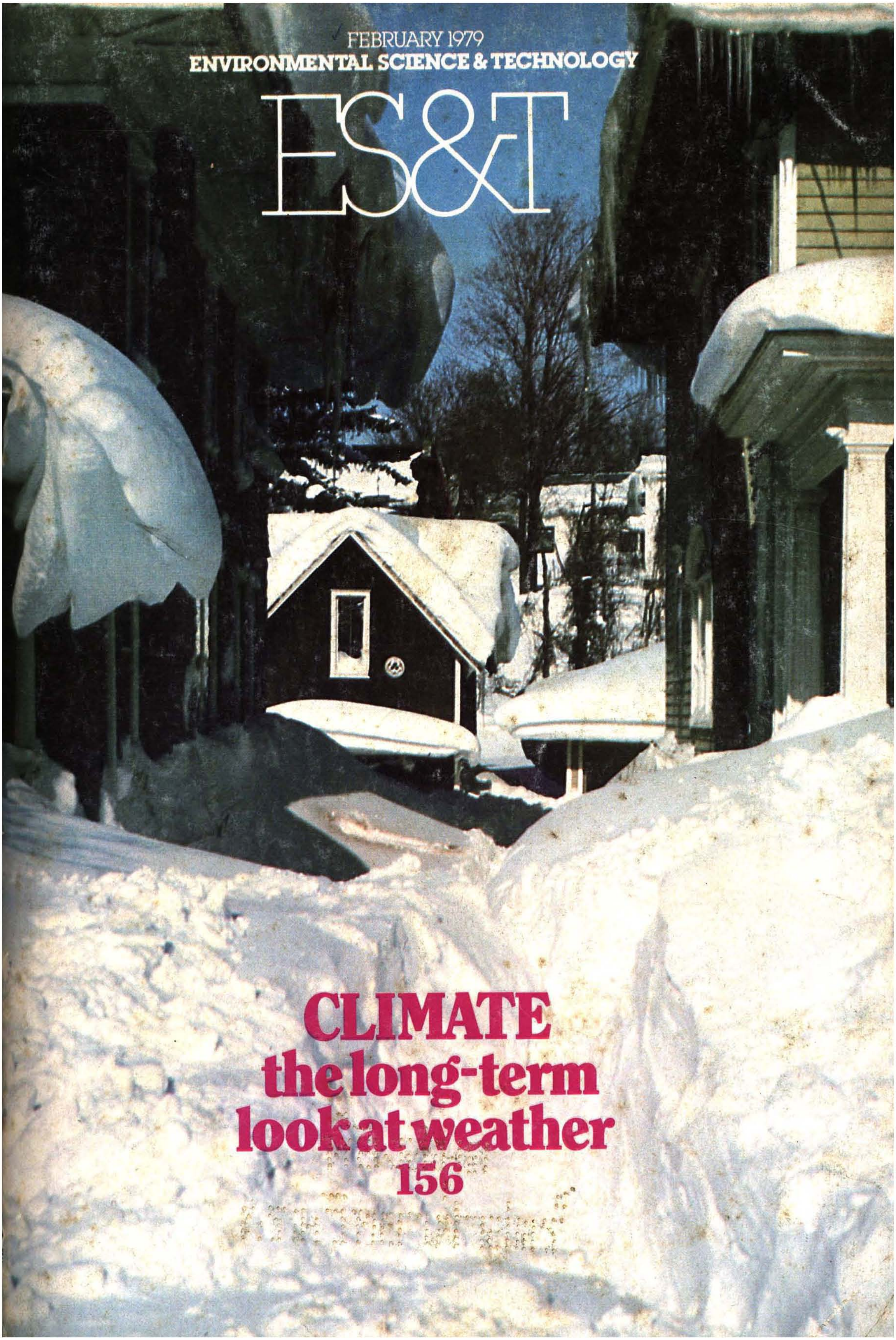
FEBRUARY 1979
ENVIRONMENTAL SCIENCE & TECHNOLOGY

# ES&T



## CLIMATE the long-term look at weather

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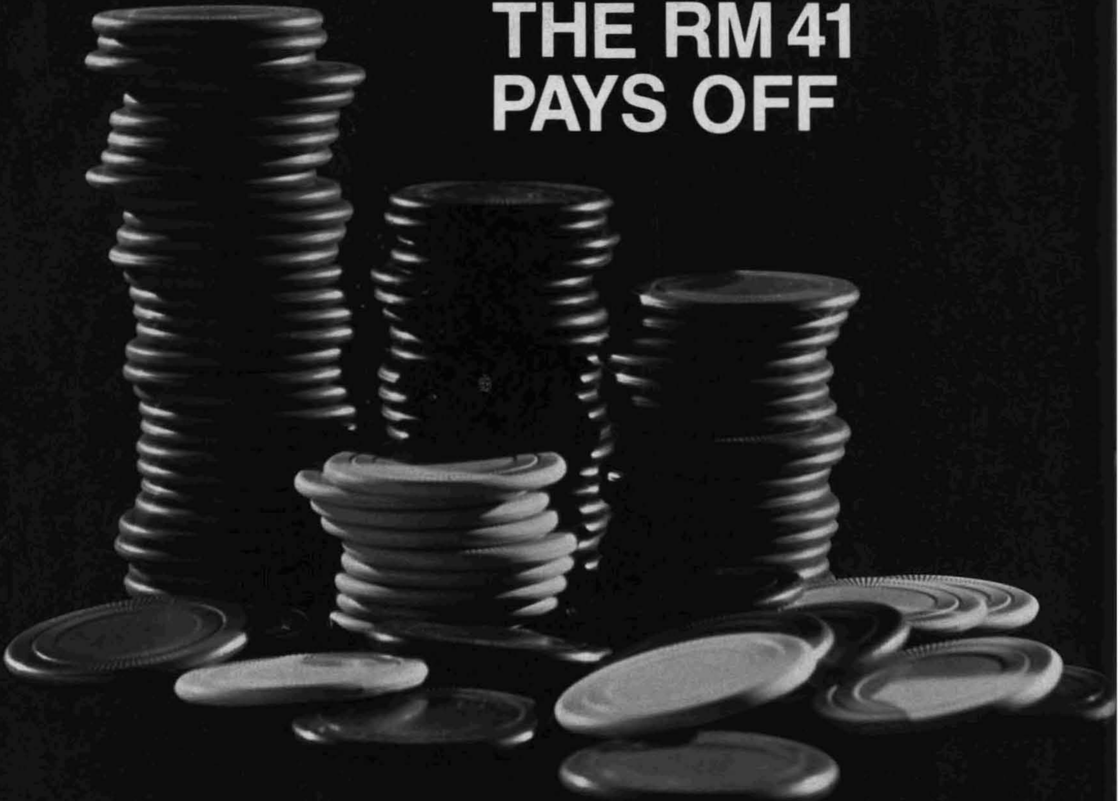
# THE RM 41 PAYS OFF



*Based on initial investment, LSI's RM41 Opacity Monitor costs a little more ... But, based on performance, it pays off. And, the pay off isn't a result of luck, it's a result of design.*

*For example:*

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You can expand to a full stack monitoring capability without costly modifications. Plus, our RM41's have demonstrated many times their ability to interface with our DP30 or your computer, allowing for easy conversion to EPA required data with minimum manpower.

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*...Lear Siegler Cares*

CIRCLE 3 ON READER SERVICE CARD


ERT NEWSLETTER
TOTAL MONITORING SYSTEMS AND SERVICES

ES&T

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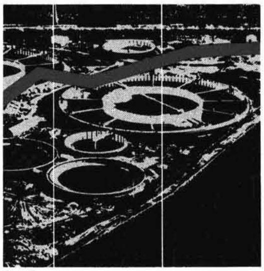

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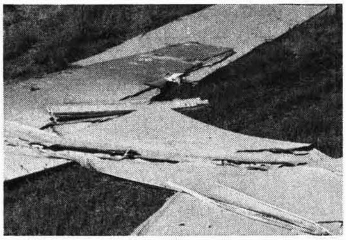

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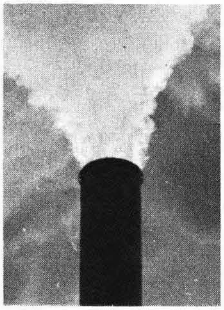

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This issue contains no papers for which there is supplementary material in microform.

## DEPARTMENTS

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Announcing a new, expanded program...

# 1979 STACK SAMPLING SEMINARS

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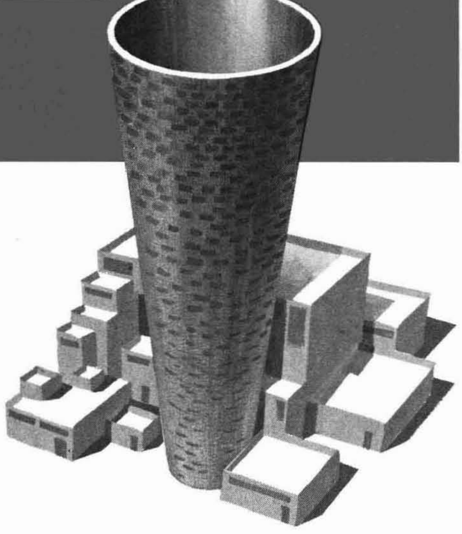

## Two-Day Technical Seminars

*Conducted by Dale Lundgren, Professor of Environmental Engineering Sciences, University of Florida,* the RAC-sponsored seminars cover all relevant parameters for accurate sampling of gaseous and particulate emissions from all types of stationary sources. These comprehensive seminars describe the methods, procedures, and types of equipment required to sample stacks and exhaust systems in accordance with *EPA Methods 1 through 8.* Each seminar is programmed to accommodate 20 participants on a first-come, prior registration basis.

## 1979 Schedule

| Location | Month | Dates | Location | Month | Dates |
|---|---|---|---|---|---|
| Tampa, FL | January | 11-12 | Denver, CO | July | 12-13 |
| Atlanta, GA | February | 1-2 | Chicago, IL | August | 2-3 |
| Houston, TX | March | 1-2 | Pittsburgh, PA | September | 6-7 |
| Dallas, TX | April | 5-6 | Boston, MA | October | 4-5 |
| Los Angeles, CA | May | 10-11 | Newark, NJ | November | 1-2 |
| San Francisco, CA | June | 7-8 | Baltimore, MD | December | 6-7 |

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CIRCLE 5 ON READER SERVICE CARD

## GUEST EDITORIAL

# Scientific questions and the courts

In November 1978, a judge in a county court in western Pennsylvania issued an injunction banning fluoridation by the West View Water Authority after lengthy hearings in a suit instituted by several residents. The most recent epidemiological and other evidence showing the benefits of fluoridation was presented to the court in support of continuing the fluoridation, as well as the lack of any credible link between fluoridation and incidence of cancer. The plaintiff's case appears to be based in large part on one study which purported to show such a connection, but which has been shown authoritatively to be invalid. Nevertheless, the judge ruled that the bulk of the evidence showed that fluoridated water can cause cancer. In a newspaper letter he stated, "I heard a great deal of scientific testimony and made my decision based upon the testimony."

As of this writing, West View has appealed to Commonwealth Court, and the issue is complicated by the jurisdictional authority of the State Department of Environmental Resources in granting permits for fluoridation. Even if West View now wins its appeal, which it should, at least on the basis of the best scientific evidence, the initial ruling is another important example of an environmental decision gone awry, and, perhaps more significantly, one involving a judicial determination.

There is no doubt that many environmental controversies involving conflicts among laws, interpretation of legislative intent, and competing interests protected by law appropriately and necessarily require a judicial determination for resolution. And certainly the courts often have to deal with scientific questions, such as in patent litigation. But are they in a position to evaluate adequately the evidence on a complex scientific question? Should they hear the competing claims and evidence and decide whether saccharin is a human carcinogen? Whether fluorocarbons are depleting ozone in the stratosphere? Or, indeed, whether fluoridation is harmful to human health?

We seem to be developing and utilizing a variety of sometimes clumsy mechanisms to deal with environmental matters, and the atmosphere is often supercharged and the voices strident. In July 1978, at the final EPA hearing concerning its proposed regulations for the control of trace organic chemicals in drinking water, there seemed to be an adversary and sometimes almost carnival milieu, hardly conducive to a calm and deliberate determination of a policy that could best advance the public interest. One useful mechanism for analyzing competing scientific claims is the National Academy of Sciences ad hoc panel report. However, even there the quality of the effort can be variable, and the recommendations not fully and thoughtfully incorporated into regulatory decisions. One example is the hasty governmental decision banning major uses of fluorocarbons, when such a report recommended additional data collection for a specified period with very little risk.

To improve our environmental decisionmaking in the public interest, what may then be needed is a greater reliance on mechanisms that can thoughtfully articulate and elucidate the status of the scientific understanding and uncertainties. It has been suggested that a "science court" could play such a role in evaluating scientific controversies impinging on public policy. The use of this court's "judgments," which in effect and hopefully would be the best available scientific concensus, would then be likely to improve the quality of such policy decisions, as well as those emerging from traditional courts that must deal with these questions.

Julian B. Andelman

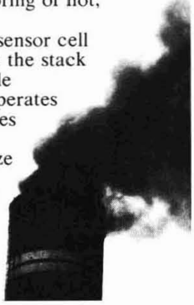
**Dr. Julian B. Andelman** *is Professor of Water Chemistry at the Graduate School of Public Health, University of Pittsburgh, Pittsburgh, Pennsylvania.*

# MSA INSTRUMENTS in the NEWS

COMBUSTION CONTROL • HEALTH & SAFETY • ENVIRONMENTAL • PROCESS

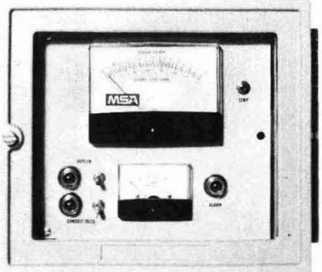
## On-stack oxygen analyzer saves fuel while measuring emissions.

MSA's new Model 803 Oxygen Analyzer was designed to solve many of the practical operating problems that you face in accurate monitoring of hot, dirty flue gases.



The Model 803 sensor cell mounts directly on the stack for shortest possible sampling line. It operates hot to keep all gases above their dew points and minimize plugging. The stabilized fuel cell sensor measures oxygen—not an effect of oxygen—so it produces a high-level signal. It analyzes 0.1% to 21% $O_2$. The lower the oxygen concentration, the better the readability on its logarithmic scale.

Users of the Model 803 Oxygen Analyzer have commented on its fast response to changes in furnace operating conditions. And its close matchup between oxygen readings and theoretical calculation of $O_2$ content gave them fuel savings that paid for the analyzer quickly.



One operator of a 120-million Btu heater fired with fuel oil had a history of plugging troubles with other analyzers until he tested a Model 803. Now he reports, "This was the first analyzer installed that successfully worked when we merely followed instructions."

Another company, operating several marine-style 20,000-lb steam boilers, liked the demonstration of the 803 so well that they kept the demonstration model and ordered another for full evaluations.

If you need a dependable, accurate oxygen analyzer that stays out of trouble and saves you fuel, get details on the Model 803.

CIRCLE 14 ON READER SERVICE CARD

Make sure/check MSA

## Factory cuts fuel bill for dryer in half by monitoring combustible solvents.

The printing and dyeing operation in a fabric finishing plant involved the removal of mineral spirits from the cloth in a gas-heated dryer. Insurance regulations called for control of solvent vapor below 15% LEL. To achieve this level, the operator was forced to change air in the dryer as often as four times a minute—wasting fuel and heat.

An MSA instrument specialist studied the problem, came up with a two-point combustible gas analyzer system with sensors mounted in strategic monitoring points. The MSA instrument system monitors and measures the concentrations of combustible vapors so accurately that the dryer can be operated safely at much higher solvent concentrations. That translates directly to fuel savings.

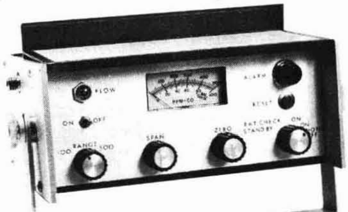
The analyzer was set up to provide an audible alarm at 20% LEL; if the vapor concentration reaches 25% LEL, it automatically shuts off the gas, starts the fan, and increases the amount of makeup air to reduce vapor concentration. Result: The plant is a safer place to work. The insurance firm has since increased the allowable top limit to 30% LEL. The company saved half of its annual fuel bill for operating the dryers, and savings have already paid for the MSA instrument system. The plant is planning a similar installation in its finishing department.

CIRCLE 15 ON READER SERVICE CARD

## New carbon monoxide indicator joins the MSA portable instrument line.

MSA now offers a battery-operated CO indicator that will work a full shift between charges. The Portable Carbon Monoxide Indicator, Model 70, provides over eight hours of detection of airborne CO in the 0-100 parts per million (ppm) range or 0-500 ppm range.

The Model 70 helps you keep track of "the silent killer" in garages, loading docks, coke plants, open-hearth furnaces, manufacturing plants, refineries and similar locations. When CO concentrations reach preset TLV levels, the instrument provides a visual alarm, plus an audible alarm if you wish. The alarm point can be set at any desired level.



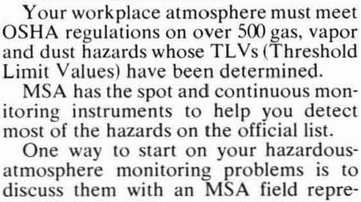
For compliance records, the Model 70 CO Indicator is calibrated for use with a 1-volt recorder, or it can be adapted easily to other recorders.

Recharging is by 115-volt ac source or from a 12-volt battery. Maintenance on this solid-state unit is simple. A calibration check kit is available for reproducible testing and certification.

Ask your MSA instrument specialist for more details or write for literature.

CIRCLE 16 ON READER SERVICE CARD

## Questions about OSHA limits on hazards?



MSA has some answers.

Your workplace atmosphere must meet OSHA regulations on over 500 gas, vapor and dust hazards whose TLVs (Threshold Limit Values) have been determined.

MSA has the spot and continuous monitoring instruments to help you detect most of the hazards on the official list.

One way to start on your hazardous-atmosphere monitoring problems is to discuss them with an MSA field representative.

CIRCLE 17 ON READER SERVICE CARD

**Call us (we're in the Yellow Pages).** Or circle the appropriate Reader Service Number. MSA Instrument Division, 600 Penn Center Boulevard, Pittsburgh, PA 15235.

# ES&T CURRENTS

## INTERNATIONAL

**By the 1990's, solar could supply 8–15% of all of Israel's energy needs,** Natan Arad, director-general of Israel's National Energy Authority, estimated. At present, 300 000 solar heaters provide one-third of that country's domestic hot water needs, thereby saving 3% of the national electricity consumption, Arad noted.

## WASHINGTON

**EPA proposes its first "cradle to grave" hazardous waste disposal regulations.** Under the proposed rules, all producers of more than 220 lbs (100 kg) of hazardous waste per month would have to establish a system to track the waste until its final disposal. Full information about the wastes' composition would have to be provided to companies transporting or disposing of the wastes. Lined landfills would have to be located at least 500 ft from any water source, and water-impervious clay soil would have to be layered over closed landfill sites. Landfills would have to be monitored continuously.

**A decade-long air quality compliance dispute between the EPA and TVA has been settled.** The Tennessee Valley Authority's Board approved an agreement with the EPA, Alabama, Kentucky and 10 citizen health and environmental groups which will, by 1983, bring 10 of its coal-fired power plants into compliance. This agreement ends the lawsuits brought against the TVA for noncompliance. Among the measures taken by the TVA to meet air quality standards are the burning of medium- and low-sulfur coal and the use of flue-gas scrubbers to remove sulfur dioxide at some plants, the use of coal-cleaning methods, and the use of electrostatic precipitators or fabric-filter baghouses to control fly ash. The pollution control equipment is expected to cost about $450 million/y in the early 1980's.

*NOAA administrator Frank*

**NOAA's administrator Richard Frank announced the U.S.' participation in a year-long global weather experiment.** The U.S. is among the 147 nations participating in this WMO- and ICSU-sponsored program. The various projects, some of which began on December 1, will help meteorologists to develop more accurate methods for forecasting the weather. Instrumention is perfuse; included will be special airplanes to take wind tests, stationary weather satellites, orbiting polar satellites, ocean buoys, research balloons and 50 wind-testing ships. The collected data will be fed to computers, assessed and used by weathermen around the world to improve their weather predicting skills.

**Despite an overall austerity budget for fiscal 1980, EPA's operating budget will increase** to $1.3 billion, up $0.1 billion from fiscal 1979. The EPA's construction grants program, however, will be slashed to $3.8 billion, down from fiscal 1979's $4.2 billion.

**EPA's fourth annual National Water Quality Report to Congress finds** some improvements, but reports that 89% of 246 river basins in the U.S. are plagued by water pollution problems from municipal discharges. Information supplied by the states on these 246 basins indicates that 72% of the river basins are affected by industrial discharges to varying degrees.

**EPA proposes the "bubble" concept which allows industry to decide the most cost-effective way of meeting air quality standards** at multiprocess plants. This move away from the traditional "command and control" approach to pollution control will permit plant management to propose the most cost-saving plant-wide mixes of pollution control so long as the overall clean air requirements are met. This more flexible regulation is seen as an incentive to industry to come up with innovative solutions to pollution control.

**The USGS has received $96 million in appropriations for water-resources studies** for fiscal year 1979; this represents about 15% of the total U.S. Geological Survey appropriation for earth science and resource investigations. The USGS monitors the quantity and quality of surface- and groundwater resources at more than 40 000 data-gathering stations throughout the U.S.

**To defray the costs of complying with the "toxics" law,** small businesses may apply for special loans from the Small Business Administration. These businesses may apply directly to SBA for long-term repayment loans available at 6⅝% interest. They would have to document the costs of new testing, plant conversions or new equipment needed to comply with the Toxic Substances Control Act.

**A call for toxicologists.** Four regulatory agencies asked the U.S. Civil Service Commission to set up a new job classification for toxicologists. The heads of the Consumer Product Safety Commission, the EPA, FDA and OSHA asked that a separate "toxicology register" be established to help them in hiring the toxicologists needed to carry out the mandates of the health and environmental laws.

## STATES

**To meet federal air-quality standards, the Washington, D.C., metropolitan area** needs a vehicle inspection and maintenance (I/M) program, according to the Metropolitan Washington Council of Governments (COG). COG also says that the area will need an extension of the compliance deadline for ozone and carbon monoxide to 1987. The District, Maryland and Virginia are planning on meeting the January 1, 1979 deadline for submitting state implementation plans. However, Virginia will only propose its I/M program to its 1979 legislative session, after January 1; and Maryland is now drafting an I/M program for submission to its 1979 legislative sessions. The District, which has an I/M program, will not enact it until the two states enact similar programs.

*TVA's Moore*

**A water quality survey of the Tennessee Valley drainage basin** finds the quality deteriorating. For example, fish in the Virginia portion of the Holston River and in an embayment of the Tennessee River near Huntsville, Ala., are contaminated with mercury and DDT, and are hazardous to health if eaten. These are the two most seriously polluted sites, but the Tennessee Valley Authority (TVA) survey found 17 other "critical" locations and 28 other "major problem" areas in the Tennessee River drainage basin. "Many people tend to think that the rivers and streams of the Tennessee Valley . . . are free of pollution problems. But unfortunately that just isn't so," said Harry G. Moore, Jr., acting director of environmental planning for TVA. The survey is entitled "Where the Water Isn't Clean Anymore."

**Ohio has adopted new air pollution rules regarding alerts caused by ozone.** The new regulations require that an alert be called whenever ozone reaches 0.2 ppm or 200 on the pollution standard index (PSI), which is twice the level of the old regulation alert. An emergency episode for ozone would be called when ozone reaches 0.5 ppm or 400 on the PSI, which is lower than the old regulation. Ohio will continue to issue a health warning to affected areas when ozone levels reach 0.08 ppm or 100 PSI. Ned E. Williams, director of the Ohio EPA says that "Our number one culprit and contributor to the ozone problem in Ohio is the automobile."

**The Minnesota Pollution Control Agency (MPCA) rejected a plan to develop a former chemical dump** site in St. Louis Park. The site was formerly owned by the Reilly Tar and Chemical Co., which used it to dispose of creosote wastes. The southern portion of the site is heavily contaminated, and agency staff believe that the contamination may have migrated into the soil and underground waters of the northern portion. The state Health Dept. ordered the closing of four wells north of the site when laboratory analysis of the well water showed trace levels of polynuclear aromatic hydrocarbons. It is feared that aquifers providing drinking water to several western Minneapolis suburban communities may be threatened. MPCA is suing Reilly Tar, now located in Indiana, for contamination-related damages.

