in Table I. Low-voltage mass spectral measurements (*5*) were applied to the Long Island Sound oysters and numerous other samples. These spectra confirmed that not only pyrene (molecular weight series 202, 216, etc.), but

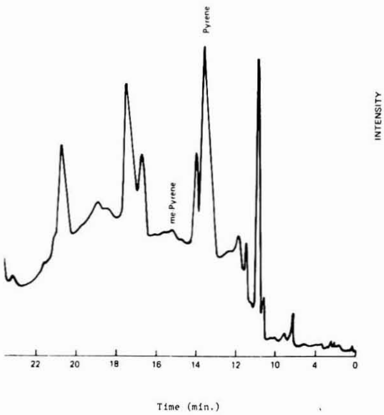

Figure 1. Gas chromatogram of Long Island Sound oysters

other PAH homologous series were comprised principally of the parent compound with much lower amounts of methyl-substituted homologs.

Samples

Figure 2 shows the origin of several samples which were studied. Included were oysters and clams from a commercial fishery in Long Island Sound near Norwalk, Conn. Crabs and menhaden were taken from Raritan Bay in New Jersey. The Long Island Sound and Raritan Bay waters are exposed to municipal and industrial wastes. Two flounder samples were analyzed; one was taken during dredging off Long Branch, N.J., and a second was collected off the R/V *Delaware II* during a cruise conducted by the NOAA Fishery Laboratory of Sandy Hook, N.J., about 10 miles off the southern coast of Long Island. Codfish came from an open area of the Atlantic Ocean.

Table I tabulates the origins for all the samples. In addition to the samples already mentioned, oysters and clams were from Chincoteague, Va., crabs from Chesapeake Bay, shrimp from a clean control pond operated by Texas A & M University in Palacios, Tex., and lake trout from a wilderness lake in Ontario, Canada. Mussels were supplied by Woods Hole Oceanographic Institute from a study of Buzzard's Bay in Falmouth, Mass. Samples were taken from the Little Sippewissett Creek which is an unpolluted area and from Wild Harbor which is considered to be polluted.

Results

Among the polynuclear aromatic hydrocarbons, BaP is the most widely studied carcinogen (*6*). Among other such hydrocarbons, BaA (a weak carcinogen) has also been measured. These compounds were therefore selected as indicators of total PAH contents. Observed concentrations for these two compounds are tabulated in Table I for 15 marine tissues. In 8 of the 15 samples, "less than" concentrations only are reported. Less than values can, as seen in Table I, vary considerably from sample to sample. The values reported depend to a large extent on the amount of residue obtained in the final step of our method. The larger the residue, the less will be the percent of the total sample injected into the GC, and accordingly the less ^{14}C material will be recovered. Since the data are related to ^{14}C recovery, the less recovered means, in effect, that a higher detectability level will be observed for some samples over others. A preponderance of these less than values are <1

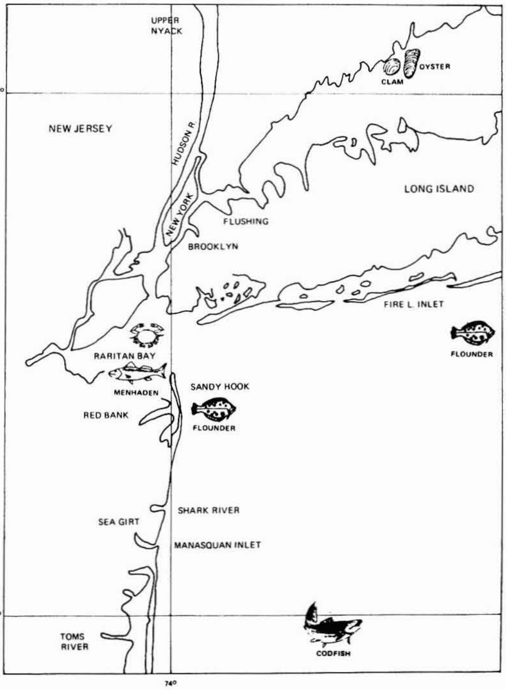

Figure 2. Origin of several samples

Table I. Summary of PNA Hydrocarbons in Marine Tissues (ppb, Wet Weight)

Location of sample	Marine tissues	BaA	BaP	Pyrene	Methylpyrene	Other individual PNA's[a]
Long Island Sound	Oyster	8	2	58	11	<2–15
Chincoteague, Va.						
Black Point	Oyster	0.1	0.2	0.5	<0.1	<0.5–0.7
Little Toms Cove	Clam	0.3	0.3	1.0	<0.2	<0.1–<0.9
Darien, Conn., Scott's Cove	Clam	1	<1	12	2.5	<1–3
Fish Market, Linden, N.J.	Clam	<1	<1	<3	<1	<0.5–<3
Chesapeake Bay	Crab	<1.5	<0.5	<0.2	<0.2	<0.5–<1.2
Raritan Bay	Crab	2	3	6	1.6	1–2
	Menhaden	<0.3	1.5	<0.3	<0.6	<0.3–1
Atlantic Ocean						
Long Branch, N.J.	Flounder	<1	<2	<1	<0.6	<1–<2
South of Long Island (40°27′N, 73°06′W)	Flounder	<1	<1	2	0.5	<1
Falmouth, Mass.						
Little Sippewissett	Mussel	<0.2	<0.5	2	0.5	<0.2–0.3
Wild Harbor	Mussel	0.6	0.5	4	1.5	<0.5–1.2
Palacios, Tex.	Shrimp	<0.2	<1	<0.3	<0.3	<0.3–<1
Atlantic Ocean, 25 mi. off Toms River, N.J. (39°57′N, 73°35W)	Codfish	<2	<1	<0.5	<2	<0.5–<5
Lake Maskinonge, Ont., Canada	Lake trout	<0.5	<1	<0.3	<0.6	<0.5–<1.5

[a] Includes chrysene, triphenylene, benzo(b)fluoranthene, benzo(e)pyrene, perylene, and benzo(g,h,i)perylene.

Table II. Benzo(a)pyrene Reported in Mussels, Codfish, and Oysters

Source	Marine tissue	BaP (ppb, wet wt)	Ref
Toulon Roads, France	Mussel	0.2–3.0[a]	Greffard and Meury *(12)*
Falmouth, Mass.	Mussel	<0.5–0.5	This study
Vancouver, B.C., Canada	Mussel		Dunn and Stich *(7)*
Remote area		0.0–0.2	
Outer harbor		2.0 ± 0.3	
Around wharf, marina, docks		18	
Inner harbor		42	
West Coventry, Greenland	Codfish	1.5[a]	Mallet et al. *(13)*
Atlantic Ocean, off N.J.	Codfish	<1	This study
Norfolk Harbor, Va.	Oyster	2–6	Cahnmann and Kuratsune *(14)*
Long Island Sound	Oyster	2	This study
Chincoteague, Va.	Oyster	0.2	This study
French coast	Oyster	0.1–7.0[a]	Mallet *(15)*

[a] Converted from dry to wet weight by factor of 0.1 *(11)*.

ppb. Concentrations of 0.1–1.5 ppb are observed for five samples, and only the oysters from Long Island Sound and crabs from Raritan Bay showed concentrations higher than 2 ppb.

The last column of Table I reports the concentration ranges as observed for six other 4-, 5- or 6-ring aromatics. Uniformly low values are observed. The single relatively high concentration of 15 ppb is that of triphenylene, a noncarcinogen, in Long Island Sound oysters.

Discussion

It is of interest to compare the results of this study with published information which is generally limited to BaP values. As shown in Table II, mussels from this study are similar to those from a remote area as analyzed by Dunn and Stich (*7*). These investigators found significantly higher BaP contents for samples from polluted areas covering from the inner to the outer harbor area of Vancouver, B.C. Long Island Sound oysters contain BaP at the lower range observed for oysters from harbor and coastal water. An even lower concentration was found for oysters from Chincoteague, Va.—a pristine area.

By comparison with other foodstuffs, neither shell nor fin fish show unusually high amounts of polynuclear aromatics. Indeed, lower concentrations occur in fish than in many common foodstuffs. For example, Malanoski et al. (*8*) report smoked meats (including fish) to contain from 0.5 to 7.0 ppb of BaP. In other cases this compound occurs at 5–13 ppb in lettuce (*8, 9*), 43.7 ppb in coconut oil (*10*), and 4 ppb in tea (*9*).

Pyrene and methylpyrene data from this study merit special mention. Absolute values are reported for these compounds in six samples. For the ratio of methylpyrene to pyrene, an approximately constant value of 0.26 was observed. In two other samples (oysters and clams from Chincoteague, Va.), the "less than" values of methylpyrene compared with the absolute values of pyrene show an even lower ratio. Predominance of the parent compound, pyrene, indicates that the hydrocarbons are not of petroleum origin. Published data (*2, 16*) show that, in petroleum, PAH's consist of homologous series in which the methyl and higher alkyl-substituted isomers significantly outnumber the parent hydrocarbons. Aromatic hydrocarbons from the combustion of fossil fuel or wood, however, contain a predominant amount of the parent hydrocarbons. It is quite possible, then, that the hydrocarbons found in marine tissue originate from such combustion. This would agree with previous findings for polynuclear aromatic hydrocarbons in soil and marine sediment where Youngblood and Blumer (*16*) suggest combustion as a direct source, and Hites (*17*) proposes as a source in situ modification of air particulates.

This reasoning does not take into account the possibility that the lower concentration of methyl isomers is caused by a difference in the rate and extent of accumulation in marine tissues. In some recent work on this subject, Bieri et al. (*18*) exposed *fundulus* to a crude oil and found that there was a temporary accumulation of naphthalenes but with no preference for naphthalene itself. A similar observation was made by Anderson et al. (*19*) who exposed oysters, shrimps, and clams to a highly aromatic fuel oil. In this study, depuration was accomplished by placing the exposed samples in clean seawater. Preferential metabolism of PAH's with side chains could also account for their relatively low concentrations. Again neither Bieri et al. (*18*) nor Anderson et al. (*19*) observed this process. More work is required to further clarify these points.

Acknowledgment

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Errors in Determination of Residual Oxidants in Chlorinated Seawater

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■ The iodometric titration procedure for residual chlorine underestimates the true values for residual oxidants in seawater by threefold or more. Chlorine added to seawater causes oxidation of the natural bromide ion. The erroneous results appear to be due to partial oxidation of iodide ion to iodate ion by bromine and hypobromous acid. Modifications of the procedure by increasing the acidity and KI concentration or the use of a back titration procedure eliminate the spuriously low results that have been false indications of a large and rapid chlorine demand in unpolluted seawater.

With the increasing recognition of the responses of aquatic organisms to low levels of "residual chlorine" (*1, 2*), measurement of the residual oxidants in the waters discharged from wastewater treatment plants and electricity-generating plants has become important in order that the environmental impact of the discharges can be properly assessed and regulated. Operation of electricity-generating plants frequently involves the use of chlorine as an antifouling agent in the cooling water system, and the large number of plants that have been built at estuarine and coastal sites during the past decade has led to much greater input of chlorinated waters. The wastewater collection systems of many coastal communities contain some seawater as a result of infiltration with brackish ground waters, and chlorine added as a disinfectant during treatment reacts with the seawater constituents during treatment and in the receiving water. We report in this paper on our observations that the analytical methods in widespread current use underestimate the residual oxidants in chlorinated seawater by as much as 70%, depending on the details of the procedures.

The addition of chlorine to waters containing sea salts leads to reaction with the natural bromide ion (65 mg/L in ocean water) to produce hypobromous acid and hypobromite ion (*3*). If ammonia is present, a mixture of monobromamine and monochloramine may be formed (*4*). In addition, reaction with organic compounds may produce a variety of brominated substances. Thus, the determination of "residual chlorine" actually corresponds to the estimation of the sum of this complex mixture and is better termed "residual oxidant determination".

The toxicity of chlorinated waters has been reported in terms of the combined residual chlorine concentration (*1*), and the results of iodometric amperometric titration measurements appear to be the most closely correlated with biologically active chlorine residuals (*5*). Since responses by fish have been found at the low concentrations of 0.001–0.01 mg/L, the high sensitivity of amperometric titration equipment with large electrodes has been attractive. The high sensitivity is attained by vigorous agitation of the sample with the danger that volatile halogen compounds may be lost, so that rapid titration has been recommended. The basic procedure (*6*) consists of adjusting the pH of the sample to 4 with acetate buffer, adding KI solution (final concentration 0.001–0.003 M depending on sample size), and rapidly titrating the liberated iodine with either sodium thiosulfate or phenylarsine oxide solutions. Similarly, the direct solid electrode amperometry (*7*) involves the continuous addition of an acetate buffer solution containing KI to the sample stream and the monitoring of the current produced by electrochemical reduction of the resulting iodine, with the refinement of using coulometrically generated iodine for periodic calibration. These procedures involving reaction of KI with the residual oxidants during a brief reaction time do not respond to all the residual oxidants in chlorinated seawater.

Experimental

The determinations of residual oxidants were carried out using reagent solutions and procedures as described in "Standard Methods" (*6*), except that the titration of iodine was followed photometrically using the apparatus and procedure outlined by Carpenter (*8*). Stock solutions of chlorine were prepared by dilution of distilled water saturated with gaseous chlorine. Stock solutions of bromine were prepared by dilution of distilled water saturated with liquid bromine.

The triiodide ion concentration in experimental solutions was monitored at 350 nm with a Beckman Model 24 spectrophotometer with a recorder.

Results and Discussion

The results of titrations for residual oxidants in chlorinated seawaters showed that Gulf Stream water filtered through 0.22-μ Fluoropore filters had a large apparent chlorine demand, even though such waters have a very low organic carbon content. In addition, the end point of the titrations was not

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persistent, and triiodide ion was slowly generated after the initial end point had been reached, with 18–24 h required for cessation of additional appearance of triiodide ion. For example, for a chlorine dosage that produced an apparent residual oxidant concentration in distilled water of 4.0×10^{-5} N (1.4 ppm Cl_2 equivalent), the same dosage in Gulf Stream seawater produced an apparent residual oxidant concentration of 2.1 and 2.5×10^{-5} N in two separate trials. The pH 4 buffer and KI reagents (final solution 0.0024 M KI) were added in less than 1 min after the chlorine dose to minimize reaction with seawater organics or decomposition. The residual oxidants reacted completely with KI in 1 min or less in solutions of pH 2 and 0.024 M KI in distilled water, and the test seawater showed a residual oxidant concentration of 3.6×10^{-5} N under these conditions.

The high "chlorine demand" of the Gulf Stream seawater appears to be due to the rapid formation of chemical species that react slowly with 0.0024 M KI at pH 4.

The addition of chlorine to seawater results in the rapid production of hypobromous acid and hypobromite ion. Based on observation of the 330-nm peak of hypobromite ion, the reaction is complete in less than 1 min. It seemed probable that the slow reacting species was formed from the bromine rather than the chlorine. This possibility was confirmed by use of the simple system of KI solutions in distilled water at various pH values to which an aqueous bromine solution was added and the absorbance to 350 nm (the triiodide peak) was monitored with time. The rate of appearance of the triiodide ion depended on the pH of the solutions and the KI concentration. For the "Standard Methods" (*6*) conditions of pH 4 and 0.0024 M KI, 70% of the total potential triiodide ion concentration appeared in less than 20 s, and further production was very slow. The slow formation of triiodide ion observed photometrically is analogous to the fading end point in the iodometric titrations. The inference is that the formation of the slow reacting species is not peculiar to seawater. The initial formation of triiodide ion was less (30–50%) if the stock KI and buffer solutions were added to brominated distilled water, as in the case of the procedures for analysis of residual oxidants, but was difficult to reproduce with precision. We used the bromination of the diluted KI solution to illustrate the formation and kinetics of the species that reacts slowly with iodide ion.

The rate of production of triiodide ion by the species formed when bromine was added depended strongly on the pH of the solutions (Figure 1). Slow reaction at pH 4 was found even in the presence of a tenfold higher concentration of KI than is normally used in the amperometric procedures for residual chlorine.

We sought to identify the slow reacting species by observing the triiodide ion concentration variation with time after the addition of iodine, chlorine, iodate, and bromate to 0.024 M KI solutions at various pH values (Figure 2). Addition of iodine produced a triiodide ion absorbance nearly instantaneously that did not vary with time or pH, showing that hydrolysis or disproportionation reactions were not responsible for the variations shown in Figure 1. Similarly, the addition of chlorine caused an absorbance that did not vary with time or pH, which supports the notion that the slow appearance of iodine in chlorinated seawater is not caused by reactions involving chlorine.

An obvious species that could cause the observed behavior is bromate ion, since the rate of reaction between iodide and bromate is strongly dependent on acidity (*9*), and the formation of bromate from bromide by hypochlorite is favored by a high concentration of chloride (*10*). As shown in Figure 2, bromate reacts with 0.024 M KI only slowly at pH 2 and does not appear to be the species that causes the results shown in Figure 1. Furthermore, we were unable to detect bromate in chlorinated seawater polarographically, unless the solutions were exposed to sunlight (*11*).

Addition of iodate to the 0.024 M KI solutions produced patterns of triiodide ion appearance with time at various pH values (Figure 2) that are similar to the results shown in Figure 1, ranging from rapid at pH 2 to very slow at pH 5. We infer that hypobromous acid or bromine (1.4×10^{-5} N) reacts rapidly with iodide (0.024 M) to produce a mixture of iodine and iodate; subsequently, the iodate reacts with the excess iodide to produce additional iodine at rates that depend on the pH.

Confirmation of the formation of iodate from iodide by added bromine at pH 4 was found from differential pulse polarograms. Differential pulse polarography was used in order that the iodate wave could be resolved on top of the large current due to the reduction of the iodine that is also present

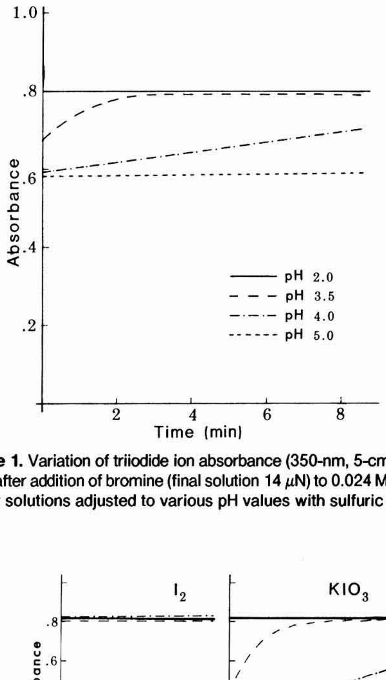

Figure 1. Variation of triiodide ion absorbance (350-nm, 5-cm path) with time after addition of bromine (final solution 14 μN) to 0.024 M KI distilled water solutions adjusted to various pH values with sulfuric acid

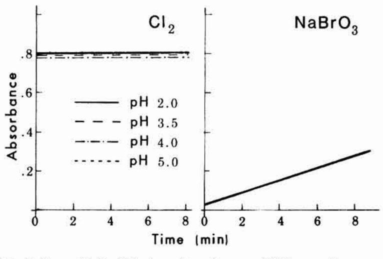

Figure 2. Variation of triiodide ion absorbance (350-nm, 5-cm path) with time after addition of either iodine, potassium iodate, chlorine, or potassium bromate (final solutions 14 μN) to 0.024 M KI distilled water solutions adjusted to various pH values with sulfuric acid. Variation with added iodate similar to variation with added bromine in Figure 1

as a result of the reaction of the iodide with the added bromine.

Comparison of Alternate Procedures

These results indicate that the amperometric standard method badly underestimates the residual oxidants in chlorinated seawater because the resulting bromine oxidizes part of the iodide to iodate. In our experiments the residual oxidant was primarily hypobromous acid because Gulf Stream seawater contains very low concentrations of ammonia and organic matter. We considered the ferrous ammonium sulfate titrimetric method with *N,N*-diethyl-*p*-phenylenediamine (DPD) end point indicator (*12*) as a possible alternate procedure for these unpolluted waters. Application of this method to Gulf Stream seawater gave only 80–85% recovery of added chlorine. The reasons for this discrepancy have not been identified. The DPD ferrous titrimetric method does not appear to be suitable for low (0.1–0.01 ppm) concentrations of residual oxidants because the visual end point is not sharp in these dilute solutions.

Another possible procedure would be a modification of the iodometric procedure at lower pH and higher potassium iodide concentrations, so that iodate would react rapidly. Greater acidity and iodide ion concentration should be limited to conditions that do not produce significant air oxidation of the iodide, and pH 2 with ca. 0.03 M KI appears to be a realistic limit. The high KI concentration has the additional virtue of reducing the volatilization of the iodine by the formation of the triiodide ion complex, but has the drawback of reducing the amperometric response since the electrode senses primarily the free iodine (*13*). In the photometric titration procedure that we used, the triiodide ion concentration is measured, and the high KI concentration is desirable.

The results of titrations for residual oxidants in chlorinated seawater, by use of variations of the iodometric procedure, are shown in Table I. The pH was adjusted and the KI solutions were added within 1 min after the addition of the chlorine solution to minimize the decomposition of the resulting oxidants. Use of pH 4 and low KI concentration produced values that are substantial underestimates, as delineated above. The chlorine disappearance in seawater has been described as involving an initial rapid decline followed by a much slower decline (*14*), and our results suggest that the apparent rapid initial decline may be partially an artifact of the analytical method.

The use of greater acidity and KI produced values that correspond to a loss or consumption of chlorine in the Gulf Stream seawater of roughly 1 to 2 μeq/L, which is possibly a reasonable result. However, the use of the back titration procedure (*6*, p 382), in which the sample was added to an excess of phenylarsine oxide solution that had been mixed with the pH 4 buffer and the KI solution and the excess phenylarsine oxide titrated with a standardized iodine solution, gave results corresponding to 100% recovery of the oxidizing capacity of the added chlorine. The reverse titration has been recommended for wastewaters to avoid reaction of the liberated iodine with the organic material in such solutions. A possible explanation for the difference between the direct titration results and the back titration results would be the reaction of the iodine with organic matter during the 10 min or so required for the photometric titration that was used. If so, this effect would be greater in estuarine and coastal waters that contain much more organic matter than the Gulf Stream seawater.

The quantitative recovery of the added chlorine oxidizing capacity with the back titration procedure suggests this procedure is suitable for residual oxidant determinations in chlorinated seawater. The procedure has the following advantages:

A low KI concentration may be used without the danger of iodine volatilization, and the response of the amperometric electrodes is not reduced, as it would be if a high KI concentration were required.

The pH 4 acetate buffer is convenient for adjusting the pH of samples.

The high pH and low KI concentration should reduce the possible effects of interference from air oxidation and ferric, manganic, or nitrite ions.

The large errors that we find with current procedures make it difficult to evaluate and compare various toxicity studies involving chlorine since the actual exposure levels probably have been underestimated substantially. Simple correction for the errors does not appear to be practical because the magnitude of the errors depends on the particulars in the analyses, such as whether pH 4 or 3.5 was used and the rate of titration. A need for careful evaluation of the analytical procedures seems obvious, particularly for water containing higher concentrations of ammonia and organic compounds than Gulf Stream water.

Table I. Apparent Residual Oxidant Concentrations in Distilled Water and Seawater with Different Analysis Procedures for Two Different Chlorine Additions[a]

Procedure	Residual oxidants, μM	Recovery, %
a	21.7	. . .
b	6.7	31
c	18.7	86
d	21.4	99
a	40.6	. . .
b	21.2	52
c	38.8	95
d	41.3	102

[a] (a) Distilled water, direct iodometric at pH 2 in 0.024 M KI; (b) seawater, direct iodometric at pH 4 in 0.0024 M KI; (c) seawater, direct iodometric at pH 2 in 0.024 M KI; and (d) seawater, back titration with standardized iodine solution after excess phenylarsine oxide solution added at pH 4 and 0.0024 M KI.

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NO_x–O_3 Photochemistry in Power Plant Plumes: Comparison of Theory with Observation

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■ Measurements were made by an instrumented aircraft in the plume from a large, coal-fired power plant. In all traverses (out to 45 km downwind), ozone concentrations within the plume were depressed below background levels. The depth of this ozone deficit and the ratio of NO to NO_x in the plume both decreased with increasing distance from the plant. A model is presented which accurately predicts the observed plume profiles of O_3, NO, and NO_x from the background conditions, plume geometry, and basic photolytic cycle. Free-radical reactions within the plume did not significantly affect oxidant concentrations at the distances sampled.

The elevated pollutant plume from a stationary combustion source is a large-scale flow reactor well suited to the study of certain photochemical reactions in the atmosphere. Samples taken in the core of the plume at increasing downwind distances show the evolution of ambient air doped with nitric oxide and other contaminants. At the same time, control samples taken adjacent to the plume show the evolution of undoped ambient air under similar meteorological conditions.

The interpretation of reactant profiles in a plume is somewhat complicated by the continual mixing which takes place at the plume boundary. Changes in reactant concentrations produced by the simple physical entrainment of ambient air must be backed out of the data before the effects of ongoing chemical transformations can be identified. Because of the simplicity of their dependence on plume geometry, much can be learned from a study of the stoichiometric invariants of the fast photochemical reactions. This paper develops such an approach and applies it to the analysis of data taken at a large, coal-fired power plant in the Midwest.

Experimental

During the summer of 1974, an instrumented light plane was used to map the flow of aerosols and trace gases within large plumes in the St. Louis area. These measurements were carried out as part of Project MISTT (Midwest Interstate Sulfur Transformation and Transport) (*1*) and were supported by intensive pilot balloon observations of winds aloft. The aerial plume mapping program is described in detail in ref. *2*, and results on sulfur chemistry and secondary aerosol production in a power plant plume have been presented elsewhere (*3, 4*). The discussion in the present paper will focus on the chemistry of nitrogen oxides in a power plant plume.

The sampling aircraft carried continuous monitors for four gases: O_3, NO, NO_x, and SO_2. Ozone was measured with a chemiluminescence detector ($O_3 + C_2H_4$) calibrated against the buffered KI method. Nitrogen oxides were measured with a chemiluminescence detector ($NO + O_3$) equipped with dual reaction chambers and a low-temperature molybdenum NO_x converter. The converter was designed to reduce only NO_2 to NO, but may have reduced higher oxides as well (*5*). Sulfur dioxide was measured with an electrochemical cell. Readings from each instrument were recorded at 0.4-s intervals on magnetic tape cartridges. The figures in this paper show data which have been averaged over 5–25 records.

On 14 August 1974 the plume from the 2200-MW coal-fired power plant at Labadie, Mo., was mapped in considerable detail out to a distance of 45 km (Figure 1). A total of 19 sampling passes were flown under hazy skies during the middle of the day, when temperatures at 455–610 m (1500–2000 ft) msl were 20–25 °C and humidities were 60–70%. Winds aloft were well suited to the characterization of pollutant flow, holding steady from the east at 3–5 m/s (11–18 km/h) and carrying the plume away from St. Louis over predominantly rural terrain. At these wind speeds the emissions of the plant had aged 3–4 h by the time they reached the 45-km sampling distance.

Figures 2–5 show cross-plume profiles of gas concentrations recorded during selected horizontal traverses of the plume. (The complete data set is available in ref. *6*.) The boundaries of the plume are apparent in the SO_2 profiles, since background SO_2 concentrations in the sampling area were generally below the detection limit of the instrument.

The concentrations on either side of the SO_2 plume represent the background from sources other than the power plant. Background NO_x concentrations were on the order of 3 pphm, and background ozone concentrations ranged from 6 to 11 pphm. On some traverses (e.g., Figure 3), ozone concentrations on the north side of the plume were higher than those on the south side; inspection of Figure 1 suggests that the power plant plume may have been on the southern shoulder of the St. Louis urban plume (*7*).