**New Jersey and New York are involved in a pilot program,** funded by the U.S. EPA, designed to gain citizen participation in the control of toxic substances. Thirty-six public-interest groups and 500 people are to participate in the program. Twenty-five of these groups will divvy up the $106 000 distributed by the EPA; 11 organizations will participate voluntarily.

**Two local New Jersey governmental entities are seeking federal funds to finalize a preliminary resource recovery system design.** The Hackensack Meadowlands Development Commission and the Bergen County Board of Chosen Freeholders are applying to the U.S. EPA for $174 275 under the President's Urban Policy for resource recovery project development. The proposed system will handle 2500–3000 tons of solid waste per day.

## MONITORING

**A portable electrostatic precipitator is being developed by the University of Denver Research Institute** under a 3-y, $2.6 million grant from the U.S. EPA. The prototype device will be built for the collection of high resistivity, fine-particle emissions at their source. The two-stage precipitator will be built on as many as four semitrailers, and will be transported to industrial sites to demonstrate its operation at different geographical locations and with various types of particulates under varied operating conditions.

## TECHNOLOGY

**Up to 99% of hydrogen chloride (HCl) is removable** with the "Mitsubishi-TESI Dry Process Poisonous Gas Treatment System," according to Mitsubishi Heavy Industries, Ltd. (Japan). The name TESI is from a U.S. firm, Teller Environmental Systems, Inc., with which Mitsubishi has a "technical tie-up." Essentially, HCl is removed by a lime slurry and filter bag system, and the product is a powder. Tests are taking place with a maximum throughput of 5000 $Nm^3/h$, at Mitsubishi's Isogo Factory at Yokohama, Japan.

**Coal gasification can be improved by use of a honeycomb catalyst** made of ruthenium. The honeycomb design replaces conventional pelleted catalysts, says Matthey Bishop, Inc. (Malvern, Pa.). The company believes that the new design is more efficient in converting the gas mixture that comes from coal, to methane. The open structure permits freer flow of reactant gases, and does not obstruct piping with "fines." Moreover, honeycomb catalysts are much easier to handle than are pelleted catalysts, Matthey Bishop says.

**This system recycles "black water" and comes up with an odorless, clear product.** It is a "closed loop" toilet system which controls, retains, and treats human wastes at the point of origin. Known as the Cycle-Let, it can be used as a no-discharge, or limited discharge system. Since the Cycle-Let requires no fresh water for operation, as much as 600 000 gpy of water can be saved by its use. No sewer hookups are needed. An electrical control system warns of any malfunction, audibly and visually. Depending upon level of usage, sludge need be removed only every 1–5 years. The Cycle-Let is made by the Thetford Corp. (Ann Arbor, Mich.).

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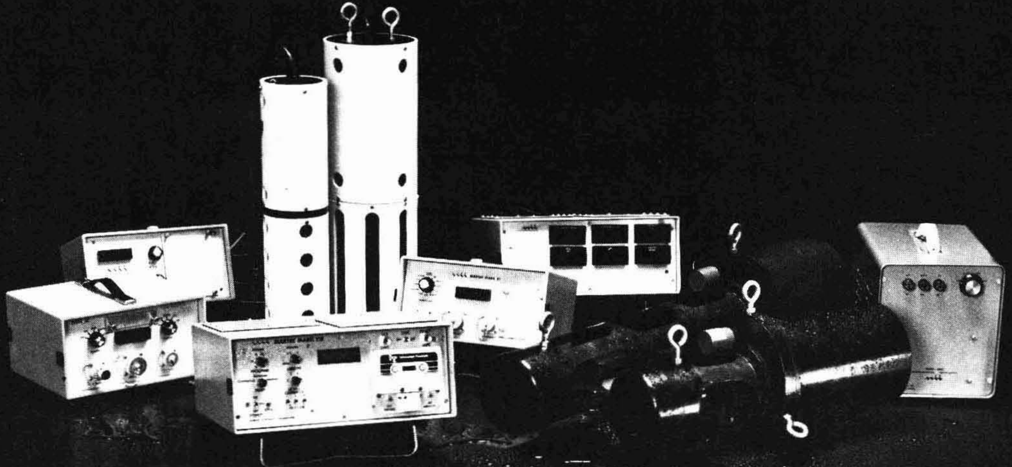

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CIRCLE 12 ON READER SERVICE CARD

*Solar cell array*

**A 3500-watt (peak) solar electric power system has been dedicated** at Schuchuli, Ariz., on Papago Indian tribal lands. It is being managed by the Dept. of Energy's National Photovoltaic Conversion Program. The system will service 96 residents with enough power for 15 four-ft$^3$ refrigerators, a wringer-type washing machine, a sewing machine, a 2-hp, 5000-gpd pump for the community well, and 40 fluorescent lights. The solar cell array has 192 photovoltaic modules, each containing 42 solar cells. Excess energy is stored in a specially-designed bank of lead-acid storage batteries. Capital cost was $108 483, with the energy cost estimated at $1.76/kWh.

**What if adipic acid can effect efficient $SO_2$ removal? Then, smaller flue gas desulfurization (FGD)** scrubbers may become possible, says Michael Maxwell of the U.S. EPA (Research Triangle Park, N.C.). What the acid does is to stabilize limestone scrubber pH drop, and make the FGD system "more responsive." Maxwell notes that $SO_2$ concentration variations do not seem to affect efficiency, so very possibly scrubbers may not have to be designed so large as to accommodate "worst case" situations. In tests at TVA's Shawnee Steam Plant (Paducah, Ky.), FGD systems with adipic acid averaged 97-98% efficient. Adipic acid is a principal component of nylon production.

**How well do ozone $O_3$ and chlorine dioxide ($ClO_2$) technologies work** to make drinking water safe? EPA/Cincinnati made a careful study and evaluation of many technologies, and of water treatment philosophies in the U.S., Canada, and Europe. Also covered is preozonation of the water with subsequent "biological activated carbon" treatment (*ES&T*, October 1978, p 1141). Fundamental uses, and engineering design of various systems are discussed in detail. The report number is EPA-600/8-78-018; it was prepared by the Municipal Environmental Research Laboratory, EPA, Cincinnati, Ohio 45268.

## INDUSTRY

**A contract to develop liquid metals as solar energy heat conductors** was awarded to Westinghouse's advanced reactors division (Madison, Pa.). The initial $25 000 contract will determine how temperature changes will affect properties of materials, such as liquid sodium, proposed as heat transfer agents.

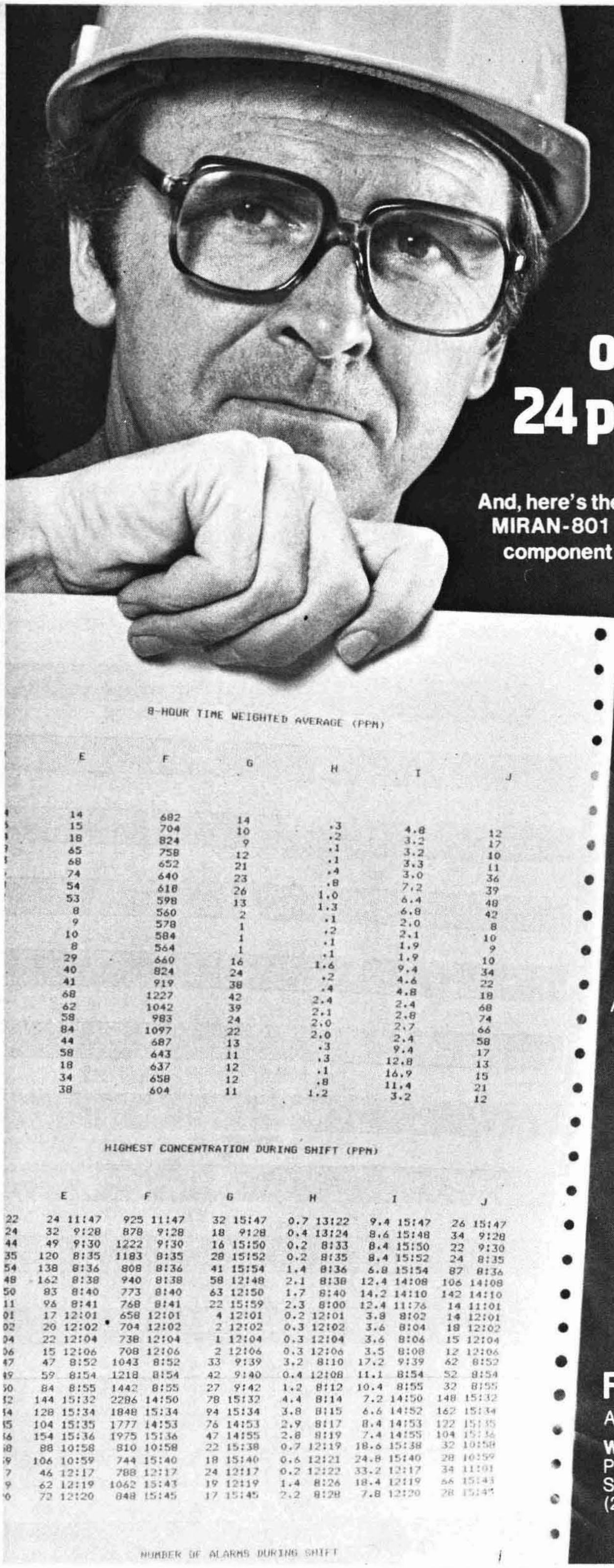
**Whether there will be severe energy disruptions in the future** will be determined by the extent to which overregulation of the nation's oil companies inhibit necessary capital investments, according to Jerry McAfee, chairman of Gulf Oil Corp. McAfee said that there were advances in "soft" areas of technical development, public awareness, and energy use, but that the critical "hard" area—regulated pricing—has not been adequately addressed. He warned that such price controls will discourage U.S. production, and serve to increase reliance on oil imports from potentially unreliable sources.

**A contract for test performance of OTEC-1 was awarded** to Global Marine Development Inc. (Newport Beach, Calif.). OTEC is ocean thermal energy conversion. The OTEC-1 test platform will be the USNS CHEPACHET (T-AO-78), which will be reclassified as an oceanographic research vessel. Ocean thermal uses a heat transfer fluid which, in vapor form, runs a turbine to generate electricity. After running the turbine, the vapor sinks to an installation in cold, deep ocean water where it condenses. The condensate is then pumped up to warm ocean depths near the surface, where it reevaporates to form the gas to run the turbine. TRW, Inc. is the principal sub-contractor.

*MCA vice president Frost*

**Society may benefit from pollution control regulations, but** investment in compliance with them would rarely, if ever, increase productivity and innovation. This is the assessment of Edmund Frost, vice president and general counsel of the Manufacturing Chemists Association (MCA, Washington, D.C.). Frost noted that the chemical industry will expend $3.4 billion on pollution control equipment this year. This expenditure will be for regulation compliance, most or all of which, Frost said, must be considered as non-productive.

**Private contractors may handle municipal waste collection more and more,** partly because of "Proposition 13" fever, William T. Lorenz & Co. (Boston, Mass.), which makes economic forecasts, believes. The 145 million t handled in 1977 will be 200 million t by 1985. Also, Lorenz predicted that industry, which spent $615 million to handle and dispose of wastes in 1977, will pay out $1.2 billion in 1985. The primary cause for this jump will be new hazardous waste standards and requirements, Lorenz foresees; also, operating expense levels for industry will go up from $1.2 billion in 1977 to almost $2.2 billion by 1985.



# "Here's an 8-hour time-weighted average of the concentrations of 10 toxic gases at 24 places in our plant."

```
                    8-HOUR TIME WEIGHTED AVERAGE (PPM)

          E             F          G          H           I           J

         14           682         14          .3         4.8         12
         15           704         10          .2         3.2         17
         18           824          9          .1         3.2         10
         65           758         12          .1         3.3         11
         68           652         21          .4         3.0         36
         74           640         23          .8         7.2         39
         54           618         26         1.0         6.4         48
         53           598         13         1.3         6.8         42
          8           560          2          .1         2.0          8
          9           578          1          .2         2.1         10
         10           584          1          .1         1.9          9
          8           564          1          .1         1.9         10
         29           660         16         1.6         9.4         34
         40           824         24          .2         4.6         22
         41           919         38          .4         4.8         18
         68          1227         42         2.4         2.4         68
         62          1042         39         2.1         2.8         74
         58           983         24         2.0         2.7         66
         84          1097         22         2.0         2.4         58
         44           687         13          .3         9.4         17
         58           643         11          .3        12.8         13
         18           637         12          .1        16.9         15
         34           658         12          .8        11.4         21
         38           604         11         1.2         3.2         12


               HIGHEST CONCENTRATION DURING SHIFT (PPM)

          E            F            G           H           I           J

22     24 11:47    925 11:47    32 15:47   0.7 13:22   9.4 15:47   26 15:47
24     32  9:28    878  9:28    18  9:28   0.4 13:24   8.6 15:48   34  9:28
44     49  9:30   1222  9:30    16 15:50   0.2  8:33   8.4 15:50   22  9:30
35    120  8:35   1183  8:35    28 15:52   0.2  8:35   8.4 15:52   24  8:35
54    138  8:36    808  8:36    41 15:54   1.4  8:36   6.8 15:54   87  8:36
48    162  8:38    940  8:38    58 12:48   2.1  8:38  12.4 14:08  106 14:08
50     83  8:40    773  8:40    63 12:50   1.7  8:40  14.2 14:10  142 14:10
11     96  8:41    768  8:41    22 15:59   2.3  8:00  12.4 11:76   14 11:01
01     17 12:01    658 12:01     4 12:01   0.2 12:01   3.8  8:02   14 12:01
02     20 12:02    704 12:02     2 12:02   0.3 12:02   3.6  8:04   18 12:02
04     22 12:04    738 12:04     1 12:04   0.3 12:04   3.6  8:06   15 12:04
06     15 12:06    708 12:06     2 12:06   0.3 12:06   3.5  8:08   12 12:06
47     47  8:52   1043  8:52    33  9:39   3.2  8:10  17.2  9:39   62  8:52
49     59  8:54   1218  8:54    42  9:40   0.4 12:08  11.1  8:54   52  8:54
50     84  8:55   1442  8:55    27  9:42   1.2  8:12  10.4  8:55   32  8:55
2     144 15:32   2286 14:50    78 15:32   4.4  8:14   7.2 14:50  148 15:32
4     128 15:34   1848 15:34    94 15:34   3.8  8:15   6.6 14:52  162 15:34
5     104 15:35   1777 14:53    76 14:53   2.9  8:17   8.4 14:53  122 15:35
6     154 15:36   1975 15:36    47 14:55   2.8  8:19   7.4 14:55  104 15:36
8      88 10:58    810 10:58    22 15:38   0.7 12:19  18.6 15:38   32 10:58
9     106 10:59    744 15:40    18 15:40   0.6 12:21  24.8 15:40   28 10:59
7      46 12:17    788 12:17    24 12:17   0.2 12:22  33.2 12:17   34 11:01
9      62 12:19   1062 15:43    19 12:19   1.4  8:26  18.4 12:19   66 15:43
0      72 12:20    848 15:45    17 15:45   2.2  8:28   7.8 12:20   28 15:45


                    NUMBER OF ALARMS DURING SHIFT
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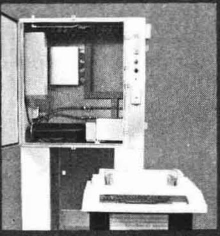

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ES&T OUTLOOK

# The pollution control industry

*Its market share could be $3.5 billion by 1983, representing a growth of 11–12% per year. Some sectors may move faster than others*

Loud, indeed, has been the hue and cry from many quarters of industry, concerning environmental regulations. That would hardly come as a surprise, when one considers capital and operating costs brought about by these regulations—many of which may not go to a directly productive purpose. But is there any sector of industry that might benefit from these regulations in some way?

Yes, there is. That sector is the pollution control industry (PCI). It has about 600 companies in all phases of air, water, and solid waste/resource recovery. In all fairness to the PCI, it should be mentioned that many of its individual component companies try to help client firms meet regulations for the lowest achievable cost, and, if at all possible, find ways to offset compliance costs.

### An update

In 1972, Arthur D. Little, Inc. (ADL, Cambridge, Mass), under a contract with the U.S. EPA, made a study on the impact of environmental regulations on the PCI. Results of the earlier study can be found in "Economic Impact Study of the Pollution Abatement Equipment Industry," Report to EPA by Arthur D. Little, Inc., December 1972 (EPA Contract No. 68-01-0553). One would think, therefore, that an update would be needed. Thus, ADL prepared such an update for the EPA, completed last year. Objectives were, essentially

- to identify any constraints on the industry's ability to meet needs and market demands stemming from the EPA's regulatory activities
- to evaluate performance of PCI companies and their attitudes toward future investments
- to estimate markets and resulting employment associated with the industry, and its role in satisfying environmental regulatory requirements.

Terry Rothermel (*ES&T,* April 1978, p 379) and five of his colleagues represented ADL for the study's preparation. EPA's project manager was Edward Brandt, who was with the Economics Division, and has moved over to the Permits Division since the report appeared. They gave the bulk of their attention to air pollution (apc), water pollution control (wpc), and resource recovery (RR) sectors of the PCI.

### Growth and profits

From 1972 to 1976, leading companies of the PCI experienced a 16–22%/y growth rate, as compared to a 9% rate for all U.S. manufacturing. Profitability was "about average" for U.S. industry—10–11% after-tax return on stockholder's equity. However, the water treatment chemicals sector did much better ($250 million in sales in 1977, with, maybe, a 19%/y growth to 1983); indeed, it was among the most profitable in U.S. industry.

For 1977, the PCI market share was about $1.8 billion. ADL foresees a market share of $3.5 billion by 1983, representing a growth of 11–12%/y, based on 1978 dollars, and a 5–7% inflation rate. RR systems and flue gas desulfurization (FGD) systems could enjoy faster growth. As for employment, job-equivalents associated with the 1977 market share numbered 35 850. This number could well rise to 43 900 by 1983, ADL forecasts.

**ADL's Rothermel**

**"EPA's interest in understanding the impacts of their policies upon the PCI made that industry very willing to provide the information vital to the preparation and completion of this study"**

**EPA's Brandt**

**"The report provides some useful insights into the economic characteristics of the industry, and how EPA policies affect decision-making and risk"**

With respect to financial resources in this industry, ADL believes that even the larger of the component companies normally have sales of $200–700 million/y. They "are not among the multi-billion dollar firms which command the greater financial resources within the U.S. manufacturing industry. Hence, the industry has been limited by the resources of its leading participants, as well as by disappointing profitability," according to the report.

Perhaps account should be taken of recent mergers/acquisitions within the industry, and by companies outside the industry, which acquire PCI companies. Cases in point are Wheelabrator-Frye's merger with Neptune, and Allis-Chalmers' acquisition of American Air Filter Co., Inc. It might be interesting to see what effect on financial resources these mergers/acquisitions might have in the near future.

### "Throw away your degree"

Several months ago, an engineer with a company serving the wpc field wryly told an *ES&T* editor: "When you compete for a municipal contract, throw away your degree . . . and come up with the lowest bid. Know-how, capabilities, experience, future reliability, alternative technical options, and cost-effectiveness don't really cut any ice."

Perhaps this assessment is somewhat exaggerated, but, be that as it may, ADL considers the municipal bidding process to have the greatest impact of concern on the PCI. This process essentially involves expenditures of federal grant money for specialized sewage treatment equipment/instrumentation systems. Of special concern, for instance, is that low-bid purchasing may impede technological innovation, and result in costly operation/maintenance problems in the future, according to ADL.

Also of concern is "bid shopping" after wastewater treatment (wwt) awards are made. Here, the municipality may procure equipment and instrumentation according to price considerations only, with resulting impairment of total system quality and performance. Construction grant funds are used to pay for equipment purchased under a bid shopping scheme. Money is saved for the general contractor's benefit—which is the whole idea of bid shopping.

Extreme concern about the bid shopping practice was expressed by EPA, and by member companies of the Water and Wastewater Equipment Manufacturers Association (WWEMA, McLean, Va.). The matter was brought up at WWEMA's Washington Affairs Forum, held at Washington, D.C., in December. New guidelines may sharply curtail this practice, and should be promulgated in the near future, according to what was heard at the Forum.

### R&D motivations

Many in the PCI feel that needed pollution control technologies—both air and water—are generally available, according to the report. Others may argue forcefully against that position on the grounds that since pollution control is largely a "non-productive"

**Major competitors**[a]

**Water pollution control**

| Equipment | Instrumentation supplies | Specialty chemical suppliers |
|---|---|---|
| Envirotech | Fischer & Porter | Nalco |
| Ecodyne | General Signal | Betz |
| Rexnord | Betz | Calgon (Merck) |
| FMC | Beckman Instruments | Drew (U.S. Filter) |
| Penwalt | Leeds & Northrup | Dearborn (W.R. Grace) |
| Neptune International | Foxboro | Mogul (Dexter) |
| Dorr-Oliver | Great Lakes | |
| Peabody International | Johnson Controls | |
| | Taylor | |
| | Honeywell | |
| | Technicon | |

**Air pollution control**

| Particulate control | $SO_x$ control | Instrumentation |
|---|---|---|
| American Air Filter | Babcock & Wilcox | Beckman Instruments |
| Envirotech/Buell | Combustion Engineering | Monitor Labs |
| Joy Manufacturing | Combustion Equipment Associates | MDA Scientific |
| Research-Cottrell | Envirotech/Chemico | Lear Sigler |
| U.S. Filter | Research-Cottrell | Environmental Data Corp. |
| Wheelabrator-Frye | UOP | Tyco |
| | | Meloy Laboratories |

[a] According to ADL report listings.

investment, users would continue to seek lower-cost solutions; hence, a motivation for R&D, ADL says.

But R&D motivation may be "wishy-washy," at best. One reason is that even the larger PCI firms enjoy only $200–700 million in annual sales, with "average" profitability within U.S. industry, so these firms—with notable exceptions, perhaps—would not be inclined to commit heavy funding to pollution control R&D. Moreover, larger, billion-dollar corporations coming into the "PCI club" may lack the necessary business know-how for this field, and thus, would approach R&D most gingerly.

On the other hand, the federal establishment's plan seems to be to look to the private sector for R&D efforts, mainly in the form of development of new, proprietary technologies. Accordingly, EPA's R&D budgets for this item have been declining. The problem is that the private sector's, particularly potential control system users', motivations for innovation may be subject to question for various reasons, ADL believes.

### Some may move faster

Earlier, with respect to apc, it was noted that FGD systems might enjoy a faster growth than that of the PCI in general. The promulgation of stringent $SO_2$, and, perhaps, particulate and $NO_x$ standards, pursuant to the Clean Air Act of 1977, may have this effect. Moreover, ADL's Rothermel reminded *ES&T* that much "catch-up" work is still needed in the FGD field. But also, stricter standards for particulate control may well extend the period of uncertainty for companies, in terms of technological performance, operating experience, and market position, according to ADL. A problem is that apc, especially with regard to particulate control, "is in danger of having technology created in the contract," instead of being developed through the medium of the pilot plant. That situation, in turn, could lead to unreliability, and a commensurate undermining of user confidence.

Also, with regard to particulate emissions control, that segment of the apc business has been the most stable and profitable, ADL noted. Its state-of-the-art has been making steady progress which could, however, be disrupted, if new, very stringent standards come into being, ADL believes.

Perhaps, then, the main question concerns the role of technology forcing, as in particulate control, for example. Now, maybe environmental concerns may require higher apc performance. But ADL queries whether a technology-forcing standard—where a technology presently exists and is progressing—might not be as effective as it could be in an alternative situation in which no pollution control technology exists, at all.

### Keeping ahead

In the past, PCI customers were largely concerned with meeting minimum regulatory requirements. The future, however, may bring about a need to keep up with, or even ahead of pollution control regulations. Thus, emphasis on capital investment and necessary technology could give some way to operating performance and costs, ADL predicts.

Later this month, there will be a good opportunity for PCI firm representatives and their customers, and regulatory people to discuss all of these matters face to face. That will be at the Third Annual Meeting of the Environment Industry Council, to be held on February 28–March 1, at Washington, D.C. For more information, contact the Environment Industry Council, 1825 K Street, N.W., Washington, D.C. 20006.

*ES&T* hopes to see y'all there. JJ

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*In the future, the main emphasis of environmental monitoring and control technology, as well as court cases, will be on*

# Compliance with regulations

Court challenges involving the various environmental laws, including the Clean Water Act of 1977 (P.L. 95-217), will continue occurring for some time. But cases governed by this law will probably concentrate more on actual *compliance*. "Courts will continue to accord wide latitude to EPA in setting general and individual standards, so long as the court is convinced that EPA did its homework, and explained its reasoning. Rightness or wrongness from a general point of view, economic or technological, does not enter heavily into the matter.

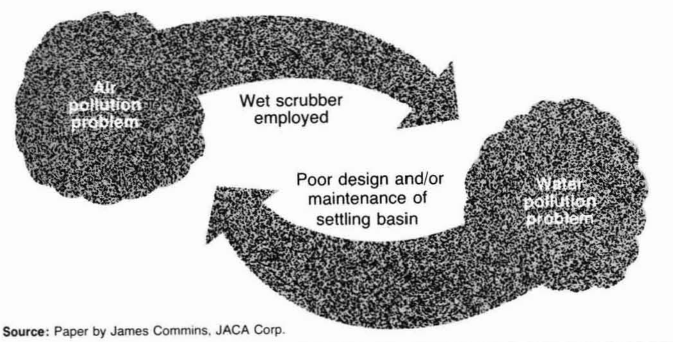
"Industries will seldom prevail in court on future review questions," George Coggins, professor of law at the University of Kansas, said at the 71st Annual Meeting of the American Institute of Chemical Engineers (AIChE), which included a 22-session program on compliance, and was held at Miami Beach, Fla., in November. He noted that "basic interpretational problems have long been ironed out, and are no longer a reasonable ground for challenge." Moreover, "the beating EPA has taken in several cases [one example was American Meat Institute v. EPA, 1975, involving regulations for that industry, developed from petroleum industry data] should lead it into using more careful and complete procedures, and better articulation of the reasons for its decisions."

*The compliance sessions were jointly sponsored by the AIChE, and the American Chemical Society.*

### Monitoring instruments

As for the technology of compliance, Coggins also observed that no significant amount was "forced." Rather, EPA, he said, has largely "confined its attention to demonstrated methods and processes, although occasionally requiring technology transfer." A case in point was California and Hawaiian Sugar Co. v. EPA. It dealt with BPT/BAT regulations based on activated sludge and sand filter technology transfer. Here, EPA prevailed. Many in the environmental field agree with that evaluation concerning technology

**The interrelationship problem**



**Source:** Paper by James Commins, JACA Corp.

forcing; certainly, many others will take issue.

Be all that as it may, monitoring instrumentation is one important aspect of technology for compliance. This instrumentation must be so developed and constructed as to meet EPA guidelines for test procedures with respect to the National Pollution Discharge Elimination System (NPDES), as Robert Booth of EPA/Cincinnati reminded an AIChE meeting session. Such instrumentation (for water) would include, for example, pH meters, ion-selective electrode meters, and many other precise analytical instruments. Documents describing quality assurance techniques needed to provide valid data are available from the EPA. Contact the Environmental Monitoring and Support Laboratory in Cincinnati. Provisions for alternative test procedures can be made in certain cases.

For the future, Booth said, instrumentation needs could encompass

- low operator dependence
- capabilities of lower detection limits with high degrees of reliability
- capabilities of monitoring specific organic compounds in comparatively complex sample matrices
- capabilities of automatically accommodating desired quality control techniques to assure data validity.

### Computer control

The computer is a principal tool for advancing compliance technology. C. Wells of Envirotech Operating Services (Belmont, Calif.) explained how a digital computer automatically controlled activated sludge process working at the 10.37-mgd Fairfield-Suisun (Calif.) Regional Water Reclamation Plant. The computer was used on one side of a parallel train to control dissolved oxygen (DO), return sludge density, and mixed density. Control of the other side of the train was manual, with identical feed, for purposes of comparison.

Computer control apparently brought about improved sludge settleability (sludge volume index, or SVI); improvement was about 40% (with manual control, the SVI was 199 ± 80 mL/g). DO was controlled to ±0.3 mg/L by computer, and to ±1.8 mg/L in the manual system. Total organic carbon was 25.4 ± 16.5 mg/L in the effluent from computer control, and 25.5 ± 16.2 mg/L in the effluent from manual control. But the computer-controlled effluent quality was achieved with one-half of the manually-controlled settling volume.

The marked SVI improvement by tight computer control allowed the plant to operate with only one secondary clarifier. For the manual system, two were required. Also, computer control of the process allowed the use of about 18% less air for the activated sludge process than the manual system needed.

The use of less air, brought about through automation of the air header, could save much electric power; electricity costs currently exceed $45 000/mo for the plant. Moreover, better control of filamentous organisms that impair the SVI was achieved through tight computer control.

### Automating the bugs

Coming "down the pike" is a handbook for automation of the liquid- and solids-train biological activated sludge process for achieving effluent compliance. The handbook should appear in June or July. To be aimed at consulting engineers and government agencies, it is being prepared for EPA by EMA, Inc. (St. Paul, Minn.), EMA president Alan Manning told AIChE meeting attendees.

One part of the book will cover successful control strategies at 23 wastewater treatment plants. The book will also show weakness in present systems, such as insufficient attention often paid to control of hydraulics. As for sludge drying, multiple-hearth incineration, rather than vacuum filtration will be emphasized. Manning says that the latter process can have poor economics, because of chemical costs, and control difficulties. But for incineration, automatic control must be very tight, and properly set up for every aspect, such as temperature control, oxygen level, combustion zone location, and similar factors, or energy costs could really mount up.

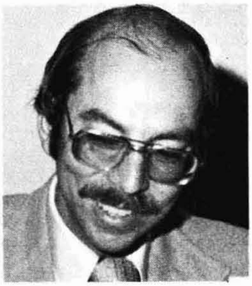
To shore up certain weak points in automated biological activated sludge systems, Manning recommended

- an integrated control scheme to be developed/demonstrated for the activated sludge process
- demonstration of feasibility and desirability of dynamic control of plant hydraulics
- a management handbook for plant operation/maintenance
- development/demonstration of a measurable filterability index, necessary for full automation of sludge dewatering processes
- better understanding, and demonstration of combustion process automation, particularly for multiple-hearth incineration
- a preventive maintenance program for instrumentation.

### Interrelationships

Any technical and economic evaluation of a planned environmental control system, to be built to comply with regulations, must take the interrelationships of air, water, and solid waste into account. If this is not done, at the outset of a system analysis, the result can be makeshift solutions not constituting a technical or economic optimum, warns engineer James Commins, president of JACA Corp. (Fort Washington, Pa.).

For example, Commins cited the case of an industrial dryer whose par-



**Stone & Webster's Siegel**
*"control only through technology"*

ticulate emissions were controlled by a wet scrubber. Scrubber water discharged to a receiving stream had to be treated for pH and suspended solids. Apparently, during the original economic analysis, water regulations were not considered. The result was a system choice whose cost-effectiveness was not optimal.

Another example was that of the asphalt batching plant that used a wet scrubber to capture particulates in its air stream. Because of new "zero discharge" water requirements, scrubber makeup water was taken from the same pond to which spent water from the demister was discharged. Improper design of that pond, and of input filters, led to the system's being out of "spec" on particulate loading. Corrective design of the water source brought the system within specifications, but because of that necessity, extra costs were incurred.

These case histories served as a warning of what happens when the water/air/solid waste interrelationships are not considered in their entirety, as they apply to an antipollution project. Commins recommended ways of considering the interplay of the environmental laws, and of technical/economic factors, so as to achieve the most cost-effective compliance.

### How not to comply

With regard to air pollution control, there are at least two new ways to fail in compliance with EPA's regulations evolving as a consequence of the Clean Air Act Amendments of 1977, according to Richard Siegel of Stone & Webster Engineering Corp. (Boston, Mass.), who coordinated the program on environmental regulations and compliance. He said that these "no-nos" are use of "compliance fuel" and tall stacks.

Instead, EPA now mandates continuous emission reduction, such that control will have to be achieved through technology. This technology will culminate in use of Best Available Control Technology (BACT), and Lowest Achievable Emission Rates (LAER) for new facilities, depending upon whether they are located in areas attaining ambient standards (BACT), or not attaining standards (LAER). LAER is a technology-forcing control level which does not consider economics as an object. Moreover, as gleaned from the compliance symposia, it is probably safe to say that to meet most pollution control requirements—which may be expected to grow ever tighter—various combinations of hardware and software systems technologies will be the key. JJ

# Regulating hazardous substances

*As one of its first major efforts, the four-agency Interagency Liaison Regulatory Group issues its report on 24 hazardous materials*

Jimmy Carter took office pledging to eliminate waste and duplication in setting regulations, thereby increasing their effectiveness while decreasing the burden on the regulated industries and the public. In the area of regulatory policies protecting the public from the untoward consequences of hazardous substances, increased efficiency is particularly important.

Carter threw out his gauntlet early. The regulatory agencies met his challenge with a vengeance.

### Together whatever . . .

One of the best ways to ensure against overregulation is through coordinative efforts among agencies having similar regulatory responsibility. Letting the "government's left hand . . .[know] what the right hand is doing," is the way OSHA's head and current IRLG chairman Eula Bingham describes it.

Two of the earliest efforts in this direction were the Toxic Substances Strategy Committee (TSSC), which has representatives from 17 agencies and is chaired by the Council on Environmental Quality, and the four-agency Interagency Regulatory Liaison Group (IRLG), which was formed in August 1977 by Susan King, Douglas Costle, Donald Kennedy and Eula Bingham, respectively the heads of the Consumer Product Safety Commission (CPSC), EPA, the Food and Drug Administration (FDA) and OSHA.

Since the formation of TSSC and IRLG, the cooperative spirit has given rise to the Interagency Toxic Substances Data Committee, the Interagency Toxic Substances Testing Committee, the Regulatory Analysis Review Group, the National Toxicology Program, and the Regulatory Council, to name just a few.

While cooperation may appear to be rampant and, to some extent, excessive, the need is apparent. Early on, the IRLG took inventory of the projects concerned with toxic substances control, and found that its four members alone had 300 ongoing projects at a cost of $39 million. Three other nonregulatory HEW agencies—NCI, NIEHS, and NIOSH—had another 600 projects whose total cost exceeded $95 million.

### Agreement on toxics

With this inventory of potential duplication, and the Carter administration's thrust to eliminate such duplicative efforts, the four agencies, on October 11, 1977, published an interagency agreement in the *Federal Register* relating to the regulation of toxic and hazardous substances. As the IRLG, the agencies agreed to share information and other resources to


CPSC's King


EPA's Costle


FDA's Kennedy


OSHA's Bingham

develop "common, consistent or compatible practices." This cooperation, it was felt, would bring about effective, cost-effective health-protection programs.

Under this October agreement, eight work groups were established. One of these groups, the Regulatory Development Work Group, chaired by Henry E. Beal of EPA, recently published "development plans" for 24 hazardous materials (box) that two or more of the agencies regulate or intend to regulate.