Analysis of Invariants

In all traverses of the Labadie plume, ozone concentrations within the plume were depressed below their levels in the background air. This ozone "deficit", which has been remarked in other power plant plumes (*8–10*), is due to scavenging of ambient ozone by the nitric oxide in the plant effluent:

$$O_3 + NO \rightarrow O_2 + NO_2 \qquad (1)$$

Reaction 1 is very fast with a rate constant of about 27 ppm^{-1} min^{-1} (*11*). In the dark it proceeds almost to completion; at every point of the early morning traverse shown in Figure 6, either ozone or nitric oxide had been exhausted.

During the day, absorption of ultraviolet radiation by nitrogen dioxide leads to the formation of ozone:

$$NO_2 \xrightarrow{h\nu} NO + O \qquad (2)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (3)$$

Reaction 3 is so fast that it can be combined with Reaction 2 for the purposes of this discussion:

$$O_2 + NO_2 \xrightarrow{h\nu} O_3 + NO \qquad (2')$$

The lumped Reaction 2′ has a rate constant at midday of 0.3–0.5 min^{-1} (*12*). It is the reverse of Reaction 1 and in daylight maintains positive concentrations of ozone and nitric oxide (Figures 2 and 4).

At atmospheric concentrations, Reactions 1 and 2′ are much the fastest known reactions in which nitric oxide, nitrogen

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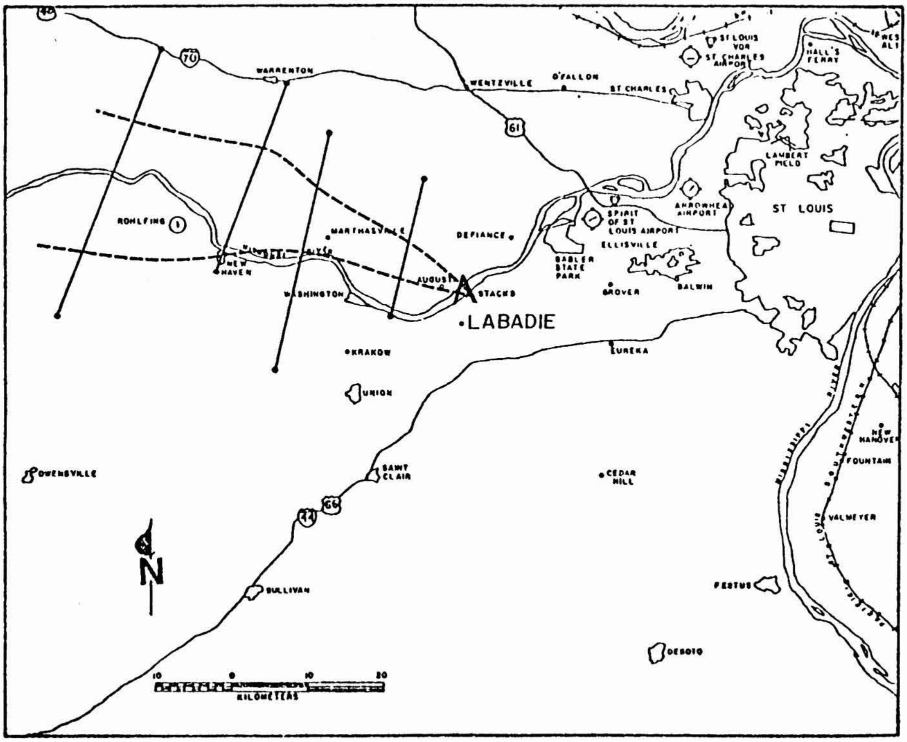

Figure 1. Outline of SO_2 plume downwind of Labadie power plant on August 14, 1974

Solid lines: sampling path. Dashed curves: region in which SO_2 concentrations above 1 pphm were measured between 455 and 610 m (1500 and 2000 ft) msl. Sampling began near plant at 1045 c.d.t., ended 45 km downwind at 1515 c.d.t.

dioxide, and ozone participate (*13*). Reactions 1 and 2′ should therefore control the short-term dynamics of the $NO/NO_2/O_3$ system, and concentrations should quickly approach a photostationary state in which (*13*)

$$[O_3][NO]/[NO_2] = k_2'/k_1 \qquad (4)$$

Although measurements of this concentration ratio are inherently noisy (Figures 4 and 5) (*14*), there is little doubt that the approximate relationship of Equation 4 obtains under conditions such as those in the Labadie plume 10 km or more downwind of the plant. The photostationary relationship leaves the $NO/NO_2/O_3$ system with two degrees of freedom, and even relatively slow competing reactions can affect concentrations within the photostationary constraint imposed by Reactions 1 and 2′.

In the absence of competing reactions, additional constraints are imposed on the $NO/NO_2/O_3$ system by the fact that $[NO_2] + [O_3]$ and $[NO] + [NO_2]$ are stoichiometric invariants of Reactions 1 and 2′. As will be shown in the next section, the concentrations of NO, NO_2, and O_3 can be expressed in terms of the quantities $[O_3][NO]/[NO_2]$, $[NO_2] + [O_3]$, and $[NO] + [NO_2]$. Reactions other than 1 and 2′ therefore affect concentrations in the $NO/NO_2/O_3$ system to the degree that $NO_2 + O_3$ ("oxidant") and $NO + NO_2$ ("NO_x") are not conserved. The conservation of a species is easily checked, since the profile to be expected of a conservative species can be calculated directly from plume geometry and background conditions.

Oxidant. In the following discussion, the term "oxidant" will be used to refer conveniently to the sum of nitrogen dioxide and ozone: $[\text{oxidant}] = [NO_2] + [O_3]$. This usage is not standard; the "oxidant" defined here is not that measured by, e.g., the KI method, which does not respond quantitatively to NO_2.

The direct impact of primary emissions on oxidant concentrations within the Labadie plume is negligible 20 km or more downwind of the plant. The oxidant profile to be expected in the absence of reactions other than 1 and 2′ is thus simply that of the background air. Very little of the nitrogen in the effluent is emitted as nitrogen dioxide; for example, on the traverse 1 km downwind of the plant shown in Figure 6, the NO/NO_x ratio was 0.90 in the core of the plume. Since the plant emits no ozone, its primary oxidant emissions are at most 10% of its nitrogen oxides emissions. In the core of the plume 22 km downwind from Labadie on August 14, this would have corresponded to a primary oxidant concentration of less than 0.5 pphm, about 6% of background oxidant levels.

Figures 2 and 3 show the oxidant profiles measured in the Labadie plume 22 and 45 km downwind from the plant on August 14. To within the accuracy of the measurements, oxidant concentrations within the plume were consistent with the background levels on either side, that is, the measured and expected oxidant profiles agree.

Nitrogen Oxides. Unlike oxidant, NO_x is emitted in significant quantities by the Labadie plant. The NO_x profile in the plume thus depends not only on the background air, but on the geometry of the plume as well. In the absence of reactions other than 1 and 2′, the NO_x concentration to be expected at a given point is $f_{NO_x}\chi + B$, where χ is the concentration of plant effluent at that point, f_{NO_x} is the fraction of NO_x in the stack gas, and B is the background NO_x concen-

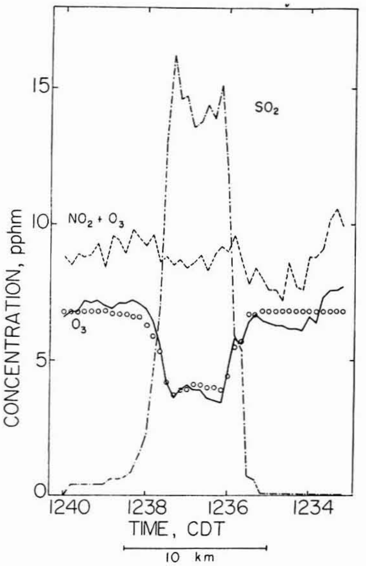

Figure 2. Concentration profiles from horizontal traverse at 455 m (1500 ft) msl, 22 km downwind of Labadie power plant on August 14, 1974

Curves: measured O_3, $NO_2 + O_3$, and SO_2 profiles. Circles: model O_3 profile calculated as described in text

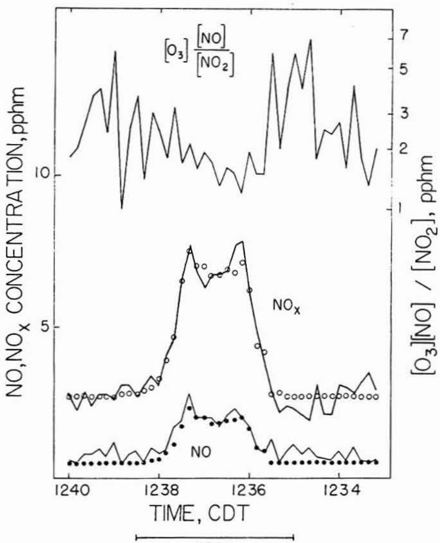

Figure 4. Further concentration profiles (see also Figure 2) from horizontal traverse at 455 m (1500 ft) msl, 22 km downwind of Labadie power plant on August 14, 1974

Curves: measured NO, NO_x, and photostationary ratio profiles. Dots and circles: model NO and NO_x profiles calculated as described in text

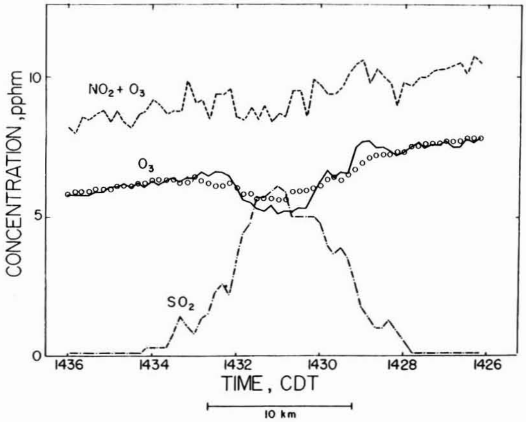

Figure 3. Concentration profiles from horizontal traverse at 610 m (2000 ft) msl, 45 km downwind of Labadie power plant on August 14, 1974

Curves: measured O_3, $NO_2 + O_3$, and SO_2 profiles. Circles: model O_3 profile calculated as described in text

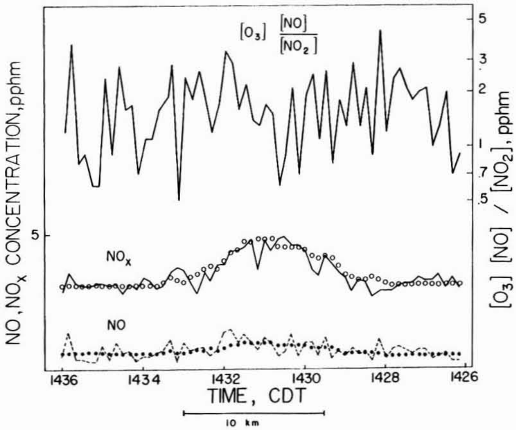

Figure 5. Further concentration profiles (see also Figure 3) from horizontal traverse at 610 m (2000 ft) msl, 45 km downwind of Labadie power plant on August 14, 1974

Curves: measured NO, NO_x, and photostationary ratio profiles. Dots and circles: model NO and NO_x profiles calculated as described in text

tration. The quantity χ can be eliminated through use of the approximation $[SO_2] = f_{SO_2}\chi$, since sulfur dioxide backgrounds are negligible and measurements of the flow rate in the August 14 Labadie plume showed no detectable loss between 10 and 45 km (*2, 3*).

Figures 4 and 5 show the NO_x profiles measured in the Labadie plume 22 and 45 km downwind from the plant on August 14. The measured NO_x profiles are compared with expected NO_x profiles calculated from the measured SO_2 profiles according to the formula

$$[NO_x] = f_{NO_x}\chi + B = 0.3[SO_2] + B$$

The background, B, was taken to be the average NO_x concentration measured outside the SO_2 plume, which was 2.6 pphm in the pass at 22 km and 3.0 pphm in the pass at 45 km. As in-stack measurements were not available, the factor 0.3 $= f_{NO_x}/f_{SO_2}$ was determined by linear regression of NO_x on SO_2 for this and other plumes. To within the accuracy of the measurements, the measured and expected NO_x profiles agree.

Simple Model

The preceding section identified three quantities, $[O_3][NO]/[NO_2]$, $[NO_2] + [O_3]$, and $[NO] + [NO_2]$, which are kinetic or stoichiometric invariants of Reactions 1 and 2′. As others have noted (*15–18*), these invariants together determine the state of the NO/NO$_2$/O$_3$ system; the following identities are easily verified:

$$[\mathrm{NO}] = \frac{1}{2}\{-\,[\mathrm{O_3}][\mathrm{NO}]/[\mathrm{NO_2}] - ([\mathrm{NO_2}] + [\mathrm{O_3}]) + ([\mathrm{NO}] + [\mathrm{NO_2}]) + X\} \quad (5)$$

$$[\mathrm{NO_2}] = \frac{1}{2}\{[\mathrm{O_3}][\mathrm{NO}]/[\mathrm{NO_2}] + ([\mathrm{NO_2}] + [\mathrm{O_3}]) + ([\mathrm{NO}] + [\mathrm{NO_2}]) - X\} \quad (6)$$

$$[\mathrm{O_3}] = \frac{1}{2}\{-\,[\mathrm{O_3}][\mathrm{NO}]/[\mathrm{NO_2}] + ([\mathrm{NO_2}] + [\mathrm{O_3}]) - ([\mathrm{NO}] + [\mathrm{NO_2}]) + X\} \quad (7)$$

where

$$X = \{([\mathrm{O_3}][\mathrm{NO}]/[\mathrm{NO_2}] + ([\mathrm{NO_2}] + [\mathrm{O_3}]) + ([\mathrm{NO}] + [\mathrm{NO_2}]))^2 - 4\,([\mathrm{NO_2}] + [\mathrm{O_3}])\,([\mathrm{NO}] + [\mathrm{NO_2}])\}^{1/2}$$

When environmental conditions are spatially uniform and reactions other than 1 and 2′ unimportant, simple formulas can be written for the profiles of the three invariants. Equations 5–7 then yield analytic expressions for the profiles of the individual reactant concentrations.

Figures 2–5 show model ozone and nitric oxide profiles calculated as above for the environment and geometry of the August 14 Labadie plume. Based on the latitude and time of day of the observations, a crude estimate was made of the photostationary ratio $[\mathrm{O_3}][\mathrm{NO}]/[\mathrm{NO_2}] = k_2'/k_1$; the optical thickness of the plume was neglected, and k_2'/k_1 taken to be 1.5 pphm throughout. The oxidant concentration was taken from ozone and nitrogen dioxide concentrations outside the plume; a constant value of 9.0 pphm was used for the pass at 22 km, and a value dropping linearly with time from 10.4 pphm at 1426 c.d.t. to 8.3 pphm at 1436 c.d.t. was used for the pass at 45 km. The NO$_x$ concentration could have been predicted with a Gaussian plume model (*17, 18*) but was instead scaled from the measured SO$_2$ concentration as described in the preceding section; basing the calculations on the observed plume geometry simplifies the interpretation of any differences between the measured and model profiles.

The correspondence between measured and model profiles is quite good for the pass 22 km from the plant. There is a suggestion that the correspondence was beginning to break down 45 km from the plant, where the observed ozone deficit was narrower and deeper than that calculated from the geometry of the SO$_2$ plume. The origin of this difference is not known. Possible explanations include the following: The profile of the background oxidant concentration was irregular; ultraviolet radiation was significantly attenuated within the core of the plume due to scattering by aerosols, depressing the rate of nitrogen dioxide photolysis; and reactions involving hydrocarbon products were important where the plume mixed into the background air, destabilizing the oxidant concentration.

An advantage of an analytic model is that its sensitivity to various input parameters is easily determined. Figure 7 shows the calculated dependence on rate constants, background oxidant, and plume dilution of the ozone concentration in the core of the August 14 Labadie plume 22 km from the plant. The calculated ozone concentration is relatively insensitive to the photostationary ratio, which is why the noisy measured $[\mathrm{O_3}][\mathrm{NO}]/[\mathrm{NO_2}]$ profile can successfully be approximated in the model by a constant one.

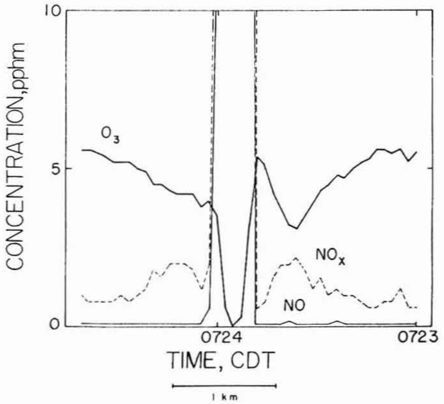

Figure 6. Concentration profiles from horizontal traverse at 550 m (1800 ft) msl, 1 km downwind of Labadie power plant on July 31, 1974
Curves: measured NO, NO$_x$, and O$_3$ profiles

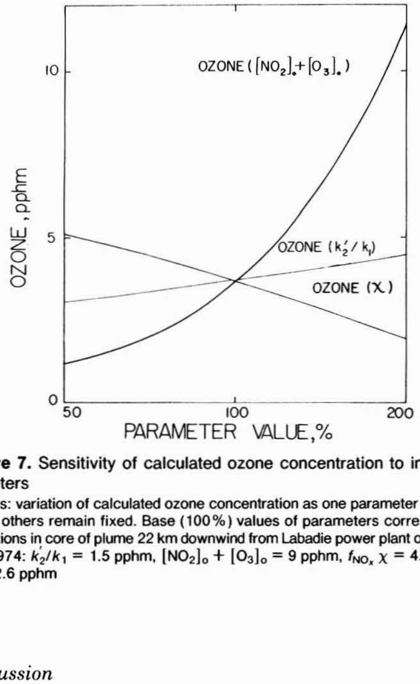

Figure 7. Sensitivity of calculated ozone concentration to input parameters
Curves: variation of calculated ozone concentration as one parameter is varied while others remain fixed. Base (100%) values of parameters correspond to conditions in core of plume 22 km downwind from Labadie power plant on August 14, 1974: $k_2'/k_1 = 1.5$ pphm, $[\mathrm{NO_2}]_o + [\mathrm{O_3}]_o = 9$ pphm, $f_{\mathrm{NO}_x}\,\chi = 4.9$ pphm, $B = 2.6$ pphm

Discussion

In polluted air, Reactions 1 and 2′ are but two of many reactions which affect the NO/NO$_2$/O$_3$ system. Some of the most interesting competing reactions are those which provide alternatives to Reaction 1 for the oxidation of nitric oxide to nitrogen dioxide. An important example is the reaction of nitric oxide with peroxy radicals formed during the oxidation of reactive hydrocarbons (*15*) or, possibly, of SO$_2$ (*8*):

$$\mathrm{NO} + \mathrm{ROO}\cdot \rightarrow \mathrm{NO_2} + \mathrm{RO}\cdot \quad (8)$$

While they are too slow to perturb the photostationary state significantly, such free-radical reactions do allow the oxidant concentration to rise:

$$\frac{d}{dt}([\mathrm{NO_2}] + [\mathrm{O_3}]) = k_8\,[\mathrm{NO}][\mathrm{ROO}\cdot] \quad (9)$$

This can be seen (Figure 8) in the hydrocarbon-rich plumes downwind of downtown St. Louis (site of concentrated automotive emissions) and Wood River, Ill. (site of a large chemical industry), where ozone and oxidant concentrations are commonly well above background (*19*).

Free-radical reactions play an essential role in determining the oxidant level of the environment into which the emissions of a power plant are injected. In this sense, they strongly influence the chemistry of the NO/NO_2/O_3 system within the plume (cf Figure 7). However, the increase in the oxidant concentration corresponding to Equation 9 was not detected in the plume downwind of the Labadie plant on August 14, although this plume was followed well beyond the distances at which oxidant production began in the St. Louis and Wood River plumes. The central conclusion to be drawn from the preceding sections is that, over the first few tens of kilometers at least, the observed impact of the hydrocarbon-poor Labadie plume on the ambient NO/NO_2/O_3 system can be understood fairly well in terms of Reactions 1 and 2′.

The advantage of restricting attention to the basic photolytic cycle is that reactant profiles can then be calculated for the exact geometry of the observed plume, and the study of plume chemistry separated from the study of plume dispersion. This is possible only because the model chemistry is in equilibrium, so that reactant concentrations at a point are determined solely by the dilution of the plume at that point

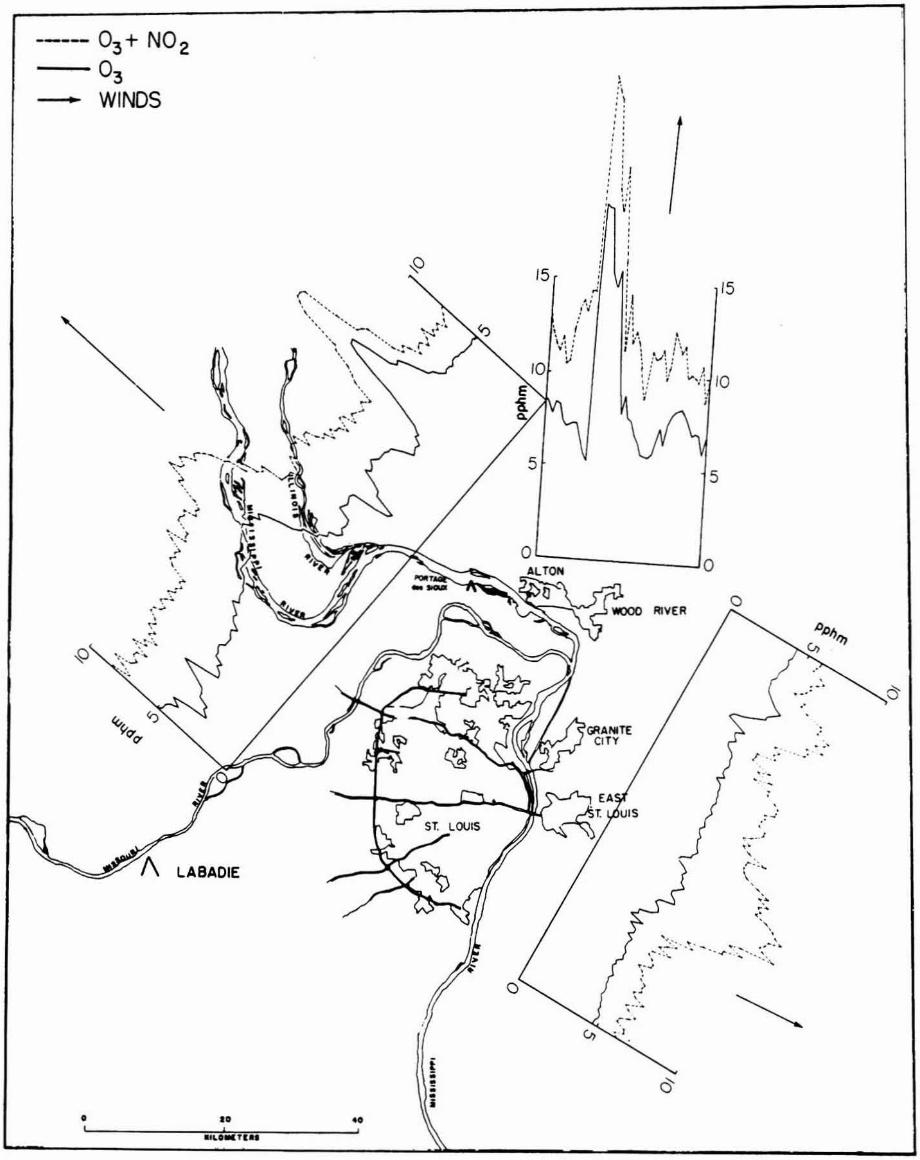

Figure 8. Concentration profiles from horizontal traverses downwind of metropolitan St. Louis under three different wind regimes

Traverses made along profile baselines at following altitudes and times: (counterclockwise from lower right) 455 m (1500 ft) msl, 0933–0952 c.d.t., 30 July 1974; 610 m (2000 ft) msl, 1145–1152 c.d.t., 12 August 1974; 455 m (1500 ft) msl, 1027–1048 c.d.t., 15 August 1974. Arrows: average winds measured in mixing layer during sampling period; their lengths equal distance covered in 1 h at average wind speed and are independent of the speed with which that dilution was reached. The addition to the reaction scheme of alternative pathways for the oxidation of NO to NO_2 destroys that equilibrium and renders the state of the $NO/NO_2/O_3$ system in a plume parcel dependent on the past dilution history of that parcel. Given the difficulty of characterizing the initial turbulent dilution of a plume, the model presented here contains, in a sense, as detailed a reaction scheme as can be compared with observation at moderate distances from the stack.

Davis et al. have reported ozone concentrations in excess of background within the plume 40 km downwind of a 1000-MW power plant on the East Coast (*8*). We have not yet observed such an ozone "bulge" at these distances in the Labadie plume. It is possible, however, that the nitrogen oxides of the Labadie plume eventually contribute to the net formation of ozone as they mix with outside air containing hydrocarbons. While the oxidant-conserving model presented here can be compared with observations of a given plume to determine whether or not net production of ozone is occurring, an understanding of the conditions under which ozone would be formed in a power plant plume must ultimately be sought in plume kinetics which incorporate a variety of reactions beyond the basic photolytic cycle (*20*).

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Nitrate Formation in Atmospheric Aerosols

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■ Equilibrium nitrate levels in aqueous solution in the presence of sodium chloride, nitric oxide, nitrogen dioxide, sulfur dioxide, carbon dioxide, ammonia, and sulfuric acid are calculated. Nitrate levels in solution are of the order of those observed in the atmosphere when the gaseous concentrations are at typical urban levels. Sulfate levels in such solutions are predicted to be relatively low in the absence of oxidation catalysts. When sulfate formation is assumed to occur by gas-phase oxidation of sulfur dioxide to sulfuric acid followed by absorption of the sulfuric acid in aerosols, predicted nitrate and sulfate size distributions are in qualitative agreement with those observed in the atmosphere.

One of the most important current problems in atmospheric chemistry is the delineation of the detailed chemical and physical paths of conversion of sulfur dioxide and nitrogen oxides to sulfate and nitrate salts. In comparison to sulfate, considerably less attention has been devoted to nitrate formation in the atmosphere.

The gas-phase formation of nitrates, such as nitrous acid, nitric acid, and peroxyacyl nitrates, has been studied experimentally (*1–3*) and theoretically (*4, 5*) and is reasonably well understood. There have been several experimental studies of nitric acid formation in smog chambers (*1, 2*) and measurements reported of nitric acid in ambient air (*6*).

There exist a number of studies in which ambient particulate nitrate levels have been measured. Lundgren (*7*) measured aerosol nitrate concentrations at Riverside, Calif., in 1968 and found high concentrations of ammonium nitrate in particles in the 0.5–2-μm-diameter size range during days of high smog (very limited visibility). A source of considerable information on particulate nitrates was the Aerosol Characterization Experiment (ACHEX) conducted in the South Coast Air Basin in 1972 and 1973 (*8, 9*). In the ACHEX study, sulfate and nitrate together often comprised more than 15%

of the total aerosol mass (*9*). The diurnal concentration behavior of sulfate was similar to that of SO_2, ozone, and total carbon. In contrast to sulfate, the diurnal nitrate pattern typically exhibited its maximum during the morning close to the time when gas-phase nitrogen oxides (NO_x) concentrations are at a maximum. Nitrate concentrations generally exhibited a second, less pronounced peak in the afternoon coincident with ozone maxima. Figure 1 shows the diurnal variation of sulfate and nitrate at West Covina, Calif., on July 23–24, 1973, in the particle size fractions above and below 0.5 μm diameter (*9*). Freshly produced sulfate seems to be associated principally with particles below 0.5 μm diameter. Of the two diurnal nitrate peaks, the morning maximum is associated predominantly with particles of diameter greater than 0.5 μm, and the afternoon peak is associated mainly with particles of diameter less than 0.5 μm diameter.

Table I shows ranges of sulfate and nitrate levels found at various locations in the South Coast Air Basin in 1973 and the mass median diameters for particles containing nitrate and sulfate on the days during which measurements were carried out. The sulfate diameters are relatively constant and, with the exception of the Rubidoux point, are consistently smaller than those of nitrate-containing particles. Observed levels of ammonium, NH_4^+, correlated closely with sulfate and nitrate levels. Observed levels of ammonium were compared with those NH_4^+ levels that would be present if all the sulfate and nitrate were present as $(NH_4)_2SO_4$ and NH_4NO_3 (*9*). The measured NH_4^+ levels ranged from 62% at Dominguez Hills, which is close to major SO_2 sources, to 103% adjacent to the Harbor Freeway. Infrared spectra studies by Grosjean and Friedlander (*10*) showed that NH_4NO_3 comprised 95% of the total nitrate aerosol. Chang and Novakov (*11*) identified in ambient aerosol from West Covina, in addition to nitrate and ammonium, two reduced forms of nitrogen that would have been produced by surface reactions of NH_3 and NO with soot particles. Sandberg et al. (*12*) presented an analysis of five years (1969–73) of sulfate and nitrate fractions from high-volume particulate samples in the San Francisco area.

As a part of the ACHEX study, Cronn et al. (*13*) measured the diurnal variation of ammonium nitrate and sodium nitrate levels at West Covina during 1973. Ammonium chloride and ammonium nitrate were observed to peak in the morning. Fairly uniform concentrations of sodium nitrate were observed over the sampling period. Peak values of NH_4Cl, NH_4NO_3, and $NaNO_3$ were 1.6, 4.6, and 0.68 $\mu g\ m^{-3}$, respectively. Moskowitz (*14*) made measurements of aerosol nitrate at three locations in the South Coast Air Basin: Pasadena, Hermosa Beach, and Chino (an agricultural area 30 miles southeast of Pasadena). An average diurnal nitrate size distribution for each location was obtained. The Pasadena distribution was bimodal; peaks exist in the two size ranges 0.05–1 and 2–8 μm. The Chino distribution possessed a significant peak in the submicron range, although the distribution appeared to be weakly bimodal. In the coastal area (Hermosa Beach) the predominant size range for nitrates was 2–8 μm. The main nitrate species in the larger coastal marine aerosol was $NaNO_3$, whereas that in the smaller inland particles was NH_4NO_3.

Recently, there have been several smog chamber experiments in which aerosol nitrate formation rates have been measured. Clark et al. (*15*) irradiated initially particle-free ambient air collected downwind of a freeway at different SO_2 levels. Sulfate, nitrate, and nitrate formation rates were measured. Harker et al. (*16*) studied further the formation of particulate nitrate through irradiation of hydrocarbon, nitrogen oxides, and SO_2 mixtures in initially particle-free ambient air. In the absence of SO_2, nitrate was the principal aerosol nitrogen species with smaller quantities of ammonium and an amine-like species. In the presence of SO_2, the nitrate levels were substantially lowered, suggesting that sulfate formation in some manner reduced particulate nitrate levels.

The object of this study is to attempt to elucidate the formation of nitrate in atmospheric aerosols. We confine our attention to aqueous aerosols; we do not consider, therefore, the role of surfaces as a catalytic agent for formation of reduced nitrogen species. Primarily we wish to determine if liquid-phase chemistry is capable of accounting for nitrate levels of the order of those observed in the South Coast Air Basin. (Although we refer to available data for the South Coast Air Basin in our discussion, the analysis is applicable to the general urban atmosphere.) We are also interested in ascertaining possible explanations for the observed differences in sulfate and nitrate size distributions (*9*).

We will discuss in general terms the paths of formation of nitrates in the atmosphere. Then we will consider the chemistry of an aqueous droplet in the presence of NaCl, NO, NO_2, SO_2, CO_2, and NH_3. A situation will be considered in which gas-phase oxidation of SO_2 to form sulfuric acid followed by absorption of the sulfuric acid into existing droplets takes place. Finally, we will speculate as to the principal atmospheric conversion mechanisms for nitrate in the types of systems studied here.

Paths of Nitrate Formation

Atmospheric nitrates can be formed by a number of pathways. Figure 2 summarizes several of these routes. Path 1 in-

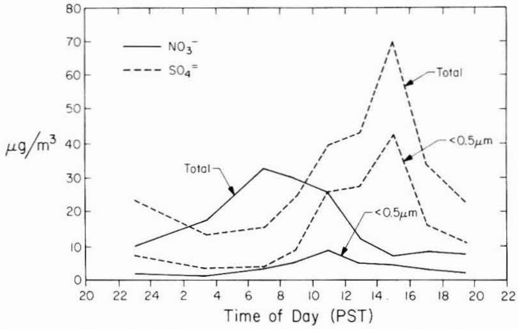

Figure 1. Diurnal variations in size distributions for sulfate and nitrate in West Covina, July 23–24, 1973

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Table I. Sulfate and Nitrate Data Obtained in South Coast Air Basin During 1973 ACHEX (*9*)

Location	Date	Sulfate	Nitrate
	24-h averages ($\mu g\ m^{-3}$)		
West Covina	Jul. 23–24	40	6
Pomona	Aug. 16–17	35	7
Rubidoux	Sept. 5–6	16	45
Rubidoux	Sept. 18–19	32	70
	Mass median diameter (μm)^a		
Dominguez Hills	Oct. 4–5	1.64	0.43
	Oct. 10–11	0.72	0.42
West Covina	Jul. 23–24	1.13	0.34
	Jul. 26^b	0.62	<0.22
Pomona	Aug. 16–17	0.68	0.39
Rubidoux	Sept. 5–6	0.33	0.33
	Sept. 18–19	0.34	0.43

^{a} Except as noted, based on 24-h size distributions obtained with five-stage Lundgren impactor. ^{b} 13-h average, 0500–1800 h.

volves the formation of nitric acid by homogeneous gas-phase reactions involving NO and NO_2. Nitric acid, once formed, may then react with NH_3 to produce NH_4NO_3 or be absorbed directly into an aerosol droplet (paths 2 and 3, respectively). Because of the relatively high vapor pressure of nitric acid, homogeneous nucleation is not expected to take place under normal atmospheric conditions (*17*). Thus, step 3 is probably unimportant when compared to other possible routes of incorporation of nitrate in a particle. Path 4 involves the direct absorption of NO and NO_2 followed by chemical reaction within the droplet. Step 6 depicts the formation of organic nitrates through free radical reactions followed by absorption of these nitrates into particles.

Homogeneous Formation of Nitric Acid. Table II lists the major gas-phase reactions involving nitric acid in the urban atmosphere. The principal homogeneous sources of nitric acid are Reactions 1 and 2 in Table II. The rates of formation of nitric acid by Reactions 1 and 2 can be estimated for typical atmospheric conditions. If we assume a hydroxyl radical concentration of 10^{-7} ppm (*19–21*), the rates of formation of nitric acid at NO_2 concentrations of 0.05 and 0.5 ppm are:

$$R_1 = 8.5 \times 10^{-5}\ \text{ppm min}^{-1}\ ([NO_2] = 0.05\ \text{ppm})$$

$$R_1 = 8.5 \times 10^{-4}\ \text{ppm min}^{-1}\ ([NO_2] = 0.5\ \text{ppm})$$

Over a 5-h period these rates, if sustained, would lead to 64.6 and 646 $\mu g\ m^{-3}$ of nitric acid in the absence of any removal mechanisms for nitric acid.

The rate of Reaction 2 in Table II can be estimated from a chemical kinetic simulation of a typical smog chamber experiment (*5*). Using $[NO]_o = 0.5$ ppm, $[NO_2]_o = 0.09$ ppm, initial total reactive hydrocarbons = 1.17 ppm, and relative humidity = 50%, the rate of formation of nitric acid by Reaction 2 at the time of occurrence of the NO_2 maximum is approximately

$$R_2 = 2.2 \times 10^{-5}\ \text{ppm min}^{-1}$$

Therefore, the homogeneous formation of nitric acid probably results primarily from Reaction 1. Although the nitric acid concentrations theoretically achievable from homogeneous reactions are substantial, removal processes serve to keep actual atmospheric concentrations lower than the theoretical maxima. As noted above, because of the relatively high vapor pressure of nitric acid, homogeneous nucleation is not expected to be an important removal process.

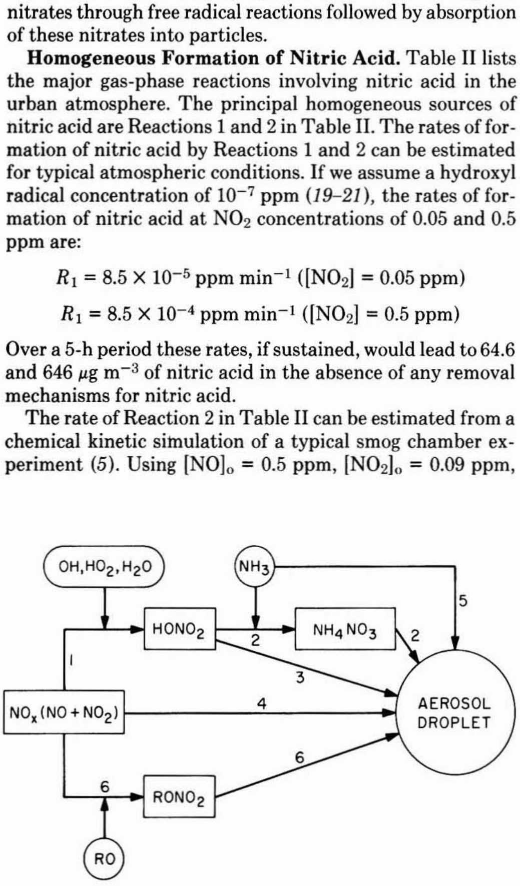

Figure 2. Nitrate formation mechanisms in atmospheric aerosols

Table II. Major Homogeneous Reactions Involving Nitric Acid in Urban Atmosphere

No.	Reaction	Rate constant @ 25 °C, $ppm^{-1}\ min^{-1}$	Ref
1.	$OH + NO_2 \rightarrow HNO_3$	1.7×10^4	*18*
2.	$N_2O_5 + H_2O \rightarrow 2HNO_3$	$1.5 \times 10^{-5\ a}$	*39*
2a.	$NO_3 + NO_2 \rightarrow N_2O_5$	5.6×10^3	*39*
2b.	$N_2O_5 \rightarrow NO_3 + NO_2$	$12.2\ min^{-1}$	*39*
3.	$HO_2 + NO_3 \rightarrow HNO_3 + O_2$	$2.5 \times 10^{3\ b}$	*4*
4.	$NH_3 + HNO_3 \rightarrow NH_4NO_3$	0.028^{c}	*38*
5.	$OH + HNO_3 \rightarrow H_2O + NO_3$	120	*18*

[a] Estimated upper limit. [b] Estimated. [c] Estimated by analogy to the reaction of NH_3 and HCl.

A possible route to convert nitric acid to the particulate phase is through Reaction 4 in Table II. As noted in Table II, a value for the rate constant of Reaction 4 is not available; the value shown is that for the analogous reaction of HCl and NH_3. If we estimate the NH_3 and HNO_3 concentrations as 0.01 and 0.005 ppm, respectively,

$$R_4 \cong 1.4 \times 10^{-6}\ \text{ppm min}^{-1}$$

Thus, the rate of Reaction 4 is approximately an order of magnitude smaller than the rate of formation of nitric acid by Reactions 1 and 2 combined. Because ammonium nitrate has a relatively low vapor pressure, a significant fraction of that formed should condense.

Heterogeneous Formation of Nitrate. The abundant evidence concerning particulate nitrate levels suggests that heterogeneous processes for nitrate formation may be important. The remainder of this work is devoted, therefore, to an evaluation of nitrate formation by heterogeneous processes.

Nitrate Formation in Aqueous Aerosols

In this section we consider the chemical equilibrium existing in a water droplet in air containing NO, NO_2, SO_2, CO_2, and NH_3. The water droplet may contain dissolved NaCl. Our object is to determine the concentration of nitrate achieved in such a solution and therefore to ascertain if aqueous equilibrium chemistry provides a possible explanation for observed ambient particulate nitrate levels.

The chemical reactions and equilibrium constants in the $NO–NO_2–SO_2–CO_2–NH_3–NaCl–H_2O$ system are given in Table III. In addition to the reactions in Table III, sulfate forms by the oxidation of sulfite (*22*)

$$SO_3^{2-} + \frac{1}{2}O_2 \rightarrow SO_4^{2-}$$

Once sulfate is formed by oxidation of sulfite, it does not reenter the chain producing the sulfite. Consequently, most of the sulfate formed in solution remains as sulfate ion (a small amount exists as bisulfate). Nitrate may form by the oxidation of nitrite by dissolved oxygen and ozone:

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^-$$

$$NO_2^-\ O_3 \rightarrow NO_3^- + O_2$$

In the absence of the above two reactions, nitrate exists in solution as a result of the reaction:

$$2NO_{2(g)} + H_2O \rightleftarrows NO_3^- + H^+ + HNO_2$$

As nitrate is formed by oxidation of nitrite, the equilibrium of the above reaction simply shifts to accommodate the new nitrate, resulting in desorption of NO_2. Consequently, nitrite oxidation to nitrate should have no effect on the nitrate level in solution and can be neglected.

The aqueous solution at equilibrium with gaseous NO, NO_2, SO_2, CO_2, and NH_3, and possibly containing dissolved NaCl, represents a simplified model for certain urban aerosols. For example, the aerosol measured by Moskowitz (*14*) at a coastal site in Los Angeles was primarily $NaNO_3$, presumably the result of the contact of aqueous sea salt aerosol with NO and NO_2. On the other hand, the nitrate aerosol sampled at Chino, an inland area in a region of high ammonia emissions (feedlots), was primarily NH_4NO_3. The Pasadena nitrate aerosol appeared to retain traces of the sea salt aerosol but was also primarily NH_4NO_3. We can employ the equilibrium chemical model to represent each of these situations by simply varying the concentrations of the gaseous species and the dissolved NaCl in accordance with expected atmospheric conditions.

The condition of electroneutrality for the system of reactions in Table III is:

$$[H^+] + [NH_4^+] + [Na^+] = [OH^-] + [HSO_3^-] + 2[SO_3^{2-}] + [HCO_3^-] + 2[CO_3^{2-}] + [NO_2^-] + [NO_3^-] + 2[SO_4^{2-}] + [Cl^-] \quad (1)$$

After using the expressions for the equilibrium constants, Expression 1 can be written as

$$\left(\frac{K_{ha}K_{1a}p_{NH_3}}{K_w} + 1\right)[H^+] + ([Na^+] - [Cl^-]) = \frac{K_w}{[H^+]\gamma_+\gamma_-} + \frac{K_{hc}K_{1c}p_{CO_2}}{[H^+]\gamma_+\gamma_-} + \frac{K_{1n}^{1/2}K_{3n}p_{NO}^{1/2}p_{NO_2}^{1/2}}{[H^+]\gamma_+\gamma_-} + \frac{K_{2n}p_{NO_2}^{3/2}}{K_{1n}^{1/2}p_{NO}^{1/2}[H^+]\gamma_+\gamma_-} + \frac{K_{hs}K_{1s}p_{SO_2}}{[H^+]\gamma_+\gamma_-} + \frac{2K_{hs}K_{1s}K_{2s}p_{SO_2}}{[H^+]^2\gamma_+{}^2\gamma_{2-}} + 2[SO_4^{2-}] \quad (2)$$

where we have neglected the contribution of $[CO_3^{2-}]$. The rate constant for oxidation of sulfite ion to sulfate ion has been proposed as (*22*)

$$k_o = 0.78 + 3540[H^+]^{1/2}\ \text{min}^{-1} \quad (3)$$

Equilibrium Expression 2 can be solved for $[H^+]$ to enable calculation of the concentrations of all species. Note that the initial concentration of NaCl must be specified. Subsequently $[Na^+]$ remains at its initial value, but chloride ion may be lost from solution through desorption of HCl. If we assume that there is no HCl initially in the gas phase, the total quantity of chlorine in the gas and liquid is equal to the initial quantity present. For those cases in which NaCl is assumed to be present, it is necessary to assume a particle volume concentration in $\mu m^3\ cm^{-3}$. Typical volume concentrations reported in ACHEX ranged from 100 to 300 $\mu m^3\ cm^{-3}$ (*8*).

The concentration of sulfate at any time can be calculated in a step-by-step fashion using $\Delta[SO_4^{2-}] = k_o[SO_3^{2-}]\Delta t$. Sulfate levels for times up to 300 min have been calculated. In all cases in which oxides of nitrogen are present, the sulfate levels attained are negligible due to the highly acidic solution. (A high $[H^+]$ inhibits sulfate formation through its effect on the sulfite concentration.) Thus, in the absence of catalysts (such as metallic ions), significant sulfate formation by oxidation of sulfite ion in solution will not take place when oxides of nitrogen are present in appreciable concentrations.

Equilibrium nitrate concentrations have been calculated as a function of vapor concentrations of NO, NO_2, SO_2, and NH_3 (CO_2 concentrations have a negligible effect on nitrate concentrations) and of the NaCl concentration in solution. Because of the pH inhibition of sulfate formation, changes in SO_2 vapor concentrations have a negligible effect on equilibrium nitrate levels. Figure 3 shows contours of constant nitrate concentration (in mol L^{-1}) in aqueous solutions containing

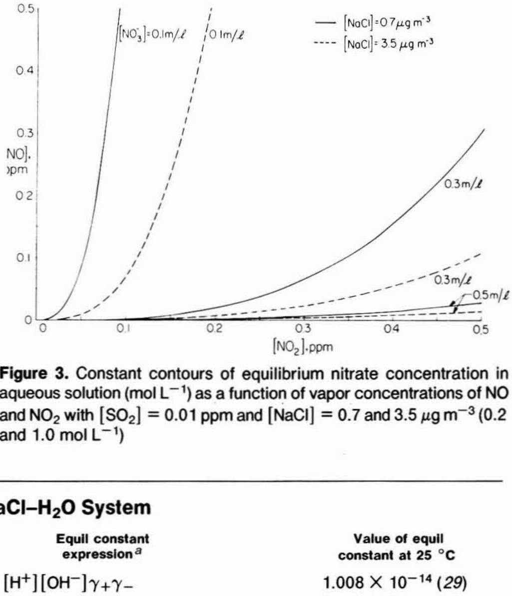

Figure 3. Constant contours of equilibrium nitrate concentration in aqueous solution (mol L^{-1}) as a function of vapor concentrations of NO and NO_2 with $[SO_2]$ = 0.01 ppm and [NaCl] = 0.7 and 3.5 $\mu g\ m^{-3}$ (0.2 and 1.0 mol L^{-1})

Table III. Chemical Equilibria in SO_2–NH_3–CO_2–NO–NO_2–NaCl–H_2O System

Reaction	Equil constant expression[a]	Value of equil constant at 25 °C
$H_2O \leftrightarrows H^+ + OH^-$	$K_w = [H^+][OH^-]\gamma_+\gamma_-$	1.008×10^{-14} (*29*)
$SO_{2(g)} + H_2O \leftrightarrows SO_2{\cdot}H_2O$	$k_{hs} = [SO_2{\cdot}H_2O]/p_{SO_2}$	1.24 (*30*)
$SO_2{\cdot}H_2O \leftrightarrows H^+ + HSO_3^-$	$k_{1s} = [H^+][HSO_3^-]\gamma_+\gamma_-/[SO_2{\cdot}H_2O]$	0.0127 (*31*)
$HSO_3^- \leftrightarrows H^+ + SO_3^{2-}$	$k_{2s} = [H^+][SO_3^{2-}]\gamma_+\gamma_{2-}/[HSO_3^-]\gamma_-$	6.24×10^{-8} (*31*)
$NH_{3(g)} + H_2O \leftrightarrows NH_3{\cdot}H_2O$	$K_{ha} = [NH_3{\cdot}H_2O]/p_{NH_3}$	57 (*32*)
$NH_3{\cdot}H_2O \leftrightarrows NH_4^+ + OH^-$	$K_{1a} = [NH_4^+][OH^-]\gamma_+\gamma_-/[NH_3{\cdot}H_2O]$	1.774×10^{-5} (*29*)
$CO_{2(g)} + H_2O \leftrightarrows CO_2{\cdot}H_2O$	$K_{hc} = [CO_2{\cdot}H_2O]/p_{CO_2}$	0.034 (*32*)
$CO_2{\cdot}H_2O \leftrightarrows H^+ + HCO_3^-$	$K_{1c} = [H^+][HCO_3^-]\gamma_+\gamma_-/[CO_2{\cdot}H_2O]$	4.45×10^{-7} (*29*)
$HCO_3^- \leftrightarrows H^+ + CO_3^{2-}$	$K_{2c} = [H^+][CO_3^{2-}]\gamma_+\gamma_{2-}/[HCO_3^-]\gamma_-$	4.68×10^{-11} (*29*)
$NO_{(g)} + NO_{2(g)} + H_2O \leftrightarrows 2HNO_2$	$K_{1n} = [HNO_2]^2/p_{NO}p_{NO_2}$	122[b]
$2NO_{2(g)} + H_2O \leftrightarrows HNO_2 + H^+ + NO_3^-$	$K_{2n} = [HNO_2][H^+][NO_3^-]\gamma_+\gamma_-/p_{NO_2}^2$	4.3×10^5 (*33*)
$HNO_2 \leftrightarrows H^+ + NO_2^-$	$K_{3n} = [H^+][NO_2^-]\gamma_+\gamma_-/[HNO_2]$	5.1×10^{-4} (*34*)
$HCl_{(g)} + H_2O \rightleftarrows HCl{\cdot}H_2O$	$K_{1h} = [HCl{\cdot}H_2O]/p_{HCl}$	19.0 (*36*)
$HCl{\cdot}H_2O \rightleftarrows H^+ + Cl^-$	$K_{2h} = [H^+][Cl^-]\gamma_+\gamma_-/[HCl{\cdot}H_2O]$	1.3×10^6 (*37*)

[a] The activities follow the Davies relation (*40*), $\log \gamma_z = (-Az^2\sqrt{I})/(1 + \sqrt{I}) + 0.2\ IAz^2$, where I is the ionic strength, $I = 1/2\ \Sigma_i[c_i]z_i^2$, and A = 0.5085 for water at 25 °C. [b] The equilibrium constant for the reaction, $NO_{(g)} + NO_{2(g)} + H_2O \rightleftarrows 2HNO_2$ (A.1), was arrived at as follows. Equilibrium constants are known for the reactions $2NO_{2(g)} + H_2O \leftrightarrows HNO_2 + H^+ + NO_3^-$ (A.2) and $3HNO_2 \leftrightarrows H^+ + NO_3^- + 2NO_{(g)} + H_2O$ (A.3) where $K_{A1} = [HNO_2]^2/p_{NO}p_{NO_2}$, $K_{A2} = [HNO_2][H^+][NO_3^-]/p_{NO_2}^2$, and $K_{A3} = [H^+][NO_3^-]p_{NO}^2/[HNO_2]^3$. We note that $K_{A1}^2 = K_{A2}/K_{A3}$. Since $K_{A2} = 4.3 \times 10^5$ and K_{A3} = 29 (*35*), we find that K_{A1} = 122.

NaCl concentrations of 0.3 and 1.0 mol L^{-1}, as a function of the vapor concentrations of NO and NO_2. In Figure 3 the vapor concentrations of SO_2 and NH_3 are assumed to be zero. Figure 4 shows contours of constant nitrate concentrations in aqueous solutions not containing NaCl as a function of the vapor concentrations of NO and NO_2 at NH_3 concentrations of 0.01 and 0.05 ppm. In Figure 4 the vapor concentration of SO_2 is taken to be 0.01 ppm. The equilibrium nitrate levels shown in Figures 3 and 4 in mol L^{-1} of solution can be converted to particulate mass concentrations in $\mu g\ m^{-3}$ of air given particle volume concentration in $\mu m^3\ cm^{-3}$. In the case in which NaCl is present, increasing the concentration of NaCl does not lead to an increased neutralizing effect. Because only a certain amount of Cl^- can be lost from the particle in the form of HCl, increasing the concentration of NaCl results in an increase in the Cl^- concentration causing the solution to become more acidic. As the acidity increases, the equilibrium concentration of nitrate decreases. In the case in which NH_3 is present, on the other hand, as the NH_3 concentration increases, more neutralization occurs; consequently, the equilibrium nitrate concentration increases.

Sulfate and Nitrate Formation in Water Droplets with Gas-Phase Conversion of SO_2

Sulfur dioxide may be converted to sulfate by homogeneous or heterogeneous paths. In clean air, SO_2 is very slowly oxidized by sunlight to sulfuric acid, at a rate of about 0.1%/h. In the ambient atmosphere, SO_2 oxidation may occur at rates exceeding 10%/h (*23*). In the gas phase, reactions with free radicals provide the major contribution to homogeneous oxidation of SO_2 (*24*). In the liquid phase, catalytic oxidation of SO_2 may take place in the presence of metallic compounds, such as manganese, iron, vanadium, aluminum, lead, and copper. In aqueous droplets an acid pH decreases the rate of SO_2 oxidation, and therefore sulfuric acid formation in the aerosol is self-limiting unless the acidity is diluted by additional water vapor or buffered by alkaline metal compounds or ammonia. In the previous section because of the high acidity of droplets containing dissolved oxides of nitrogen in addition to SO_2 and NH_3, virtually no sulfate will form in the droplet through oxidation of sulfite ion (in the absence of metallic catalysts). Thus, we turn to the homogeneous oxidation of SO_2 to sulfuric acid vapor followed by absorption of the sulfuric acid into the aerosol as a possible alternative mechanism to liquid-phase sulfate formation to explain observed sulfate levels in aerosols. (Clearly, since we are not considering catalysis by dissolving metals or soot particle surfaces, our model of the atmospheric aerosol is incomplete.)

We consider the conversion of SO_2 to particulate sulfate to take place in two steps:

$$SO_2 \xrightarrow{1} H_2SO_{4(g)} \xrightarrow{2} H_2SO_{4(p)} \tag{4}$$

Step 1 depicts the overall rate of conversion of SO_2 to sulfuric acid vapor. We will assume that the rate of step 1 can be represented as first order with respect to SO_2 concentration. The rate of conversion of SO_2 to sulfuric acid vapor is probably not strictly first order although SO_2 conversion rates are generally reported as if the rate were first order. The rate constant k_1 depends on details of gas-phase chemistry (*24*). For our purposes we will specify the value of k_1 based on typical atmospheric conditions.