The document, "Hazardous Substances Summary and Full Development Plan," inventories the regulatory activities currently in progress for 24 wide-ranging toxic materials—from acrylonitrile to substances present in waste disposal to agricultural land. For each substance or group (some of the categories are not single compounds), the report summarizes

- the agencies' statutory authority to regulate
- the history of regulations in effect
- the adverse biological effects
- the opportunities for avoiding conflicts in standards setting, and for eliminating duplicative efforts
- the economic ramifications of proposed or pending regulations
- recommendations for future action.

To call the document "development plans" is, however, an exaggeration. The recommendations—which Toby Clark, special assistant to EPA administrator Costle, acknowledges as not being an outstanding feature of the document—are in many cases vague or nonexistent. With poor or no recommendations, can these be called development plans? Clark accepts this criticism, but emphasizes that the document represents the first evolutionary stage—which he terms coordination—in the regulation of hazardous substances.

An evolutionary process it is. The Regulatory Development Work Group's efforts appear to be fluid and ongoing. For example, plans have already been made to publish quarterly updates of the present 24 schemes. Expansion of these quarterly reports may also occur whenever an agency begins regulatory action on a new hazardous material; should this occur, the other agencies would be made aware of the new initiative through an "alert" system, which has already been set in motion.

To ensure that the coordinative effort is self-sustaining, new regulations are to describe in their prefaces how the IRLG agencies "worked together, and the effect such joint effort has on the regulation."

### 24 hazardous materials for regulation

Acrylonitrile
Arsenic
Asbestos
Benzene
Beryllium
Cadmium
Chloroform & chlorinated solvents
  Trichloroethylene
  Perchloroethylene
  Methylchloroform
Chlorofluorocarbons
Chromates
Coke-oven emissions
Dibromochloropropane
Diethylstilbestrol
Ethylene dibromide
Ethylene oxide & residues
Lead
Mercury & mercury compounds
Nitrosamines
Ozone
PBBs
PCBs
Radiation
Sulfur dioxide
Vinyl chloride; polyvinyl chloride
Waste disposal to food-chain land

Source: IRLG's Hazardous Substances Report

Hopefully these joint efforts will have the desired effect enunciated by EPA administrator Costle: "The plans aim at . . . minimizing the risks associated with [the careless manufacture, use or disposal of] these compounds while maximizing their benefits."

### And now to the details

Costle cites asbestos as an example. Here he says "Our goal . . . is not to halt essential uses such as fire proofing material but to ensure that these can be done in ways that don't jeopardize people's health or environmental quality."

Asbestos is a good example. A recent HEW report (*ES&T*, January 1979, p 15) estimates that 8–11 million workers have been exposed to this mineral. All four agencies have set standards for the substance. Millions of dollars have been spent on health-effects research. Yet controversy still rages over the health consequences of ingesting asbestos and asbestiform fibers; therefore, more studies are being conducted.

The asbestos "development plan" recommends closer cooperation with the Dept. of Transportation, which has relevant jurisdiction under its Hazardous Materials Transportation Act, and HEW's Subcommittee to Coordinate Asbestos/Asbestiform Research, and relevant programs within the Public Health Service. No other recommendations are made. Conspicuously absent are recommendations concerning coordinative health-effects research projects.

One hazardous substance for which all four agencies are contemplating regulatory action is cadmium. OSHA is planning workplace standards, and EPA is considering air-pollution controls. The CPSC, EPA and FDA recently issued a joint voluntary standard to control the leaching of this metal (and lead) from cadmium-containing decorations on glassware.

Here, the recommendations appear reasonable. The regulatory work group, it is suggested, should serve as the informal coordinator of the various cadmium-exposure analyses being carried out in the four agencies, and it should also review waste-disposal criteria for the metal; and the implications of cadmium carcinogenicity, mutagenicity and teratogenicity data.

The recommendations for the class of compounds labeled chloroform and chlorinated solvents are also more forthcoming than those for asbestos. Although, even here, vagueness creeps in. To wit: "As the results of on-going contracts and studies come in, more meetings should be held so that regulatory considerations can be a joint effort."

Regulation of nitrosamines, the report uncovers, is just over the horizon. The EPA will address the nitrosamine issue in its development plan for a National Ambient Air Quality Short-Term Standard for Nitrogen Dioxide; it is assessing the hazards of pesticides containing nitrosamines, and has already proposed a nitrosamine water standard. The FDA and the Dept. of Agriculture are considering regulating nitrite and nitrate preservatives in cured meats; these substances, when ingested, are nitrosamine precursors in humans.

For nitrosamines, the IRLG development plan recommends that "policy decisions and statutory language [be] clarified to clearly delineate FDA and EPA responsibility in regard to nitrosamines in water." The plan urges the development and validation of analytical methods for determining nitrosamines. Most importantly, the plan recommends the pooling of information and other resources regarding this substance in air, water and food to determine whether regulatory action "should be taken."

### A first step

The 24 summaries should only be considered a first effort; in those cases where the recommendations are vague or nonexistent, corrections ought to be made in the quarterly updates. Nevertheless, despite the generally poor quality of the recommendations, this inventory effort did make two significant contributions: it delineated the areas for cooperation and sharing of resources, and it uncovered important areas of research that have received little or no funding support.

In testimony before the House Subcommittee on Environment and Atmosphere, FDA Commissioner Kennedy outlined research areas needing further scrutiny. Among these are: the development of short-term tests for measuring neurotoxicity; methods to quantify risks; and more predictive animal models and risk/benefit analyses.

These are areas that the IRLG or the four agencies individually are likely to pursue in the future. In fact, the EPA and the FDA have already established a joint laboratory in North Carolina to study the subtle neural and behavioral effects of toxic materials.

### Achievements to date

The four agency heads touted IRLG's first-year achievements at the first interagency forum on December 12, 1978. In addition to the "Hazardous Substances" document, they cited the development of programs for inspection referrals whereby an inspector from one agency can refer possible violations of other laws to the pertinent agencies. Also, the four agencies have agreed upon a joint computerized information system on toxic substances that will list all regulations and relevant legal decisions. The agencies are now in the process of developing uniform health testing guidelines; the first seven are expected to be published early this year.

With the specter of deregulation hanging over their heads, the four agencies are working very hard at making the IRLG effort successful. If successful, the prospect of a legislative veto—a concept that has reared its head in Congress intermittently over the last several years, and one that, in these inflationary times, is likely to find a very favorable climate for taking hold in the 96th Congress—can be staved off.

The fatal flaw in this whole scheme of cooperation may be the zealous formation of interagency groups. What, for example, are the coordinative conduits among the IRLG, the TSSC and the Regulatory Council? Are these merely overlapping jurisdictions or compatible efforts? Has another layer of bureaucracy merely been superimposed on the once individual regulatory fiefdoms, or will these cooperative efforts produce more government efficiency?

It is still too early to answer these questions. For the moment, it is certain that the regulated industries now have the added burden of keeping a close watch on the regulatory agencies and the rapidly growing crop of interagency liaison groups and committees.

LRE

# Pittsburgh Conference: the environmental papers

*We will see you at this year's conference in Cleveland, at its convention center on March 5–9. Plan to attend and hear the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy*

## Monday, March 5
## SYMPOSIUM
### The Application of High Pressure Liquid Chromatography to Environmental Problems—Practical Applications and Regulatory Considerations

arranged by
P. C. Talarico,
Waters Associates, Inc.

**Monday Morning, Room 235A**
*P. C. Talarico, Presiding*

8:30 (041) **Keynote Address—Impact of HPLC on the Monitoring Requirements for Trace Organics**—*W. May,* U.S. Bureau of Standards

9:00 (042) **Uses of LC in Analyzing Non-Volatile Organics in Waste-Effluent**—*H. Walton,* University of Colorado

9:30 (043) **Use of HPLC in Monitoring Trace Level Organics for Chronic Toxicity**—*G. Wilson,* E G & G Bionomics

10:00 **Recess**

10:20 (044) **Cleanup and Concentration of Environmental Samples for HPLC**—*C. Creed,* LCS Laboratories, A. Wolkoff

10:40 (045) **Determination of Polynuclear Aromatics in Industrial Hygiene Samples by High Performance Liquid Chromatography**—*G. Gibson,* U. S. Department of Labor

11:20 (046) **Determination of Selected Carcinogens by HPLC**—*W. Hendricks,* U.S. Department of Labor—OSHA

**Monday Afternoon, Room 235A**
*C. Creed, Presiding*

1:30 (131) **Monitoring Waste Water for Munitions by HPLC**—*D. Helton,* Midwest Research Institute

2:00 (132) **HPLC Determination of Pesticides in Water**—*T. Steinheimer,* U.S. Geological Survey

2:30 (133) **Analysis of Industrial Waste Waters by HPLC**—*R. Hites,* Massachusetts Institute of Technology

3:00 **Recess**

3:50 (134) **Use of HPLC to Isolate a Mutagen from a Plant Waste Effluent**—*K. Carlberg,* NEIC/USEPA, R. H. Laidlaw

4:20 (135) **Analysis of Pesticides in Fish in HPLC**—*J. Moore,* Gulf Breeze ERL

## Environmental Analysis—Water Pollution I

**Monday Morning, Room 235B**
*C. E. Gonter, Presiding*
NUS Corporation

8:30 (047) **Organic Compound Characterization of Wastewater for an Environmental Assessment Study**—*M. F. Marcus,* H. H. Miller, P. H. Cramer, Midwest Research Institute

8:50 (048) **Determination of Arsenic in Natural Waters**—*W. A. Richards,* M. A. Thomas, S. R. Goode, University of South Carolina

9:10 (049) **Metal Transport: Role of Naturally Occurring Organic Substances in Aqueous Systems**—*C. A. Crumm,* O. T. Zajicek, University of Massachusetts

9:30 (050) **The Analysis of Trace Water-Soluble Polymers in Waste Water by HPLC**—*A. C. Hayman,* G. Dallas, Du Pont Instruments

9:50 (051) **Some Improvements in Analysis of Industrial Wastes for Priority Pollutants**—*W. Averill,* J. E. Purcell, Perkin-Elmer Corporation

10:10 **Recess**

10:20 (052) **Analysis of the Consent Decree PAHs in Water**—*K. Ogan,* E. Katz, W. Slavin, The Perkin-Elmer Corporation

10:40 (053) **D. C. Argon Plasma Emission Spectrometry Applied to Environmental Water Samples**—*M. S. Hendrick,* D. Eastwood, U.S. Coast Guard Research and Development Center

11:00 (054) **The ICP-ES Analysis of NURE Surface Waters of the Rocky Mountain States and Alaska**—*C. T. Apel,* B. A. Palmer, D. V. Duchane, L. B. Cox, J. V. Pena, A. D. Hues, D. L. Gallimore, Los Alamos Scientific Laboratory

11:20 (055) **Determination of pH in Soils and Specific Conductance in Wastewater using an Automated ISE System**—*A. Buccafuri,* J. Potts, R. B. Roy, Technicon Industrial Systems

11:40 (056) **Oxidative Methods for Minimizing Reagent Blank in the Determination of Low-Range Oxygen De-**

**mand**—*L. Stookey,* B. Klein, Manchester Laboratories, Inc.

## Environmental Analysis— Water Pollution II

**Monday Afternoon, Room 235B**
*A. Pollock, Presiding*
Harshaw Chemical Company

1:30 (136) **Reduction of Foaming in the Analysis of Volatile Organics in Industrial Effluent Waters when using Purge and Trap GC Techniques**—*B. N. Colby,* M. E. Rose, Systems, Science and Software

1:50 (137) **The Ultratrace Determination of Thallium In Natural Waters by Differential Pulse Anodic Stripping Voltammetric Techniques**—*J. E. Bonelli,* H. E. Taylor and R. K. Skogerboe, U. S. Geological Survey

2:10 (138) **Isolation of Polynuclear Aromatic Hydrocarbons from Water by Adsorption on Membrane Filters**—*F. Amore,* Illinois State Water Survey

2:30 (139) **Analytical Problems Encountered During the Restoration of a Mercury-Contaminated Public Water Supply**—*J. C. Cooper,* C. Hackbarth, C. M. Hellwig, D. L. Venezky, U.S. Naval Research Laboratory

2:50 (140) **An Automatic Sampler for Trace Organics in Water**—*J. D. Pope, Jr.,* A. W. Garrison, U.S. Environmental Protection Agency

3:10 **Recess**

3:20 (141) **A Statistical Evaluation of the DR-EL/4 Portable Wastewater Laboratory vs. Standard Methods**—*B. Culver,* S. Schuler, D. Miller, C. Gibbs, Hach Chemical Company

3:40 (142) **Spectrophotometric Determination of Phenols by Their Oxidation with Sodium Metaperiodate**—*L. R. Sherman,* University of Akron

4:00 (143) **High-Pressure Liquid Chromatography of Nitrophenols**—*A. F. Haeberer,* U.S. Environmental Protection Agency

4:20 (144) **Determination of Acrylonitrile in Water at the PPB Level**—*J. Going,* K. Thomas, Midwest Research Institute

4:40 (145) **Sample Preparation for Environmental Analysis**—*D. R. Lorenz,* H. Rodriguez, Waters Associates

## Tuesday, March 6
## Environmental Analysis— Air Pollution I

**Tuesday Morning, Room 235B**
*J. Frohliger, Presiding*
University of Pittsburgh

8:30 (222) **A Portable Plasma Emission System for the Determination of Mercury and Mercury Species in Air**—*D. D. Gay,* U.S. EPA, K. O. Wirtz, L. C. Fortmann, H. L. Kelley, C. W. Frank

8:50 (223) **Statistical Studies of 1975-1977 Air Pollution and Weather Data for the Phoenix, Arizona Metropolitan Area**—*M. L. Parsons,* Arizona State University, L. Y. Hara, D. D. Pratt

9:10 (224) **Analysis of Air, Stack Gas, and Solution Particulates by Secondary Target Energy—Dispersive X-Ray Fluorescence**—*D. J. Kalnicky,* Exxon Research Engineering Company

9:30 (225) **Determining Trace Quantities of Acrylonitrile in Air**—*R. L. Campbell,* D. R. Marrs, N. W. Standish, Vistron Chemical Company

9:50 (226) **Preparation and Evaluation of Silica and Asbestos Reference Materials for Pollution Studies**—*J. A. Mackey,* National Bureau of Standards, O. Menis, P. D. Garn

10:10 **Recess**

10:20 (227) **Polymer Combustion: Analysis of Volatile Smoke Products by GC and GC/MS**—*R. O. Gardner,* R. F. Browner, Georgia Institute of Technology

10:40 (228) **Experimental Improvements in Chromatographic Analysis of Ambient Level Hydrocarbons**—*R. Denyszyn,* Scott Specialty Gases, J. M. Harden, D. L. Hardison

11:00 (229) **Quantitative Determination of Sulfur Gases by Gas Chromatography**—*E. R. Kebbekus,* Matheson

11:20 (230) **The Evaluation of PPM Level Sulfur Gases in $N_2$ and Air Contained in High Pressure Aluminum Cylinders**—*F. J. Kramer, Jr.,* S. G. Wechter, Airco Industrial Gases

11:40 (231) **New Digitally Controlled API Mass Spectrometer Based System**—*N. M. Reid,* J. A. Buckley, J. B. French, C. Poon, Sciex, Inc.

## Environmental Analysis— Air Pollution II

**Tuesday Afternoon, Room 235B**
*H. Ryba, Presiding*
Alcoa Laboratories

1:30 (308) **Determination of Ammonia in the Atmosphere by Multiple Wavelength Absorption Spectrometry**—*J. M. Shekiro, Jr.,* K. R. O'Keefe, Colorado State University

1:50 (309) **Application of a Trapping Concentrator/GC System to the Trace Analysis of Volatile Organics in Polymer and Air**—*E. J. Levy,* Chemical Data Systems, Inc.

2:10 (310) **A Simple Tenax Collector/Injector for Atmospheric Sampling**—*F. H. Jarke,* IIT, Research Institute, S. Cotton, A. Dravnieks

2:30 (311) **The Laboratory Environment—Air Pollution Control**—*J. Librizzi,* Heat Systems-Ultrasonics, Inc.

2:50 (312) **Surface Analysis Techniques as Probes of Metal Speciation in Environmental Samples**—*R. W. Linton,* M. Bednar, M. E. Farmer, University of North Carolina

3:10 **Recess**

3:20 (313) **A Microcomputer Controlled Infrared Spectrometer for Ambient Air Analysis**—*J. G. Kocak,* D. K. Wilks, Foxboro Analytical

3:40 (314) **Standards for Quantitative Gas Analysis**—*E. R. Kebbekus,* D. D. Murray, Matheson

4:00 (315) **Computerized Display of Chromatographic Data for Environmental Analyses**—*R. E. Clement,* F. W. Karasek, University of Waterloo

4:20 (316) **A Microprocessor Controlled Process Gas Chromatographic System for Area Monitoring**—*J. M. Clemons,* E. Leaseburge, Bendix Environmental and Process Instrument Division

4:40 (317) **Photoacoustic Spectra of Organic Compounds on Coal Fly-Ash**—*T. Mauney,* D. F. S. Natusch, Colorado State University

## Wednesday, March 7
## SYMPOSIUM
## Environmental Organic Analysis of Water and Sediment

arranged by
David H. Freeman,
University of Maryland

**Wednesday Morning, Room 235A**
*D. H. Freeman, Presiding*

8:30 **Introduction to the Symposium**—*D. H. Freeman*

8:35 (383) **Organics in the Environment: Statistical Sampling and Instrumental Analysis**—*H. S. Hertz,* National Bureau of Standards

9:20 (384) **Implications of Transport and Transformation for Environmental Pollutant Analysis**—*G. L. Baughman,* Environmental Research Laboratory

10:05 **Recess**

10:20 (385) **Strategies for Ultratrace Analysis of Prevalent Environmental Organic Contaminants**—*C. S. Giam,* Texas A & M University

10:45 (386) **Methodless Methodology—Strategy for Alkyl Phthalate Measurement in Marine Sediments**—*D. H. Freeman,* J. C. Peterson, University of Maryland

11:10 (387) **Nonvolatile Organic Impurities in Wastewater by Liquid Chromatography**—*H. F. Walton,* University of Colorado

11:35 (388) **Aromatic Hydrocarbon Biogeochemistry in a Model EcoSystem**—*N. M. Frew,* A. C. Davis, K. Tjessem, J. W. Farrington, Woods Hole Oceanographic Institution

## Environmental Analysis— Air Pollution III

**Wednesday Morning, Room 235B**
*A. J. Kavoulakis, Presiding*
ALKAV Analytical Laboratories, Inc.

8:30 (389) **Analysis for Selected Toxic and Carcinogenic Organic Vapors in Ambient Air**—*J. W. Bozzelli,* J. Kemp, J. LaRegina, B. Kebbekus, New Jersey Institute of Technology

8:50 (390) **Evaluation of Sorbents for Trapping of Organic Vapors from the Ambient Atmosphere**—*B. Kebbekus,* R. Vaccaro, J. W. Bozzelli, New Jersey Institute of Technology

9:10 (391) **Chemical Characterization of Trace Elements in Ashes from Refuse Fueled Processes**—*G. M. Trischan,* Midwest Research Institute

9:30 (392) **Analysis of Coal Liquefaction Products by MIKES**—*D. Zakett,* V. M. Shaddock, R. G. Cooks, Purdue University

9:50 (393) **Sampling and Analyzing Techniques of Air Bag Inflator Effluents**—*B. M. Joshi,* E. L. Stokes, Ford Motor Company

10:10 **Recess**

10:20 (394) **Determination of Vinyl Chloride Monomer in the Ambient Air Near Point Source Emissions**—*J. L. Lindgren,* G. Speller, Texas Air Control Board

10:40 (395) **Analysis of Ambient Particulate Matter using a Fourier Transform Infrared Spectroscopic Technique**—*K. H. Shafer,* Battelle Columbus Laboratories, W. M. Henry, R. J. Jakobsen, R. Burton

11:00 (396) **Sample Preparation in the Determination of Free Crystalline Silica in Respirable Dust from Steelmaking Environments**—*O. P. Bhargava,* A. S. Alexiou, H. Meilach, W. G. Hines, Steel Company of Canada

11:20 (397) **Development of a Purging Technique for the Determination of Volatile Organic Pollutants in Biological Matrices**—*M. D. Erickson,* L. C. Michael, S. P. Parks, J. L. Barclay, E. D. Pellizzari, Research Triangle Institute

11:40 (398) **Application of Proton Induced X-Ray Analysis for Aerosol in the Atmosphere**—*S. Tanaka,* Keio University, R. Chiba, H. Kutsuna, Y. Osada, Y. Hashimoto

## SYMPOSIUM
## The Use of ICAP Emission for Environmental Analysis

arranged by
R. W. Freedman,
United States Bureau of Mines

**Wednesday Afternoon, Room 235A**
*R. W. Freedman, Presiding*

1:30 (470) **ICAP Analysis of Environmental Samples—Successes and Failures**—*F. N. Abercombie,* D. J. Koop, R. B. Cruz, Barringer Research Ltd.

2:15 (471) **Inductively Coupled Plasma Atomic Emission Spectroscopy—Questions Often Asked and Their Answers**—*V. A. Fassel,* Iowa State University

3:00 **Recess**

3:20 (472) **Practical Application of ICAP to Environmental Analysis**—*C. D. Carr,* Applied Research Laboratories

4:10 (473) **Analytical Aspects of ICAP in Water Quality Control**—*A. F. Ward,* Jarrell-Ash Division

## Environmental Analysis—General

**Wednesday Afternoon, Room 235B**
*J. P. McKaveney, Presiding*
Occidental Research Corporation

1:30 (474) **The Determination of Tracer Compounds by Liquid Scintillation Counting after Preparation of the Samples by Oxidation of the Host Matrix**—*J. E. Caton,* Oak Ridge National Laboratory, M. P. Maskarinec, G. M. Henderson, R. W. Harvey, M. R. Guerin, Z. K. Barnes

1:50 (475) **Some Limitations in the Determination of Labile Species by Anodic Stripping Voltammetry**—*P. M. Figura,* B. McDuffie, State University of New York at Binghamton

2:10 (476) **Time Resolved Solvent Leaching for Surface Characterization of Particles**—*M. D. M. Tucker,* University of Illinois, D. F. S. Natusch

2:30 (477) **GC-MS Analysis of Volatile Organics from Atmospheres Impacted by the Amoco Cadiz Oil Spill**—*B. J. Dowty,* J. W. Brown, F. N. Stone, J. Lake, J. L. Laseter, University of New Orleans

2:50 (478) **Determination of Several Polyaromatic Hydrocarbons at Selected Sites in Texas**—*J. L. Lindgren,* Texas Air Control Board, H. J. Krauss, M. A. Fox

3:10 **Recess**

3:20 (479) **Determination of Polyaromatic Hydrocarbons not Collected by Particulate Filter Media**—*J. L. Lindgren,* Texas Air Control Board, H. J. Krauss, M. A. Fox

3:40 (480) **Partial Chemical Speciation Techniques for Aquatic Humic-Metal Complexes**—*D. S. Chase,* J. D. Ingle, Jr., Oregon State University

4:00 (481) **Determination of Fly Ash in Biological Tissue from Animals Exposed to Coal Combustion Fly Ash**—*S. H. Weissman,* L. C. Griffis, R. F. Henderson, Lovelace Biomedical and Environmental Research Institute

4:20 (482) **Determination of Total N-nitrosamines in Cutting Oils**—*R. D. Cox,* C. W. Frank, University of Iowa

4:40 (483) **Determination of Nitrate and Nitrite at the Parts Per Billion Level**—*R. D. Cox,* University of Iowa

## Thursday, March 8
## SYMPOSIUM
## Analysis of Oil and Other Organic Pollutants

arranged by
A. P. Bentz,
U. S. Coast Guard Research & Development Center

**Thursday Morning, Room 239**
*A. P. Bentz, Presiding*

8:30 (527) **Artificial Oil Weathering Techniques**—*C. P. Anderson,* University of Connecticut, T. J. Killeen, J. B. Taft, A. P. Bentz

8:50 (528) **Interlaboratory Comparison of Environmental Analyses Associated with Increased Energy Production**—*F. R. Guenther,* H. S. Hertz, L. R. Hilpert, W. E. May, S. A. Wise, J. M. Brown, S. N. Chesler, National Bureau of Standards

9:10 (529) **Laser-Excited Matrix-Isolation Molecular Fluorescence Spec-**

**trometry of Polycyclic Organic Compounds**—*E. L. Wehry,* R. B. Dickinson, Jr., R. R. Gore, University of Tennessee

9:30 (530) **Investigation of the Use of Molecular Fluorescence for Identification of Hazardous Materials**—*L. P. Giering,* J. T. Brownrigg, Baird Corporation

9:50 **Recess**

10:00 (531) **GPC Enrichment and Carbon Chromatographic Fractionation of Hydrocarbons and Other Environmental Contaminants**—*J. D. Petty,* D. L. Stalling, L. M. Smith, Columbia National Fisheries Research Laboratory

10:20 (532) **Problems with the Chemical Analysis of Marine Sediments**—*F. E. Franklin,* J. Borges, V. Dunning, C. W. Brown, University of Rhode Island

10:40 (533) **A Facile Method for the Determination of Trace(sub-ppm) Hexamethylenediamine in Water**—*J. Hanrahan,* Allied Chemical Corporation

11:00 (534) **Detection and Determination of Acetohydroxamic Acid in Industrial Wastewater**—*D. Richton,* Allied Chemical Corporation

11:20 (535) **Infrared Spectrophotometric Determination of Neopentylester Lubricating Oils in Water**—*G. J. Gottfried,* Biospherics, Inc., T. S. Yu, D. G. Shaheen

## Environmental papers in other sessions for the serious environmental watcher*

### Monday, March 5

**Room BR**
9:30 (064) **Determination of Lead in Environmental Water Samples using Flameless Atomic Absorption Spectrophotometry**—*R. J. Faust,* Calgon Corporation

**Room BR**
10:20 (066) **Determination of Total Phosphorus in Industrial Process Waters by Flameless Atomic Absorption**—*E. L. Henn,* Calgon Corporation

**Room 239**
11:00 (018) **A New Fully Integrated GC/MS/DS System**—*M. S. Story,* D. M. Taylor, T. R. Stevens, Finnigan Corporation

**Room MH**
11:00 (078) **A New Glass Capillary Gas Chromatograph for the Analytical Needs of Tomorrow**—*T. A. Rooney,* R. R. Freeman, Hewlett-Packard Company

**Room MH**
11:20 (079) **Designing a New Chromatograph for Tomorrow's Applications**—*L. Mikkelsen,* M. Murphy, Hewlett-Packard Company

### Monday afternoon

**Room MH**
2:10 (164) **Industrial Hygiene Air Samples Analysis—Improved Results Through Automation Using Glass Capillary Columns and a Multi-Channel Data System**—*R. C. Domingo,* J. W. Bailly, D. R. Brezinski, DeSoto, Inc.

**Room 3A**
2:50 (115) **A Coupled HPLC/GC System: Instrumentation and Automation**—*S. P. Cram,* A. C. Brown III, E. Freitas, R. E. Majors, E. L. Johnson, Varian Instrument Division

**Room 3A**
3:20 (116) **A Coupled HPLC/GC System: Applications**—*R. E. Majors,* E. L. Johnson, S. P. Cram, A. C. Brown III, E. Freitas, Varian Instrument Division

**Room LT**
3:25 (149) **Application of Ion Chromatography to the Analysis of Atmospheric Pollutants**—*J. D. Mulik,* United States Environmental Protection Agency

**Room BR**
4:20 (160) **Evaluation of Simultaneous Multielement Atomic Absorption—Electrothermal Atomization Analysis Applied to Natural Water Matrices**—*R. G. Rowley,* P. R. Beaulieu, J. L. Maglaty, K. R. O'Keefe, Colorado State University

### Tuesday, March 6

**Room BR**
8:50 (239) **The Thermal Environment of Furnaces of the Massmann Design**—*S. Myers,* D. C. Manning, F. J. Fernandez, Perkin-Elmer Corporation

**Room MH**
10:15 (250) **Environmental Analysis with Glass Capillary Columns**—*W. Bertsch,* University of Alabama

**Room BR**
10:20 (243) **Comparison of Proton-Induced X-Ray Emission (PIXE) with AAS for the Determination of Acid Leachable Trace Metals in Marine Sediments**—*G. C. Grant,* R. K. Jolly, D. C. Buckle, The College of William and Mary

**Room 235A**
11:00 (219) **Direct Monitoring of Airborne Heavy Metal by Air Plasma Spectrometry**—*S. Hanamura,* National Measurement Laboratory

**Room 205**
11:20 (190) **Laser Optoacoustic Detection of $NO_2$ in a Flow System**—*A. Fried,* National Center for Atmospheric Research, D. H. Stedman

### Tuesday afternoon

**Room 235A**
1:30 (297) **Ion Chromatography Coupled with Ion Exclusion (IC/IE): Instrumentation and Applications**—*W. Rich,* F. C. Smith, Jr., L. McNeill, Dionex Corporation

**Room 235A**
2:10 (299) **Application of Ion Chromatography to Analysis of Industrial Process Waters**—*J. A. Rawa,* Calgon Corporation

**Room LT**
2:25 (319) **Utilizing a Microprocessor in a Dedicated Analytical Instrument**—*C. J. Sitek and R. B. Edwards,* LECO Corporation

**Room 235A**
2:50 (301) **Anion Analysis by HPLC**—*K. Harrison,* The Separations Group, D. Burge

**Room 239**
2:50 (271) **Surface Analysis of Particulates**—*C. J. Powell,* T. Jach, National Bureau of Standards

**Room LT**
3:30 (320) **Applying a Microprocessor to Multicomponent Infrared Analysis**—*P. Wilks,* Wilks-Foxboro Analytical

**Room MH**
3:15 (334) **Screening for Priority Pollutants in Industrial Waste Waters**—*T. Sabatino,* Rutgers University

**Room 240**
3:40 (258) **Low Level Nitrogen Analysis with a New Elemental Analyzer**—*R. F. Culmo,* Perkin-Elmer Corporation

**Room CRB**
3:40 (293) **The Analysis of Some Waste Lubricating and Residual Fuel Oils by High Performance Liquid Chromatography**—*J. M. Brown,* W. E. May, National Bureau of Standards

**Room MH**
4:35 (337) **Column Selection for Pesticide and PCB Analyses in Water—Advantages and Pitfalls**—*F. Onuska,* Canadian National Water Research Institute

### Wednesday, March 7

**Room 240**
9:10 (340) **Magnetic Resonance and Infrared Spectral Studies of Structural Changes during Coal Liquefaction**—*M. R. Hough,* H. L. Retcofsky, T. A. Link, D. H. Finseth, U.S. Department of Energy

**Room 205**
9:10 (350) **Application of an Inductively Coupled Plasma/Direct Reading Polychromator to the Multielement Analysis of Stream Sediment Extracts**—*G. F. Larson,* R. W. Morrow, L. E. White, Union Carbide Corporation—Nuclear Division

9:30 (351) **Sequential Determination of 60 Elements in Geochemical and Environmental Matrices by Inductively Coupled Plasma-Atomic Emission Spectrometry**—*M. A. Floyd,* A. P. D'Silva, V. A. Fassel, M. Tschetter, Iowa State University

**Room 3A**
9:30 (366) **Identification and Determination of Minerals in Whole Coal by Diffuse Reflectance Infrared Spectrometry**—*M. P. Fuller,* P. R. Griffiths, Ohio University

**Room BR**
11:40 (418) **The Fate of Trace Metals in a Batch Type Coal Gasification Unit**—*P. M. Grohse,* S. K. Gangwal, D. E. Wagoner, Research Triangle Institute

### Wednesday afternoon

**Room 205**
2:10 (436) **Total Sulfur in Hydrocarbons by Oxidative Microcoulometry:**

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* LT is the Little Theatre, MH the Music Hall, CRB, the Club Room B, and BR, the Ballroom of the Convention Center.

**10 ppb to 10%**—*R. T. Moore,* Envirotech, P. Clinton, V. Barger

**Room 205**
2:50 (438) **Trace and Minor Element Analyses of Liquefaction Products From West Virginia Coal**—*R. G. Lett,* R. R. DeSantis, J. W. Adkins, R. A. Hahn, U.S. Department of Energy

**Room CRB**
2:50 (464) **A Semi-Automatic Standard Addition Method for the Analysis of Pesticide Formulations**—*R. J. Obremski,* J. Bernard, J. W. Mohar, Beckman Instruments, Inc.

**Room 240**
3:20 (429) **A Resonance Raman Method for the Rapid Detection and Identification of Bacteria in Water**—*W. F. Howard,* W. H. Nelson, J. Sperry, University of Rhode Island

**Room 205**
3:40 (440) **Determination of Total Organic Carbon (TOC) in Sea Water by UV Promoted Persulfate Oxidation**—*Y. Takahashi,* Envirotech

**Room 205**
4:20 (442) **Total Nitrogen in Hydrocarbons by Automated Chemiluminescence Detection System: 20 ppb to 1%**—*J. M. Castro,* R. T. Moore, Envirotech

**Room 205**
4:40 (443) **PPB Sulphate Determination by MECA-VAP**—*S. L. Bogdanski,* A. Townshend, I. S. A. Shakir, University of Birmingham

**Room 240**
4:40 (433) **Use of the Molecular Microprobe for Analysis of Sulfur Compounds in Coal and for Monitoring of P-N Junctions**—*F. Adar,* R. Grayzel, D. Landon, Instruments SA, Inc.

## Thursday, March 8

**Room 240**
8:50 (508) **Analysis of Synfuel Waste Water by Second-Derivative Synchronous Luminescence Spectroscopy**—*T. Vo-Dinh,* R. B. Gammage, A. R. Hawthorne, Oak Ridge National Laboratory

**Room BR**
8:50 (576) **Data Reduction for GC/MS Analyses of Water and Water Extracts for EPA's Priority Pollutants**—*J. M. Rombough,* NUS Corporation

**Room 205**
9:30 (520) **Electrochemical Detection of Mercury**—*D. D. Nygaard,* Bates College

**Room BR**
10:20 (580) **Application of Capillary Column GC/MS to Water Pollutant Analysis**—*E. M. Chait,* T. A. Blazer, E. I. du Pont de Nemours & Co.

**Room 205**
10:40 (523) **Advances in Ion Selective Electrodes Technology**—*J. Driscoll,* E. Atwood, J. Fowler, HNU Systems, Inc.

**Room 235A**
10:40 (562) **Nebulizers for ICPOES and AAS: Aerosol Characterization**—*J. W. Novak,* R. F. Browner, Georgia Institute of Technology

**Room 235B**
11:30 (570) **Development of an Instrument for Continuous, Automated and Low-Cost Monitoring of the Organic Loading in Water**—*W. J. Cooper,* U.S. Army Medical Bioengineering R & D Lab.

**Room 3A**
11:40 (545) **Applications of a New Infrared Spectrophotometer with Microprocessor Control**—*I. A. Steer,* R. C. J. Osland, Pye Unicam Ltd.

## Thursday afternoon

**Room BR**
2:30 (665) **Chemical Compound Glass Separation in Shale Oil Analysis**—*P. C. Uden,* F. P. DiSanzo, S. Siggia, University of Massachusetts

**Room 235B**
2:30 (653) **An Evaluation of Continuous Monitoring Procedures for Cyanide**—*B. Fleet,* S. das Gupta, HSA Reactors Ltd.

**Room BR**
2:50 (666) **Applications of High Resolution Glass Capillary Gas Chromatography in Analysis of Synthetic Fuels From Coal**—*C. M. White,* U.S. Department of Energy, D. L. Vassilaros, M. L. Lee

**Room 235B**
3:40 (656) **A New On-Line Colorimetric Analyzer for Water and Wastewater**—*R. Clemens,* J. Chisholm, C. Hach, P. Larson, D. Schoonover, Hach Chemical Company

## Friday, March 9

**Room 235A**
8:30 (722) **The Du Pont "Prep 1"—A Rapid Automatic Sample Processor for LC/GC Analysis**—*A. P. Goldberg,* G. Dallas, Du Pont Instruments

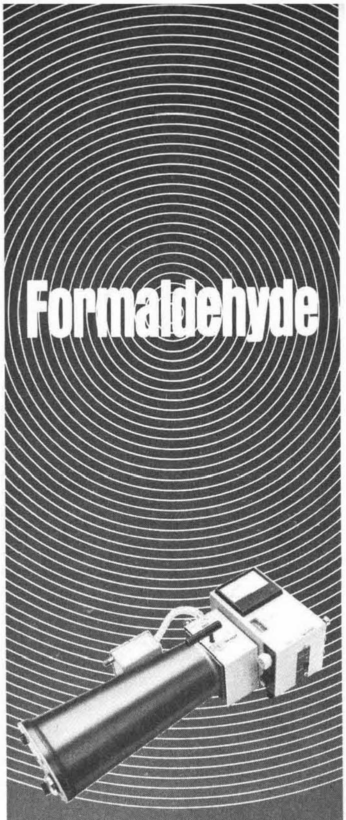
**Room LT**
8:50 (713) **The Evaluation of a Low Cost Computerized ICAP Direct Reading Spectrometer for the Routine Analysis of Ecological Samples**—*J. P. Maney,* V. J. Luciano, L. F. Marciello, A. F. Ward, Jarrell-Ash Division

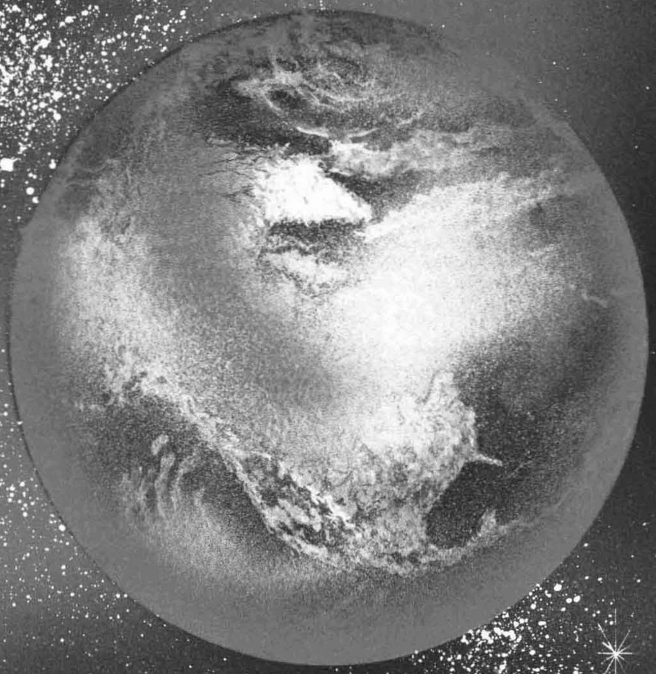
**Room 205**
9:30 (695) **Analysis of Coal and Coal Ash by Energy Dispersive X-Ray Fluorescence**—*B. D. Wheeler,* N. Jacobus, EG&G ORTEC, Inc.

**Room 205**
10:40 (698) **Standardless Determination of Some Heavy Metals in Airborne Particulate Matters by X-Ray Fluorescence Spectrometry**—*K. Ohno,* National Research Institute for Metals

**Room 240**
10:40 (688) **ASTM Method of Testing for Determining the Arrhenius Kinetic Constants for the Screening of Potentially Hazardous Materials**—*R. B. Cassel,* W. P. Brennan, R. L. Fyans, A. P. Gray, Perkin-Elmer Corporation

**Room 240**
11:00 (689) **Measurement of Critical Thermal Stability Parameters for Potentially Hazardous Materials**—*R. L. Blaine,* P. S. Gill, Du Pont Instruments





## REGULATORY ALERT

# Economic penalties in CAAA

**Michael R. Deland**
*ERT, Concord, MA*

The Clean Air Act Amendments of 1977 (CAAA) substantially increased the enforcement powers of EPA and the States by adding two new types of economic penalties. The two are court-imposed "civil penalties," which may be assessed for violations going back to Aug. 7, 1977, and "noncompliance penalties," which will commence to run for violations after Aug. 7, 1979.

Both of these new sanctions reflect Congressional frustration with continuing delays in the attainment of the health-related standards. Two civil penalty provisions are an extremely powerful new tool in the regulatory arsenal, particularly when complemented by the noncompliance penalties, which are triggered automatically, and over which EPA and the States have very little discretion.

### A new test

The civil penalty provision supplements the criminal penalty sanctions for "knowing and willful" violations. (The criminal provision was toughened to make "any responsible corporate officer" personally liable.) The new civil penalties provide much more leverage for enforcement officials because civil liability need only be proven by a "preponderance of the evidence," a substantially lighter burden than the criminal standard of "beyond a reasonable doubt." Additionally, "knowledge" or "willfulness" are not elements of the civil provision, so only the occurrence of the violation must be proved.

The premise of the civil penalty provision is that it is unfair for a relatively small number of sources to continue to violate when the majority have made the effort and capital outlay to comply. The amount of the penalty (up to $25 000 per day per violation) may be determined by considering the size of the business, the economic impact of the penalty on the business and the seriousness of the violation. It is intended to be used as a punitive sanction as well as an economic incentive for compliance.

The calculation of the amount of the civil penalty is highly structured. Not only are specific formulas provided, but the amount of the penalty to be sought in each case is reviewed by a panel of top officials from EPA, the Department of Justice, and some state agencies. The amount approved by this panel is a minimum, and the U.S. Attorneys and others negotiating settlements of these cases are instructed not to settle for less than the approved amount.

### For noncompliance

The other new economic sanction requires a *mandatory* assessment of "noncompliance penalties" against nearly every violating source of air pollution after Aug. 7, 1979. Similar to the civil penalty promise, this penalty is designed to eliminate any financial incentive to defer pollution control investments. There are only a limited number of exemptions from these *automatic* penalties (for example, for innovative technology or insignificant violations). EPA draft regulations describe in detail the method for calculating the amount of the penalty and the procedures governing the federal and state systems of penalty assessment and collection.

The basic approach of the proposed penalty calculation formula is to determine the present value of the pollution control investments that *should have been made* and the present value of the investments that *are being or will be made*, and to take the difference between the two as the source's economic benefit of not timely complying with the pollution control regulations. Obviously, if major control equipment such as scrubbers is required, the penalties will be substantial.

The details for administering the noncompliance penalty system may vary in those states where the state agency has submitted and received approval for a plan for assessing and collecting these penalties. Such plans must fulfill the requirements of EPA's draft regulations.

### Calculation of penalty

The source owner or operator must calculate the penalty owed and establish a payment schedule. If the source fails to calculate the penalty, the enforcement agency may hire an outside contractor to do the calculation and add the contractor's fee to the amount of the penalty. The enforcement agency must, within 30 days, review the calculation and either accept it, request more information or recalculate it. The source may request a hearing to challenge any recalculation.

The regulations sharply restrict both the subjects that can be raised in a petition for a hearing and the discretion of the hearing officer. Only two defenses against assessment of a penalty may be allowed in a petition for a hearing: the violation did not occur, or the source is eligible for an exemption (or both).

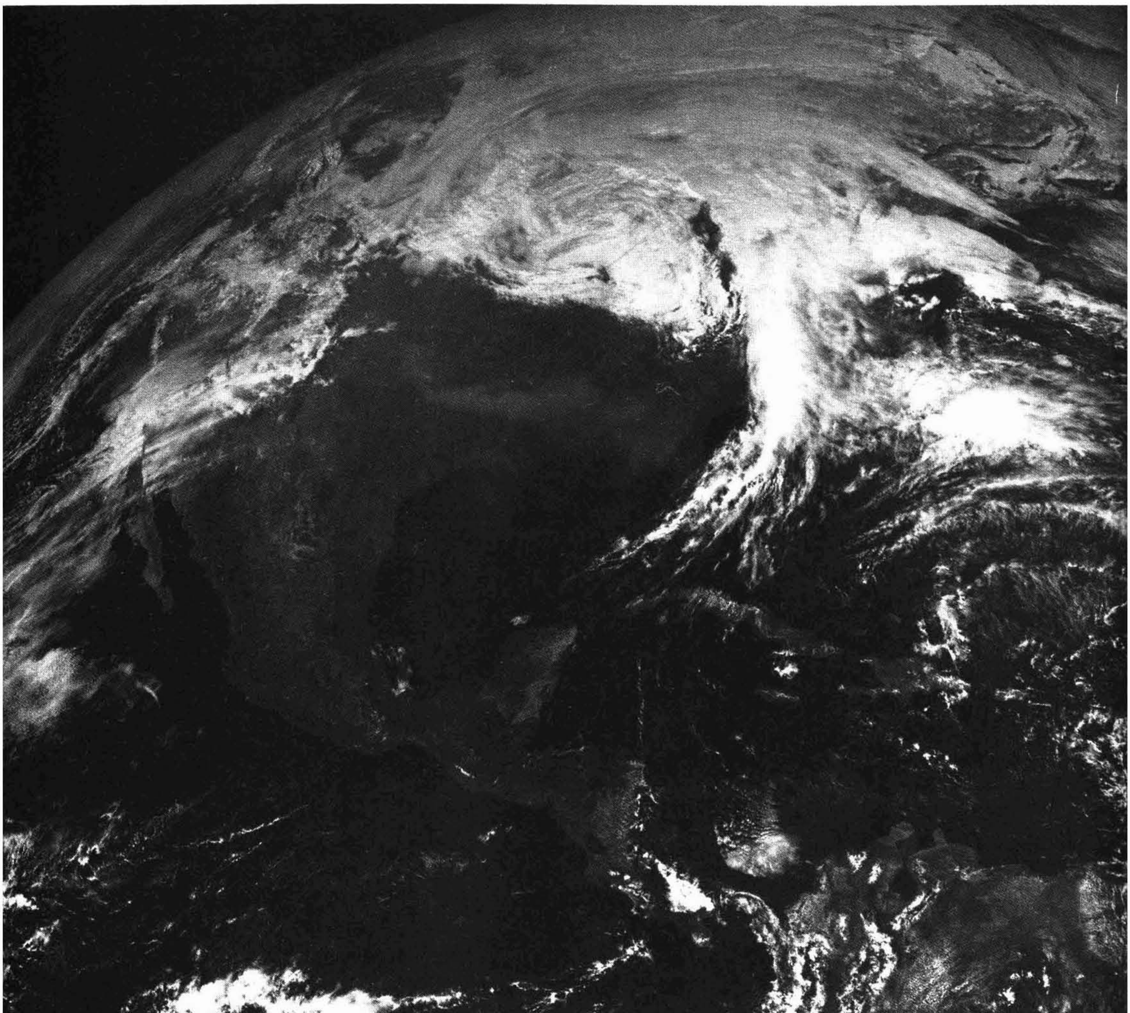
The regulations envision a fast-paced and simple hearing procedure, with final disposition of the case within 90 days of receipt of a petition. Given the severe economic consequences of these automatic penalty provisions, the calculation formula, and other crucial aspects, should be carefully scrutinized and comments submitted before the regulations are finalized.

Once the penalties start to run on Aug. 7, 1979, very little flexibility will remain with the regulatory agencies. The Amendments provide that civil penalties can be assessed in addition to the mandatory noncompliance penalties. Whether individually or in tandem, these new economic sanctions substantially increase the incentives to comply with the Act.

ES&T FEATURE

# Focus on climate

*An international gathering of experts, the first World Climate Conference, meets in Geneva, Switzerland, from February 12–23 to assess and integrate current knowledge of climate with knowledge from other disciplines which, in combination with climate, affect human activities and the environment*



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**F. Kenneth Hare**
*Institute for Environmental Studies*
*University of Toronto*
*Toronto, Ontario M5S 1A4*

The 1970s may well go down in history as a decade when climate became a major destabilizing factor in the world economy. In no previous decade, except the 1930s, was as much attention given to climatic anomalies and their impact on mankind. The 1930s saw severe drought in many crop-producing areas, and there was considerable damage to soils. But the world's demand for food was then much smaller, in part because the population was only half of what it is now and, in part, because of poverty. Yet, in the midst of crop failures and bread-lines, we had surplus supplies.

In the 1970s it has been different. The world is now richer and more populous. Large populations lie at the margin of self-sufficiency even in good climatic years. And the world grain trade is readily upset by quite small climatic differences, even though production from year-to-year varies by less than 1% on either side of the upward trend observed since 1950.

### Politicians, scientists respond

Many politicians have become receptive to the idea that world action may be needed to combat the impact of hostile climate. In Africa this view is almost unanimous. The same attitude prevails in the central and western states and provinces of North America, where the specter of drought has once again shown itself. Along with bumper crops, the Soviet Union has also had two disastrous growing seasons—1972 and 1975—in this decade.

Faced with predictions in the media that events like these periodic droughts are the forerunners of a lasting shift toward worse conditions, the political world has had to take account of the climatic problem.

The scientific and technical world has not been slow to respond. This month, the World Meteorological Organization (WMO, a UN agency), in conjunction with several other world bodies, is to stage the first World Climate Conference (WCC). This conference will, it is hoped, draw up a plan of action for a World Climate Program (WCP), to which WMO is already committed in principle. WMO has an excellent record in organizing and executing world research and observational programs, so these meteorological ventures are likely to succeed.

But they will be new and strange exercises for a profession—meteorology and climatology—structured, as it is, on the physical sciences, chiefly physics, mathematics and chemistry. Meteorologists are comfortable with tackling problems of climatic research. And there will be a large research component in WCP, which will be jointly carried out, as was the Global Atmospheric Research Program, with the International Council of Scientific Unions (ICSU), which brings together the various nongovernmental scientific unions.

However, when it comes to the impact of climate on humanity, meteorologists and climatologists are on less familiar ground. And the social scientists to whom they might turn are not as internationally organized as are the members of ICSU.

The idea of a conference was deliberated at the 1975 U.N. Conference on Food, where hostile climate was seen as a serious threat to future food supplies. Quite independently, the WMO Executive Committee's Panel of Experts on Climatic Change put forward similar views. In January 1974, and again in June 1975, the Rockefeller Foundation also held small but influential conferences on climatic impact.

The 1975 Rockefeller Foundation Conference (which I chaired) was held at the Villa Serbelloni in Italy. Its report somehow reached Henry Kissinger's table, and he used it as a basis for a message to the U.N. The Soviet Union, at that time, also supported the idea of a world parley, and has since strongly backed the preparations for this month's meeting.

"This Conference is a response by the WMO and other U.N. agencies to the growing worldwide concerns about the impacts of natural variations in climate upon world food production, energy supply and demand, water resources, land use, and other aspects of society. It is also a response to the ominous indications that man, through his own activities, may cause significant changes in climate. There are now sufficient indications that some of these potential changes, such as those that might result from increased amounts of atmospheric carbon dioxide, could have a pervasive impact upon the nations of the world and may require unprecedented forms of international actions to deal with them effectively."

**Robert M. White**
*Chairman,*
*World Climate Conference*

### Conference's structure . . .

It was decided by WMO's Executive Committee that the first-stage conference should be a consultation of invited experts, drawn mainly from disciplines or professions outside the atmospheric sciences. About 100 experts will attend, reinforced in the first week, which will be devoted to overview papers, by 300 others who wish to be there.

The list of persons invited is broadly representative of expert knowledge of areas *impacted* by climate. It includes foresters, agriculturists, marine scientists, fisheries experts, energy specialists and many others. All major parts of the world are represented. There is also a small nucleus of senior atmospheric scientists, who will present what is known about climatic variation and variability.

The difficult task of picking the experts was left by the organizing committee to its bureau, which has had the job of detailed planning. Its chairman, and that of the conference, is Robert M. White, until recently the administrator of NOAA, and now chairman of the Climate Research Board, National Academy of Sciences. The other members are Jim Dooge, the former president of the Irish Senate, and a distinguished hydrologist; and Yu. Sedunov, first deputy chief of the Hydrometeorological Service of the U.S.S.R.

I have served with the bureau as consultant to the secretary-general of WMO, and have convened the overview papers. William W. Kellogg, of the National Center for Atmospheric Research, who plays a similar role with respect to WCP, has also had much to do with the input to the conference.

The main input will be a series of 25 overview papers, written by a remarkable team of authors who met in April 1978, at Laxenburg, Austria, (as guests of the International Institute of Applied Systems Analysis) to concert their efforts. Two versions of these reports will be available. A summary version (averaging about 3000 words each) will be translated into all the conference's official languages (English, French, Russian, and Spanish). The more complete version (averaging 10 000 words) will be published after the conference in book form, and will constitute the most thorough analysis of climatic impact ever published.

### . . . And its content

The conference will be opened by a keynote address from the chairman, Dr. White, summarizing the reasons why the group has been convened, and stressing its role in relation to the forthcoming World Climate Program. The keynote address will be followed by the opening overview paper, on climate and society, given by academician Yevgeny K. Fedorov, a member of the Praesidium of the Supreme Soviet, and one of the pioneers of the remarkable Soviet research program on the north polar pack-ice.

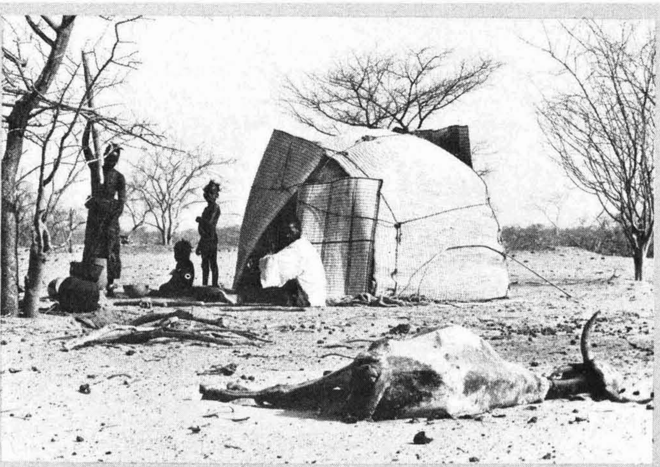
Fedorov discusses philosophically the extent to which political systems can usefully absorb better climatological information and services. He gently pulls the western world's leg by pointing out our inability to plan, and to identify the decisionmakers. But no ideological gap opens between his paper and White's. Indeed the whole documentation displays a degree of unanimity rare in international affairs.

The second group of papers has to do with climate itself. They are written for lay audiences by professionals, and cover most aspects of current knowledge of climate. Larry Gates of Oregon State University has written on the fundamental causes of climate and its variation. Bert Bolin, of the University of Stockholm, writes (with UNESCO sponsorship) on climate and global ecology, laying stress on the fundamental assumption of the conference—that climate is an interactive system involving soil, plants, animals and oceans. The intrusion of man into this system is reviewed in a paper by R. E. Munn of the University of Toronto and Lester Machta of NOAA. I contribute a paper on climatic variability and variation, and Ju. P. Izrael, chief of the Board of the Hydrometeorological Services of the Soviet Union, deals with the monitoring of climate and climatic change. Academician I. P. Gerasimov of Moscow writes about variation of climate during geological history, drawing extensively on geological and paleobotanical evidence.

A third series of papers deals with the scientific modeling of climate, and of its sensitivity to human interference. Academician G. I. Marchuk of the Siberian Academy of Sciences Central Computing Center at Novo-Sibirsk deals exhaustively with the fundamentals of atmospheric modeling itself: a giant problem made even larger by the need to include the two-way relation with human society. John Mason, head of the U.K. Meteorological Office, then analyzes what modeling studies have actually taught us about such questions as the potential impact on climate of stratospheric pollution and of carbon dioxide build-up. Hermann Flohn, of the University of Bonn, sketches scenarios of future climates by another kind of analysis. He delves back into the past to find analogs of what may happen in the future.

The conference will then go on to the chief areas of climatic impact. The series of papers on agriculture was coordinated by Michel Frère of the Food and Agricultural Organization. M. S. Swaminathan of the Indian Council of Agricultural Research presents a comprehensive overview of the present world food situation, and its vulnerability to climatic and other disturbances.

A series of sectoral papers then follows. Francesco Mattei, of the Ufficio Centrale di Ecologia Agraria, Rome, writes on the notoriously vulnerable agriculture of the semiarid tropics. A specific study of the problems of Africa during the Sahelian drought, and at other times of stress, conducted by Julius Oguntoyinbo of the University of Ibadan and Richard S. Odingo of the University of Nairobi, is presented by these scientists. Hayao Fukui of the Center for Southeast Asian Studies, Kyoto, gives a very detailed analysis of the agricultural problems of the humid tropics, dealing not only with irrigated rice, but with rainfed agriculture and



### Economic, political repercussions of recent climatic events[a]

- **1970:** The Sahel, the southern border areas of the Sahara Desert, experienced a 5-y drought; the result was widespread death and famine. A costly, sometimes ineffectual international food-aid program fed nomadic populations at refugee camps.
- **1972:** First a severe winter freeze, then an extreme summer heat wave and drought reduced Russian grain production by 12%. Massive grain purchases by the Soviet government in the world food-grain market sent prices skyrocketing.
- **1972:** El Niño, a warming of coastal waters associated with changes in atmospheric circulation, and overfishing brought on the collapse of the anchovy harvest off the coast of Peru. The impact was felt on international supplies of animal protein and world demand for soybeans.
- **1974:** Poor monsoon rains in India and Southeast Asia resulted in reduced food production in that region.
- **1975:** Half the coffee trees in Brazil were destroyed by a severe frost. World coffee prices increased dramatically.
- **1977:** Abnormally severe cold weather in the eastern and midwestern U.S. drained the finite supplies of natural gas. The result was the closing of schools and industries, and widespread unemployment.

[a] Adapted from Robert M. White.

tree crops as well. James McQuigg of Columbia, Missouri, deals with the impact of climate on middle latitude agriculture and its offshoot, the international grain trade. Juan Burgos writes of climate-related problems in Latin America. Chinese authors, Chang Chia-cheng, Wang Shao-wu and Cheng Szu-chung, present a case history of climatic change in the People's Republic of China, and its impact on agriculture.

In the same genre, A. Baumgartner of the University of Munich deals extensively with forest-climate interactions. Like many other authors, he lays stress on the role of vegetation in modulating the carbon cycle. David H. Cushing, of the Fisheries Laboratory, Lowestoft, England, discusses world marine fisheries, especially those of the Atlantic, and shows how the recent spell of relative warmth (essentially 1910–1960) had dramatic impacts on recruitment of fish stocks, and looks at the effect of the 1972 El Niño on the Peruvian anchovy catch. A paper by T. F. Gaskell, executive secretary of the International Oil Industry Group on Exploration and Production, London, deals with the relation of climate and weather to the exploitation of the ocean's bottom resources, chiefly oil, and the transportation of the product. His paper, too, was sponsored by UNESCO.

**Drought.** *Total precipitation, which was several inches below normal for the Bath, S.D., area, was responsible for the loss of this corn crop*

### Other interacting forces

The major question of energy-climate interaction, which also has a major bearing on the carbon dioxide problem, is dealt with in a study by a group from the International Institute for Applied Systems Analysis, Jill Williams (now at the National Center for Atmospheric Research, Boulder, Colo.), Wolf Haefele and Wolfgang Sassin.

Water resources interactions, yet another area highly sensitive to climatic fluctuations, are treated in a paper by John C. Schaake, of NOAA's Hydrologic Services Division, and Z. Kaczmarek, Director of the Institute of Meteorology and Water Management, Warsaw. Health impacts are covered in a WHO-sponsored paper by W. H. Weihe of the University of Zurich's Biologisches Zentrallaboratorium.

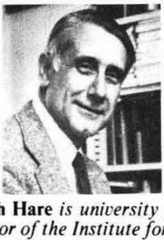
Finally, the overall impact of climate on human economic concerns is covered by two papers from well-known U.S. economists. Ralph D'Arge, of the University of Wyoming, deals with the impact of climate on the world economy, using chiefly the work which he directed under the U.S. Climatic Impact Assessment Program Kenneth Arrow of Harvard, a former meteorologist and Nobel Laureate in economics, considers decisionmaking problems.

### A plan of action

Out of this welter of authoritative information, plus its own expertise, the conference will fashion a plan of action. The second week will be devoted to working group sessions aimed at such a plan, aided by careful preparatory work done in a series of informal planning meetings. It would be impertinent to try to foresee the contents of such a plan in detail, but no doubt it will have to cover, *inter alia,* at least these points:

- The virtual unanimity in the overview papers that the build-up of carbon dioxide and contaminants in the atmosphere will induce significant climatic change within the next century; and that it is vital to try to foresee the character of this change, so that its impact may be mitigated, or conceivably exploited.