Step 2 depicts the transfer of sulfuric acid to the particulate phase. This transfer may occur by homogeneous nucleation of sulfuric acid with water or by heterogeneous condensation of sulfuric acid on existing particles. Jerskey et al. (*25*) have shown that at typical urban particle concentrations the rate of homogeneous nucleation of sulfuric acid with water is negligible compared to that of heterogeneous condensation on existing particles. The rate of transfer of sulfuric acid vapor to an existing population of particles is given by

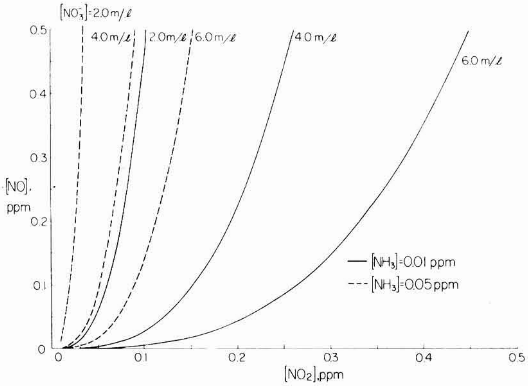

Figure 4. Constant contours of equilibrium nitrate concentration in aqueous solution (mol L^{-1}) as a function of vapor concentrations of NO and NO_2 with $[SO_2] = 0.01$ ppm and $[NH_3] = 0.01$ and 0.05 ppm

$$L_c = V_L^{-1}\left(\frac{\pi}{2}\right)\int_0^\infty D_p^2\left(\frac{dD_p}{dt}\right)n(D_p, t)dD_p \tag{5}$$

where dD_p/dt is the rate at which a particle of diameter D_p grows by condensation, V_L is the volume of a molecule of sulfuric acid in the condensed state, and $n(D_p, t)$ is the particle size distribution function, so that $n(D_p, t)dD_p$ is the number of particles per unit volume of air having diameters between D_p and $D_p + dD_p$. The quantity $(\pi/2)(D_p^2)(dD_p/dt)$ is the rate at which the volume of an individual particle grows and is, in general, dependent on the particle size. Hence, L_c depends not only on the number of particles present, but also on the size distribution of these particles. In general, a detailed description of the aerosol size distribution is required to determine the mass of material condensing on existing particles. The rate of step 2 can be represented as first order with respect to the concentration of sulfuric acid vapor.

The relationship for the steady state flux of gas molecules to a spherical particle depends on the Knudsen number of the particle, $Kn = 2\ \lambda/D_p$, where λ is the mean free path of the background gas, i.e., air. The flux of H_2SO_4 molecules to a particle can be expressed as (*26*)

$$\phi = \frac{2\ \pi D_p \mathcal{D} N_{H_2SO_4}}{1 + 1Kn} \tag{6}$$

where

$$1 = \frac{1.333 + 0.71\ Kn^{-1}}{1 + Kn^{-1}} \tag{7}$$

and where $\mathcal{D}$ is the molecular diffusivity of H_2SO_4 in air, and $N_{H_2SO_4}$ is the molecular number density of H_2SO_4. The number of H_2SO_4 molecules striking a particle of diameter D_p per second is given by Equation 6. The rate of depletion of H_2SO_4 molecules by condensation has been represented as $L_c = k_2\ N_{H_2SO_4}$ ($cm^{-3}\ s^{-1}$). Thus, the first-order rate constant k_2 is given by

$$k_2 = 2\ \pi\mathcal{D}\int_0^\infty \frac{D_p n(D_p, t)}{1 + 1Kn}dD_p \tag{8}$$

The values of $\mathcal{D}$ and λ relevant to our interest are 0.054 $cm^2\ s^{-1}$ and 0.066 μm, respectively.

If $k_2 \gg k_1$, then the sulfuric acid vapor concentration can be assumed to be in a pseudo-steady state, given by

$$[H_2SO_4] = \frac{k_1[SO_2]}{k_2} \tag{9}$$

By assuming a value of k_1 and a size distribution $n(D_p, t)$, the validity of the steady state approximation for sulfuric acid vapor can be tested by comparing k_2 and k_1. Jerskey et al. (*25*) have evaluated k_2 for typical observed urban aerosol size distributions and have shown that for all cases of practical interest k_2 is many orders of magnitude larger than typical values of k_1. Therefore, the steady state approximation for sulfuric acid vapor can be considered to be valid.

Our object in this section is to study the growth of aqueous atmospheric aerosols in the presence of the continuous conversion of SO_2 to sulfuric acid vapor. Of particular interest are the predicted size distributions of sulfate and nitrate in the particles as a function of time. The basic problem is to calculate the growth rates and compositions of aqueous aerosols in the presence of oxides of nitrogen, ammonia, sulfur dioxide, and sulfuric acid. Qualitatively, at any time each particle will have an internal composition subject to constraints of the chemical equilibria in the previous section. The growth of each particle results from the continuous absorption of sulfuric acid vapor produced in the gas phase by the oxidation of SO_2. The absorption of sulfuric acid in the droplet lowers the vapor pressure of water in the droplet, inducing water vapor in the atmosphere to diffuse spontaneously to the drop. Similar models for atmospheric aerosol growth have been used by Foster (*27*) and Wadden et al. (*28*), except in those studies the production of sulfuric acid was assumed to take place in the particle by catalytic oxidation of dissolved SO_2.

A rigorous calculation of the growth of a multicomponent droplet requires knowledge of the thermodynamic properties of the solution, such as the vapor pressures of each of the dissolved species. For the type of solution considered here, the necessary data for a rigorous calculation are not available. Therefore, we adopt the following procedure. We assume there exists an initial population of particles the size distribution of which is known. Each particle is in equilibrium with the gas phase which is specified to contain given concentrations of NO, NO_2, SO_2, CO_2, and NH_3. At $t = 0$ it is assumed that the droplets are free of sulfate. At that time an initial quantity of gaseous SO_2 begins to be converted by first-order reaction to H_2SO_4, so that $[SO_2] = [SO_2]_o \exp(-k_1 t)$. (Because the sulfate formed by oxidation of sulfite in solution is negligible, the sulfate in the particles is due virtually completely to absorbed H_2SO_4.) Over a time interval Δt a certain quantity of sulfuric acid will be absorbed in the particles (in quantities differing for each particle depending on the size of the particle). The absorbed sulfuric acid lowers the vapor pressure of water over each drop causing a spontaneous absorption of water vapor to return each particle to vapor-liquid equilibrium. This process of absorption and growth continues for a specified time. Because data on the vapor pressure of water over solutions of the type considered here are not generally available, it will not be possible to incorporate the water vapor equilibrium into our calculation. Thus, it will not be possible to compute the change in size of each particle. Nevertheless, it is possible to calculate the rate of accumulation of sulfate and nitrate in a given population of particles, with particular interest in the relative size distributions of sulfate and nitrate.

We are interested in computing the dynamic behavior of a population of particles exposed at $t = 0$ to an atmosphere containing NO, NO_2, NH_3, and SO_2 and in which SO_2 is being converted to H_2SO_4. Particles of different sizes will grow at different rates because the rate of diffusion of H_2SO_4 to a particle depends on the size of the particle and because the compositions of particles of different sizes will be different. The initial size distribution was chosen to be log-normal:

$$n(D_p, 0) = C_o \exp\left\{-\frac{1}{2}\left[\frac{\log D_p - \log \mu}{\log \sigma}\right]^2\right\} \qquad (10)$$

with $C_o = 7.5 \times 10^4$, $\log \mu = -0.8$, and $\log \sigma = 0.2$. This distribution has total particle surface area and volume of 2812 μm^2 cm^{-3} and 156 μm^3 cm^{-3}, respectively. The surface area and volume for this distribution are in the range of those measured in the ACHEX program (*8*).

Figure 5 presents a comparison of the sulfate and nitrate size distributions at t = 5 h. The conditions of Figure 5 are $[NO] = [NO_2] = 0.2$ ppm, $[SO_2] = 0.01$ ppm, and $[NH_3] = 0.01$ and 0.05 ppm. The effect of ammonia on the nitrate size distribution is evident. As noted above, the quantity and size distribution of sulfate are independent of the ammonia level as long as the primary mechanism for sulfate formation is homogeneous oxidation of SO_2. (Of course, this is not actually the case since water vapor equilibrium will influence droplet growth and hence the sulfate size distribution. Nevertheless, the water vapor effect should not change the relative sulfate and nitrate size distributions greatly from those calculated here.) From Figure 5, sulfate tends to accumulate in the smaller particles and nitrate in the larger particles.

The sulfate and nitrate mass median diameters at t = 5 h were 0.2 and 0.35 μm, respectively. Referring to Table I, we note that measured sulfate mass median diameters are consistently less than nitrate mass median diameters. However, the diameters given in Table I are generally larger than those calculated here. A number of factors may be responsible for this discrepancy. First, the atmospheric aerosol size distributions although unknown, were almost certainly different from the idealized log-normal distribution used in our calculations. Second, since we have neglected the role of water in the chemical dynamics of the particle, we expect that our predicted particle sizes will be generally less than they should be.

Sulfate and Nitrate Concentrations and Size Distributions. Having specified the SO_2 concentration and the aerosol size distribution, concentrations of sulfate and nitrate in the aerosol resulting from gas-phase conversion of SO_2 to H_2SO_4 followed by absorption of H_2SO_4 in the particles and from absorption of NO, NO_2, NH_3, and SO_2 directly into the particles can be calculated. (The role of NaCl was not considered in these studies.) Total sulfate and nitrate concentrations can then be obtained at any time by integrating over the entire particle size distribution. Sulfate and nitrate concentrations at 1, 3, and 5 h are given in Table IV.

We note that whereas sulfate concentrations are steadily increasing with time, because of the conversion of SO_2 to sulfate, nitrate concentrations decrease somewhat with time. The nitrate decrease is due to the decreasing pH of the

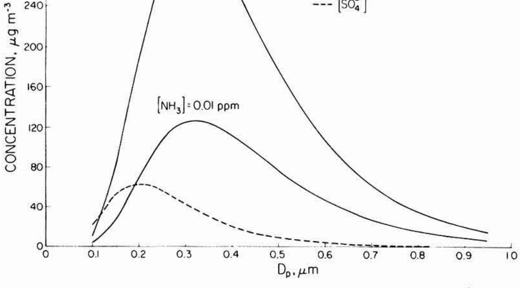

Figure 5. Particulate nitrate and sulfate concentrations ($\mu g\ m^{-3}$) as a function of particle diameter at t = 5 h for initial size distribution of Equation 10, $[NO] = [NO_2] = 0.2$ ppm, $[SO_2]_o = 0.01$ ppm, and $[NH_3]$ = 0.01 and 0.05 ppm

Table IV. Total Sulfate and Nitrate Concentrations ($\mu g\ m^{-3}$) as a Function of Time for Initial Size Distribution of Equation 10.[a] $[NO] = [NO_2] = 0.2$ ppm. $[SO_2]_o = 0.01$ ppm and $k_1 = 0.1\ h^{-1}$

t, h	Sulfate	Nitrate
	$[NH_3] = 0.01$ ppm	
1	4.04	54.86
3	10.94	50.93
5	16.53	48.21
	$[NH_3] = 0.05$ ppm	
1	4.04	125.8
3	10.94	121.4
5	16.53	118.2

[a] Total particle surface area and volume equal to 2812 $\mu m^2\ cm^{-3}$ and 156 $\mu m^3\ cm^{-3}$, respectively.

droplets as more sulfate is added. As expected, ammonia level has a strong influence on the nitrate level. Sulfate levels are independent of NH_3 concentration, since the mechanism for formation of sulfate from SO_2 is independent of NH_3. The total nitrate concentration is dependent on the volume of particulate matter present because nitrate formation occurs within the particle. Sulfate concentrations, on the other hand, are dependent on the surface area of particles present since the transfer of H_2SO_4 to the particles depends on the available particle surface area. The nitrate and sulfate values are within the range of observed atmospheric levels (*9*). The behavior indicated in Table IV is generally consistent with the observations of Harker et al. (*16*).

Ammonium Concentrations. A quantity of interest in the evaluation of atmospheric particulate sulfate and nitrate concentrations is the ratio of the actual concentration of ammonium ion to the stoichiometric concentration of ammonium needed if all the sulfate and nitrate existed as their ammonium salts, i.e.,

$$\frac{[NH_4^+]}{[NO_3^-] + 2[SO_4^{2-}]}$$

In solutions in equilibrium in the presence of NO, NO_2, SO_2, and NH_3, with no gas-phase production of sulfuric acid, the above ratio is essentially 1.0. Thus, ammonium ion exists essentially stoichiometrically with nitrate ion (sulfate concentrations being negligible in this case). When SO_2 is converted to sulfuric acid in the gas phase, followed by absorption of sulfuric acid in the particle, the above ratio drops to about 0.43. This effect is expected since the sulfate is assumed to be added externally, independently of the pH of the solution. Observed values of the ammonium to nitrate plus sulfate ratio in Los Angeles range from about 0.6 to 1.0 (*9*). Our neglect of the interaction between the solution composition and the rate of sulfuric acid addition is probably responsible for the relatively low value of this ratio that we predict.

Discussion and Conclusions

With mounting evidence that chemical composition and particle size are important factors in disease effects related to urban aerosols, there is a strong impetus to understand as fundamentally as possible the factors which govern the composition of aerosols. Sulfates and nitrates are two of the most prolific secondary aerosol constituents, constituents for which there is evidence (at least for sulfates) of related disease effects. Clearly, complete understanding of the physics and chemistry of atmospheric aerosols is a large undertaking, which almost certainly cannot be accomplished without much more extensive data than are currently available. This paper has focused on one aspect of the aerosol problem, namely, a study of the factors governing nitrate concentrations in atmospheric aerosols.

We first presented estimates of the rate of homogeneous formation of nitric acid in the urban atmosphere and then studied in some detail the formation of nitrates by heterogeneous, aqueous-phase processes. (The role of particle surfaces or dissolved metallic ions as catalytic agents for sulfate or nitrate formation was not considered.) We have neglected the dynamics of particle growth associated with absorption of water vapor in response to chemical changes with aerosol particles. In spite of the simplifications made, the predictions that we have reported are in qualitative agreement with available observational data. Nitrate levels predicted are in the range of those observed, and relative sulfate and nitrate size distributions can be explained if sulfate formation occurs homogeneously and nitrate formation occurs heterogeneously.

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Chemical Behavior of Fluorine in Production of Wet-Process Phosphoric Acid

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■ A study was made to determine the fate of fluorine in the production of wet-process phosphoric acid and to explore methods of effective pollution control. Results indicated that the quality of the acid is improved by precipitation of the metallic impurities as complex fluoride compounds, and up to 85% of the fluorine can be immobilized as an insoluble compound in the by-product gypsum solids. Twelve different fluorine compounds were identified as possible precipitates in the production of wet-process phosphoric acid. Fluorite and chukhrovite were sufficiently insoluble in aqueous solutions to suggest long-term storage in gypsum ponds without undergoing reactions that will release fluorine to the atmosphere or natural waters.

Fluorine is a major pollutant in the conversion of phosphate rock to phosphate fertilizer. The recently established pollution abatement requirements have increased the necessity for the fertilizer industry to restrict its output of fluorine to the environment. The primary objective of this study was to determine the reaction mechanisms that control the fate of fluorine during the early stages of phosphate processing.

The chemical factors that control the precipitation of fluorine during the initial reactor stage in the production of wet-process phosphoric acid are poorly understood, but the chemical forms of by-product fluorine and their distribution pattern in subsequent process steps affect both the product quality and the potential for pollution by liquid and solid by-product effluents.

Commercial phosphate concentrates used as raw materials for wet-process acid production differ in fluorine content as well as in their relative contents of soluble sodium, potassium, magnesium, calcium, aluminum, and silica, among others. In preliminary studies these constituents were identified as having the major influence over the composition of fluorine precipitates and the eventual distribution of fluorine in gaseous effluents, by-product gypsum cake, wash liquors, and the intermediate acid product. Thus, the fate of the fluorine is determined by the compositional type of phosphate raw material as well as by the particular manufacturing process. The types and amounts of impurities solubilized during acidulation interact with fluorine and govern its precipitation. A better knowledge of the fate of the precipitated fluorine in the solid and liquid wastes discharged to gypsum storage ponds will lead to more effective control of evolved gaseous fluorine and improved methods for prevention of discharge of fluorine to pond and surface waters. Thus, the precipitated forms of fluorine in reactor solids and their solubility properties in wash solutions, pond waters, and pure water presented a complex characterization problem that had not been studied adequately.

Characterization and Preparation of Fluorine Compounds for Solubility Studies

The initial objective was to identify, isolate, and characterize the fluorine compounds that can be precipitated from filter-grade wet-process phosphoric acid. Salts such as K_2SiF_6 (*1*), Na_2SiF_6 (*1*), $Ca_4SO_4AlSiF_{13}\cdot 10H_2O$ (*2*), $MgSiF_6\cdot 6H_2O$ (*3*), $CaNaAlF_6\cdot H_2O$ (*4*), $MgNaAlF_6\cdot 2H_2O$ (*5*), Na_3AlF_6 (*6*), $CaSiF_6\cdot 2H_2O$ (*7*), and CaF_2 (*8*) have long been recognized as contaminating phases in many phosphate fertilizer products. MgF_2, which is isotypic with CaF_2, is likewise implicated.

To confirm that these compounds are possible precipitates in filter-grade acids (32% P_2O_5), factorial tests were made with simulated acids containing impurities at levels that are compatible with those found in Florida rock products. Except for variations designed to test the effect of individual components, each solution contained 0.51% Na_2O, 0.14% K_2O, 0.28% MgO, 0.96% Fe_2O_3, 1.1% Al_2O_3, and 3.5% F and was equilibrated with excess solid gypsum. The chemical analysis, reported elsewhere (*9*), of the salts used in the solubility study agreed well with the empirical formulas shown in Table I. The SiO_2 content varies considerably in wet-process phosphoric acids, and an initial series of tests was designed to determine the significance of an increasing SiO_2 content at Al_2O_3 concentrations of 0.5 and 1.0%. The SiO_2 concentration was varied from 0.1 to 1.4% in increments of 0.05% and maintained at 65 °C for 24 h with agitation. The results showed that the concentration of silica was not the significant factor in controlling the forms in which fluorine precipitated. Of the possible fluorine compounds that may precipitate from filter-grade H_3PO_4, only five were found in this test; all except one were present in essentially all simulated acid compositions, regardless of the silica content.

Characterization studies by optical and x-ray methods identified four of the salts as Na_2SiF_6, $NaKSiF_6$, $MgNaAlF_6\cdot 2H_2O$, and Na_3AlF_6. The fifth salt, found only at low SiO_2 levels, was poorly formed as small rosette aggregates which at first appeared to be either pachnolite or its dimorph thomsenolite, $CaNaAlF_6\cdot H_2O$. Its x-ray pattern, however, did not agree with the published data for these dimorphic salts.

Table I. Preparation Methods for 12 Fluoride Salts from Filter-Grade Wet-Process Phosphoric Acid[a]

Na_2SiF_6 K_2SiF_6	Precipitates from acidic solutions of H_2SiF_6 by addition of respective cation salt. pH must be maintained below 6.0
$NaKSiF_6$	Forms from 30% P_2O_5 acid containing 0.2% K, 0.15% Na, and 0.5% H_2SiF_6. Better crystals obtained by slow addition of Na_2SiF_6 to slurry of K_2SiF_6 in 30% P_2O_5 acid. Microscopic observations confirm dissolution of each end-member as coarse crystals of double salt become the homogenous solid phase
$Ca_3(AlF_6)_2{\cdot}4H_2O$	Forms slowly as small rosette aggregates of needle crystals when 10 g $CaSO_4{\cdot}2H_2O$ charged to 300 g of solution comprising 160 g of 60% P_2O_5 acid (reagent H_3PO_4), 28 g of 48% HF solution, 16 g of amorphous $AlPO_4{\cdot}2.5H_2O$, and 96 g water. Equilibration period about 2 weeks; excess gypsum removed by soaking solids in 5% HCl
$Ca_4SO_4SiAlF_{13}{\cdot}10H_2O$	Precipitates slowly from solution containing 30% P_2O_5, 0.4% Al, 2.5% F, 2% Ca, 0.3% Si, 2% SO_4, and saturated with $CaSO_4{\cdot}2H_2O$. Excess gypsum removed by soaking product in 5% HCl
$MgNaAlF_6{\cdot}2H_2O$	Precipitates slowly from solution comprising 30% P_2O_5, 0.35% Na, 0.2% Mg, 0.25% Al, and 3.5% F
Na_3AlF_6	Prepared by stoichiometrically adding constituent ions to 30% P_2O_5 acid
NaK_2AlF_6	Precipitates from 30% P_2O_5 acid containing 1.2% K, 4% F, 0.7% Al, and 1.5% Na
$MgSiF_6{\cdot}6H_2O$	Prepared by reacting stoichiometrically $MgCO_3$ and H_2SiF_6 in 2% P_2O_5 acid until first stable precipitate forms, then filter. Coarse crystals of $MgSiF_6{\cdot}6H_2O$ grow as filtrate slowly evaporates
$CaSiF_6{\cdot}2H_2O$	Prepared similarly as magnesium salt by use of $CaCO_3$
CaF_2 MgF_2	Prepared by adding constituent ions to dilute acid solution of HF

[a] Recommend polyethylene containers.

Subsequent chemical studies showed that this salt had the composition of $Ca_3(AlF_6)_2{\cdot}4H_2O$ and could be prepared according to the procedure shown in Table I, which gives the preparation methods for salts used in this study. Petrographic and x-ray data have been reported (*5, 7, 8, 10*) for most of these salts, and the optical data for $Ca_3(AlF_6)_2{\cdot}4H_2O$, $CaSiF_6{\cdot}2H_2O$ (dimorphs A and B), and $NaKSiF_6$ are given in Table II with the x-ray powder diffraction data for $Ca_3(AlF_6)_2{\cdot}4H_2O$ and $NaKSiF_6$ in Table III. Dimorph B of $CaSiF_6{\cdot}2H_2O$ precipitates initially in acid solutions but is metastable and converts to the stable form, A, after a few hours.

The compositional parameters of the possible fluoride compounds are discussed in the following section with reference to known or suspected variations. These considerations are pertinent to preparation procedures and especially so when precipitated from impure wet-process phosphoric acid solutions.

$Ca_3(AlF_6)_2{\cdot}4H_2O$. Preparation of this compound in filter-grade wet-process acid compositions free of sodium established it to be a stoichiometric calcium fluoroaluminate, rather than a pachnolite-type composition.

$CaNaAlF_6{\cdot}H_2O$. After considerable effort, pachnolite and thomsenolite, $CaNaAlF_6{\cdot}H_2O$, were eliminated as possible precipitates from filter-grade acids. This can never be ascertained completely; however, since many compositional adjustments between Ca and Na produced only $Ca_3(AlF_6)_2{\cdot}4H_2O$ or Na_3AlF_6 and no other salts, it became apparent that conditions for the formation of $CaNaAlF_6{\cdot}H_2O$ did not exist in a wet-process phosphoric acid production train. The preparation of $CaNaAlF_6{\cdot}H_2O$ from solutions other than filter-grade (30–32% P_2O_5) acids appeared to be irrelevant to our investigation and was not attempted.

$Ca_4SO_4AlSiF_{13}{\cdot}10H_2O$. Chukhrovite, $Ca_4SO_4AlSiF_{13}{\cdot}10H_2O$, which occurs frequently in wet-process filter acids is reported to have a variable composition (*11*) as a result of (Al + RE^{3+}) substitution for Ca and Si. No satisfactory method of preparation was known, and the concentration factors that control its precipitation or influence its composition had not been established. A 1937 British patent (*2*) states that precipitation of chukhrovite-type compositions from wet-process filter acid (30–32% P_2O_5) is promoted by maintaining high concentrations of calcium and fluorine, although specific details about other impurities in the acid compositions were not disclosed. In an exploratory test at high calcium and fluorine levels, a simulated acid was prepared that yielded well-crystallized chukhrovite. The acid mixture contained 30% P_2O_5, 3.0% CaO, 1.0% Al_2O_3, 1.0% SiO_2, and 3.8% F, and also an excess of solid $CaSO_4{\cdot}2H_2O$. After equilibration for 3 days at 35 °C, the solids were essentially homogeneous chukhrovite, along with traces of residual gypsum which were removed by extraction with 1:10 HCl.

The composition of this synthetic chukhrovite is compared with similar material from two commercial acids, and all have compositions that are essentially equal to the stoichiometric composition shown in Table I. Thus, it appears that the chukhrovite phases that precipitate from wet-process acids will not show the wide variations in composition that have been reported previously (*11*). Further confirmation of this was obtained in the subsequent experiment.

As a further test, a factorial experiment was designed to test the effects of F, Al, and Si on the precipitation and composition of chukhrovite. A simulated wet-process acid was prepared to contain 30% P_2O_5, 3.0% CaO, 2.0% SO_3 with F levels of 1.0, 2.5, and 4.0% and with Al_2O_3 and SiO_2 levels of 0.5 and 1.5%. The mixtures prepared according to this design with excess gypsum were equilibrated for 4 days at 25 °C with frequent shaking, after which the precipitated solids were filtered, washed with dilute acid to remove gypsum, and then water washed and air dried for petrographic and x-ray analysis.

Chukhrovite precipitated from all except two of the compositions, and was usually associated with other solid phases such as gypsum, CaF_2, or $CaSiF_6{\cdot}2H_2O$. The characterization studies showed that the 10 chukhrovite precipitates were well-crystallized cubic salts with nearly identical refractive indices (1.429–1.430), indicating essentially no variation in chemical composition. This further confirmed the results in Table I and eliminated the necessity of selecting a representative chukhrovite composition for use in the solubility characterization studies.

It is obvious that factors other than the concentrations of Ca and F as claimed in the British patent are involved in the formation of chukhrovite. The concentration ranges and possible interactions of all likely impurities affecting the precipitation of chukhrovite from filter-grade wet-process phosphoric acid were studied next.

The choice of impurities and their concentration levels used to prepare the simulated acids were based on a typical central Florida phosphate rock with an average composition of 30.0% P_2O_5 (66 BPL), 3.8% F, 0.6% Na_2O, 0.3% MgO, 1.0% Al_2O_3, and 1.0% Fe_2O_3.

The acid compositions were prepared with fixed concentrations of P_2O_5 (30%), Fe_2O_3 (1.0%), F (3.8%), and SO_3 (2.0%, maintained by gypsum saturation) and variable amounts of Al_2O_3 (0.5–1.0%), SiO_2 (0.5–1.0%), MgO (0.3–0.6%), and Na_2O (0–0.5–1.0%) according to a factorial design. These concentration ranges were selected to represent a wide range of ore variability with regard to accessory mineral impurities.

The equilibrium cells were prepared from reagent-grade (60% P_2O_5) H_3PO_4 with $AlPO_4 \cdot nH_2O$ (30% Al_2O_3, 42% P_2O_5) for the aluminum source, $FePO_4 \cdot nH_2O$ (41% Fe_2O_3, 36% P_2O_5) for the iron, H_2SiF_6 (30% solution containing 12% SiO_2, 14% F) for the Si and F with additional F from 48% HF solution (46% F), $MgCO_3$ (40% MgO) for magnesium, $NaHCO_3$ (57% Na_2O) for sodium, and H_2SO_4 for the excess (1.5%) SO_3 and H_2O for dilution to the desired concentration. The fluoride components were charged last to avoid premature precipitation, and each cell was charged with an excess of $CaSO_4 \cdot 2H_2O$. The mixtures were equilibrated at room temperature (25–27 °C) until cessation of fluoride precipitation and dissolution of the gypsum component, after which the aqueous phases were sampled for chemical analysis, and the solid phases were prepared for petrographic examination to determine the types and relative abundance of the equilibrating fluoride compounds.