- The recognition of the need for extensive research and modeling exercises whose scope will be extended to the whole climatic system, whose sensitivity to human interference can hence be tested.
- The obvious need for more formal techniques for climatic impact assessment. This will have to include the development of new and sophisticated interdisciplinary modes of research and operation, with a larger input from economics and ecology than has been usual in the past.
- The vital need to determine the degree of resilience or vulnerability of the various national economies to climatic impact, and to consider ways and means of assistance to those countries or peoples who may in the future find themselves in jeopardy as some major anomaly strikes.

There will be many other items in the plan, especially as regards climatic services, applications and data gathering. At the root of all this, however, will be the unspoken motto of the conference: understanding climate in the service of mankind.



**F. Kenneth Hare** *is university professor, and director of the Institute for Environmental Studies at the University of Toronto. Dr. Hare is a Fellow of the Royal Society of Canada and the American Association for the Advancement of Science.*

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# Textile plant wastewater toxicity

*A study collected baseline data on priority pollutant concentrations and chemical toxicity, in support of BATEA standard-setting*

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In mid-1974 and mid-1976, two U.S. Environmental Protection Agency (EPA) regulatory events occurred which led to a large research effort designed to evaluate the toxicity of textile plant wastewaters, and to determine the most effective treatment technology.

The first one occurred in June 1974, when EPA's Effluent Guidelines Division set forth guidelines for the degree of effluent reduction attainable through the application of the "Best Practicable Control Technology Currently Available" (BPCTCA), and the "Best Available Technology Economically Achievable" (BATEA), to be achieved by existing textile manufacturing (SIC 22) point sources by July 1, 1977 and July 1, 1983, respectively. However, on October 1, 1974, the textile manufacturing industry, represented by the American Textile Manufacturers Institute (ATMI), Northern Textiles Association, and Carpet and Rug Institute, filed a petition with the U.S. Fourth Circuit Court of Appeals, asking for a review of the proposed 1983 effluent guidelines.

Grounds for the suit were that the BATEA had not been demonstrated for the textile manufacturing industry. Thus, ATMI and EPA filed a joint motion for delay of the petition, stating that additional information would be developed through a cooperative grant study by ATMI and EPA's Industrial Environmental Research Laboratory at Research Triangle Park, N.C. (IERL-RTP).

### BATEA determination

The objective of the ATMI/EPA Grant Study was to gather enough technical and economic data to determine the BATEA for reducing criteria pollutants from textile wastewaters. Criteria pollutants for the textile industry include 5-day biochemical oxygen demand ($BOD_5$), chemical oxygen demand (COD), color, sulfide, pH, chromium, phenol, and total suspended solids (TSS). On January 3, 1975, the Court instructed ATMI and EPA to proceed as promptly as possible to a completion and review of the study.

To evaluate the best available technology, two mobile pilot plants were constructed and operated by ATMI's contractor, Engineering Sciences, Inc. This strategy allowed for real-time flowthrough treatability studies. Each pilot plant contained five tertiary wastewater treatment unit operations. In addition, a tertiary treatment technology was laboratory tested. One of the mobile plants was scheduled to visit 12 textile plants, and the other to visit 11.

Treatment operations in each mobile unit included a reactor/clarifier (using combinations of alum, lime, ferric chloride, and anionic and cationic polyelectrolytes), two multimedia filters, three granular activated carbon columns, ozonation, and dissolved air flotation. Powdered activated carbon treatability tests were performed in the laboratory, instead of in the field, with the pilot plant. From these six-unit operations, ATMI and EPA selected seven treatment modes for evaluation (Figure 1).

Each of the seven treatment modes was to be individually set up, with operational and pollutant data collected over a 2- to 3-day period. Based on those data, the "best" system for each plant was to be set up for 2 weeks of operational evaluation. These data were then to be forwarded for economic evaluation.

Prior to pilot plant field testing, the second EPA regulatory event occurred, and formed the basis for the toxicity study. On June 7, 1976, the U.S. District Court of Washington, D.C., issued a consent decree (resulting from Natural Resources Defense Council, et al. *vs* Train) requiring EPA to accelerate development of effluent standards for 21 industrial point sources, including textile manufacturing. Among other requirements, the Court's mandate focused federal water pollution control efforts on potentially toxic and hazardous chemical compounds.

The original consent decree required that "65 classes" of chemical compounds be analyzed in wastewater samples. Recognizing the difficulty of analyzing for all chemical species present in each category of compounds, EPA developed a surrogate list of 129 specific compounds representative of the classes of compounds listed in the consent decree.

These compounds are referred to as "priority pollutants," and are divided into the following fractions for sampling and analytical purposes: volatile organics, nonvolatile organics, pesticides, polychlorinated biphenyls, metals, asbestos, cyanide, and phenol. EPA also developed a sampling and analytical procedures manual to be

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used as a laboratory guide for the analysis of these priority pollutants.

The consent decree obliges EPA to identify which priority pollutants are present in industrial wastewaters, and to determine the ability of various wastewater treatment technologies to remove priority pollutants. Therefore, EPA, with ATMI's cooperation, decided to conduct a separate study parallel with the EPA/ATMI Grant Study designed to measure priority pollutants. Also, since the consent decree focused on the issue of wastewater toxicity, ATMI agreed to have samples collected for bioassay testing, in order to have a complete and comprehensive wastewater characterization data base. Thus, the bioassay testing program established by EPA for evaluating the reduction in toxicity of water samples by control technologies and outlined in Figure 2 was integrated into the program. The overall EPA-IERL/RTP textile program consists of two separate projects, each with different activities running parallel in time, but converging toward the same goal: determination of BATEA for textile wastewaters.

### Program objectives

Monsanto Research Corporation (MRC) collected and analyzed the samples for priority pollutant analysis and bioassay testing under EPA Contract 68-02-1874. The fundamental objective of the textile plant wastewater toxicity study was to determine the reduction in toxicity, and priority pollutant concentrations achieved by the tertiary treatment technologies being tested at 23 plants in the EPA/ATMI Grant Study.

The study conducted at MRC's Dayton Laboratory was divided into two phases, in order to gather the most information in a cost-effective manner. Phase I was designed to collect baseline toxicity and priority pollutant data on secondary effluents from the 23 plants before the pilot plant program began. In this manner, 23 samples were to be subjected to the battery of bioassay tests. Only those plants with toxic secondary effluents would be selected to determine reduction in toxicity by tertiary treatment systems. Also, appropriate bioassays could be selected, instead of performing the entire battery of tests for Phase II. Phase II was designed to collect samples before and after each tertiary treatment unit operation to determine reduction in toxicity and priority pollutant concentrations at the plants selected from Phase I.

In addition to collecting samples for priority pollutant analysis and bioassay testing, EPA included the new Level I environmental assessment technology developed by EPA's Process Measurements Branch, IERL/RTP. Level 1, the first part of a three-phased environmental assessment approach, was designed to focus available resources on emissions that have a high potential for causing measurable health or ecological effects. Based on the results of the pilot test, approaches for Levels 2 and 3 could be developed.

### Field sampling

The basic textile plant wastewater treatment plant consisted of an aeration lagoon with several surface aerators, followed by conventional clarifiers and chlorination. Raw waste and secondary effluent samples were collected at the points indicated in Figure 3. Secondary effluent samples were collected between the clarifier and chlorination, because that is the stream that would flow into a tertiary treatment system.

Raw waste samples were collected over an eight-hour period during a normal working day, with automatic composite samples. Eight individual secondary effluent samples were collected by grab sampling techniques, by use of a 3-gal Teflon®-lined stainless steel bucket. Aliquots were removed

FIGURE 1

**Tertiary treatment nodes for "best available technology" evaluation**

Mode A: Reactor/clarifier → Multimedia filter

Mode B: Multimedia filter → Granular activated carbon columns

Mode C: Multimedia filter → Ozonator

Mode D: Ozonator

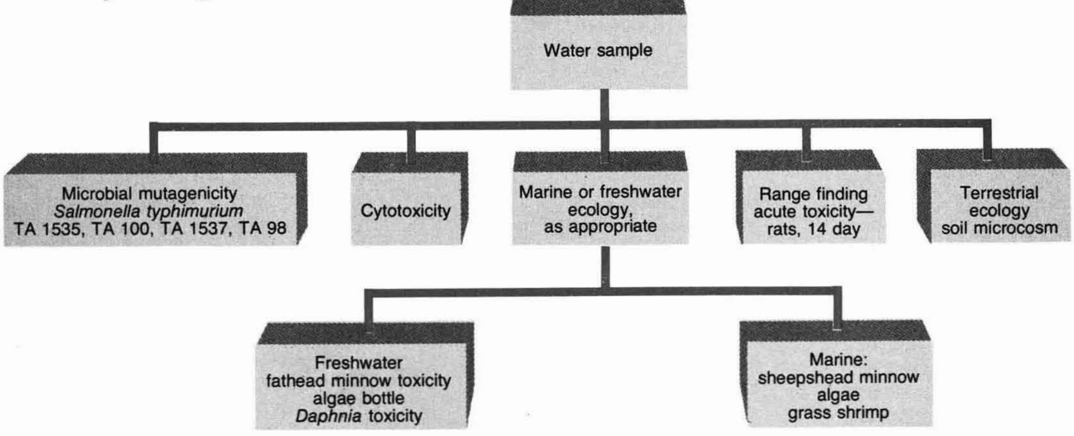
Mode E: Reactor/clarifier → Multimedia filter → Granular activated (Optional) carbon → Ozonator

Mode F: Coagulation → Multimedia filter

Mode G: Dissolved air flotation

FIGURE 2

**Bioassay testing**



from the bucket, and poured into appropriate sample containers. Care was taken to ensure that the sample remained homogeneous throughout each of the 10-min pouring sessions. Containers for volatile organics analysis were filled first, and sealed to minimize possible evaporation losses. All samples were preserved in the field according to EPA specifications. Samples were then packed in ice and shipped via commercial air freight to the appropriate laboratory for analysis.

### Priority pollutants detected

Analysis of raw waste and secondary effluent samples (totaling 64 samples) for the 129 priority pollutants were performed by MRC in accordance with the analytical methodology recommended by EPA. It is important to realize that the purpose of EPA's analytical scheme is to screen samples to determine which of the 129 chemical species are present, and to estimate their general concentration range. With a narrowed list of species, later verification studies will more accurately quantify species concentrations in a cost-effective manner.

Currently, the recommended analytical protocol is in the developmental stage and requires further verification and validation. Therefore, the analytical results of textile plant wastewater samples must be looked upon as reliable estimates of which priority pollutants were present, with concentrations accurate to within a factor or two.

The 114 organic priority pollutants are divided into four categories for analysis: voltatile organics, base/neutral organics, acid organics, and pesticides and PCB's. Volatile organics were sparged from the sample with helium and adsorbed onto a Tenax column. Adsorbed species were later thermally desorbed for identification and quantification with a Hewlett-Packard 5981 gas chromatograph/mass spectrometer (GC/MS) with a 5934 Data System.

Base/neutral and acid organics were determined by extracting the sample with methylene chloride first at pH >11, and then the aqueous phase at pH <2. Extracts were then dried on a sodium sulfate column and concentrated to 1 mL in a Kuderna-Danish evaporator with a Synder column. Concentrates were then analyzed with the GC/MS system.

Pesticide and PCB species were similarly processed. However, they were extracted instead, with a mixture containing a volume ratio of 15% methylene chloride and 85% hexane.

Since raw waste samples were collected with automatic samplers with a peristaltic pump and Tygon tubing, sample blanks were collected to determine if the sampler was contributing to the presence of organic priority pollutants. Laboratory-prepared organic-free water was passed through the sampler, and collected. Results are presented in Table 1.

Results of GC/MS analyses of 64 textile plant raw waste and secondary effluent samples for organic priority pollutants are available. Of the 114 organic compounds in the priority pollutant list, a total of 44 different compounds were identified in textile wastewaters, 38 in raw waste samples and 33 in secondary effluent samples. On an individual plant basis, the greatest number of organic compounds detected in a raw water and secondary effluent sample were 14 and 8, respectively, with an average number per plant of 7 in the raw waste and 5 in the secondary effluent. The predominant compounds were bis (2-ethyl hexyl)-phthalate in 54 samples (0.5 $\mu$g/L–300 $\mu$g/L), toluene in 44 samples (0.4 $\mu$g/L–300 $\mu$g/L), and ethylbenzene in 30 samples (0.7 $\mu$g/L–3000 $\mu$g/L). A summary of the 13 priority pollutant metals and cyanide concentrations in raw waste and secondary effluent samples is given in Table 2.

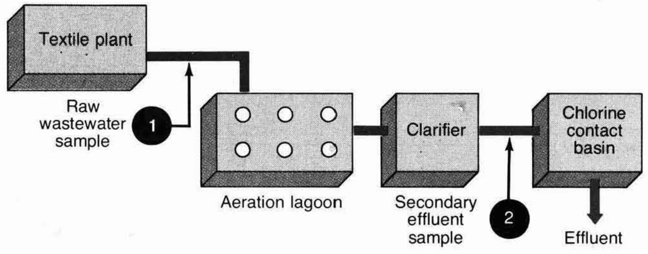
On an individual plant basis, it was frequently observed, especially for the metals data, that the concentration of a specific pollutant was greater in the secondary effluent sample than in the raw waste sample. This phenomenon is due, in part, to the hydraulic retention time of the wastewater treatment facility. Since raw waste and secondary effluent samples were collected simultaneously, concentrations in the secondary effluent were caused by raw waste loads that entered the treatment system 1–30 days prior to sampling. The average retention time for the 23 plants was about 5 days.

### Level 1 chemical analyses

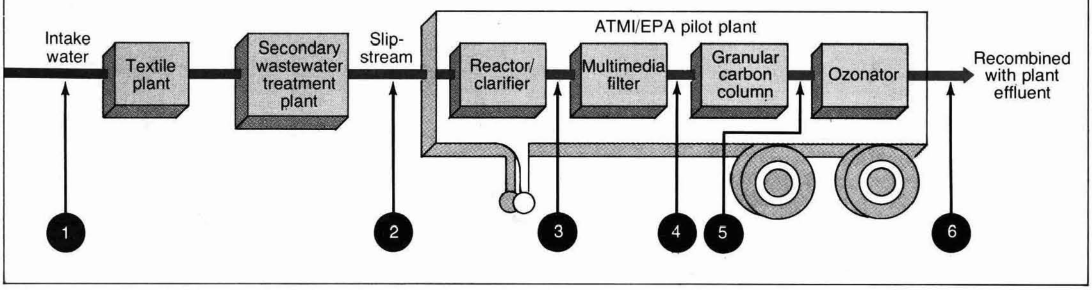
Level 1 chemical analyses were performed on secondary effluent

FIGURE 3

**Water toxicity sampling locations for Phase I . . .**



**. . . and for Phase II**



samples from 15 of the 23 basic textile plants. Level 1 protocol identifies classes of compounds present in environmental samples, and measures the general concentration range. Results indicate that total concentration of methylene chloride extractable organics ranges 3 mg/L–64 mg/L.

In the Level 1 procedure, each sample was fractionated by a liquid chromatography column into eight fractions based on polarity. Infrared analysis of each fraction indicated the presence of aliphatic hydrocarbons, esters and acids: aromatic compounds, phthalate esters, and fatty acid groups. Low resolution mass spectrophotometric analysis of the eight fractions of each sample detected the following types of compounds: paraffinic/olefinic, bis (hydroxy-*t*-butyl phenol) propane, tri-*t*-butyl benzene, alkyl phenols, dichloroaniline, toluene-sulfonyl groups, vinyl stearate, and azo compounds.

### Bioassay results

The primary objective of the entire wastewater toxicity study is to determine the level of toxicity removal from secondary wastewater achieved by the tertiary treatment technologies selected in the ATMI/EPA BATEA study. To this end, the purpose of this screening study was to provide chemical and toxicological baseline data on secondary effluents from the 23 textile plants, and to select plants for the toxicity reduction study.

Bioassays used were selected by EPA and included tests for assessment of both health and ecological effects. Health effects tests estimated the potential mutagenicity, potential or presumed carcinogenicity, and potential toxicity of the secondary effluent wastewater samples to mammalian organisms. Ecological effects tests focused on the potential toxicity of samples to vertebrates (fish), invertebrates (daphnids and shrimp), and plants (algae) in freshwater, marine, and terrestrial ecosystems.

Biological testing, as well as chemical and physical parameters, should be considered when assessments of the potential impact of industrial or municipal/industrial wastewaters on the aquatic environment are made. Biological testing involves determination of toxicity for samples of treated effluents. In a toxicity test, aquatic organisms will integrate the synergistic and antagonistic effects of all the effluent components over the duration of exposure.

Although toxicity tests with aquatic organisms can be conducted by applying wastewater samples directly to the test organisms, or by injection or feeding, most tests are conducted by exposing the test organisms to test solutions containing various concentrations of effluent samples. One or more controls are used to provide a measure of test acceptability by giving some indication of test organism health and the suitability of dilution water, test conditions, handling procedures, etc.

A control test is an exposure of the organisms to dilution water with no effluent sample added. Bioassay tests are exposures of test organisms to dilution of water with effluent samples added.

Generally, the most important data obtained from a toxicity test are the percentages of test organisms that are affected in a specified way by each concentration of wastewater sample added. The result derived from these data is a measure of the toxicity of the effluent sample to the test organisms under the test conditions.

Acute toxicity tests are used to determine the level of a toxic agent that produces an adverse effect on a specified percentage of test organisms in a short period of time. The most common acute toxicity test is the acute mortality test. Experimentally, 50% effect is the most reproducible measure of the toxicity of a toxic agent to a group of test organisms, and 96 h is often a convenient, reasonably useful exposure duration. The 96-h median lethal concentration (96-h $LC_{50}$) is most often used with fish and macroinvertebrates. Thus, the acute mortality test is a statistical estimate of the $LC_{50}$, which is the concentration of toxicant in dilution water that is lethal to 50% of the test organisms during continuous exposure for a specified period of time.

However, the 48-h median effective concentration (48-h $EC_{50}$), based on immobilization, is most often used with daphnids. The terms median lethal concentration ($LC_{50}$) and median effective concentration ($EC_{50}$) are consistent with the widely used terms median lethal dose ($LD_{50}$) and median effective dose ($ED_{50}$), respectively. As used in this study, "concentration" is the percent of effluent wastewaste per unit volume of test solution to which the organisms were exposed; "dose" refers to the measured amount of effluent wastewater given to the rats (mg/kg).

TABLE 1

**Summary of organic priority pollutants found in automatic sampler tubing blanks**

| Fraction | Compound found | Concentration range, μg/L |
|---|---|---|
| Base/neutrals | Naphthalene | 2 |
| | Dimethylphthalate | 16 |
| | Diethylphthalate | 0.5 to 10.2 |
| | Bis(2-ethyl hexyl)phthalate | 1.5 to 46 |
| | Di-*n*-butylphthalate | 1.3 to 1.7 |
| Acids | Phenol | 0.6 to 1.1 |
| Volatiles | Toluene | 2.6 to 55 |
| | *Trans*-1,2-dichloroethylene | 3.2 |
| | Trichloroethylene | 2.4 |
| | Ethylbenzene | 8.3 |

TABLE 2

**Summary of priority pollutant metals**

| Element | Concentration range, mg/L<br>Raw waste sample | Secondary effluent sample |
|---|---|---|
| Antimony | 0.0005 to 0.06 | 0.0005 to 0.07 |
| Arsenic | 0.005 to 0.2 | 0.005 to 0.02 |
| Beryllium | <0.0001 | <0.0001 |
| Cadmium | 0.0005 to 0.05 | 0.0005 to 0.01 |
| Chromium | 0.0002 to 0.9 | 0.0002 to 2.0 |
| Copper | 0.0002 to 2.4 | 0.0002 to 0.3 |
| Cyanide | 0.004 to 0.2 | 0.004 to 0.2 |
| Lead | 0.001 to 0.2 | 0.001 to 0.2 |
| Mercury | 0.0005 to 0.004 | 0.0005 to 0.0009 |
| Nickel | 0.01 to 0.2 | 0.01 to 0.2 |
| Selenium | <0.005 | <0.005 |
| Silver | 0.005 to 0.1 | 0.005 to 0.1 |
| Thallium | <0.005 | <0.005 |
| Zinc | 0.03 to 8.0 | 0.07 to 38 |

A total of 8 biological systems were used for wastewater toxicity evaluation. Twenty-one different tester organisms were utilized.

Under guidance of appropriate EPA technical advisors, four of the eight bioassays were performed at five commercial laboratories, including MRC, experienced with the bioassays. The remaining four bioassays were performed by the EPA technical advisors.

### The measure of toxicity

The viability test was a measure of the cells' ability to survive exposure to the effluent. The adenosine triphosphate (ATP) test measured the quantity of the coenzyme ATP produced, indirectly measuring cellular metabolic activity.

$EC_{50}$ for the algal tests means the concentration of secondary effluent, which caused a 50% reduction in algal growth as compared to a control sample. The freshwater algae test was performed over a 14-day period, and the marine algae test over a 96-h period.

For the fathead minnow, sheepshead minnow, and grass shrimp bioassays, death was used to measure toxicity, which was expressed as Lethal Concentration 50 ($LC_{50}$). $LC_{50}$ indicated the calculated concentration of secondary effluent that was expected to cause the death of 50% of the test species. Since rats were given a specific quantity of secondary effluent, toxicity was expressed as Lethal Dose 50 ($LD_{50}$). $LD_{50}$ indicated the quantity of material fed to the rats that resulted in the death of 50% of the test animals.

The measure of toxicity to a soil microcosm was the quantity of carbon dioxide ($CO_2$) produced after effluent exposure, as compared to that evolved from a control sample. The quantity of $CO_2$ produced over a 3-wk period, after subtraction of the quantity produced by the control, was plotted on graph paper. The slope of the curve then represented the rate of increase or decrease in $CO_2$ production brought about by exposure to the effluent.

Results of the freshwater ecology series showed enough variation in responses to permit relative ranking of the toxicity of effluent samples. However, no general rule can be formulated concerning the relative response between fathead minnows and daphnia. For example, Plant E's effluent was found to be toxic to daphnia but not to fathead minnows; at Plant T, the reverse was true.

For the marine ecology series, the data indicate the grass shrimp were more sensitive than sheepshead minnows. Also, fathead minnows were more sensitive, in the majority of the samples, than sheepshead minnows.

In terms of mutagenicity, none of the 23 effluent samples produced a positive response to any of the bacterial tester stains. Also, no acute toxicity was observed in any of the rat tests when rats were given the maximum dosage of 10 mL/kg of rat body weight.

### Data interpretation

An objective of the Phase I screening study was to rank textile plants according to the toxicity of their secondary wastewater, and to select plants for detailed toxicity evaluation in Phase II. To accomplish this objective, members of the EPA Bioassay Subcommittee met to evaluate the bioassay data.

From the results, the subcommittee recommended that the following nine textile plants ranked in relative order of toxicity being tested to determine the reduction in toxicity achieved by the tertiary treatment technologies tested in the ATMI/EPA Grant Study: N, A, W, C, T, V, L, S, and P. (Plant R was also recommended for study under Phase II, because its secondary effluent samples were inadvertently collected before the effluent reached the settling pond.) In addition, the subcommittee recommended that the freshwater ecology series and Ames test be used to measure reduction in wastewater toxicity by the treatment technologies. The marine ecology series was not selected because none of the textile plants discharge wastewater into a marine environment.

During Phase II of this project, samples will be collected at the 10 plants selected before and after each of the tertiary treatment unit operations being tested in the pilot plant. In addition, samples of the textile plant intake water and secondary effluent will be collected. In Figure 3 is an example of sampling locations for a typical treatment train.

### Toxicity ranking

Phase I toxicity screening provided several significant results. Of the 129 priority pollutants, only 45 of the 114 organic species were detected. On an individual plant basis, the largest number of organic species detected in a single effluent sample was eight, with an average number of five. Thallium was not detected in any of the samples.

Data collected from the battery of technology-based bioassays indicated it was possible to rank effluents based on relative toxicity. In general, toxic effects detected in one test system were also detected in other systems. None of the effluent samples, however, produced positive mutagenicity responses or resulted in acute toxicity effects in rats.

Results of these tests were used to select plants with relatively more toxic effluents with which to study the reduction in toxicity by selected tertiary treatment wastewater control technologies. Results of the Phase II work will be available in mid-1979.

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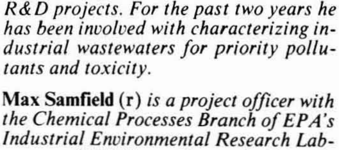

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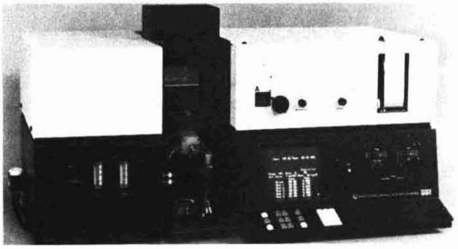

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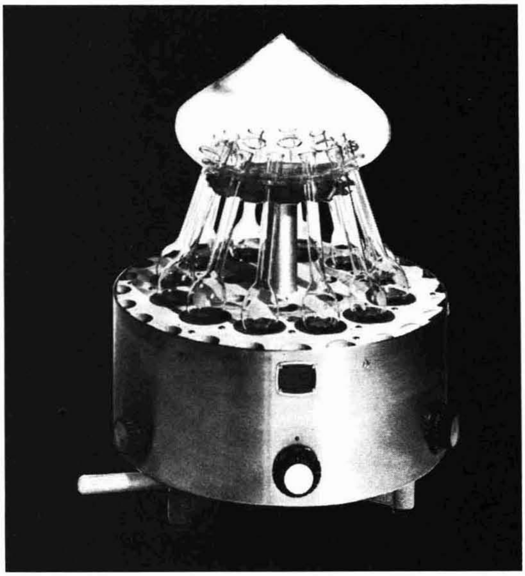

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# RECYCLING HAZARDOUS WASTES

*A successful California pilot experiment, soon to be expanded, offers incentives for conservation and environmental protection plus economic rewards for participating industries*

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Recently, the California Department of Health, Hazardous Materials Management Section (HMMS) undertook a program to locate and identify the waste streams of various companies in the San Francisco Bay Area whose components might be recycled. The purpose of the program was to conserve energy and chemical resources by reusing materials which normally would be disposed of, and to reduce the volume of materials going into disposal sites.

Philosophically, the Department believes that land burial of hazardous waste should be used only as a last resort. Burial of highly toxic wastes presents hazards that project into the future over an indefinite period; for example, there is little assurance that the Class I sites so carefully selected to confine hazardous waste materials today will function in this capacity forevermore.

This is not to say that land burial does not have its place as a disposal method. It should be used judiciously, but whenever possible, alternate methods should be considered. The best procedure for solving waste problems is to reuse the waste material in other production processes to reduce its generation. This, of course, is not a novel idea; but what is new is the use of hazardous waste materials in new and different applications.

## Economic feasibility

Almost all materials are recyclable, but to be viable the reuses must offer economic incentives. All materials are not economically recyclable; in some, more energy will be expended in recovery than the recovered value warrants. Hence, many factors need to be weighed. Recycling programs require careful scrutiny and evaluation to assure that a viable solution to the problem will be achieved. Mixture complexity, the processing equipment required, available technology, technical capability and geographic location are all factors that need to be addressed. And, of course, most important of all is the question of whether or not a net gain of value is obtained.

If suitable processing or reclamation equipment and technology are not available, the material may or may not be reusable. A case in point is a mixture of epichlorohydrin, methyl ethyl ketone, methyl isobutyl ketone, ethanol, propylene chlorohydrin and water. This mixture is the result of an epoxy resin process and is rectified and recycled on a routine basis by a large epoxy resin manufacturer. A small operator would find this material to be an unseparable mixture, essentially nonrecyclable.

Simple mixtures, as a rule, are easier to process than multicomponent mixtures. For this reason, the HMMS encourages industry to keep waste streams separated and as simple as possible. However, this cannot always be done and, as a result, some nonreusable waste streams are generated under the best conditions. These waste-solvent mixtures may still be useful as fuels, however.

Geography, as well, plays a key role with regard to the reusability of a waste. Many times optimum utilization of a waste requires its combination with a waste that is at a different location. The feasibility of reuse in this situation is completely dependent upon the proximity of the two wastes. Transportation costs can quickly negate such opportunities.

## Department's efforts

The hazardous waste recycling program has involved the investigation of many waste streams from a variety of industries. Because of the unrestricted opportunities for exploring the waste streams of completely different

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types of industries, the Department has been able to "marry off" wastes of companies that normally would have little or no contact with one another. The Department has supported only a low key effort to date. One man in the San Francisco Bay Area has initiated a pilot program which has proven so successful in promoting waste recycling that it will probably be greatly expanded over the next year.

The most productive means of obtaining the needed information for waste reuse is by personal interview, which identifies a potentially useful product that is presently being wasted, and uncovers potential consumers. Furthermore, by personal interview a relationship is established that is helpful in not only locating useful waste streams, but also in convincing companies to investigate the use of a waste stream in their production line.

An alternate method is the clearing house concept. As the name implies, this involves the collection and wide dissemination of information regarding industrial waste resources. Information describing the type of waste material, concentration, impurities or contaminants, as well as the physical location of each waste is obtained. The use of a questionnaire is the usual way the data are accumulated, although personal interviews may be used. The information can be computerized and/or published and disseminated in the form of a list of materials available, and a list of materials being sought.

The clearinghouse idea, however, does not automatically solve the problem. It is merely a tool that can be used to expedite waste information exchanges. The system does not automatically assure that waste exchanges or uses will develop. Recycling and recovery need to be worked at; they require many hours of technical discussions, the services of technical personnel, consultation and hand holding to fit waste streams into present technology. While there is a need for the establishment of a data bank, the passive clearinghouse concept does not work well without active support.

## The problems with a list

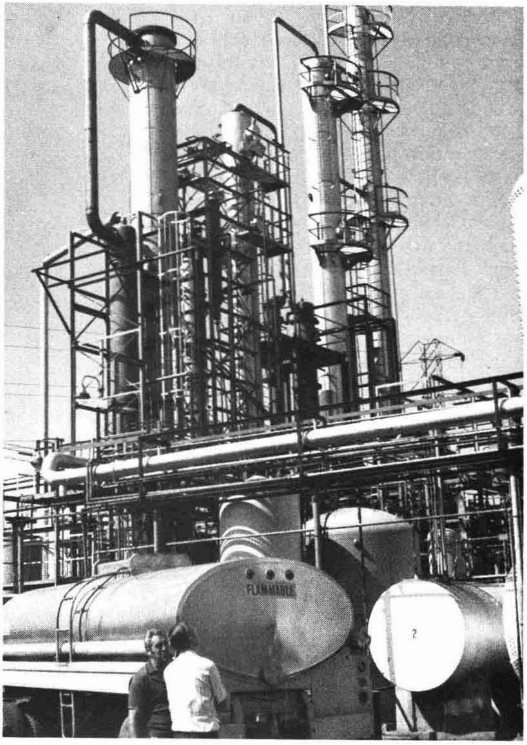
In regard to the computerized lists generated under the clearinghouse concept, several difficulties are associated with the periodic mailing of a waste list to potential users. The list may not get into the hands of the right person, especially in large companies; consequently its value is lost.

The time required to assemble and

*Prior to treatment this heavy clay soil supports only light crops of salt grass*

*Wallboard and paper fiber sludge amendment is applied to the heavy clay soil*

*Lime-sulfur sludge from a nearby chemical plant is being applied to a field*



*Right. This plant processes waste solvents*

*Below. Pickle acid from this steel plant is chlorinated to produce ferric chloride, which is used to treat sewage at a sanitary disposal facility*

distribute a list is relatively long (usually one month), but an arrangement might be made for the information to be published in a newspaper on a daily basis. This is not inconceivable. However, most companies are not receptive to the idea of holding waste materials on-site for extended periods of time.

In reality, however, a waste producer may not have a steady production of waste; he may produce, for example, 30 drums of "spent" acid over a period of time. Usually, he is not receptive to the idea of keeping the material any longer than necessary. He wants a more positive response than to store the material on-site hoping that someday someone will take it away.

Most industries interviewed have indicated that a list sent by mail probably would not even be read unless they were actually looking for a specific material. Several reasons are cited.

Companies have a great fear of changing an established process that has been proven successful over a long period of time. To interchange a pure feedstock for somebody's waste stream takes a great deal of investigation and thought; a mistake could prove to be extremely costly. In addition, companies require assurance of a continued level of purity and quantity. Hence, in a great many cases, companies will not seek out a source of materials that may jeopardize either their production rate or quality.

In the personal technical interview, some of these fears can be allayed. Problems of this kind can be discussed in detail and possible solutions addressed. A complete description of the waste can be given and arrangements for samples made.

### Hindrances

Many industries are sensitive about protecting information regarding their production rate and manufacturing procedures. The types and amounts of waste components generated are sources of information that a competitor can use to his advantage to obtain valuable production data. Hence, in a recycling program it is necessary to address and solve this problem.

Another problem that occurs with mailed questionnaires involves reported accuracy of the composition of the waste streams. Incomplete or deficient information can lead to poor experiences. A case in point involved the transfer of 48 drums of 92% acetic acid which was shipped to the recipient and subsequently returned. The generator had failed to note that the acid also contained 2% chromic acid!

Another factor that frustrates the efficient use of the clearinghouse procedure involves interaction of governmental agencies. It is sometimes difficult to obtain clearance to recycle without the services of an intermediary agency.

For example, a galvanizing waste pond located in the San Francisco Bay Area contained sufficient zinc and iron content to be of use for soil application in the Brentwood area (40 miles away) where these elements are deficient. A farmer was located who needed the material and was willing to test it on his soil.

The Department of Health Services analyzed the material to assure that no heavy metals deleterious to the land were present in any significant concentrations. Agriculturists at the University of California at Davis agreed that the material might indeed have beneficial effects on the soil to which it would be applied. The problem now revolved around the location of the pond and the area in which the material was to be used.

The pond was located in an area under the jurisdiction of the San Francisco-Oakland Water Quality Control Board. This agency was concerned about removing this potentially hazardous material as soon as possible (probably to a Class I disposal site) since they wanted the assurance that the pond would be properly phased out. The exigency of time revolved around the fact that the company had ceased operations in the area and was indeed preparing to abandon the area as a production site.

The agency, which had control over the area where the material was to be disposed, wanted to be assured, as did the farmer, that the pond contents would be beneficial before applying 3.5 million gallons of the material broadly and indiscriminately over the land. The agency also wanted to make a test plot which involved raising a crop and evaluating the results. This, of course, would postpone the removal of the pond contents for six months to a year.

The problem was solved by the Department's Hazardous Management Section in bringing Water Quality Control Board representatives, the farmer, the prospective hauler and the producer of the waste all together at a meeting where all questions could be addressed and answered to the satisfaction of all those involved. This problem could not have been rectified by just using the clearinghouse concept.

Perhaps one of the most difficult problems regarding the clearinghouse concept is the fact that there is a tendency to collect all the "dogs." The useful components we assume will eventually be used or put to work. If things work, the easily recyclable waste will be quickly removed from the list. But some materials may have a very low potential for recycling and these will tend to accumulate. The clearinghouse concept makes assessment difficult, but the dynamic technical interview concept allows for an appraisal to be made at the time of the interview—before the material is entered into a recycling list.

### Interview approach works

Making a list of materials available and distributing the list is a minor part of a recycling program, but it has its place. A more dynamic approach involves interviews in which technical discussions are held regarding the waste streams. Quantity, contaminants, and other discretionary information of importance can then be secured. Many such interviews are required before a recycling program really begins to "tick" and gain momentum. Then the industry will respond to this "fee-free brokerage" service.

When this occurs, another facet of the program can be invoked. Assistance can be rendered by suggesting alternative procedures for waste usage that can be of great economic value to a company. These alternate procedures, which may not be apparent to the waste producer, are the direct results of the interviewer's vast knowledge of industrial information accumulated by his contacts in the industry.

Although the task of interviewing a myriad of companies to define their waste streams might seem formidable if not impossible, the process can be greatly shortened. A practical means of achieving this goal, and accumulating a large amount of information, is to become familiar with the effluents from the various types of industry. For example, most steel processing plants have a waste stream known as "pickle" acid. It usually contains about 10–15% ferrous chloride or sulfate and a few percent of acid. If a need for this type of material arises, a large portion of the steel industry is available as a source.

Industrial participation in the program has been gratifying. In most cases, complete cooperation has been received. Industry has not only sanctioned the program, but is gratified to learn that the state has instituted a program to help it solve its disposal problems. To some, the service offers income from an unexpected source; to others, it reduces the amount of money spent on disposal fees; and to still others, both incentives are provided.

At the present time, most plant managers are willing to discuss their processes and waste streams with state interviewers. Recycling advice is given whenever appropriate. At other times, technical advice, which allows the generator of a waste stream to convert it into a useful and valuable by-product, is supplied. These services are given without cost.

The Department learns of potentially useful waste products in other ways, notably through our disposal-site-surveillance activities. Inspections of waste disposal sites, both Class I and II, by field personnel frequently reveal that large quantities of high-quality commercial materials are being disposed of. Large loads of chemicals in unopened bags and drums are frequently discarded. The operators of the disposal sites are asked to contact our office if materials suspected of having recoverable value are brought to the site. Cooperation between the site operators and our inspectors results in the retrieval of much valuable material that has been delivered for disposal.

Managers usually welcome recycling advice and, in most cases, quickly follow up the contacts that are suggested. After all, the alternative to recycle is disposal, usually at considerable expense. When two parties are brought together, the work of the Department has ended. Our sole function is to bring the right parties together to avoid disposal. The details of the transactions such as whether the material is sold, given away outright, or who pays for transportation are left to the two principals involved. There have been times when the transactions have been unsuccessful, but this is the exception rather than the rule.

### Reclaiming nonhazardous wastes

Much useful nonhazardous material is being thrown away also. This usually occurs because disposal is easy and convenient and relatively inexpensive. A case in point involved a breakfast-food manufacturer who discarded 18 semitrailer loads of breakfast food into a Class II (domestic refuse) site. This material was boxed and "cartoned" and ready for distribution at the time of disposal. Why was it discarded? Too much vegetable oil had inadvertently been used during manufacturing, thus possibly affecting the shelf life of the product. It was cheaper for the manufacturer to dispose of the material than to reopen the boxes and recover the breakfast food for animal consumption.

Our program was explained to the breakfast-food manufacturer, whereupon he offered to cooperate with us for alternate disposal in the event of future problems. Six weeks later, the manufacturer contacted us about another batch of breakfast food damaged by an overhead sprinkler failure. We contacted a pheasant farmer who was delighted to receive the material; he saved $4000 on his feed bill for that year!

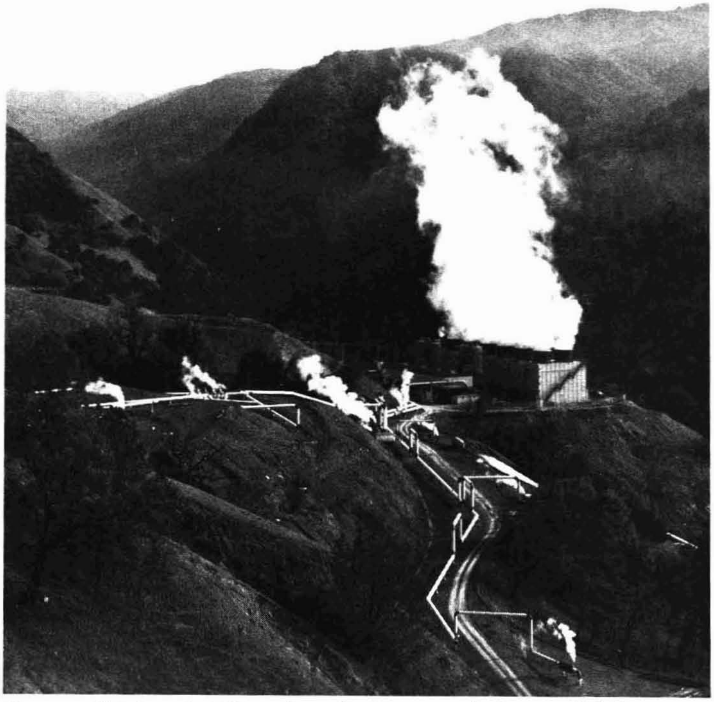
Many other examples of nonhazardous waste disposal of usable materials have been observed. Whenever possible, we assist in recovering nonhazardous industrial waste materials for reuse as well as the hazardous materials.

### Categories of hazardous wastes

Our interviews with company personnel indicate that about five broad categories of hazardous waste are being generated. These include:

- materials or "articles" of commerce
- process wastes that are reusable without treatment
- materials that are reusable with treatment
- waste materials that have little or no value
- materials that no one wants to recover.

In the first category, materials of



*Ferrous sulfate is used at this geothermal well to remove hydrogen sulfide from steam prior to reinjecting the steam into a return well*

commerce, we have found many kinds of materials being discarded. For example, many gallons of concentrated caustics and sulfuric, nitric, and hydrochloric acids are being disposed of daily. These are in addition to the nonusable dilute solutions that are being thrown away. Needless to say, unused materials of commerce are the easiest materials to recycle. In addition to known users of these materials, or those who have expressed an interest in such products during our original interview, there are a number of competent, dependable chemical brokers in the San Francisco Bay Area who are delighted to take these so-called waste materials off the hands of the generator. Usually they are able to purchase these products at discount rates.

Many drums of useful chemicals are discarded on a regular basis. Why are they being discarded? Many times the products are "outdated" or have been discovered during a clean-up or have been stored for a long period of time and are being disposed of because they are no longer of value to the owner.

A frequently encountered reason for disposal is the very tight quality-control restrictions that are imposed by some industries. This is especially true of the food and semiconductor industries where chemicals of generally acceptable quality are discarded because they cannot meet the very tightly-controlled standards of these industries. These materials are discarded rather than returned for credit because the producer does not want to risk contamination of future batches of the same product.

In the second category are processing wastes that are reusable without treatment. These are waste materials that can be reused as industrial feed stocks per se. In this category belong the cardboard for pulping, copper, and other metal solutions for metal recovery, certain solvent streams, and a diversity of other materials. They also include filter charcoals, oils that can be used for fuel, used diatomaceous earth filter cakes which provide siliceous materials for cement manufacturers, a variety of valuable metal materials, and sludges which sometimes may require simple separation from water suspensions.

Caution is required to assure that these materials, when reused, will not cause untoward effects. For example, cardboard is repulpable and is commonly repulped to make more cardboard. However, if the cardboard is contaminated with polychlorinated biphenyls (PCB's), pesticides or chemicals, the new cardboard should not be used for food packaging, but it can be used for other purposes such as the manufacture of concrete foundation forms.

Another example of "reuseable without treatment" waste involves a paper recycling company which has a certain percentage of paper that is not repulpable. This they biodegrade to make a loam used in lawn preparation. During our interview, it was brought out that they would really like to make a complete fertilizer by the addition of nitrogenous and phosphorous materials. Tanneries produce a highly proteinaceous material from their dehairing process. This is difficult to dispose of since it contains caustic sodium sulfides and undissolved hair as well as various other proteinaceous organic materials. The tannery oxidizes the waste to convert the sulfides, neutralizes with sulfuric acid, and sends the products to a disposal site.

This material is ideal as a nitrogenous soil amendment when used with the biodegradable paper loam. We suggested that the tannery contact the paper company for disposal. The tannery volunteered to use phosphoric acid in place of sulfuric acid to neutralize the alkalinity and upgrade the nutritional value of the soil amendment.

There was only one catch. The distance between the two sources was too far and the sales price of the product could not justify the transportation costs. This brings us to another point. Resource recovery and recycling would be greatly aided and abetted if more stringent restrictions were put on disposal and the cost of disposal increased.

### Opportunities are plentiful

A good example of the successful recycle of a waste product is "galvanizers pickle acid." This material contains about 8-10% zinc sulfate as well as some iron salts. It can be used as an agricultural additive in areas deficient in zinc; it is commonly used in citrus orchards.

The pickle acid can be fortified with baghouse dust produced by some scrap steel processors. Baghouse dust from this source contains as much as 25% zinc oxide. So this material in conjunction with more waste sulfuric acid is used to increase the zinc sulfate concentration in "galvanizers pickle acid." Higher concentrations are more amenable to the recovery of solid zinc-iron sulfate by a dehydration process. This process is presently in operation in California.

Another "steel pickle acid" contains 10-15% ferrous sulfate. This product is being used to treat the steam being used to develop electrical power in the geothermal area around Calistoga. The Air Pollution District in that area does not allow venting of the hydrogen sulfide in the steam, so it is treated with ferrous sulfate solution. A sludge consisting of iron sulfide and elemental sulfur is recovered, which in itself is useful as a soil amendment in many areas.

These and other developed uses have created a shortage of "pickle acid" in the Bay Area. Now that is pretty unusual! A shortage has developed for a material which at one time was a prime pollutant of the rivers and the bay of this area.

Opportunities for recycling waste are manifold and pop up in many strange places. For example, a relatively small company is involved in the business of recovering metals such as nickel, copper, and some gold and silver from waste streams arising from an ammonia copper solution waste produced by printed circuit board manufacturers.

A caustic waste stream containing sodium sulfide is produced by a nearby refinery. Both the metal-containing waste and the sulfide-containing waste are considered hazardous waste in California and require rather costly disposal in our Class I disposal sites.

The treatment of the metal-containing solution with the sulfide caustic precipitates the heavy metals which are recovered. The amount of heavy metal remaining in residual waste is at a concentration which allows disposal to the sanitary sewer system.

The third category of wastes have potential use, but require some ingenuity or inventiveness to convert them to useful materials. These are usually disposed of by using the alternate methods approach. One example involves the semiconductor industry, which produces a large amount of acid stripper—a mixture containing 96% sulfuric acid, and 2% chromic acid. It's the bane of the industry and is usually buried. This material can be used for refining used crankcase oil. Used crankcase oil contains heavy metals such as lead, calcium and barium, so adding a little bit of chromium isn't going to do any harm. The oil and waste acid are mixed and allowed to separate into sludge and treated oil. The sludge is very acidic and normally contains about 10 000–20 000 ppm lead and varying amounts of other heavy metals. But now we have enriched it with 2% chromium.

The problem now is to separate the metals from the acid sludge. If we neutralize the acid sludge with ammonium hydroxide, we make ammonium sulfate, a marketable agricultural fertilizer. The fertilizer can be sold directly or returned to the ammonia producer for credit, and the filter cake, which contains a rich concentration of heavy metals, primarily lead and chromium, can be profitably processed for metal recovery. Recycling possibilities such as these are at hand. The problem is getting somebody to do it.

Another tough example of a waste needing innovative thinking is a waste mixture called mixed acid etch. The etch is used in the semiconductor industry to process so-called silicon wafers. It should be called "the seven-year-etch" because it just doesn't go away. This material contains 60% nitric acid, 20% hydrofluoric, and 20% acetic acid. This waste is extremely dangerous, but when handled correctly, "it just lays down and rolls over."

The secret is to mix it with lime or acetylene lime plus calcium hydroxide—a waste stream coming from the manufacture of acetylene from calcium carbide. Lime neutralizes the acids and, after treatment, we have a solution containing calcium nitrate, calcium fluoride, and calcium acetate. Calcium nitrate is a first-class fertilizer. It commands a premium price and is used on golf courses and by lettuce growers.

The second useful product generated by this process is calcium acetate. The calcium acetate in the neutralized acid etch behaves in a manner similar to lime or gypsum in the soil, but is fast acting because, as a liquid, it penetrates the soil better than gypsum, which requires tilling to be effective.

The third useful product generated by this treatment is calcium fluoride. This material is useful in cement manufacture and as a raw material for hydrofluoric acid manufacture. In the latter use, high-grade calcium fluoride brings $200–300 per ton.

The last category involves those materials that no one wants to recover. This category includes chemical carcinogens, polychlorobiphenyls (PCB's), dibromochloropropane (DBCP), DDT, and other materials, which, when buried, wait in their subterranean lair for the opportunity to rear their ugly heads and plague our environment sometime in the future. These materials should be destroyed in an incinerator capable of eradicating them forever. But even these materials, if properly handled, can be of some value as fuels.

PCB's and DDT solutions can be incinerated in cement kilns, which are ideal for this purpose. The flame temperature of the kilns are in excess of 2000 °F and the residence time is long. The hydrochloric acid that results from the burning of these chlorinated materials reacts with some of the limestone that is used to make cement. This reaction has the desirable effect of reducing the free alkalinity in the cement, and the calcium chloride that is formed is useful in controlling the set time and temperature of the cement.

### A one-man effort

As previously stated, the Department of Health Services' Waste Recycle Program has been a one-man pilot effort in San Francisco Bay Area. The primary approach has been detailed technical personal interviews with industries. This is a time-consuming job, but it is more productive than questionnaires because it allows the interviewer to follow unexpected leads as they are generated. A low-key, fee-free state-controlled waste brokerage office can be greatly instrumental in forestalling the tremendous amount of waste that is now going into disposal sites.

The State of California has enacted a law, AB 1593, which among other provisions, requires the disposer to justify not having recycled recoverable, useful waste products. It also mandates the recovery and recycle of usable materials whenever it is economically possible. Chapter 6.5, Article 7, 25170 of the California Health & Safety Code calls for the investigation of the market potential, and the feasibility of using hazardous wastes and the recovery of resources from hazardous wastes. The law further addresses itself to the promotion of recycling and recovery of resources from hazardous waste, and to the establishment of a clearinghouse to assist in the recovery of useful wastes.

It is clear that California is intent on applying a program that has been demonstrated to offer great incentives for conservation and environmental protection, as well as economic profitability for those who participate. The initial success of our low-key efforts assures us that the goals of the Lockyer Bill, AB 1593, will be attained.

**Carl G. Schwarzer** *is a waste management specialist with the state of California. He has been involved in the development of a program for reusing industrial discards.*

Coordinated by LRE

# NSPS: Critique of proposed rulemaking

*The control technology issues are highlighted for the revision of new source performance standards for electric utility steam-generating units, which EPA is expected to finalize next month*