The final compositions of these simulated acid solutions and the petrographic identification of the solid phases after cessation of fluorine precipitation are available elsewhere (*9*). The solid-phase compositions so obtained indicated that the appropriate combination of impurity elements was considered in the factorial design to achieve maximum precipitation of chukhrovite.

The approximate weight percent of chukhrovite precipitated in the various simulated acid compositions was calculated from the change in solution composition with respect to fluorine and cations, and the composition of fluoride solids was determined petrographically. These results are shown in Table IV and reveal the pronounced suppressant effect of sodium on the chukhrovite precipitation process, but there was no direct dependence on silica concentration.

In the eight tests where only chukhrovite precipitated, the amounts of aluminum or silica were sometimes the limiting factors. When SiO_2 was present at the low level (0.5%), the maximum possible amount of chukhrovite would be about 6.8 wt %; when Al_2O_3 was present at the low level (0.5%), the maximum amount of chukhrovite that could form would be about 7.2%. The actual chukhrovite weights ranged from 6.0 to 7.2%. When Al or Si were at the high level (1.0%), fluorine (3.8%) became the limiting factor, with the maximum amount of chukhrovite being 11.4 wt %, whereas the maximum amount observed was 9.66%. Thus, complete removal of fluorine by the chukhrovite precipitation process is not possible.

Table III. X-ray Diffraction Patterns[a] of $Ca_3(AlF_6)_2 \cdot 4H_2O$ and $NaKSiF_6$

$Ca_3(AlF_6)_2 \cdot 4H_2O$		$NaKSiF_6$			
d, Å	*I*	*d*, Å	*I*	*d*, Å	*I*
13.31	100	4.86	15	2.37	15
3.14	40	4.64	15	2.30	20
3.06	40	4.31	90	2.05	40
2.23	10	4.26	70	2.02	15
2.02	40	3.40	35	1.925	20
		3.38	45	1.918	15
		3.34	100	1.815	15
		2.61	20	1.651	15

[a] Scanned at 0.5° 2 θ/min. Intensities read from goniometer tracings and reported as percent of strongest line.

Table II. Microscopic Characterization

Compound	Crystal system	Refractive indices	Optical properties
$Ca_3(AlF_6)_2 \cdot 4H_2O$	Orthorhombic needle crystals as rosette clusters	$N_F \sim 1.413$ $N_S \sim 1.420$	Length slow needles with parallel extinction $D_{calc} = 2.40$
$MgSiF_6 \cdot 6H_2O$	Hexagonal, trigonal, $\bar{6}$, rhombohedral. Highly modified $(10\bar{1}1)$ prisms or hexagonal rods exhibiting $(10\bar{1}0)$ terminated by $(10\bar{1}1)$ and elongated along c. Interpenetration twinning gives strained, distorted crystals with pseudobiaxial figures ranging up to $2V = 20°$	$N\omega = 1.342$ $N\epsilon = 1.360$	Uniaxial (+) $D_{calc} = 1.70$
$NaKSiF_6$	Orthorhombic, mmm. Stout rods flattened on (010), elongated along *a* and exhibiting forms: {111}, {011}, and small {110}	$N\alpha = 1.323$ $N\beta = 1.326$ $N\gamma = 1.328$	Biaxial (−) $2V = 70°$ (calc 77°) $D_{calc} = 2.46$ $a:b:c = 0.5317:1:0.9209$ $D_{calc} = 2.46$
$CaSiF_6 \cdot 2H_2O$-A	Monoclinic, 2/M, rod crystals elongated on *c* with prominent {110} and terminated by (101) and (101)	$N\alpha = 1.412$ $N\beta = 1.416$ $N\gamma = 1.419$	Biaxial (−), $2V = 75°$ (81°). $b = X$ and $Y \Lambda C =$ 17° in acute β on (010), $\beta = 98°$ $D_{calc} = 2.65$ $D_{detn} = 2.68$ $D_{x\text{-}ray} = 2.68$
$CaSiF_6 \cdot 2H_2O$-B	Monoclinic, 2/M, (010) plate crystals modified by (100) and {111}	$N\alpha = 1.369$ $N\beta = 1.388$ $N\gamma = 1.391$	Biaxial (−), $2V = 45°$ (43°). $Y = b$ and $Z\Lambda$ $c = 3°$ in acute β $\beta = 97°$. $D_{calc} =$ 2.60

The percent of input fluorine removed from the initial acid composition as solid fluorides in the gypsum cake is shown in Table V. In general, chukhrovite was much more effective than alkali fluorosilicate in immobilizing fluorine; a maximum of 85% of the input fluorine (3.8% F, corresponding to a typical Florida feed rock) was removed in the filtercake solids, whereas in commercial practice, usually no more than about 20–40% of the fluorine is removed with the by-product solids. Thus, the chukhrovite precipitation process offers a way for greatly decreasing the residual fluorine content of the phosphoric acid intermediate, and at the same time, render it insoluble during subsequent transport and storage in disposal ponds.

The results show that the total quantity of residual metallic impurities (Ca, Mg, Na, Al, and Si) in the acid summarized in Table VI was affected by the chukhrovite precipitation process. Although the initial acid compositions (based on Florida rock composition) contained up to about 4% of these oxide impurities, the final filter-acid compositions after fluorine precipitation only contained from 0.17 to 2.00% total impurities.

The single most important variable was magnesium; increasing the MgO content from 0.3 to 0.6% more than doubled the amount of dissolved impurities retained in the acid (0.52 vs. 1.28%). The effect of magnesium was to depress all fluorine precipitation processes, which strongly indicates a competing process of complex formation. Consequently, the total impurities were as low as 0.24% at maximum fluorine precipitation, but at high concentrations of magnesium and sodium, the concentration of dissolved impurities was almost an order of magnitude higher (2.0%).

Gypsum is the main source of calcium and sulfate required for the precipitation of chukhrovite, but the mole ratio of Ca:SO_3 in this solid phase is 4. Consequently, high sulfate concentrations parallel the removal of fluorine as chukhrovite. In commercial practice, this precipitation mechanism would return SO_3 in acid recycle to the reactor in proportion to the amount of calcium removed as chukhrovite.

In these simulated acid products this differential in acid consumption amounted to 2.6% SO_3 (weight percent increase in SO_3 content from about 2.0 to 4.6%).

Both magnesium and sodium tend to depress the final SO_3 content because they compete for fluorine and interfere with the formation of chukhrovite.

Since the relationships affecting chukhrovite precipitation, fluorine removal, retention of metallic impurities, and final SO_3 content involve a consideration of interactions of impurities, the data in each of Tables IV–VI were subjected to an analysis of variance. Summarized in Table VII are the effects of each variable with significance at the 95% confidence level (F^*), and at the 99% confidence level (F^{**}).

As shown in Table VII, aluminum, sodium, magnesium, and the first-order interactions of these elements with silica influence the formation of chukhrovite as well as the associated fluoride salts. Quite obviously, fluorine precipitation is not controlled by silica or any other single component as a function of its concentration.

Also shown in Table VII are the means for the main effects. The highly significant effects of aluminum and the Al × Si interaction tend to favor precipitation of chukhrovite, whereas the highly significant effects of sodium and magnesium act to depress precipitation. The petrographic analyses (*9*) show that sodium competes for the fluorine and silica to form Na_2SiF_6, while magnesium forms soluble fluoride complexes.

Increasing the aluminum concentration has a greater effect on promoting chukhrovite formation than an increase in silica. This suggests that the acidulation of high alumina phosphate rocks, whole matrix, phosphatic clay slimes, or phosphate rock with an alumina amendment may favor the chukhrovite precipitation process over the formation of $(Na,K)_2SiF_6$, so as to offset the adverse effect of sodium. The presence of significant sodium in the compositions of highly substituted apatitic phosphates appears to account for the preferential precipitation of fluorine as $MgNaAlF_6{\cdot}2H_2O$ alone, or in combination with Na_2SiF_6, rather than as chukhrovite. With phosphate rocks of this composition, it is unlikely that aluminum amendments would be effective in promoting the precipitation of chukhrovite. The best alternative would be to adjust rock composition to favor precipitation of fluorine as alkali fluorosilicates rather than as ralstonite, since the latter is usually fine grained and therefore has an adverse effect on gypsum filtration rates.

Table IV. Weight Percent of Chukhrovite Precipitated from Simulated Filter-Grade Phosphoric Acids[a]

		Si (−)		Si (+)	
		Al (−)	Al (+)	Al (−)	Al (+)
Mg (−)	Na (−)	6.60[b]	9.66[b]	6.00[b]	5.70[b]
	Na (0)	3.30	7.29	5.20	6.95
	Na (+)	1.00	1.41	(3.26)	4.12
Mg (+)	Na (−)	7.20[b]	9.09[b]	6.90[b]	3.90[b]
	Na (0)	(2.22)	5.13	1.99	2.30
	Na (+)	(0.62)	3.03	(1.12)	(1.65)

[a] Levels of concentration: SiO_2 = 0.5 and 1.0%; Al_2O_3 = 0.5 and 1.0%; MgO = 0.3 and 0.6%; Na_2O = 0, 0.5, and 1.0%. [b] Essentially 100% chukhrovite; the remainder contain Na_2SiF_6 as a coprecipitate, and the samples enclosed in parentheses contain three or more fluoride phases.

Table V. Percent of Input Fluorine Removed in Gypsum Filter-Cake Solids[a]

		Si (−)		Si (+)	
		Al (−)	Al (+)	Al (−)	Al (+)
Mg (−)	Na (−)	58	85	53	50
	Na (0)	53	77	55	74
	Na (+)	71	71	63	53
Mg (+)	Na (−)	63	80	61	34
	Na (0)	34	50	21	45
	Na (+)	45	47	16	63

[a] Levels of concentration: SiO_2 = 0.5 and 1.0%; Al_2O_3 = 0.5 and 1.0%; MgO = 0.3 and 0.6%; Na_2O = 0, 0.5, and 1.0%. Fluorine removal based on residual fluorine concentration (*R*), as compared to the initial concentration (3.8% *F*).

Table VI. Effect of Chukhrovite Precipitation on Total Residual Metallic Impurities (Ca, Mg, Na, Al, Si) in Filter-Grade Acids[a]

		Sum of metallic oxide impurities, wt %[b]			
		Si (−)		Si (+)	
		Al (−)	Al (+)	Al (−)	Al (−)
Mg (−)	Na (−)	0.24	0.24	0.56	1.09
	Na (0)	0.57	0.17	0.34	0.74
	Na (+)	0.41	0.44	0.49	0.94
Mg (+)	Na (−)	0.39	0.35	0.70	1.80
	Na (0)	1.24	1.49	2.00	1.59
	Na (+)	1.22	1.81	1.90	0.85

[a] Levels of concentration: SiO_2 = 0.5 and 1.0%; Al_2O_3 = 0.5 and 1.0%; MgO = 0.3 and 0.6%; Na_2O = 0, 0.5, and 1.0%. [b] Based on compositions of clear supernatant acids shown in Table II; in addition, all acids contain 1% Fe_2O_3, which was unaffected by the chukhrovite precipitation.

$MgNaAlF_6{\cdot}2H_2O$, Ralstonite. A factorial study was made of acid compositions to determine the range of conditions

Table VII. Analysis of Variance: Chukhrovite Precipitation

Source of variation[a]	*F*-value	*F**	*F***
Aluminum	10.81	5.12	10.56
Magnesium	11.58	5.12	10.56
Sodium	55.76	4.26	8.02
Al × Si	10.38	5.12	10.56
Mg × Si	6.40	5.12	10.56
Na × Si	7.49	4.26	8.02

Means for main effects: SD = 0.92%

		Mean wt % chukhrovite at concn levels		
Single factors	1	2	3	Effect
Silica	4.71	4.09		Not significant
Aluminum	3.78	5.02		Increase pptn
Magnesium	5.04	3.76		Decrease pptn
Sodium	6.88	4.30	2.03	Decrease pptn
Interactions		Si-1	Si-2	
Al × Si	Al (−)	3.49	4.08	Increase in silica counteracts effect of increasing alumina
	Al (+)	5.94	4.10	
Mg × Si	Mg (−)	4.88	5.21	Increase in silica enhances depressant effect of magnesium
	Mg (+)	4.55	2.98	
Na × Si	Na (−)	8.14	5.63	Increase in silica reduces depressant effect of sodium on chukhrovite pptn
	Na (0)	4.49	4.11	
	Na (+)	1.52	2.54	

[a] Includes only those factors and first-order interactions that are significant (95%, *F**) or highly significant (99%, *F***).

Table VIII. Factorial Levels Used to Determine Ralstonite Composition

	Concn, %, at indicated level			
Component	(−)	(0)	(+)	(++)
MgO	0.1	0.3	0.6	. . .
Al_2O_3	0.1	0.5	1.0	1.5
Na_2O	0.1	0.5	1.0	1.5

required to precipitate ralstonite-type salts and to obtain the variation in the ralstonite compositions. Portions of simulated filter-grade phosphoric acid (30% P_2O_5, 1.5% SO_3, 3.5% F, and 1.0% Fe_2O_3, but no silica) were treated with MgO, Al_2O_3, and Na_2O according to the factorial design in Table VIII.

The 48 solution compositions were allowed to equilibrate for 3 weeks at 25 °C with frequent shaking to promote precipitation. Most of the precipitated solids were fine grained and were recovered by centrifuging, washed with acetone, and then air dried. Traces of iron and aluminum phosphate gels that were precipitated by the acetone treatment were flash extracted with 1:10 HCl without visible effect on the fluorine solid phases. The results in Table IX show that an increase in concentration of any given component (Mg, Al, or Na) tended to increase both the amount of total solids and the amount of the metal component in the solid phase. This effect was particularly pronounced for magnesium at low concentrations of sodium (0.1 and 0.5% Na_2O). A maximum of 77% fluorine removal was obtained over the range of compositions studied.

Sodium appeared to have the greatest effect on the type of fluorine compounds that precipitated. At the highest concentrations of aluminum (1.0 and 1.5% Al_2O_3), an increase in sodium concentration favored the formation of cryolite over ralstonite, regardless of changes in the magnesium concentration (0.1–0.6% MgO). This effect of sodium was even more striking at the 0.5% Al_2O_3 level. At the 0.1% Al_2O_3 level, however, magnesium appeared to control the form of the fluorine precipitate.

As expected, the ralstonite had a range of compositions with as much as one-half of the aluminum being replaced by (Mg + Na + H). The compositions of the ralstonite products in Table IX that were verified by x-ray diffraction as being reasonably homogeneous phases are shown by empirical formula in Table X. The empirical formula $Na_xMg_xAl_{2-x}(F,OH)_6 \cdot H_2O$ assigned by Pauly (*5*) on the basis of natural ralstonites implies unlimited replacement of aluminum, an atomic ratio of Na:Mg of unity, and an atomic ratio F:OH close to 2.

As shown in Table X, Pauly's empirical formula must be modified to include the wide range of magnesium-to-sodium ratios found in our synthetic ralstonites. Our ralstonite compositions indicate that the atomic ratio Mg:Na is not unity but varies over the range 0.24–2.50, depending upon the ratio of $MgO:Na_2O$ in the acid. It also appears that little, if any, OH substitutes for F in these synthetic ralstonites so that the number of moles of hydrate water should be 2, rather than 1 as indicated by Pauly. Furthermore, it appears that only one-half of the aluminum can be replaced, so that the limiting composition can be represented by the formula $Mg(Na,H)AlF_6 \cdot 2H_2O$ and not $2[Al(F,OH)_3 \cdot H_2O]$.

Solubility Characterization of By-Product Fluorine Compounds

The solubilities of the 12 fluorine compounds that may precipitate along with gypsum in the acidulation step of the production of wet-process phosphoric acid and thus enter the gypsum disposal pond system were studied in distilled water and in four solutions that simulate the conditions for the manufacture of wet-process phosphoric acid and the disposal of waste products from the process.

Distilled water was used as a reference solution. The 5% P_2O_5 phosphoric acid solution simulates the first wash-water composition to come in contact with the freshly precipitated fluorine salts after precipitation and filtration from the filter-grade acid. A typical pond-water solution was prepared from reported analytical data (*12*) and simulates the liquid effluent slurry destined for pond storage. Its final adjusted composition was 0.44% P_2O_5, 0.14% Ca, 0.73% SO_3, 0.28% F, 0.10% Si, 0.01% Fe, and 0.01% Al; its pH was 1.05. The 15% P_2O_5 phosphoric acid solution is comparable in ionic strength to the first wash liquor after sulfate conversion in hemihydrate processes, and the 30% P_2O_5 acid is a filter-grade acid.

The mixtures were equilibrated at 25 °C for four months; the solid phases were examined microscopically to be certain that an excess of the equilibrating salt was present and to identify incongruent dissolution as indicated by the precipitation of other phases. The solution compositions (*9*) after four months have been summarized in Table XI as the weight percent solubility of each salt. These solubility values show good agreement with equilibrium solubility values calculated from molal solubility products (*9*), even where incongruent dissolution or SiF_4 evolution occurred. The chemical analyses frequently indicated the evolution of SiF_4 or HF and the precipitation of calcium fluoride when fluorosilicate salt exceeded 0.2% solubility in pond water. Likewise, chukhrovite precipitated in the pond systems as fluoroaluminates dissolved. Freshly precipitated calcium fluoride tends to be of a gelatinous form, which might make it an undesirable phase in storage pond systems.

Except for the potassium salt the fluorosilicates are relatively soluble in all solutions, especially when they are exposed to a higher acidic environment where SiF_4 and HF are volatile components. However, the data show that very minor quantities of potassium can decrease the solubility of fluorosilicate and consequently the evolution of SiF_4. The data show a phenomenal decrease in the solubility of $MgSiF_6 \cdot 6H_2O$ with increasing acid strengths. These results are shown in Figure 1 which shows that the extrapolated solubility at 60% P_2O_5 is 0.5% or the equivalent of 0.05% Mg, 0.05% Si, and 0.21% F. Thus, at this level the MgO concentration in a 10-34-0 liquid prepared from this acid would be 0.04%. The unusually low fluorine concentration required for removal of the magnesium in 60% P_2O_5 acid is economically attractive.

The fluoroaluminates and simple fluorides are much less soluble than the fluorosilicates but tend to lose HF in strong acids at much lower concentration levels. Supersaturation is indicated for CaF_2 since the experimental value of 0.04% in

Table IX. Precipitation of Fluorine from Simulated Wet-Process Acids

XR sample no.	Factorial compn, wt %			Solids, %	Compn of solids, %					*F* removed, %	Major solid phases by x-ray[a]
	Al_2O_3	Na_2O	MgO		Al_2O_3	F	Na_2O	MgO	H_2O (diff)		
2031	1.5	1.5	0.1	4.3	25.8	50.2	34.2	2.5	30.5	62	r, C
2032	1.5	1.5	0.3	6.1	23.7	50.5	28.7	6.7	33.0	71	r, C
2033	1.5	1.5	0.6	7.1	21.2	47.8	20.9	10.9	39.1	77	R, C
2034	1.5	1.0	0.1	4.7	31.7	53.5	27.6	2.8	30.1	57	R, C
2035	1.5	1.0	0.3	4.9	28.8	53.0	22.7	7.5	32.9	59	R
2036	1.5	1.0	0.6	4.9	23.0	50.2	15.7	12.1	40.0	57	R, C
2037	1.5	0.5	0.1	1.3	32.6	52.3	23.4	4.7	32.4	15	R, c
2038	1.5	0.5	0.3	2.9	29.5	51.2	15.6	10.1	36.1	43	R
2039	1.5	0.5	0.6	4.3	27.7	48.9	10.7	14.5	18.8	60	R, c
4-A	1.5	0.1	0.1	0.0	No solid phases					...	...
4-B	1.5	0.1	0.3	0.0	No solid phases					...	...
2040	1.5	0.1	0.6	3.8	27.5	49.5	4.8	17.1	21.9	54	R
2041	1.0	1.5	0.1	2.8	21.5	49.5	42.9	2.3	4.6	40	C
2042	1.0	1.5	0.3	3.3	21.0	49.6	34.7	5.2	10.4	47	r, C
2043	1.0	1.5	0.6	3.4	21.4	49.6	31.1	9.4	9.4	49	r, C
2044	1.0	1.0	0.1	2.1	23.3	50.7	36.3	3.8	7.3	35	r, C
2045	1.0	1.0	0.3	2.5	21.2	48.1	32.2	8.4	10.3	34	r, C
2046	1.0	1.0	0.6	2.5	21.4	48.5	26.9	11.9	11.7	34	r, C
2047	1.0	0.5	0.1	1.4	28.4	53.2	25.0	6.4	9.4	21	R, C
2048	1.0	0.5	0.3	2.4	23.7	46.6	14.0	13.8	21.5	27	R, C
2049	1.0	0.5	0.6	2.5	19.5	46.4	12.3	17.0	24.3	33	R, C
2050	1.0	0.1	0.1	0.6	26.8	48.7	10.3	12.8	21.9	8	R
2051	1.0	0.1	0.3	0.4	27.5	51.9	7.3	16.4	18.7	6	R
2052	1.0	0.1	0.6	2.3	21.5	48.2	6.3	20.4	23.9	31	R
2053	0.5	1.5	0.1	0.7	21.4	48.8	37.0	5.0	8.4	9	C
2054	0.5	1.5	0.3	1.3	17.3	49.0	30.0	13.5	10.8	19	C
2055	0.5	1.5	0.6	1.6	15.1	48.0	16.1	24.9	16.2	23	C
2056	0.5	1.0	0.1	1.0	20.7	48.6	3.6	34.1	13.5	14	C
2057	0.5	1.0	0.3	0.6	17.7	48.6	10.5	28.6	15.1	9	C
2058	0.5	1.0	0.6	0.7	15.7	42.2	15.7	24.9	15.8	8	C
2059	0.5	0.5	0.1	1.0	26.0	48.4	10.4	19.6	16.0	14	R, C
2060	0.5	0.5	0.3	1.4	18.9	46.3	16.6	13.1	24.6	18	R, C
2061	0.5	0.5	0.6	0.6	14.2	47.9	26.7	7.1	24.3	35	R, C
2062	0.5	0.1	0.1	0.5	25.2	48.9	15.0	7.7	23.8	7	R
2063	0.5	0.1	0.3	1.1	23.3	49.7	5.8	18.7	23.5	16	R
2064	0.5	0.1	0.6	1.2	15.9	47.4	3.1	27.8	15.8	16	R, MgF_2
2065	0.1	1.5	0.1	0.6	13.6	40.3	14.6	13.3	35.2	7	R, MgF_2
2066	0.1	1.5	0.3	0.7	5.7	44.6	3.9	37.9	26.7	10	MgF_2
2067	0.1	1.5	0.6	0.7	2.3	47.4	1.1	44.4	24.8	9	MgF_2
2068	0.1	1.0	0.1	0.1	...	...	...	...	...	...	R, C
2069	0.1	1.0	0.3	0.3	5.6	45.6	3.3	39.9	24.8	3	MgF_2
2070	0.1	1.0	0.6	0.4	3.1	46.5	1.4	44.6	24.0	6	MgF_2
2071	0.1	0.5	0.1	0.4	13.7	41.5	13.4	14.5	...	5	R, C
2072	0.1	0.5	0.3	0.5	6.2	44.7	3.7	39.0	...	6	MgF_2
2073	0.1	0.5	0.6	0.5	5.8	45.5	2.4	42.8	...	7	MgF_2
2074	0.1	0.1	0.1	0.1	...	...	...	...	...	...	R, C
2075	0.1	0.1	0.3	0.3	5.4	45.0	3.8	39.0	...	4	R, MgF_2
2076	0.1	0.1	0.6	0.7	3.5	43.8	1.4	42.1	...	9	MgF_2

[a] R = ralstonite, C = cryolite; capital letter denotes major or bulk phase, lower-case letter denotes minor phase.

distilled water is higher than the reported equilibrium value of 0.002%.

The calculation of the molal solubility product (*9*) for each salt after four months' equilibration in gypsum pond water as compared to the value calculated from the original pond water composition shows that two salts are stable in by-product gypsum storage ponds. These are CaF_2 and $Ca_4SO_4AlSiF_{13}\cdot 10H_2O$, both of which effectively immobilized fluorine in the pond water solids and prevent the recycle of fluorine in wash liquors or the discharge of gaseous fluorine from storage ponds. Except for magnesium and calcium fluorosilicates, which are not stable in neutral solutions, the data also show a significant decrease in solubility of each salt in distilled water as compared to pond water, indicating that neutralization of pond waters could result in precipitation of any of these fluorine compounds.

Several important features of the fluorine redistribution process are shown by these results. The fluorosilicates, with the exception of K_2SiF_6, may be expected to largely or wholly disappear as stable solid phases upon discharge into storage ponds. The fate of the fluorine released by this dissolution is determined by two competing equilibrium processes—one of serious environmental concern. Dissolved fluorosilicate tends to establish equilibrium with volatile gaseous components (SiF_4, HF). Or dissolved fluorosilicate may be reprecipitated due to supersaturation, with respect to a solid phase such as chukhrovite. The latter process is influenced by other dissolved impurities. Thus, the overall process of *F* distribution is not congruent nor simply related to solubility limits of the incoming fluorine compounds, as measured in pure solvents.

Table X. Empirical Formula for Ralstonite, $(Al_xMg_yNa_z)AlF_6\cdot nH_2O$

X-ray sample no.	Mol/mol AlF_6 Al_x	Mg_y	Na_z	H_2O [a]	Mol ratio Mg:Na
2035	0.21	0.40	1.57	3.9	0.24
2038	0.28	0.56	1.12	4.4	0.50
2040	0.25	0.98	0.36	2.9	2.70
2050	0.22	0.74	0.78	2.9	0.95
2051	0.19	0.89	0.51	2.3	1.75
2052	0.00	1.19	0.48	3.1	2.50
2062	0.21	0.87	0.58	3.1	1.50
2063	0.04	1.06	0.43	3.0	2.50

[a] By difference.

Sodium and Potassium Fluorosilicates

Potassium in very low concentrations has a marked effect on $(SiF_6)^{2-}$ behavior by converting other fluorosilicates to the less soluble phase, K_2SiF_6. The limiting concentration of potassium was about 0.05% K. Thus, K_2SiF_6 and possibly $NaKSiF_6$ are potential solid-phase components in pond solids if small additions of potassium could be economically justified. The potassium content of phosphate rock is usually well below 0.1% K_2O but may vary widely depending upon the nature of the accessory minerals. These small amounts, nevertheless, have a large effect on the fate of Na_2SiF_6.

Since phosphate rocks may show wide variation in alkali content [weight ratio Na:K about 3–10 (*13*)], the solubility relationships between Na_2SiF_6, K_2SiF_6, and the double salt ($NaKSiF_6$) were investigated to determine how sodium and potassium compete to precipitate as fluorosilicates. These results (*9*) are plotted in Figure 2.

Two important features are revealed by this plot. First, the mole fraction Na:Na + K has to be about 0.6 for the double salt to form in the filter acid composition. Secondly, since the quantity of sodium, which is derived from the apatite, is usually much greater than the quantity of potassium, which is derived from accessory minerals, the conditions for precipitation of K_2SiF_6 will rarely be encountered.

Figure 2 also shows the three- to fourfold increase in solubility of Na_2SiF_6 in pond and distilled water as compared to filter-grade acid. Since Na_2SiF_6 is often the major fluoride associated with gypsum filter cakes (*12*), it is thus likely to redissolve in pond systems and contribute to release of fluorine gas.

Summary

The aluminofluorides, ralstonite and cryolite, because of their very low solubilities in water and phosphoric acid, were initially considered as possible compounds for removing fluorine from wet-process acid and immobilizing it in storage pond systems. However, they showed a marked instability in 30% P_2O_5 acid in association with gypsum, where $Ca_3(AlF_6)_2\cdot 4H_2O$ precipitated as the fluoroaluminates dissolved.

Of the two simple fluorides, only CaF_2 appears likely to persist as a stable phase in storage ponds. The MgF_2 phase is decomposed slowly by soluble calcium (from the associated gypsum) and converts to CaF_2. Despite the very low solubility of CaF_2 in the simulated pond mixtures and vast reservoir of Ca^{2+} ions from gypsum, it failed to control the precipitation of soluble fluorine in most of the mixtures tested.

This study, which was based on simulated acid compositions such as would be expected from Florida phosphate rock

Table XI. Stability of Fluoride Compounds from Wet-Process Phosphoric Acid

Fluoride salt	Solubility, wt %, 25 °C 30% P_2O_5 + gypsum	15% P_2O_5 acid	5% P_2O_5 acid	Pond water + gypsum	Distilled water
Na_2SiF_6	0.20	0.69	0.87	1.11	0.50
K_2SiF_6	0.25	0.24	0.21	0.23	0.14
$NaKSiF_6$	0.26	0.59	0.68	1.13	0.72
$CaSiF_6\cdot 2H_2O$	1.80	15.0	23.6	28.8	28.6
$MgSiF_6\cdot 6H_2O$	4.00	21.8	32.8	35.2	36.0
Na_3AlF_6	0.4	0.26	0.08	0.51	<0.02
NaK_2AlF_6	0.50	0.19	<0.10	0.36	<0.03
$Ca_3(AlF_6)_2\cdot 4H_2O$	0.2	0.15	<0.09	0.36	<0.02
$MgNaAlF_6\cdot 2H_2O$	0.5	0.15	0.07	~0.25	<0.04
$Ca_4SO_4AlSiF_{13}\cdot 10H_2O$	0.2	0.2	0.2	<0.01	<0.04
CaF_2	0.1	0.12	0.07	<0.01	0.04
MgF_2	0.5	0.37	0.23	0.31	<0.02

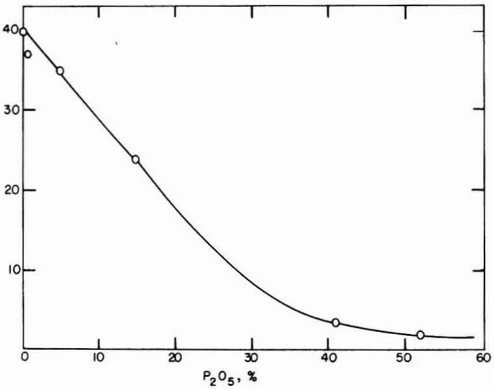

Figure 1. Solubility of $MgSiF_6 \cdot 6H_2O$ in H_3PO_4, 25 °C

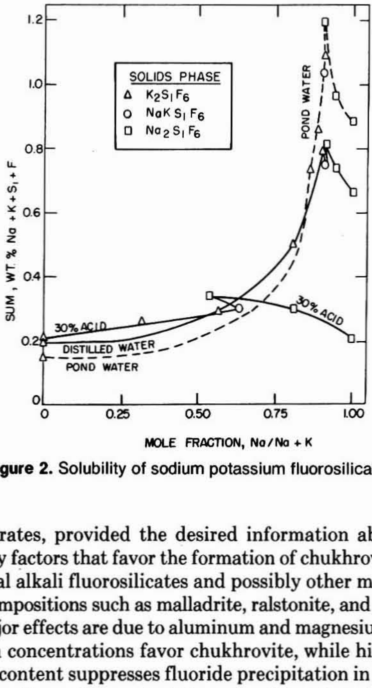

Figure 2. Solubility of sodium potassium fluorosilicate

concentrates, provided the desired information about the impurity factors that favor the formation of chukhrovite over the usual alkali fluorosilicates and possibly other major fluoride compositions such as malladrite, ralstonite, and cryolite. The major effects are due to aluminum and magnesium. High alumina concentrations favor chukhrovite, while high magnesium content suppresses fluoride precipitation in general. Increasing the sodium content favors the formation of Na_2SiF_6 as a competing precipitation process with chukhrovite.

As discussed earlier, in the treatment of pond waters, gypsum must redissolve to supply calcium as fluorine precipitates as chukhrovite.

The results of this study demonstrate that the preferential precipitation of chukhrovite during the rock digestion stage can remove as much as 85% of the input fluorine, effect an overall decrease in the total dissolved metallic impurities, decrease sulfuric acid reagent requirements, and immobilize the fluorine in the by-product cake in a salt that will minimize fluorine redistribution in gypsum storage ponds. The large decrease in fluorine content in the intermediate acid product significantly decreases the fluorine evolution problem during subsequent concentration steps to merchant-grade or superacid compositions.

Further tests of aluminum amendments to feed rock or simulated filter-grade acid compositions will be made to test the practical limits of removing fluorine by the chukhrovite route. This type of process may be highly attractive for high alumina rocks, whole matrix, or leached zone-type ore, provided they have a low magnesium content. It appears unlikely that conditions favoring chukhrovite formation can be found for highly substituted apatitic rocks such as North Carolina rocks, which have contents of MgO (0.6–0.8%) and Na_2O (1.0–1.4%) that represent the upper limits of the concentration levels tested in this factorial experiment. No single impurity constituent can control fluoride precipitation. Instead, the competitive reaction between aluminum and silica for the fluorine and then the interaction of magnesium, sodium, and calcium for the fluoroaluminates and fluorosilicates present a complex chemical problem for which a simple solution will be difficult to obtain.

This study demonstrates the interdependence of phosphate raw material composition, acidulation chemistry, and pond chemical systems. Fluorine emission models that ignore this interrelationship are thus overly simplistic.

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Relative Photochemical Reactivity of Propane and *n*-Butane

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■ A smog chamber study was undertaken to investigate the relative photochemical reactivity of propane and *n*-butane. The use of lower, more realistic initial nitric oxide concentrations and longer irradiation times in the photochemical reaction mixture permitted ozone concentrations to reach higher levels compared to the classical experiment utilizing an initial nitric oxide concentration of 1–2 ppm and a 6-h irradiation time. Thus, the ozone yields and, therefore, the relative photochemical reactivity of moderately reactive compounds such as propane are increased. The study indicates that hydrocarbon reactivity experiments should be carried out as closely as possible to conditions that occur in the atmosphere to determine realistic potentials for ozone production.

In this report we examine the results of experiments carried out in the evacuable irradiation chamber of the Laboratories of the California Air Resources Board (ARB). These experiments are intended to give insight into the question of the relative organic photochemical reactivity of propane and *n*-butane. The ARB has recently adopted a three-class hydrocarbon reactivity scale (*1*) which places all paraffinic hydrocarbons with three or more carbons in Class II (moderate reactivity organics). Dimitriades (*2*) considers all paraffinic hydrocarbons with four or more carbons to be of moderate reactivity (Class III of a five-class scheme) but places propane in the nonreactive classification (Class I) along with methane and ethane. The classification of Dimitriades is based on older smog chamber studies that were carried out at unrealistically high nitrogen oxides concentrations (*2*) and for irradiation times that are significantly less than those which occur in the ambient atmosphere (*3*). Therefore, there is a need to examine this aspect of reactivity with additional experiments. The implications of the experimental results for oxidant control strategies are considered.

Experimental

Experiments were carried out in a borosilicate glass-lined evacuable chamber (see ref. *4* for details of chamber construction and operation) with a volume of 4.11 m^3. The inner surface area is 17.7 m^2, and the surface area-to-volume ratio is 4.31 m^{-1}. The photochemical lighting system consists of three parallel Pyrex tubes that extend through the chamber and are oriented axially between the side walls and the chamber center axis. The UV light intensity inside the chamber yields dioxide photolysis, k_1, of 0.2 min^{-1} within the chamber which is less than that observed in the ambient atmosphere (*3*). The half-life for ozone decay in the dark chamber is in excess of 50 h.

Prior to each experiment the desired volumes of the hydrocarbon and the nitrogen oxide were premeasured and then injected into the evacuated chamber. Zero air (supplied by Scott Research) was then introduced as the diluent gas to a total pressure of 16 psi. Water sufficient to give an initial relative humidity of 50% was introduced into the chamber with the diluent air as it is passed through a heated bubbler containing deionized distilled water. The chamber is customarily evacuated to 10^{-6} torr between experiments to maintain day-to-day system integrity and to prevent the possible accumulation of reaction products on the interior surfaces. A 10-h irradiation of zero air alone yields less than 0.02 ppm of ozone.

Sampling for oxides of nitrogen (TECO Corp. analyzer, Model 12-A) and ozone (Meloy Corp. analyzer, Model OA 325) is continuous. The ozone and nitrogen oxides analyzers are calibrated with a Monitor Labs Model 8500 calibrator. Concentrations of ozone (up to 1.0 ppm) are simultaneously monitored during calibration with a DASIBI UV photometer (DASIBI Corp., Model 1003H) which has been standardized against a UV photometer. Hydrocarbons are analyzed by standard gas chromatographic techniques. The gases are sampled by means of Pyrex probes extending 2.5 ft beyond the interior walls of the chamber center axis. Each of the experiments was duplicated as similar reactant concentrations and yielded similar results. The data reported represent two single experiments.

Results and Discussion

For these experiments it was decided to investigate the ozone yield from the irradiation of a nitric oxide/air mixture with each of the hydrocarbons individually. In this way the experiments would be comparable to similar experiments upon which Dimitriades (*2*) based his reactivity analysis. A major departure from the earlier studies, however, is that in the present work the initial nitric oxide concentrations of 0.2 ppm and the initial concentration of hydrocarbon of 7.5 ppmC are significantly lower, i.e., the earlier studies involved nitric oxide concentrations in excess of 2 ppm and hydrocarbon concentrations in excess of 2 ppm compound. The initial concentrations used in these experiments were designed to approximate more closely realistic in terms of existing atmospheric conditions. The total irradiation time of 10 h also approximates more closely the 10–12 h of irradiation time available in the atmosphere (*3*) during the late spring and summer.

Figures 1 and 2 give typical results for the irradiation of *n*-butane and propane, respectively, under the conditions described above. The most important observation is that both hydrocarbons produce substantial amounts of ozone during the 10-h irradiation period. Furthermore, the ozone yields during these irradiations are nearly peaked at the end of the irradiation period, rather than earlier in the time period. Table I summarizes some of the parameters from the above experiments. The nitrogen dioxide maxima in both experiments are reached at 2.5 and 3.5 h for the butane and propane experiments, respectively, and the peak value for the propane experiment (Figure 2) is only slightly lower than that for *n*-butane. After reaching a peak the nitrogen dioxide exhibits a steady decline in concentration, as expected. The onset of

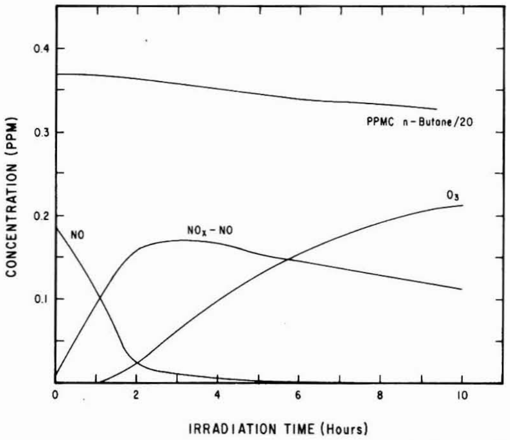

Figure 1. Ozone production from *n*-butane/NO photooxidation in ARB high-vacuum irradiation chamber

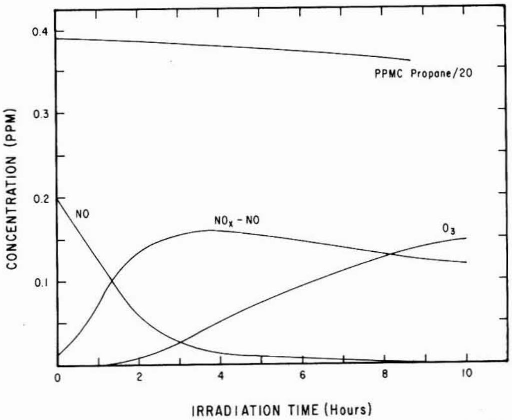

Figure 2. Ozone production from propane/NO photooxidation in ARB high-vacuum irradiation chamber

Table I. Reaction Parameters for *n*-Butane and Propane Irradiations

	Initial concn, ppm					
Compound	Nitric[a] oxide	Hydro-carbon[b]	Nitrogen dioxide[a]	NO_2 max[a]	Time to NO_2 max, h	Max ozone[a]
n-Butane	0.19	7.4	0.01	0.17	2.5	0.22
Propane	0.19	7.8	0.02	0.16	3.5	0.15

[a] Concentration expressed in units ppm. [b] Concentration expressed in ppmC units.

Table II. Reactivity Comparison of Hydroxyl Radical-Hydrocarbon Rate Constant

Compound	Ozone yield, ppm	Relative reactivity	k_{HO}[a]	Ref	(HO)[b,c]
Propane	0.15	0.68	2.2×10^{-12}	5	1.2×10^6
n-Butane	0.22	1.00	3.0×10^{-12}	6	1.2×10^6

[a] Units: cc/mol/s. [b] Units: mol/cc. [c] Estimated from the total hydrocarbon loss over a 7-h period.

ozone formation occurs after approximately 50% of the NO has been converted to NO_2. The maximum ozone for the *n*-butane experiment is 0.22 ppm after 10 h, compared to a value of 0.15 ppm for propane. Thus, the ozone yield for propane over the 10-h irradiation time is very significant compared to that for *n*-butane, establishing that propane must be considered to be a reactive compound in terms of ozone production.

It is worthwhile to consider the reasons for the observed reactivity of propane in more detail. It was indicated above that previous reactivity experiments used high concentrations of nitric oxide (>1 ppm) in the initial reaction mixture. The use of such a high initial nitric oxide concentration in the previous studies would increase the time to reach peak nitrogen dioxide concentrations beyond the 2.5 h observed in these experiments. Because significant ozone formation does not occur until the nitrogen dioxide concentration has peaked, there is little remaining time in a 6-h irradiation period to observe ozone buildup. The atmosphere, on the other hand, provides a significantly longer 10–12-h irradiation time. Most of the earlier experiments upon which Dimitriades and others rely were carried out over a 6-h irradiation period. Thus, the apparent reactivity based on maximum ozone yield for propane and other moderately reactive organics would then be severely diminished, compared to the reactivity that is consistent with realistic atmospheric air contaminant concentrations.

Table II compares the maximum ozone yields obtained in these experiments with the relative rate constants for the reaction of hydroxyl radical with the test hydrocarbon. The ratio of the rate constants, 0.73, is in excellent agreement with the observed relative reactivity for propane of 0.68. The reactivity measurements were made at equal ppmC concentrations while the rate constants are in volumetric units. Therefore, agreement may be fortuitous. These data would indicate, on the one hand, that for moderately reactive organics, the rate constant for the reaction of the organic compound with hydroxyl radicals could be a good measure of the compound's reactivity in terms of ozone yield. However, as the HO rate constant increases and the organic structure becomes more complex, it is not anticipated that a linear relationship will still be valid, because of expected complexities in the reaction mechanism. The last column in Table II gives the average hydroxyl radical concentrations calculated from the hydrocarbon loss over a 7-h irradiation period. In both cases a concentration of 1.2×10^6 mol/cc was calculated. This value is lower but in general agreement with hydroxyl radical concentrations determined from modeling calculations.

Conclusions

The results of this study show that propane will produce significant levels of ozone in smog chamber irradiations. Comparison of the relative reactivity of propane with *n*-butane indicates that the ARB classification of propane as a moderately reactive hydrocarbon is confirmed under conditions which approximate those in the atmosphere. The use of lower, more realistic initial nitric oxide concentrations and longer irradiation times in organic reactivity studies permits ozone concentrations to reach higher levels when irradiating HC/NO_x mixtures containing low and moderately reactive organics, thus indicating more realistic potentials for ozone production.

Acknowledgment

The authors express their appreciation to D. Daymon for his aid in carrying out these experiments.

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Comparison of Levels of Trace Elements Extracted from Fly Ash and Levels Found in Effluent Waters from a Coal-Fired Power Plant

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■ Trace elements were extracted from a coal-fired power plant electrostatic precipitator ash with nitric acid, hydrochloric acid, citric acid, redistilled water, and ammonium hydroxide as extractants. Effluent waters at this plant were sampled to assess the elevation of trace element concentrations compared with intake waters. The results showed a positive correlation between those elements most extractable by water (B, F, Mo, and Se) or acid (As, B, Cd, F, Mo, and Se) and those elements most elevated in effluent waters (As, B, F, Mo, and Se).

The expanding use of coal for electric power generation in the southwestern U.S., along with the high ash content of these coals, will necessitate the disposal of massive amounts of coal ash. The possible contamination of waters and soils by such coal ash disposal requires investigation. The solubility behavior of trace elements in the alkaline waters of this region may indicate that different elements are of concern here than those found in more acidic aquatic environments. A study has been initiated to identify which trace elements are most extractable from ash and to compare them with those elements that are observed at elevated concentrations in effluent waters from a coal-fired power plant in the southwestern U.S.

Experimental Methods

Electrostatic precipitator ash for the extraction experiment, influent waters, and effluent waters were collected at a large coal-fired power plant at Fruitland, N.M. A flow diagram of water usage at this plant is given as Figure 1.

Influent and effluent waters were sampled at four locations: (A) cooling lake intake; (B) cooling lake outlet at the base of the dam; (C) decant channel—effluent water from the ash settling pond; and (D) ash pond—surface water. Ash slurry from the venturi scrubbers is sent to the ash pond where the ash settles and the water is decanted. Surface water in the ash pond was sampled for comparison with ash pond effluent water in the decant channel. The outlet of the cooling reservoir was sampled for comparison with cooling lake intake and ash pond effluent, as well as to approximate scrubber intake water. Coal ash effluents discharged into the cooling lake (*1*) may also influence trace element concentrations in the outlet.

Each sample was filtered in the field with a Whatman No. 41 prefilter, a 0.45-μm Millipore membrane filter, and a backing pad; the filtered samples were acidified in the field and later frozen. The sampling train and bottles were made from plastic materials.

Trace elements in the precipitator ash were extracted using an ash-to-extractant ratio of 1:4. The extractants included 0.1 M $H_3C_6H_5O_7$ (citric acid), 1.0 M HCl, 1.0 M HNO_3, 0.1 M HNO_3, 0.01 M HNO_3, 0.001 M HNO_3, redistilled H_2O, and 0.1 M NH_4OH. The ash-extractant mixture was agitated for 3 h and then filtered through Whatman No. 41 followed by Whatman No. 542 filter paper. The filtrates were acidified and frozen in polyethylene bottles. Complete details of the extraction experiment are reported elsewhere (*2*).

Analytical Procedures

Fluoride was measured in the sample solutions with an Orion Model 94-09A specific ion electrode and a Corning Model 112 digital volt meter (*3*). The boron content was determined by thermal neutron capture prompt γ-ray analysis (*4*) by evaporating 10 mL of the solutions to dryness on small polyethylene sheets. The capture γ-ray facility at the Los Alamos Omega West Reactor was described by Jurney et al. (*5*). The remaining elements in solution were measured by flameless atomic absorption with a Perkin-Elmer Model 306 spectrophotometer equipped with a deuterium background corrector and a HGA-2000 graphite furnace. Perkin-Elmer electrodeless discharge lamps were used for As, Cd, and Se determinations, and Perkin-Elmer hollow cathode lamps were

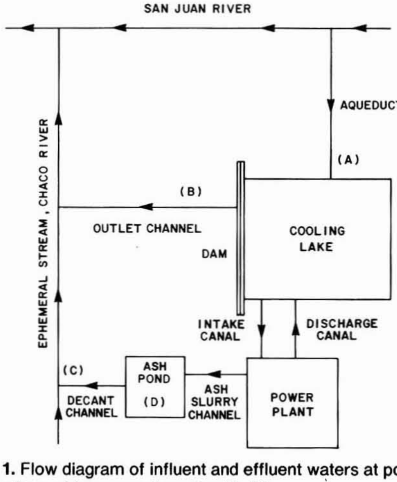

Figure 1. Flow diagram of influent and effluent waters at power plant and locations of four sampling sites (A–D)

Table I. Percentage of Trace Element Content of Ash Extracted by Each Solution and Trace Element Content of Precipitator Ash

Molarity	1.0 M	1.0 M	0.1 M	0.1 M	0.01 M	0.001 M		0.1 M	
Solution	HNO_3	HCl	Citric acid	HNO_3	HNO_3	HNO_3	H_2O	NH_4OH	
Initial pH[a]	0.5	0.5	2.2	1.4	2.2	3.1	7.4	11.3	Concn in precipitator ash, μg/g
Final pH[b]	0.5	0.6	3.6	4.1	11.7	11.9	11.9	11.9	
	%	%	%	%	%	%	%	%	
As	64	78	59	0.65	0.31	0.17	0.10	0.51	12
B	78	24	94	55	3.9	1.4	1.5	<0.05	260
Be	8.6	12	6.1	1.7	<0.09	<0.09	<0.09	<0.09	4.7
Cd	48	32	33	35	3.8	0.28	<0.14	0.14	0.29
Cr	15	14	13	1.2	0.53	0.38	0.33	0.29	34
Cu	7.3	7.9	4.6	3.3	0.11	<0.01	<0.01	<0.01	58
F	75	63	86	83	11	8.1	7.2	8.7	120[c]
Mo	120	120	110	4.7	57	55	59	54	4.2
Se	78	35	46	5.1	11	5.9	5.1	4.5	8.0
V	20	28	16	0.04	0.02	<0.01	<0.01	<0.01	98
Zn	3.1	3.1	1.8	1.2	0.27	<0.03	<0.03	0.07	160

[a] pH determined before ash was added to the extractants. [b] pH determined after agitation of ash-extractant mixture. [c] The fluorine concentration given is the mean concentration reported by the Southwest Energy Study (*6*) and Woodward Envicon (*7*).

used for Be, Cr, Cu, Mo, V, and Zn. Furnace parameters and other details may be found in Dreesen et al. (*2*).

The trace element content of the ash was determined by flameless atomic absorption for As, Be, Cd, Cr, Mo, Se, V, and Zn; by instrumental neutron activation analysis for As, Cr, Cu, and Se; and by both neutron capture prompt γ-ray analysis and emission spectroscopy for boron. Dissolution of the precipitator ash was carried out in either open beakers or Teflon-lined Parr bombs by use of a mixture of HF, H_2SO_4, and HNO_3.

Results and Discussion

The results of the extraction experiment and the trace element content of the precipitator ash are shown in Table I. The data are summarized as extractability categories in Table II. Specific acid anionic effects are not considered; however, such effects for the common mineral acids should not alter the qualitative conclusions of this study.

As expected, strongly acid extractants were efficient mobilizers of a number of trace elements; decreasing extraction of trace elements with increasing pH was found for all elements except Mo. Small (*8*) describes a similar pattern of solubility as a function of pH for Se, As, V, Cr, and Zn in extractants having a pH range of 1–5. Increased solubility of trace elements in fly ash under acidic conditions is reported by Theis (*9*) for As, Pb, Cu, Zn, Cd, Cr, and Hg.

Although the extractability of trace metals except for Mo was very slight at high pH's, elements with strong anionic character were mobilized to a significant extent as shown in Tables I and II. The acid neutralizing character of this fly ash is demonstrated by a final pH of 11.9 for the redistilled water extraction.

The trace element concentrations in the influent and effluent waters sampled at the power plant are given in Table III. The discharge of power plant effluents into the cooling lake and evaporation probably account for the higher levels of As, B, F, Mo, and V in the outlet water. The evaporative losses from the cooling lake are expected to concentrate dissolved constituents by a factor of about 2.5 (*11*). (Water will also be lost to the atmosphere from the scrubbers; however, the effect of this loss on concentrating elements in the scrubber fluids is not known.)

Table II. Extractability Categories for Trace Elements in Extraction Experiment for Strongly Acidic and Basic Extractants

Extractability, %	Strongly acid extractant (1.0 M HNO_3) final pH = 0.5	Strongly basic extractant (H_2O) final pH = 11.9
>30	As, B, Cd, F, Mo, Se	Mo
10–30	Cr, V	. . .
1–10	Be, Cu, Zn	B, F, Se
0.1–1.0	. . .	As, Cr
<0.1	. . .	Be, Cd, Cu, V, Zn

Table III. Trace Element Concentrations in Influent (A), (B) and Effluent (C), (D) Waters in ng/mL (ppb)

Element	(A) Cooling lake intake, ng/mL	(B) Cooling lake outlet, ng/mL	(C) Ash pond effluent, ng/mL	(D) Ash pond surface, ng/mL
As	2.6	7	27	33
B	<100[a]	950	12000	11000
Be	<0.2	<0.2	<0.2	<0.2
Cd	1	1	1	1
Cr	<1	1	2	3
Cu	3	2	3	2
F	220	3700[a]	16000	ND[b]
Mo	<1	23	170	160
Se	<1	1	57	60
V	2	60	130	140
Zn	590	350	440	580

[a] Data for September 1975, from the New Mexico Environmental Improvement Agency (*10*). [b] No data.

The trace element concentration ratios in the ash pond effluent (C) relative to the cooling lake intake (A) and outlet (B) are presented in Table IV. There is a correspondence between those elements most extractable in water and those elements exhibiting elevated concentrations in the effluent waters. This correspondence also holds for those elements readily extractable in acid.

Table IV. Trace Element Concentrations in Ash Pond Effluent Water (C) Relative to Cooling Lake Intake (A) and Outlet (B)

Concn ratio	Ash pond effluent (C)/cooling lake intake (A)	Ash pond effluent (C)/cooling lake outlet (B)
>50	B, F, Mo, Se, V	Se
10–50	As	B
2–10	. . .	As, Cr, F, Mo, V
<2	(Be),[a] Cd, (Cr), Cu, Zn	(Be), Cd, Cu, Zn

[a] Elements in parentheses have uncertain enrichment factors due to analytical uncertainties and detection limits.

There are two important factors which could influence the distribution of trace elements in the extracts and effluents. One is the surface predominance of certain trace elements on ash particles (*12*), making them more available for mobilization; these elements (Mo, F, Se, B, As, and Cd) are among those extractable in acids. The second factor is that anionic species would remain soluble in alkaline environments while the more metallic cations would be precipitated (*9*). Therefore, molybdate, borate, fluoride, selenate, and possibly arsenate, chromate, and vanadate would occur in soluble forms; whereas Be, Cd, Cu, and Zn would be either precipitated after dissolution with increasing pH or not extracted from the ash initially. Thus, an important consideration is whether the trace element compounds in the ash are soluble in the acidic environment of the venturi scrubbers or further downstream in the ash disposal system where more alkaline conditions are found.

In conclusion, it appears that Mo, F, Se, B, and As are most significantly elevated in effluent waters of the elements considered and are of prime interest for future studies of soluble contaminants from coal ash disposal in alkaline environments.

Acknowledgment

The authors' appreciation is extended to George Trujillo for his technical assistance in the extraction experiment.

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Lead-Containing Particles on Urban Leaf Surfaces

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■ London plane tree [*Platanus acerifolia* (Ait.) Willd.] leaf samples collected from an urban environment were examined with an electron microanalyzer and electron microscope equipped with an energy-dispersive x-ray analyzer. Lead-containing aerosol particles found upon these leaves contained no detectable chlorine or bromine. The lead appeared to be associated with sulfur and phosphorus in the form of lead sulfate and lead orthophosphate.

Tree surfaces (leaves, twigs, stems) accumulate numerous trace metals in roadside and urban environments (*1–4*). Because of its abundance, potential toxicity, and biologic nonessentiality, lead has been of particular interest. The interaction of phylloplane microorganisms and particulate heavy metals is potentially important and incompletely appreciated (*5*). Lead particle abundance, distribution, size, and chemistry in situ must be evaluated before the significance of foliar lead particles to leaf surface microbes can be determined. This report presents our preliminary findings of lead particle chemistry on tree leaf surfaces.

Experimental

Leaf samples were collected from the lower canopy of mature London plane trees [*Platanus acerifolia* (Ait.) Willd.] every two weeks throughout an entire growing season. The trees lined a busy (average daily traffic ~5000 vehicles) street in downtown New Haven (pop. 140 000). Lead contamination was monitored by analyzing unwashed leaves with an atomic absorption spectrophotometer. Leaves collected in August when the foliar lead burden was relatively high (Figure 1) were observed and analyzed with a scanning electron microscope (Autoscan Model U-3, Etec Corp.) equipped with an energy-dispersive x-ray spectrometer (Model E-2, Kevex Corp.) and with an electron microanalyzer (Model MS-64, Acton Laboratories Inc.). Discs were cut from representative sample leaves, air dried, and coated with several hundred Å of

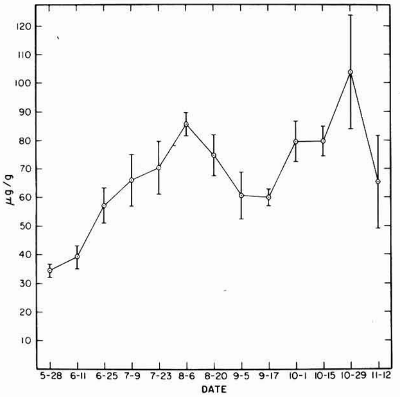

Figure 1. Total lead contamination throughout entire growing season of streetside London plane tree leaves (unwashed, dry wt basis) determined by atomic absorption spectrophotometry

Mean and standard error given for each sample which consisted of approximately 25 leaves collected from each of three trees

Table I. Elemental Ratios, Relative to Lead, for Selected Lead-Containing Tree-Leaf Particles

	Particle no.					
Element	**1**	**2**	**3**	**4**	**5**	**6**
Pb	1.0	1.0	1.0	1.0	1.0	1.0
S	0.012[a]	0.138[a]	0.307[a]	0.084[a]	0.415[a]	0.593[a]
P	0.003[a]	0.612[a]	0.196[a]	0.685[a]	0.474[a] [0.653][b]	0.471[a] [0.482]
Si	0.011[a]	0.364[a]	21.9[a]	4.156[a]	1.187[a]	0.545[a]
Al	. . .	. . .	42.9[a]	0.615[a]	1.306[a] [0.734]	1.200[a] [1.03]
Mg	. . .	. . .	8.314[a]	1.421[a]	4.986[a]	7.390[a]
Ca	. . .	. . .	. . .	. . .	[0.340]	[1.030]
K	. . .	. . .	. . .	. . .	[0.228]	[0.094]
Fe	. . .	. . .	. . .	. . .	[ND][c]	[0.016]

[a] Obtained by microprobe analysis. [b] [ ] obtained by energy-dispersive x-ray spectrometer. [c] ND: not detected.

graphite. Leaf disc surfaces were systematically scanned for lead-containing particles. Spectrometers were calibrated using metallic oxide, or in the case of the halogens, salt standards. Spectra were corrected for such factors as fluorescence yield, detector counting efficiency, and other accountable factors.

Results and Conclusions

Lead particles were infrequently encountered among the myriad of particles associated with the leaf surfaces. Lead particle size was variable with their maximum dimension ranging from 1.0 to 25 μm. The instrumentation available in this study had a minimum detectable particle size of $\sim$1.0 μm. The particles were generally composed of highly angular, planar sheets in either microcrystalline or crystalline microaggregate arrangement. The elemental composition of six particles was examined (Table I). Both systems gave similar results—especially with regard to the absence of halides in the particles studied. Sulfur and phosphorus were associated with the majority of these particles. Silicon, aluminum, and magnesium were also common. Chlorine and bromine were not associated with any of the lead particles (<10 ppm). One particle (number 1) was deficient in sulfur, phosphorus, and silicon. Physically, this particle was also unique as it appeared to be singular, spherical, and pitted.

The calculated Pb content, employing S and P elemental ratios from Table I and assuming $PbSO_4$ (Pb:S = 1.0) and $Pb_3(PO_4)_2$ (PB:P = 1.5) chemistry, was 1.056 (particle 2), 0.601 (particle 3), 1.112 (particle 4), 1.128 (particle 5), and 1.300 (particle 6). The average calculated Pb content (±SD) for these particles is, therefore, 1.039 ± 0.261. If all the lead were in the form of $PbSO_4$ and $Pb_3(PO_4)_2$, the Pb content for these particles would equal 1.0. The agreement of these values supports the conclusion that Pb was present in the particles as mixed $PbSO_4$ and $Pb_3(PO_4)_2$. The particles were apparently in association with, or in close proximity to, soil particles containing large amounts of Si and Al. The extensive variation in Pb:Si and Pb:Al ratios suggests a physical rather than a chemical association. Soil particles high in Si, Al, and Mg were extremely abundant on the leaf surfaces. Particle 1 was most probably lead oxide or lead carbonate.

While lead sulfate, phosphate and oxide have been detected in motor vehicle exhaust, lead chlorobromide is generally assumed to be the primary lead salt introduced into the atmosphere from the tailpipe (*4, 6, 7*). Lead particles leaving the exhaust system are generally in the submicrometer to 5-μm range (*4, 8–10*). Absence of lead halides on the leaves suggests that alterations of lead particle chemistry may occur in the atmosphere, in the roadside soil, or on the leaf surface. Size distributions on the leaves also suggest aggregation in the atmosphere, in the soil, or on foliar surfaces. The particles we observed may have been soil particles reentrained by vehicular turbulence and deposited on the leaf surfaces.

The form of lead residues on plant surfaces in natural environments has not been intensively investigated. Heichel and Hankin (*11*) employed an electron microprobe to examine roadside twig and bark tissue and, in contrast to our results, did detect chlorine and bromine in association with lead particles. Fleischer and Parungo (*12*) detected lead on tobacco leaf trichomes with x-ray spectrometry, but did not suggest the anion associated with it.

It is critically important to ascertain the chemistry of lead particles on plant surfaces so that the biological significance of these contaminants can be determined. In the absence of this information, we have arbitrarily employed lead nitrate to make preliminary judgments concerning the in vitro toxicity of lead to various components of the leaf surface microflora (*13–15*). We now judge that lead sulfate, phosphate, carbonate, and oxide should be screened.

Acknowledgment

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CORRESPONDENCE

SIR: The paper, "Particle Collection Efficiencies of Air Sampling Cyclones: An Empirical Theory" by Tai Chan and Morton Lippmann [*ES&T* **11** (4), 377 (1977)], contains several serious errors with reference to the theory of Leith and Licht as cited.

In Table I and in the discussion, this is classed as a "semiempirical theory" with the comments "empirical fit of cyclone collection efficiency data" and "weak dependence of D_{pc} to Q predicted". It is also stated that this theory "make(s) an analogy to electrostatic collection of particles".

The facts are: (a) there is nothing whatever empirical about the theory, and there are no empirical constants in it; (b) the dependence of D_{pc} on Q is precisely the same as that given for the "conventional" (Type I) theories, namely, $D_{pc} = K \cdot Q^{-1/2}$, and this is clearly stated in the cited reference; (c) there is no analogy whatever drawn with electrostatic collection in the explanation of the theory.

The line purporting to represent the Leith and Licht theory in Figure 1 is incorrect. It must have a slope of $-\frac{1}{2}$ on a plot of log D_{pc} vs. log Q, and therefore be parallel to the lines for the other Type I theories represented.

Our theory was developed for use in the design of industrial size cyclones and without reference to its possible application to the very small cyclones used for respirable dust sampling. We are naturally very interested in any investigation of the relevance of the theory to this small scale of cyclone operation. However, any conclusions drawn from such an investigation must at least be based upon a correct knowledge of our theory.

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SIR: It has come to our attention that there were computational errors in the data presented in Figure 1 in our recent paper (*1*) corresponding to the Leith and Licht theory (*2*). The corrected version is presented here, showing a slope of −0.5 for the Leith and Licht theory.

Although most cyclone theories in Figure 1 seemed useful in predicting performances of air cleaning cyclones, they were shown to be unsatisfactory in describing the collection characteristics in the miniature air sampling cyclones. For the industrial size air cleaning cyclones, the high loading factor improves collection efficiencies due to kinematic coagulation (*3*), but also favors losses due to particle rebound and reentrainment. In contrast, the operating conditions of the air sampling cyclones are quite different since the concentration of the airborne particulates hardly exceeds a few mg/m^3. Particle reentrainment effects were shown to be negligible at dust concentrations below 300 μg/m^3, although particle rebound is probable (*4*). The empirical theory presented in our paper includes these complicating factors.

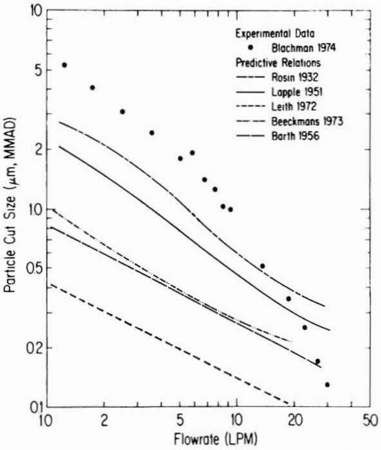

Figure 1. Comparison of experimental data vs. theoretical predictions for 10-mm nylon cyclone.

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

The Leith and Licht theory should be classified under semiempirical theories since the original equation (*5*) includes an empirical constant n, termed the vortex component. The Leith and Licht equation was written as:

$$\eta = 1 - \exp\,[-2(C\psi)^{-1/2n+2}]$$

where C = cyclone design number, ψ = inertial deposition parameter, and n = vortex component.

$$n = 1 - \left[1 - \frac{(0.394\,D_c)^{0.14}}{2.5}\right]\left(\frac{T}{283}\right)^{0.3}$$

We regret the misinterpretations of the Leith and Licht theory which were unfortunately based on faulty arithmetic computations.

Literature Cited

(1) Chan, T., Lippmann, M., *Environ. Sci. Technol.*, **11** (4), 377 (1977).
(2) Leith, D., private communication, 1977.
(3) Fuchs, N. A., "The Mechanics of Aerosols", p 319, Pergamon, New York, N.Y., 1964.
(4) Lippmann, M., Chan, T., *Am. Ind. Hyg. Assoc. J.*, **35**, 189 (1974).
(5) Leith, D., Mehta, D., *Atmos. Environ.*, **7**, 527 (1973).

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INDUSTRY TRENDS

Beckman Instruments, Inc. (Fullerton, Calif.) will install 10 light-duty consoles to measure automobile emissions for Ford Motor Co.

MikroPul Corp. (Summit, N.J.) has been selected to supply a large fabric-filter air pollution control system to Southern Colorado Power. The system, costing almost $1.3 million will handle 12 086 lb/h of fly ash with 99+% efficiency.

Xonics, Inc. (Van Nuys, Calif.) has a $4.5 million EPA contract to operate and maintain EPA air monitoring systems for the Community Health Air Monitoring Program (CHAMP), to provide air quality information in support of epidemiological studies.

AG Brown Boveri & Cie (Baden, Switzerland) has set up a Department for Water Treatment and Environmental Protection, responsible for planning, designing, and building sewage plants based on the latest technology.

Sybron Corp., and **Zurn Industries, Inc.,** have reached an agreement "in principle" to sell Sybron's subsidiary, The Permutit Co., Inc., to Zurn for an undisclosed amount of cash.

Wheelabrator-Frye Inc. will supply a three-field electrostatic precipitator for a paper mill at Willamette Industries (Albany, Oreg.). It will clean 73 000 acfm at a collection efficiency of 99.57%.

Tracor, Inc. (Austin, Tex.) recently delivered 5 Air Pollution Monitoring trailers to the Savannah River Plant of Du Pont. It monitors SO_2, H_2S, and residual sulfurs in air down to parts-per-billion levels. The trailers, costing $20 000 each, were delivered within 90 days of order.

Nichols Engineering and Research, a subsidiary of Neptune International Corp., will build a powdered carbon regeneration plant for CPC International at Argo, Ill., for more than $3.5 million.

Enviro-Systems & Research, Inc. (Roanoke, Va.) has a $138 000 contract to supply its SD-10 Fabric Filter Collector for a coal-fired heating plant at the University of Iowa.

C-E Power Systems (Windsor, Conn.) has a $52 million order from the Texas Municipal Power Agency (Waco) for a 400-MW Texas Lignite-fired steam generator, air quality control system, and related equipment.

WESMAR (Seattle, Wash.) has a large contract to supply liquid level monitors to Metro Water District of Southern California. They work by ultrasonic, non-contact monitoring.

The **National Coal Policy Project** (Washington D.C., *ES&T,* July 1977, p 646) is developing recommendations for application of the new federal strip mine law to northern Appalachian coal.

Monitor Labs (San Diego, Calif.) announced that it has shipped its 1000th Model 8500 Calibrator for air pollution monitoring, and that it has sold more than $3 million worth of them worldwide over the last 5 years.

The **Manufacturing Chemists Association** (Washington, D.C.) is questioning EPA's proposal to regulate benzene as a hazardous air pollutant under Section 112 of the Clean Air Act.

Recon Systems, Inc. (Princeton, N.J.) has substantially expanded its capabilities in industrial wastewater treatment, environmental impact, laboratory services, and related fields.

The **Beverage Industry Recycling Program** (BIRP, Phoenix, Ariz.) has held meetings in New Mexico to see about starting what it hopes can become a national program. The name BIRP is authorized for any state wishing to develop a recycling program through the BIRP system.

Underwriters Laboratories Inc. (Chicago, Ill.) has released the First Edition of its Standard for Flow-Through Marine Sanitation Devices, UL 1119. It is available for $3 at 207 E. Ohio St., Chicago 60611. With future revisions, the price is $8.

IU Conversion Systems (Philadelphia, Pa.) has contracts totaling several million dollars for its Poz-O-Tec scrubber sludge stabilization systems for two electric power plants in Illinois. The system will stabilize 1 million tpy of sludge.

Fluor Corp. has contracts for about $42 million to design, engineer, procure, and construct a proposed 45-MW geothermal power plant using geothermal brine. It will be the largest plant of its kind in the U.S.

The **Willis & Paul Corp.** (Hillsdale, N.J.) will design, supply, and build a fly ash, lime, and limestone handling and stabilized sludge disposal system for the Rural Electrification Administration (Hattiesburg, Miss.).

Zurn Industries, Inc., and **Sybron Corp.** have formally signed an agreement to sell Sybron's subsidiary, The Permutit Co., to Zurn. Terms called for $12 million in cash, with closing in late August.

Process Engineering Co. (Männedorf, Switzerland) will build a plant for the Government of Kenya, Africa, to utilize 60 000 t of local agricultural wastes to produce several basic items for Kenya's food and chemical industries. This will create at least 700 jobs.

National AirOil Burner Co. (Philadelphia, Pa.) has named United Engineering Development & Trading Co., of Kuwait, to represent National AirOil in the Middle East.

The **Buell Emission Control Division** of Envirotech (Lebanon, Pa.) has a turn-key contract for more than $17.9 million for precipitators for two 490-MW generating units in Sullivan County, Ind. They will collect up to 1900 tpd of fly ash.

Research-Cottrell's Metcalf & Eddy Division has received approval to design a 1600-tpd refuse processing facility for Metropolitan Toronto, Canada. The facility is to produce 1200 tpd of fuel, equivalent to 600 tpd of coal.

Combustion Equipment Associates, Inc., has a letter of intent from The Toledo Edison Co., whereby Toledo Edison would purchase CEA's low-sulfur, refuse derived fuel called ECO-FUEL (600 tpd).

M&T Chemical Inc., a subsidiary of American Can Co., will study the feasibility of a low-technology processing plant to recycle newspaper, glass containers, and metal cans, for Garden State Paper Co., Inc.

Apollo Chemical Corp. has recently developed and patented a means whereby the flow of coal ash and slag, and its quick removal from boiler systems, resulting in less unscheduled outages, are enhanced.

Nalco Environmental Services is conducting studies at four fossil-fueled power stations in central New York, for New York State Electric & Gas Corp. The studies, being conducted on central New York waterways, are for proposed plant sites on Lake Ontario and the Hudson River.

Public Service Co. of New Mexico and nine other southwestern utilities have joined together to study the distribution of solar radiation in that region, in order "to match the right equipment to local radiation."

U.S. Ozonair Corp. (South San Francisco, Calif.) will run an $80 000 mobile unit across the U.S. to demonstrate its approach to ozone treatment of water. Capacity is 12–100 gpm.

Met-Pro Systems, Inc. has shipped a pilot water treatment system to San Diego Gas & Electric (21 gpm) for the Sundesert Nuclear Power plant site (Blythe, Calif.). Scale-up to 30 mgd is planned.

Resources Conservation Co. (Seattle, Wash.) will design a multimillion dollar wastewater recovery system (WWRS), and install it at the San Juan Generating Station of Public Service Co. of New Mexico, and Tucson Gas & Electric Co. The WWRS will purify/recycle over 2 mgd.

Peabody International Corp. has reached an agreement with Welltrade Middle East Ltd., to expand testing and inspection services overseas, especially in the Middle East and Africa.

EG&G's Bionomics subsidiary *(ES&T,* April 1976, p 322) has a $1.6 million contract to provide to the EPA special expertise for determining fate and effects of selected chemicals in the aquatic environment.

Dames & Moore (Los Angeles, Calif.) was retained by Wisconsin Power & Light Co. to monitor air quality and conditions along the Wisconsin and Mississippi Rivers, to identify sites potentially suitable for coal-fired power stations.

Alaskan Arctic Gas Pipeline Co. is essentially disbanding, and its member companies plan to consult with and assist organizations aiming to win approval of the Alcan gas pipeline project.

Bob West Associates, Inc. has been formed at Greenwich, Conn., to provide interdisciplinary services to the health care and chemical industries, especially with regard to EPA, FDA, OSHA, and the Toxic Substances Act.

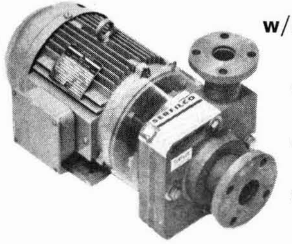
Thermal Processes, Inc. was formed at La Grange, Ill., to supply fluidized-bed combustion equipment to generate steam, hot water, hot air, or high-temperature combustion gases.

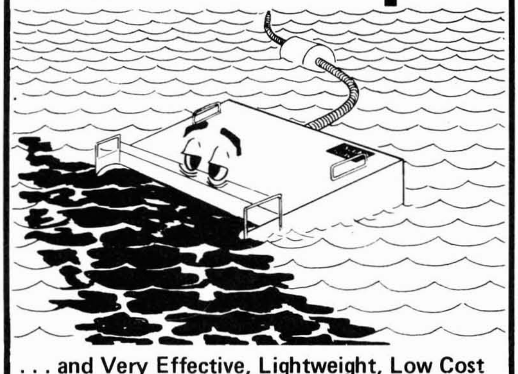
Proler International Corp. is constructing two new processing plants at Randolph, Ariz. One will recover tin from cans and other scrap; the other will convert detinned steel and other light-gauge scrap into precipitation iron.

URS Corp. (San Mateo, Calif.) has completed the design of a 4-level, 65 000-ft^2 solar office building for the Tri-County Metropolitan District of Oregon (Portland). It includes 4500 ft^2 of collectors, and a buried 4500-gal hot water storage tank.

Clow Corp. has provided 48 "Yeoman" surface aerators to treat wastewater at Syracuse, N.Y. Each 100-hp unit will contribute to treating up to 110 mgd when the plant is completed.

The **Electric Power Research Institute** (Palo Alto, Calif.) gave a contract for $4.6 million to San Diego Gas & Electric to support design/construction of the first commercial U.S. power plant to use geothermal hot water for power production.



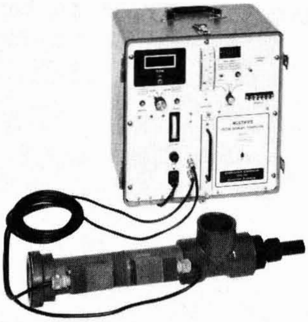


NEW PRODUCTS

Acid mist neutralizer
This additive eliminates sulfuric acid mist and reduces corrosion produced by burning sulfur-containing fuels. The powder additive removes more than twice its weight of sulfur trioxide. Chemed Corp
103

Gas analyzer/monitor
The system is capable of continuously monitoring room or ambient environments for any number of preselected gases for quantitative measurements. Sensitivity is in ppm range. An alarm system is available as an option. CVC Products 108

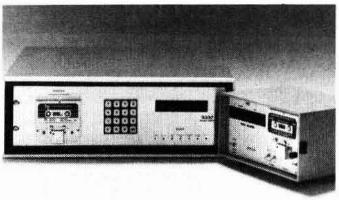
Liquid sampler
This surface sampler is suitable for sampling, measuring and analyzing oil slicks on the surface of liquids. The device can also be used to sample sewage treatment tanks. This surface sampler is an accessory to the company's oil recovery system. Oil Recovery Systems 115



Flowmeter
Designed specifically for open channels or sewers, this system consists of a fully sealed flow tube containing permanently mounted ultrasonic transducers, and a computer that provides flow indication, recording, totalization and sampler control. The flow tube is available in sizes to accommodate sewer pipes from 4–48 in. Controlotron Corp. 101

Flocculant
The high-molecular weight polymer was designed for activated sludge conditioning prior to dewatering. It is supplied in a soluble micro-bead form. Allied Colloids
102

High temperature RO
This reverse osmosis system is capable of operation on feed waters with temperatures of up to 130 °F. The permeate rate is 15 gpm. The system will find application in potable water production and wastewater recycling of water. Osmonics
104



Microprocessor
This data acquisition system is designed for the collection of air quality and meteorological data. During programmed operation, the unit samples analog or BCD inputs every 30 s, accumulates the samples for 1-h periods, averages the data, computes wind vector, records data on tape and serially "outputs" the data for remote transmission. Martek Instruments
105

Standby pulpit
This 8-man welded steel enclosure, specifically for use by coke battery personnel, incorporates a HEPA-type power filter and an air conditioner that comply with OSHA coke oven emission standards. James Campbell Smith 106

Cyclone preseparator
Samples wind-blown dust from coal storage piles and roadway construction sites. The unit attaches to the holder of standard hi-vol samplers and collects all particles greater than 5 μ in diameter. Particles less than 5 μ pass through the cyclone to be collected on the hi-vol filter paper. Sierra Instruments 107

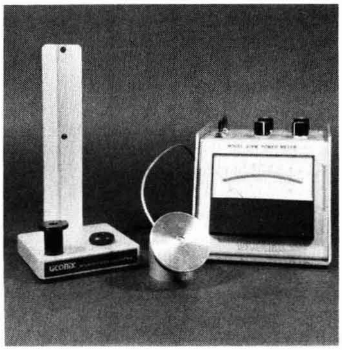
Arsine/phosphine monitor calibrator
The device verifies the proper operation of the arsine/phosphine monitor that continuously monitors the air for these gases and signals an alarm when toxic levels are reached. Matheson 109

Flow monitoring system
The ultrasonic flow monitor, consisting of a sensor and electronics in separate enclosures, monitors and records the volume of flow and takes water samples. The sensor, mounted above a flume, weir, pipe or channel, acts as a transmitter/receiver. Environmental Measurement Systems 110

Water demineralization plant
The systems consists of a membrane stack or stacks and a factory-assembled steel skid containing the dc power supply/control unit, feed water filter, pumps, valves and other hydraulic equipment. It produces 100 000–264 000 U.S. gal/d of fresh water from brackish water. Ionics
111

LC/MS interface
The interface can be used to combine liquid chromatograph and mass spectrometer systems. It permits a choice of electron impact or chemical ionization and does not interfere with GC/MS or solid probe studies. It is especially useful in the mass spectral analysis of pesticides and polycyclic aromatic compounds. Finnigan
112

Portable pH recorder
The instrument, only 15 lb, features three selectable pH ranges, an 8-in. circular chart and a peripheral junction-type electrode. The instrument can be field calibrated for proper operation. Manning Environmental Corp. 113



Solar power meter
Designed to measure the power of normally incident solar radiation, the meter is expected to be valuable to workers in the field of solar power conversion. Readout in kilowatts/meter squared is displayed on an analog scale. The meter is also calibrated to read laser power at three wavelengths. LiCoNix 114

Filtration media
Available in felt and fabric forms, the "Teflon" filtration media offers high-heat resistance, excellent release properties and excellent chemical and flex-fatigue resistance, according to the manufacturer. It can be used to collect titanium dioxide and carbon black, and to remove fly ash in power generation baghouses. Du Pont 116

Thermal reductor
The conically-shaped rotating ignition chamber thermally oxidizes the waste stream while continuously discharging noncombustible material. The resultant gases are re-ignited in a secondary combustion chamber and channeled to a waste heat boiler before being scrubbed. The unit can dispose of gases, liquids, solids and sludges. Stack emissions are pollution-free. Progressive Equipment Co.
117

Turbidimeter
This laboratory turbidimeter features a digital readout of JTU/ppm silica measurements and is insensitive to color and color changes in the fluid. Resolution is 0.01 JTU/ppm and dynamic range is 0–1000 JTU/ppm. Monitek **118**

Oxygen/toxic gas monitor
Simultaneously measures the concentration of oxygen in the atmosphere and, cumulatively, a specific toxic gas. Currently hydrogen sulfide can be detected, but carbon monoxide, chlorine, sulfur dioxide and ammonia detection sensors are under development. When oxygen levels fall below 17% concentration, an audible alarm and a flashing yellow light are activated. Neotronics Ltd. (England) **119**

Dust abatement compound
Composed of soluble resins, penetrants and plasticizers, this product, when diluted with water, can be sprayed, fogged, painted or drenched on surfaces to control dust. Easton R/S Corp. **120**

Continuous level indicator
The indicator is designed to provide continuous level indication for solids or liquids with stable dielectric constants. Measuring range (span) is 10–4000 pf and temperature range is 0–140 °F or −20 to 60 °C. Endress and Hauser **121**

Top feed centrifuge
This fully automated sludge dewatering centrifuge is capable, according to the manufacturer, of dewatering a variety of waste sludges with little or no polyelectrolyte treatment. De Laval Separator Co. **122**

Organic vapor dosimeter
This dosimeter meets OSHA standards for benzene monitoring. It is accurate at concentrations of benzene of 1 ppm. The clip-on pocket unit contains an activated carbon collection element that is removed for analysis by NIOSH-recommended procedures. The dosimeter can be refilled with a new collection element and reused. Abcor, Inc. **123**

Spectrophotometer
The instrument, a UV/visible double-beam ratio-recording grating unit, provides spectral analysis in the 195–800 nm range. Six forward scan speeds permit high resolution and rapid survey recording. Two selectable response times are provided and bandpass is adjustable in four steps. Perkin-Elmer **127**

Soil stabilizing membrane
This polypropylene filter fabric can control water seepage rate and prevent the passage of fine particle sand or soil without clogging under varying water flow conditions. It has high tensile and burst strength, and is chemically resistant to fresh or salt water, and to alkaline or acid soil conditions. Staff Industries **124**

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

Tubular filter
Constructed of stainless steel, the filter is rated to 300 psig, 300 °F. It can be cleaned manually or by shock backwashing. The Duriron Co. **133**

Speed reducer system
Specifically designed for application in wastewater treatment plants, the units reduce motor speed and convert horsepower to the torque capacity required to drive aeration, clarifying, and solids handling processes. Ex-Cell-O corp. **129**

Sludge level detector
The sealed detector combines an optical sensing head with a solid-state audio signal receiver to provide audible indication of sludge and slurry levels in water and wastewater treatment plants. Keene Corp. **128**

Adsorbent
These non-dusting dry carbonaceous beads are purported to remove and recover organic chemicals from fluids. They were designed to serve as an alternative to activated carbon and polymeric adsorbents. Rohm and Haas **130**

NEW LITERATURE

Advanced wwt. Bulletin 17.71 describes packaged wastewater treatment (wwt) system for liquids-solids separation. Typical users are electroplaters, automotive and electronics plants, and the like. Crane Co. **151**

Products from starch. "Guide to Starch Processing Product Possibilities" lists numerous products that can be made from starch for many applications. Stone & Webster **152**

Air doors. Brochure describes air doors that can keep air from entering or escaping, and can, among other things, exclude insects, dust, dirt, and fumes. Temperature can be controlled. Mars Air Doors **153**

Organic vapors. Bulletin 769 outlines OSHA-recommended methods for determining organic vapors in the industrial atmosphere. These methods are outlined in great detail. Supelco, Inc. **154**

Glassware. Catalog 700 is a 464-page listing of scientific glassware. Included are items for chromatography and pollution control. Many connections use no grease. Ace Glass Inc. **155**

Waste screens. Bulletin 12000 describes broad line of "Link-Belt" screens for water, sewage, and industrial waste. Facilities for large and small solids are listed, as are degritters. FMC Corp. **156**

Jet-type filters. Bulletin EMT-077-F1 describes EMTROL line of advanced pulse jet type filters for air pollution control and product recovery. Applications in pulp/paper, coal, minerals, others. Emtrol Corp. **157**

Fuel conditioning. Brochure lists fuel additives for oil-fired boilers, diesel engines, and gasoline turbines. Increase efficiency, reduce particulates, smoke, corrosion. Uses manganous amine complex. The Rolfite Co. **158**

Energy recovery. Bulletin 54-100M lists a line of pyrolytic incinerators that can be equipped with optional energy recovery systems. Company says that landfill disposal problems can be virtually ended. Kelley Co. Inc. **159**

Scale inhibition. Bulletin No. 502 describes corrosion- and scale-inhibiting programs for cooling water systems with non-polluting chemical products. Services are also described. Zimmite Corp. **160**

Refuse handling safety. ANSI booklet tells how company's waste handling equipment can meet ANSI Z245.1-1975 safety standards. All levels of the industry are concerned. Marathon Equipment Co. **161**

Precipitator controls. Brochure GEA-9607A tells about maximum efficiency, improved protection, and quick start-up capabilities of the precipitator control, as well as safe, easy adjustment. General Electric Co. **162**

Resource recovery. Brochure, "Resource Recovery and Energy Systems", describes 4-step program for a resource recovery system to help solve growing solid waste problems. Combustion Engineering, Inc. **163**

Granular media filters. Bulletin 900 lists virtually all types of commercially available granular media filters for industrial waste and process water recycle. Ecodyne Corp. **164**

Treatment plants. Brochure describes "Activator" modular prestressed concrete wastewater treatment plants. Modular design permits future expansion; plant uses activated sludge. Pollution Control, Inc. **165**

Groundwater protection. Brochure describes impervious, concrete-like mixture that can prevent seepage into groundwater or surface waters by means of Underground Pollution Barriers. ChemBar, Inc. **166**

Precipitators. Fifty-page brochure provides a complete discussion of electrostatic precipitators. There is also an international system of units, glossary, and keyword index. United McGill Corp. **167**

Oil skimmers. Bulletin OS-5 details the Series 7000 Oil Skimmers and their ability to recover floating oils from water and other liquids. Works on oils of almost all viscosities. Met-Pro Systems, Inc. **168**

Thermal processes. Bulletin SC-230 lists thermal processes for environmental/energy control/recovery; airless solvent drying; sludge disposal; solid waste pyrolysis; and many other applications. Midland-Ross Corp. **169**

Respirators. Data Sheet 10-00-05 gives detailed information in respirators to protect workers against certain air pollutants during welding, and similar operations. Mine Safety Applicances Co. **170**

Municipal water treatment. Bulletin 5890 lists water impurities in source supplies, together with recommended municipal treatment methods. Flow diagrams are given. The Permutit Co., Inc. **171**

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

Slime control. "Application of HTH Dry Chlorine Granular in Industrial Plants" tells how dry chlorine granular controls slime, bacteria, and certain toxic pollutants in industrial water operations. Olin Corp. **172**

Corrosion-resistant pumps. Bulletin 330 lists a series of corrosion-resistant plastic horizontal pumps. Full specifications and technical details are provided. Sethco Mfg. Corp. **173**

Chemical pumps. General Bulletin 477 lists pumps for various chemical feed systems. Neptune Chemical Pump Co. **174**

Sludge drying. Bulletin No. D-73389-477 tells how the rotary dryer can reduce sludge moisture from 80–90% to 5–10%. Only 1500 Btu evaporated 1 lb of water. Solid wastes or waste heat can power the system. The Heil Co. **175**

Fabric filters. "ENELCO Pulse Jet Fabric Filters" explains how coal-burning, metal-producing, and other industry emissions are controlled. Much data are given. Environmental Elements Corp. **176**

Chlorine leaks. Bulletin 11030 describes the ADVANCE chlorine leak detector with remote sensing, no need for chemicals, fail-safe devices, and other features. Capital Controls Co. **177**

Combustion control. "Oxygen Trim for Combustion Control" tells how correct control of oxygen input can reduce economic loss and pollution. Can be used on new and existing systems. Reliance Instrument Mfg. Corp. **178**

Monitoring station. Flyer sheet depicts and describes fully instrumented station for housing air quality or other monitors on a short-term basis. Ample work space. Radian Corp. **179**

Sludge injection. Brochure tells how sludge with up to 8% solids can be subsurface-injected, and how that is an environmentally and economically feasible alternative. Briscoe-Maphis Environmental **180**

Odor control. Form No. 423-ADV illustrates and describes a full line of immediately available odor control units. They use activated carbon and other adsorbents, and have many applications. Zurn Industries, Inc. **181**

Water intakes. Brochure describes static screen designs for water intake that minimize plugging and the need for cleaning. Fully submersible. Full siting freedom. Johnson Division, UOP Inc. **182**

BOOKS

Solar Energy: Technology and Applications. J. Richard Williams. 176 pages. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1977. $9.95, hard cover.

This book is a revised edition that discusses many solar energy aspects. It tells how to build a heating/hot water system, and how to select the proper collectors. It also discusses industrial and agricultural applications, air conditioning, ocean-thermal power, wind, geosynchronous power plants, and other timely topics.

Environmental Impact Assessment. Larry W. Canter. xiv + 331 pages. McGraw-Hill Book Co., 1221 Ave. of the Americas, New York, N.Y. 10020. 1977. $16.50, hard cover.

The National Environmental Policy Act says that just about any project on which one wishes to embark must be preceded by an Environmental Impact Statement (EIS). This book discusses the Act, and sets forth detailed instructions for the correct preparation of an EIS.

Energy from Bioconversion of Waste Materials. Dorothy J. De Renzo. ix + 223 pages. Noyes Data Corp., Mill Rd. at Grand Ave., Park Ridge, N.J. 07656. 1977. $32, hard cover.

Energy from sludge—methanation of urban trash, animal waste digestion—all these are technologies under scrutiny. But what is the latest state-of-the-art in this field? What materials does one use? This book covers the latest technology and practice in bioconversion.

Chemical Reactions as a Means of Separation: Sulfur Removal. Billy L. Crynes, Ed. ix + 345 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, N.Y. 10016. 1977. $29.75, hard cover.

This work completely addresses the removal of sulfur in energy processing industries. It covers scrubbers, tail gases, coal gases, coal liquefaction, "resid", and stock gases. Technology is covered exhaustively.

Energy Technology Handbook. Douglas M. Considine, Ed. xxvii + 1857 pages. McGraw-Hill Book Co., 1221 Ave. of the Americas, New York, N.Y. 10020. 1977. $49.50, hard cover.

"You name it, this book has it." Petroleum, gas, coal bioconversion, chemical fuels, nuclear, solar, geothermal—they are all covered. Environmental problems arising from energy production/use are also extensively discussed.

Environmental Chemistry. J. O'M. Bockris, Ed. xi + 795 pages. Plenum Publishing Co., 227 W. 17th St., New York, N.Y. 10011. 1977. $49.50, hard cover.

This work discusses interactions between pollutants and air and water. It also covers exhaustive consumption of natural resources; development of non-polluting forms of energy; political aspects; sewage treatment; food source development; and monitoring. Many other related and pertinent subjects are discussed.

Animal Wastes. E. Paul Taiganides, Ed. xvi + 429 pages. Applied Science Publishers Ltd., 22 Rippleside Commercial Estate, Barking, Essex, England. 1977. $50, hard cover.

Animal wastes are a formidable nuisance and water pollution source. They can spread disease. But they can also be a fine source of compost and fertilizer, as well as a medium for producing gaseous fuels. This book covers all of these ramifications of animal wastes, and is an outgrowth of a symposium on the subject, held at Bratislava, Czechoslovakia.

Environmental Law Handbook, 4th ed. J. Gordon Arbuckle et al. 350 + pages. Government Institutes, Inc., 4733 Bethesda Ave., Bethesda, Md. 20014. 1977. $33.50, hard cover.

What is the latest environmental law and legal terminology? This book treats those subjects, and discusses NEPA, water/air pollution control, land use, pesticides, hazardous materials, toxics, noise, and solid waste/resource recovery. It tells what the law "really says."

Mercury Contamination: A Human Tragedy. Patricia A. and Frank M. D'Itri. xxii + 311 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1977. $17.95, hard cover.

Remember Minamata Disease? The mysterious epidemic in Iraq? Mercury contamination was at the root of these, and other episodes. This book explains the mechanism of mercury (methylmercury) contamination and poisoning, and its origins. It also offers recommendations as to how citizens and government agencies can combat this menace.

Manpower For Environmental Pollution Control. xxiv + 443 pages. Printing and Publishing Office of the National Academy of Sciences, 2101 Constitution Ave., N.W., Washington, D.C. 20418. 1977. $11.25, paper.

Here is a publication that looks closely at availability of personnel, where they are needed, and rationales for personnel policy. It is the outgrowth of a long, in-depth study chaired by Earnest Gloyna, and coordinated for the Academy's National Research Council by Stanton Ware (*ES&T,* March 1976, p 222).

Water and Waste Treatment Data Book. xvi + 143 pages. The Permutit Co., Inc., E49 Midland Ave., Paramus, N.J. 07652. 1977. $3, ring-bound.

This revised edition contains up-dated charts and sections of data for practicing engineers, and others who work in water and wastewater treatment. It includes the most current technology in practical use. For more information, contact A. W. Pieper.

Marine Pollution. R. Johnston, Ed. xiv + 729 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1977. $51, hard cover.

Marine pollutants are many and varied. This book looks at the problems they engender, discusses heavy metals, sewage, legal controls, and other related topics. Pipeline discharges, oil spills, inputs from the air, and mineral resource exploitation are also covered, as are marsh and deep-sea habitats.

Solid Wastes. George Tchobanoglous, Hilary Theisen, Rolf Eliassen. xv + 621 pages. McGraw-Hill Book Co., 1221 Ave. of the Americas, New York, N.Y. 10020. 1977. $22, hard cover.

The technology of solid waste management is rapidly changing and expanding. This book discusses this progress, examines necessary engineering principles, and looks at essential management issues in depth. Problems are worked out in a step-by-step format.

Advances in Environmental Science and Technology. Vol. 7. James N. Pitts et al., Eds. 520 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1977. $30, hard cover.

This volume discusses new perspectives on pollution control. It also looks into vehicular emissions and their control; fate of NO_x and H_2S; environmental health assessment: and statistical models. Other pertinent topics of air pollution control, including photochemical smog and economics of enforcement, are also covered.

Particulates and Fine Dust Removal: Processes and Equipment. Marshall Sittig. xv + 605 pages. Noyes Data Corp., Mill Rd. at Grand Ave., Park Ridge, N.J. 07656. 1977. $48, hard cover.

What is the latest technology in this field? This book gives a complete answer to that question, and emphasizes reduction of such emissions at the source. Complete, up-to-date information concerning the nature of the problem, and practical technology and patents aiming at its solution are given.

MEETING GUIDE

October 16–19 Los Angeles, Calif.
Oceans '77. Oceans '77 Headquarters

Conference will explore developing technology and its impact on public policy with a focus on the Pacific rim. *Write:* Oceans '77, Suite 504, 615 S. Flower St., Los Angeles, Calif. 90017

October 17–19 Richland, Wash.
17th Hanford Biology Symposium. ERDA and Battelle Memorial Institute/Pacific Northwest Laboratories

Theme is "Developmental Toxicology of Energy-Related Pollutants." *Write:* Mrs. Judith A. Rising, symposium secretary, Biology Dept., 331 Bldg., Battelle-Northwest, Richland, Wash. 99352

October 17–19 Hampton, Va.
Noise-Con 77. NASA Langley Research Center/NASA and the Institute of Noise Control Engineering

Write: Conference Secretariat, Noise-Con 77, P.O. Box 3469, Arlington Branch, Poughkeepsie, N.Y. 12603

October 17–20 Niagara Falls, N.Y.
ISA/77 Fall Industry-Oriented Conference and Exhibit. Instrument Society of America

There will be sessions on the automatic control of municipal wastewater treatment, and automatic control of municipal water supply. *Write:* Peter Vestal, ISA/77, 400 Stanwix St., Pittsburgh, Pa. 15222

October 17–20 Washington, D.C.
91st Annual Meeting. Association of Official Analytical Chemists

Environmental topics will be discussed. *Write:* L. G. Ensminger, executive secretary, AOAC, Box 540, Benjamin Franklin Station, Washington, D.C. 20044

October 17–21 San Francisco, Calif.
ASCE Annual Convention and Exposition. American Society of Civil Engineers (ASCE)

Environmental topics will be discussed. *Write:* ASCE, 345 E. 47th St., New York, N.Y. 10017

October 18–20 Louisville, Ky.
NCA/BCR Coal Conference and Expo IV. National Coal Association and Bituminous Coal Research, Inc.

Write: National Coal Association, 1130 17th St., N.W., Washington, D.C. 20036

October 18–20 Detroit, Mich.
Finishing '77. Association for Finishing Processes of the Society of Manufacturing Engineers (AFP/SME)

Environmental topics will be discussed. *Write:* AFP/SME, 20501 Ford Rd., P.O. Box 930, Dearborn, Mich. 48128

October 20–21 Myrtle Beach, S.C.
Ninth Annual Carolinas Air Pollution Control Association's Fall Technical Sessions and Equipment Show. Carolinas Air Pollution Control Association (CAPCA)

Write: Don O'Gormann, 2600 Bull St., 203 Sims Building, Columbia, S.C. 29201

October 23–28 St. Simons Island, Ga.
Storage for Solar Energy and Transportation Applications. Engineering Foundation

Write: Engineering Foundation Conferences, 345 E. 47th St., New York, N.Y. 10017

October 24–28 Tucson, Ariz.
International Conference on Energy Use Management. Energy Use Management Conference

Write: Energy Use Management Conference, P.O. Box 64369, Los Angeles, Calif. 90064

October 26–27 Stateline, Nev.
6th Annual Lake Tahoe Wastewater Treatment and Water Reuse Seminar. Culp, Wesner, Culp

Write: Culp, Wesner, Culp, Box 40, El Dorado Hills, Calif. 95630

October 30–November 3 Washington, D.C.
Annual Meeting. American Public Health Association

There will be a session on "Environmental Impact on Human Health." *Write:* American Public Health Association, 1015 18th St., N.W., Washington, D.C. 20036

October 31–November 1 Miami, Fla.
Energy and the Oceans. Institute on Man and the Oceans

Write: Thomas R. Post, Institute on Man and the Oceans, Inc., P.O. Box 012436, Flagler Station, Miami, Fla. 33101

October 31–November 3 Tucson, Ariz.
13th American Water Resources Conference. American Water Resources Association (AWRA)

Write: Daniel D. Evans, Ph.D., Dept. of Hydrology and Water Resources, University of Arizona, Tucson, Ariz. 85721

October 31–November 4 Gatlinburg, Tenn.
2nd Conference on Water Chlorination: Environmental Impact and Health Effects. Oak Ridge National Laboratory, ERDA and the EPA

Write: Robert L. Jolley, Chemical Technology Division, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tenn. 37830

November 1–3 Pittsburgh, Pa.
38th International Water Conference. Engineers' Society of Western Pennsylvania

Write: Engineers' Society of Western Pennsylvania, William Penn Hotel, 530 William Penn Place, Pittsburgh, Pa. 15219

November 1–3 Atlanta, Ga.
International Pollution Engineering Congress. Clapp & Poliak, Inc.

Write: Clapp & Poliak, Inc., 245 Park Ave., New York, N.Y. 10017

November 1–3 Cincinnati, Ohio
Fifth National Conference on Energy and the Environment. American Institute of Chemical Engineers, the Air Pollution Control Association and others

Write: Dr. Edmund J. Rolinski, Air Force Materials Laboratory, AFML/LPJ, Wright-Patterson Air Force Base, Ohio 45433

November 2–4 Augusta, Ga.
Energy and Environmental Stress in Aquatic Systems. Savannah River Ecology Laboratory

Write: James H. Thorp, III, symposium chairman, Savannah River Ecology Laboratory, Drawer E, Aiken, S.C. 29801

November 3 Cherry Hill, N.J.
2nd Annual New Jersey and Pennsylvania Water Pollution/Treatment/Test Seminar. Rossnagel & Associates

Write: Mrs. M. Hanna, Rossnagel & Associates, 1999 Rt. 70, Cherry Hill, N.J. 08003

November 3–4 New York, N.Y.
The Outlook for Natural Gas. The Energy Bureau

Write: Robert W. Nash, executive director, The Energy Bureau, Inc., 101 Park Ave., New York, N.Y. 10017

November 3–4 Arlington, Va.
Environmental and Safety Briefing Sessions. The Bureau of National Affairs, Inc.

Write: Briefing Conference Secretary, Bureau of National Affairs, Inc., Room 413, 1231 25th St., N.W., Washington, D.C. 20037

November 3–4 Bangor, Me.
Northern New England Environmental Control Exposition. Gorham International

Write: Alvin G. Keene, Gorham International Inc., Gorham, Me. 04038

November 3–5 Seattle, Wash.
Third Annual Meeting. The Coastal Society

Theme is "Energy Across the Coastal Zone." *Write:* M. L. Schwartz, Dept. of Geology, Western Washington State College, Bellingham, Wash. 98225

November 4 West Chester, Pa.
Dual Water Supply for Urban Water Management. Weston Corp.

Write: Dr. Arun K. Deb, director, Dual Water Supply Seminar-Workshop, Weston, Weston Way, West Chester, Pa. 19380

(continued on page 1030)

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for water pollution control publications. Environmental engineering or related degree required. Publications experience desirable (writing, editing, manuscript evaluation). Responsibilities commensurate with qualifications. Send resume and salary requirements to: **Editor, Water Pollution Control Federation, 2626 Pennsylvania N.W., Washington, D.C. 20037.**

Air Pollution Control Director

REQUIRES: B. S. Degree in Engineering, Chemistry, or allied field with 5 years experience in the field of air pollution control. Responsible for engineering, field enforcement, administrative and technical services provided by a staff of 13. All inquires confidential. Send resume and salary requirements, before December 1, 1977, to: **Director of Administration, Canton City Health Department, Canton, Ohio 44702**

The Department of Civil Engineering, University of Illinois at Urbana-Champaign invites applications for an assistant professorship in environmental engineering. Applicants preferably should have advanced training in the principles of reactor analysis and design and the physical and chemical principles of water quality control processes. Research competence in the chemical and/or physical aspects of water quality control is desired. Individuals with research and teaching competence in the area of aqueous chemistry associated with air pollution control processes will also be considered. A Ph.D. degree is required.

Duties will involve teaching a graduate course in water quality control processes as well as undergraduate courses in water quality and pollution and water quality control processes. The successful candidate will be expected to develop and supervise research in his area of interest and advise graduate students in the same area.

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Resumés should be addressed to **Dr. C. P. Siess, Head, Department of Civil Engineering, University of Illinois at Urbana-Champaign, 1114 Civil Engineering Building, Urbana, Illinois, 61801. Phone (217) 333-3924.**

ENVIRONMENTAL SCIENTIST—Background in aquatic Biology, M.S. required, 2–3 years experience with industrial problems. Duties to include preparation of environmental reports, conducting field studies, and project management. Submit resume to **R. Francis, Envirodyne Engineers, 12162 Lackland Road, St. Louis, Mo. 63141.**

MEETING GUIDE *(continued)*

November 6–8 Washington, D.C.
The Role of Utility Companies in Solar Energy Utilization. Institute of Gas Technology (IGT)

Write: Wendell W. Waterman, IGT, 3424 S. State St., Chicago, Ill. 60616

November 6–11 New Orleans, La.
4th Joint Conference on Sensing of Environmental Pollutants. American Chemical Society, EPA, ERDA and others

Write: Mrs. Barbara R. Hodsdon, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036

November 7–8 Washington, D.C.
NEPA Conference. Environmental Law Institute

Write: Joan Habib or Karla Heimann, Environmental Law Institute, 1346 Connecticut Ave., N.W., Suite 620, Washington, D.C. 20036

November 7–11 Detroit, Mich.
FACSS IV. Federation of Analytical Chemistry and Spectroscopy Societies

Environmental topics will be discussed. *Write:* Mitch Kapron, Ethyl Corp., 1600 W. Eight Mile Rd., Ferndale, Mich. 48220

November 7–11 Seattle, Wash.
20th Navy Occupational Health Workshop. Dept. of the Navy

Write: Navy Environmental Health Center, 3333 Vine St., Cincinnati, Ohio 45220

November 8–9 Washington, D.C.
First Annual International Conference on Energy. Energy Magazine

Write: Energy Magazine, P.O. Box 2070C, Stamford, Conn. 06906

November 8–10 Chicago, Ill.
Energy Efficiency in Wood Building Construction. Forest Products Research Society (FPRS)

Write: Connie Walling, FPRS, 2801 Marshall Court, Madison, Wis. 53705

November 8–11 Hollywood, Fla.
Symposium on Flue Gas Desulfurization. EPA

Write: Franklin Ayer, Research Triangle Institute, P.O. Box 12194, Research Triangle Park, N.C. 27709

November 13–17 New York, N.Y.
70th Annual Meeting. American Institute of Chemical Engineers (AIChE)

There will be a session on "Fluidization of Large Particle Systems." *Write:* AIChE, 345 E. 47th St., New York, N.Y. 10017

Courses

October 17–28 Austin, Tex.
Design of Fixed Offshore Platforms. University of Texas at Austin/College of Engineering

Environmental considerations will be discussed. Fee: $625. *Write:* Registrar, Fixed Offshore Platform Design Program, c/o Engineering Institutes of the College of Engineering, Cockrell Hall 2.102, University of Texas at Austin, Austin, Tex. 78712

October 19–20 Madison, Wis.
Second Annual Municipal Sludge Management Institute. University of Wisconsin–Extension

Fee: $125. *Write:* Vitte V. Yusas, program director, Dept. of Engineering, University of Wisconsin–Extension, 432 N. Lake St., Madison, Wis. 53706

October 20–21 Los Angeles, Calif.
Environmental Law Course. Government Institutes, Inc. (GII)

Fee: $320. *Write:* Nancy McNerney, GII, 4733 Bethesda Ave., N.W., Washington, D.C. 20014

October 26–28 Washington, D.C.
Financing Energy Conservation Opportunities in Existing Buildings. The George Washington University

Fee: $370. *Write:* Director, Continuing Engineering Education, The George Washington University, Washington, D.C. 20052

October 31–November 4 Austin, Tex.
Advanced Water Pollution Control. The University of Texas at Austin/College of Engineering

Fee: $300. *Write:* Engineering Institutes, College of Engineering, Cockrell Hall 2.102, The University of Texas at Austin, Austin, Tex. 78712

November 1–4 Pittsburgh, Pa.
Practical Mass Spectrometry. Extranuclear Laboratories, Inc.

Fee: $395. *Write:* Jody Kelsey, manager, Dept. of Administration, Extranuclear Laboratories, Inc., P.O. Box 11512, Pittsburgh, Pa. 15238

November 15–17 Washington, D.C.
Industrial Noise Control. George Washington University

Fee: $365. *Write:* Martha Augustin, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

November 14–18 Cambridge, Mass.
4th Special Workshop on Acoustical Modeling. Massachusetts Institute of Technology

Fee: $500. *Write:* Special MIT Workshop on Acoustical Modeling IV, Room 9-335, Center for Advanced Engineering Study, Massachusetts Institute of Technology, Cambridge, Mass. 02139

Call for Papers

October 15 deadline
Third Annual Conference on the Treatment and Disposal of Industrial Wastewaters and Residues. Hazardous Materials Control Research Institute, University of Houston, American Institute of Chemical Engineers and Information Transfer Inc.

Conference will be held March 14–17, 1978. *Write:* Treatment and Disposal of Wastewaters Conference, c/o Hazardous Materials Control Research Institute, 1160 Rockville Pike, Suite 202, Rockville, Md. 20852

Environmental Specialists

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Aquatic Ecology Specialist

Advanced Degree in Ecological Sciences with specific orientation toward aquatic ecology with coursework in biostatistics and chemistry and 5 years experience in conducting aquatic ecology studies of thermal electric generating plants is required. You must be familiar with regulatory procedures. You will help determine the need for and develop ecological information acquisition programs undertaken to assess the impact of power plant construction and operation.

Environmental Health Specialist

Bachelor's Degree in a Biological/Physiological/Medical Science discipline with specific orientation toward Environmental Health (Advanced degree preferred) and 5 years of related industrial experience is required. Experience in the electric power industry is preferred. You will participate in the design, evaluation, coordination and direction of Environmental Health Studies oriented toward acquisition of permits for construction and operation of power generating facilities and in the selection of consultants for such studies.

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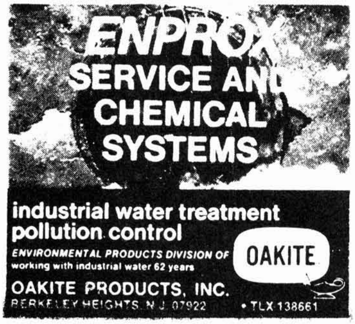

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