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On September 19, 1978, the Environmental Protection Agency (EPA) published proposed New Source Performance Standards (NSPS) for electric utility steam-generating units (43 FR 42154). In the preamble to the proposed rulemaking, EPA discussed several alternate standards for sulfur dioxide ($SO_2$), particulate matter (PM), and nitrogen oxides ($NO_x$). The agency stated that they would continue to examine the various options possible for the final standard during the 60-day public comment period on the proposal, since all the data necessary for final rulemaking were not yet available. EPA held public hearings on the proposed standards on December 12–13, 1978 and will promulgate final regulations in March 1979. This article presents the proposed standards and discusses the technological options available to meet these standards.

## Background

Under Sec. 111 of the Clean Air Act, NSPS are required to be applied nationwide to specific source categories. The first new source standard for steam generators was established on December 23, 1971 for three criteria pollutants: $SO_2$, $NO_x$, and PM. An emissions limitation was required for each pollutant, as follows:

| | Emissions limitations (lb/million Btu) | |
|---|---|---|
| Pollutant | Solid fuel | Liquid fuel |
| $SO_2$ | 1.2 | 0.80 |
| PM | 0.10<br>(20% opacity) | 0.10<br>(20% opacity) |
| $NO_x$ | 0.70 | 0.30 |

The 1.2 lb/million Btu emission level for $SO_2$ allowed sources to comply by either burning low-sulfur fuel or using a technological system of control in conjunction with burning higher-sulfur fuels.

On August 6, 1976, the Sierra Club petitioned EPA to revise the standard for $SO_2$ to reflect changes in control technology that had occurred since the original standard had been promulgated. On August 7, 1977, the 1977 Amendments to the Clean Air Act, containing major changes in federal regulation of air pollution, were signed into law. In particular, with respect to electric utility steam generators, the Amendments require that EPA issue revised NSPS within one year. The Act mandates that the NSPS revision for electric utility steam generators:

- reflect application of the *best technological system of continuous emission reduction* that EPA determines has been adequately demonstrated,
- establish a *limitation on maximum allowable emissions* that EPA determines is "achievable,"
- require *"a percentage reduction in emissions,"* and
- take into consideration cost, non-air-quality health and environmental impacts, and energy requirements. The September 19, 1978 EPA proposal was published in response to the 1976 Sierra Club petition as well as the requirements of the Clean Air Act.

The standards shown in Table 1 would apply to new, modified, or reconstructed units on which construction is begun after September 18, 1978, and that are capable of firing more than 73 megawatts (MW) of heat input (250 million Btu per hour). The standards include both a limitation on the maximum rate of emissions and a percent reduction in total emissions. Separate standards for coal-, gas-, and oil-fired units were established.

## Technological issues

Several of the most important issues that have arisen in the standard-setting process for the revised NSPS for electric utility steam generators are associated with specific emission limitation/percentage reduction requirements for $SO_2$, PM, and $NO_x$, and the control technologies available to meet the standards. The major technology-related issues associated with the proposed standards include:

- sulfur dioxide standard: technological feasibility of meeting the emission reduction/averaging time requirements proposed in the standard for boilers burning various types of coal
- particulate standard: adequate demonstration of available control technology (electrostatic precipitators, baghouses) to meet the proposed standard; and potential adverse impacts of FGD systems on particulate control levels (acid mist formation)
- nitrogen oxides standard: status of combustion modifications for $NO_x$ control.

## The $SO_2$ standard

Debate on the appropriateness of the $SO_2$ standard has centered on the three key elements of the standard and their alternatives: the 85% uniform percentage reduction requirement, the 0.2 lb/million Btu "emissions floor," and the 1.2 lb/million Btu "emissions ceiling." The preamble to the proposed rulemaking specified alternatives being considered by EPA; these are displayed by a graph in Figure 1.

EPA has proposed an 85% reduction requirement for sulfur dioxide emissions (24-h average) with 75% reduction allowed no more than three days per month. This requirement is equivalent to long-term removal efficiencies at or above 90%.

The Department of Energy (DOE) and the electric utility industry have both argued strongly for percentage reduction requirements less stringent than this for low- and medium-sulfur coals. The Natural Resources Defense Council (NRDC) and other environmentalist groups, on the other hand, have argued strongly for more stringent percentage reduction requirements, such as a 90% (24-h average) requirement and an emissions limitation ceiling less than 1.2 lb per million Btu.

EPA has proposed that the standard include a maximum control level (known as an "emissions floor") of 0.2 lb/million Btu below which no percentage reduction requirement would apply. A control level of 0.2 lb would require almost all coal-fired plants (regardless of the type of coal burned) to meet the 85% reduction (24-h average) requirement—including plants burning low-sulfur coal. Hence, EPA's proposed $SO_2$ standard is commonly referred to as the "full control" option.

On the other hand, specification of a higher maximum control level such as 0.8 lb would permit certain plants firing low-sulfur coal to reduce their emissions by less than 85% without the need for full scrubbing; this has been termed a "partial control" option. Figure 1 shows two partial control regulatory options that have been suggested. Both require some percentage reduction at all emission levels, but these would be non-uniform reductions.

One option, suggested by DOE, establishes a minimum 33% reduction requirement below the 0.8 lb floor; coals with potential emissions between 1.2 lb and 5.3 lb per million Btu would be governed by percent reduction requirements equivalent to the 0.8 lb floor (33 to 85% reduction). Another partial control option, advocated by the electric utility industry, would substitute staged percent reduction requirements for the floor, utilizing a minimum 20% reduction for very low-sulfur coals, and progressively

TABLE 1

**Proposed NSPS revisions (43 FR 42154, 19 September 1978)**

|  | Emission limitation | Percent reduction requirement |
|---|---|---|
| **Sulfur dioxide ($SO_2$)** |  |  |
| Solid fuels | 1.2 lb/MM Btu (24-h compliance averaging period—exemption allowed 3 days/month) | 85% averaged daily (24-h compliance averaging period—75% exemption allowed 3 days/month) |
| Gaseous/liquid fuels | 0.8 lb/MM Btu | 85% averaged daily (75% allowed 3 days/month) |
| **Particulate matter (PM)** |  |  |
| Solid fuels | Opacity of emissions limited to 20% (6 min average)—27% allowed 6 min/h[a] | 99% |
| Gaseous/liquid fuels | 0.03 lb/MM Btu | 70% (oil only) |
| **Nitrogen oxide ($NO_x$)[b]** |  |  |
| Bituminous coal | 0.6 lb/MM Btu | 65% |
| Subbituminous coal, shale oil, coal-derived fuel | 0.5 lb/MM Btu | 65% |
| **New technologies[c]** |  |  |

[a] A source-specific opacity standard may be established if opacity is >20% even when complying with the particulate emission limitation.

[b] Limitations (fuel-specific) for liquid and gaseous fuels are unchanged from the 1971 standard except as above. Required percent reductions: 70% for liquid fuels, 75% for gaseous fuels.

[c] EPA (in consultation with DOE) would issue commercial demonstration permits for the first three full-scale demonstration facilities of each of the following: solvent-refined coal, atmospheric and pressurized fluidized-bed combustion, coal liquefaction. For solvent-refined coal and fluidized bed combustion, 80% reduction of $SO_2$ (24-h average) is allowed with emission limitations for PM and $NO_x$ as above. For coal liquefaction, an $NO_x$ emission limitation of 0.7 lb/MM Btu is required. Additional permits up to a maximum of 15 000 MW equivalent of collective generating capacity may be issued if required. Subsequent facilities would be required to meet the NSPS as above.

higher percent reduction requirements up to 85% removal for a coal with potential $SO_2$ emissions of 8 lb per million Btu.

EPA has proposed an emissions "ceiling" for coal-fired units of 1.2 lb/million Btu heat input (24-h average), except for up to three days per month coincident with the three days of 75% control in the percent $SO_2$ reduction standard. The emissions ceiling retains the 1.2 lb per million Btu standard in the current NSPS, but the current standard does not require continuous 24-h compliance. (40 CFR 60 Subpart D requires reporting of excess emissions when average emissions over any three-hour period exceed the 1.2 lb standard. Compliance, however, is based on a short-term performance test conducted after system start-up and at such other times as may be required by the Administrator.) Hence, the proposed emissions ceiling represents a more stringent emission limitation than the current standard because of the 24-h averaging time.

In the notice to the proposed standard, the Agency has stated it will continue to examine the need for exemptions from the ceiling and the appropriateness of specifying more stringent maximum allowable emission levels (such as 1.0 or 0.8 lb per million Btu). EPA selection of the 1.2 lb/3-day exemption ceiling is based upon present estimates of the potential impact of such a ceiling on national and regional coal production.

Based on a modeling assessment, EPA believes the proposed limitation with exemptions will allow the use of substantial Midwestern coal reserves. Without exemptions, use of these reserves might be precluded, even if coal cleaning were used as a precombustion treatment. Additional modeling work to consider such impacts more precisely was scheduled for late 1978 under joint DOE/EPA sponsorship.

### Flue gas desulfurization capabilities

Assessment of the technological capabilities of FGD systems (for example, scrubbers) to remove $SO_2$ from flue gases has been the subject of numerous studies over the past decade. Although a number of interrelated technical issues are involved, the principal issue associated with the proposed standard concerns the specification of a maximum level of percentage $SO_2$ removal capability and the averaging time for enforcement.

The two parameters (percent removal/averaging time) are closely linked, as an examination of Figure 2 shows. Here, the probability of meeting 24-h $SO_2$ removal efficiencies are plotted for a number of full-scale U.S. scrubber installations (EPA data, drawn from the supplemental background information document for the $SO_2$ standard). For example, for one period involving 25 days of data, the Mitchell station scrubber (Wellman-Lord system) had about a 10% probability of being less than 87% efficient and a 50% probability of being less than 90% efficient. This scrubber also showed greater than 92% efficiency about 10% of the time.

For the time period studied, then, the Mitchell scrubber satisfied EPA's suggested daily percent removal standard (85% removal except for 3 days per month); this scrubber also satisfied a longer term (here, 25 days) 90% removal standard. Other scrubber performance data shown on this plot indicate better performance by the Eddystone station scrubber (magnesium oxide system; 8 days of data), and poorer performance by the Bruce Mansfield scrubber (thiosorbic lime system; 11 days of data for Test II, 20 days of data for Test I) and the Cane Run scrubber (carbide lime system; 89 days of data). EPA's projection of future FGD performance capabilities is shown on Figure 2 as the "Line of Improved Performance."

This projected performance capability is based on data assembled at the 10-MW Shawnee prototype facility, and on observations at full-scale scrubber facilities in the U.S. and Japan, including facilities for which data are displayed in Figure 2. Note that none of the scrubber systems referenced in Figure 2 represent conventional lime/limestone systems, the base technology invoked by the standards.

Although FGD performance efficiency for a given averaging time can probably best be stated in these probabilistic terms, system performance is typically cited only with terms such as "90% efficiency," without reference to the averaging time over which this capability has been demonstrated. In addition, past vendor performance guarantees have generally been based on short-term acceptance tests (6–8 h duration), not on system performance over continuously sequential 24-hour tests. As a result, confusion exists regarding the performance capabilities of FGD systems currently in service, and there is a general difficulty in comparing the performance of various FGD systems.

Much debate centers about the interpretation of FGD performance data gathered at various prototype, pilot-scale, and full-scale facilities. Valuable design and performance capability information can be gained in each size range. Controversy, however, centers about the use of information gathered at prototype and pilot scales to infer performance capabilities at full-scale facilities. The fundamental questions here are what constitutes a reliable design basis for full-scale FGD system applications, and whether such a design basis has been developed, at the performance levels demanded by the standard.

EPA's proposed 85% $SO_2$ removal standard (24-h averaging time, with three exemptions allowed per month down to 75%) is based on specific Agency assertions that:

- An FGD system that could achieve a long-term mean $SO_2$ removal of 92% would comply with the proposed 24-h requirement (the "line of improved performance" on Figure 2).
- Lime/limestone FGD systems can achieve such long-term $SO_2$ removal capabilities, if certain changes (for example, improved pH controls) are made in design, operation, and maintenance practices. With more reactive absorbents, even greater long-term removal capabilities can be achieved.

The first of these EPA conclusions is based on EPA's observations and statistical analysis of continuous monitoring data at full-scale FGD facilities (Figure 2). The second EPA conclusion is based on EPA's projection of FGD performance capability, from the data base assembled at the 10-MW Shawnee prototype facility and from observations at full-scale facilities, both U.S. and Japanese.

DOE has recognized that long-term average performance in excess of 90% is necessary to guarantee daily attainment of an 85% $SO_2$ removal standard (the first of EPA's assumptions). However, DOE does not agree that FGD technology will perform reliably at such levels as early as 1983, when new plants will begin to operate under the revised standard.

The Department has concluded that data on currently operating FGD systems do not provide a suitable design basis to predict scrubber performance at the levels required by EPA's proposed standard. DOE makes the engineering judgment that the proposal for 85% removal averaged daily "pushes FGD technology too fast."

The electric utility industry, as represented by the Utility Air Regulatory Group (UARG), also questions EPA's conclusions regarding projected FGD performance capability, but agrees that the revised NSPS should require the use of FGD or equivalent control technologies for new coal-fired plants. The UARG percentage reduction proposal (Figure 1) is partially based on UARG's belief that a sliding scale requirement affords technological flexibility for new plants that burn high-sulfur coal. UARG argues that this requirement would allow plants that burn high-sulfur coal and "find the scrubber does not meet design expectations" to shift to a slightly lower sulfur coal with a lower percent $SO_2$ removal standard, thereby ensuring compliance.

Environmental groups, on the other hand, argue that FGD technology capabilities are greater than the capability demanded by EPA's proposal. The Natural Resources Defense Council, Inc. (NRDC), for example, states that the technological evidence now available "indicates that scrubbers can achieve, and have routinely and reliably achieved, in a cost-effective manner, removal efficiences in excess of 90%, averaged over more demanding averaging times than a day."

The technological capability issue pivots on differing interpretations of the existing data base for operational FGD technology. Perhaps the most critical challenge to be faced prior to final NSPS promulgation is the resolution of these divergent interpretations of FGD capability. Current DOE/EPA agreement on the linkage (in a probabilistic sense) between percent $SO_2$ removal and averaging time effects is an important step forward, inasmuch as scrubber performance data can now be compared over different averaging times.

### The PM standard

The particulate matter standard has been proposed in three parts:

- an emission limitation of 0.03 lb/million Btu
- an opacity standard unchanged from the standard now in force
- a percentage reduction requirement defined so that compliance with the emission limitation will result in compliance with the percentage reduction requirement. Hence, the one issue associated with the rulemaking is the proposed emission limitation.

Two principal factors associated with the 0.03 lb limit have received attention; each is briefly discussed here.

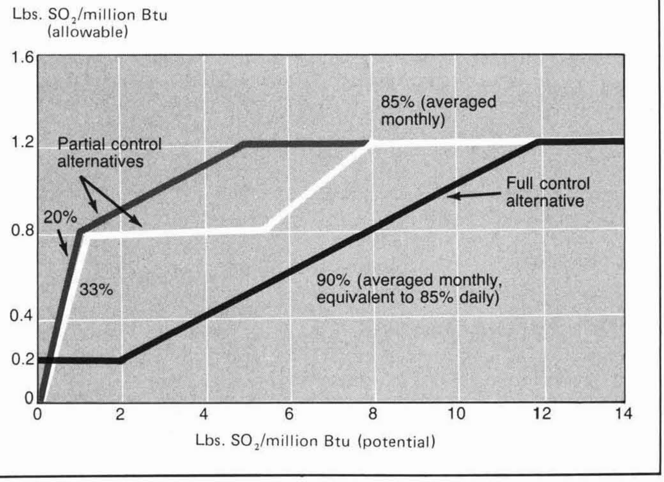
### PM control technology capabilities

EPA has based its proposed standards on the performance of a "well designed and operated baghouse or electrostatic precipitator (ESP)." The Agency's determination that these control systems are the best adequately demonstrated systems for particulate control at these emission levels was based on a number of factors, including:

- analysis of emission test results

FIGURE 1

Graphical comparison of $SO_2$ control alternatives



from steam generators employing either fabric filters (baghouses) or ESPs for particulate control

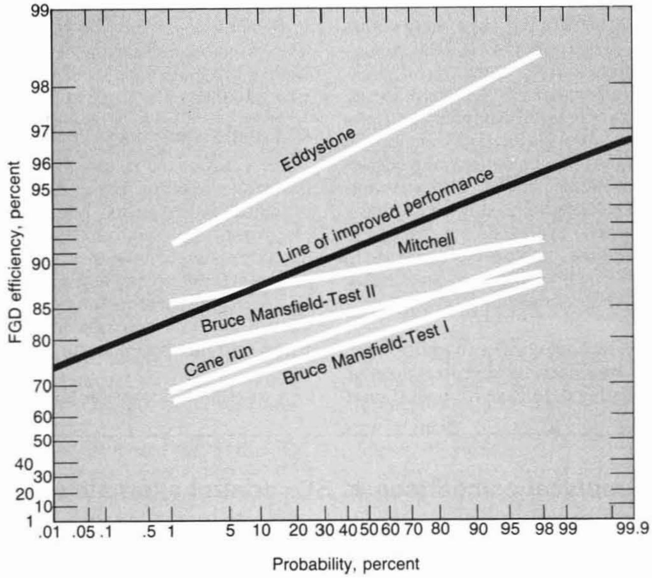
- consideration of the technological barriers to operation of baghouses or ESPs at the performance level chosen
- consideration of current construction or commitments for construction of fabric filter systems for coal-fired steam generators.

EPA's emission tests of existing baghouses or ESPs have indicated that some existing units (6 of 8 baghouse units on coal-fired plants; 9 of 22 ESP units on coal-fired plants) would meet the proposed emission limitation. The baghouse tests were performed on relatively small units (6-44 MW), including one 44-MW utility boiler firing pulverized coal. The ESP tests were performed on larger units (46-1300 MW) with seven tests on units representing "difficult particulate emission control cases." Typically, the latter tests were on units firing low-sulfur coal, where high efficiency collection of particulates by ESP units is more difficult (one of these units met the proposed standard).

Based on these emission tests and projections of performance, EPA has concluded that ESPs can be used for high-sulfur coal applications to meet the proposed standards at reasonable costs. The Agency also concludes that a baghouse control system could be applied on utility-size facilities firing low-sulfur coal at a lower cost than an ESP.

FIGURE 2

**FGD 24-h average efficiency distribution**



**FGD system parameters**

| Utility/Station | FGD Type | MW | Mean Inlet $SO_2$ lb/million Btu | No. of Testing Days |
|---|---|---|---|---|
| Philadelphia Electric/ Eddystone | MgO | 325/3 | 5.1 | 8 |
| Northern Indiana Public Service/Mitchell | Wellman-Lord | 115 | 6.3 | 25 |
| Louisville Gas & Electric/ Cane Run | Carbide Lime | 181 | 5.75 | 89 |
| Pennsylvania Power Company/ Bruce Mansfield (Test I) | Thiosorbic Lime | 825 | 6.3 | 20 |
| Pennsylvania Power Company/ Bruce Mansfield (Test II) | Thiosorbic Lime | 825 | 5.4 | 11 |

DOE has expressed concern that the proposed standard would preclude the use of ESPs on low-sulfur coal, and baghouse technology has not been adequately demonstrated for utility-scale application. The Department suggests that the standard be set at a higher level (0.05-0.08 lb) which would not preclude the use of ESPs.

The electric utility industry believes that baghouses are not a demonstrated technology for large coal-fired units, particularly those firing higher sulfur coals; that no long-term data exist on bag life at large bituminous coal-fired electric generating facilities, and that there are "no grounds for confidence" that the limited operating experience gained to date on small boilers can be "realistically extrapolated to predict the performance of much larger installations on utility boilers firing coals with widely varying characteristics." The industry also suggests that when costs are taken into account, ESPs are not adequately demonstrated for achieving a 0.03 standard. UARG has therefore recommended an emission limitation standard in the range 0.05-0.08 lb.

The central issue here, similar to the argument concerning $SO_2$ scrubber capabilities, is the issue of what constitutes a reliable commercial design base for future large-scale applications of particulate control units for commercial utility boilers. For the case of fabric filter controls, two large systems have recently been activated in the West (the 750-MW Monticello Station of Texas Power and Light Company and the 350-MW Harrington Station of Southwestern Public Service Company). EPA had plans to test emissions at the Harrington Station of Southwestern Public Service Company in late 1978 and these tests are expected to influence the rulemaking.

### FGD systems & PM emissions

In setting the particulate matter standard, EPA considered a higher emission limitation (0.05 lb) that the Agency believed could be met by wet particulate matter scrubbers. This option was rejected in favor of the 0.03 lb limit; *the proposed standard will effectively require a flue gas train in which particulate collection (by baghouse or ESP) precedes $SO_2$ removal (typically by a wet scrubber).*

Since there were no existing plants available for testing where a high-efficiency ESP or baghouse was followed by an FGD system, the *proposed standards are based on emission measurements taken at particulate control devices prior to any FGD treatment.* Compliance with the standard, however, will be based on measurements taken at the outlet of the flue gas treatment train (after the FGD unit).

There is a potential for FGD units to increase particulate emissions, either by entrainment of scrubber liquids at the mist eliminator, or by particulate matter generation through condensation of sulfuric acid mist. On the other hand, FGD units may also remove additional particulates from the flue gas stream after primary removal by an ESP or baghouse.

Tests conducted by the Agency on FGD units at plants firing low-sulfur coal, lead EPA to conclude that the proposed particulate matter standard can be met at such plants. In the case where an FGD system is used with higher sulfur coal, EPA suggests sufficient data are not yet available to fully assess the potential of the FGD unit to increase particulate emissions. EPA has scheduled tests at the Louisville Gas and Electric Cane Run Station to investigate this subject, *and these tests may influence the rulemaking.*

### The $NO_x$ standard

EPA's proposed $NO_x$ standards incorporate separate emission limitations for:

- the combustion of subbituminous coal, shale oil, and any solid, liquid, or gaseous fuel derived from coal (0.5 lb/million Btu)
- the combustion of bituminous coal (0.6 lb/million Btu).

Standards for units that burn gaseous and liquid fuels not derived from coal are unchanged from those originally promulgated in 1971 (40 CFR 60, Subpart D); standards for lignite are unchanged from those promulgated in early 1978 (43 FR 9276); the exemption of coal refuse from the Subpart D standards is continued. Percent reduction requirements for $NO_x$ are proposed for the various fuel categories, but these requirements are not controlling. Hence issues associated with this part of the rulemaking are concerned with the new 0.5 and 0.6 lb/million Btu emission limitations

### Status of $NO_x$ control

The new standards are based on emission limitations achievable through combustion modification techniques. These techniques limit $NO_x$ formation in the boiler by flame temperatures and by minimizing the availability of oxygen during combustion. However, there are potential side effects as a result of the modifications including boiler tube wastage (corrosion), slagging, increased emissions of other pollutants, boiler efficiency losses, and possible operating hazards (explosions). EPA believes only boiler tube wastage could be a potential problem at the $NO_x$ emission levels necessary to meet the proposed standards.

Viable techniques for reducing $NO_x$ emissions via combustion modification include staged combustion, use of low excess air, and use of reduced heat-release designs. Staged combustion is accomplished by redistributing the air flow to the boiler such that a cooler secondary combustion zone is encountered by the combustion gases after they leave the flame front. Low excess air reduces the oxygen available for $NO_x$ formation and is accomplished via operational adjustments.

Reduced heat release lowers combustion gas temperature and is accomplished by increasing the combustion chamber size for a given firing rate. Combinations of these techniques are used by the four major boiler manufacturers (Combustion Engineering Inc., Babcock and Wilcox Company, Foster Wheeler Corporation, and Riley Stoker) to achieve low $NO_x$ emission operation.

Based on emission test results and an assessment of the technology, EPA has concluded that if the potential side effects associated with low $NO_x$ operation were not considered, it would be reasonable to establish an $NO_x$ emission limit for pulverized coal-fired units at 0.5 lb/million Btu heat input.

However, for high-sulfur Eastern coals where tube wastage is a potential problem, EPA does not believe an emission limit below the proposed 0.6 lb level would be reasonable, even though emission data alone would tend to support a lower limit. For low-rank Western coals, where there is a much smaller tube wastage potential at low $NO_x$ levels, EPA proposes the 0.5 lb/million Btu emission limit.

UARG suggests that available data demonstrate that only one manufacturer (Combustion Engineering) could meet the proposed standards on a continuous basis. The industry has expressed concern that the proposed standards could therefore have an anticompetitive effect.

### Manufacturer capabilities

Based on a study by a consultant (KVB), the industry has assessed each boiler manufacturer's capabilities as follows:

- Combustion Engineering (CE): Although some units subject to current NSPS have emissions at or above the recommended limitations, CE's unique tangential fired boilers have the greatest potential for low $NO_x$ emissions;
- Babcock and Wilcox (B&W): This manufacturer should be able to achieve the 0.6 and 0.5 lb emission limitations for bituminous and subbituminous coal with its wall-fired boilers, new dual register burners, and redesigned windbox. However, more development and demonstration work will need to be accomplished to confirm this;
- Foster Wheeler (FW): No data exist on FW units on subbituminous coal. The one unit firing bituminous coal will marginally meet a 0.6 lb per million Btu limitation. FW is in the process of developing a new low $NO_x$ burner, but has not yet demonstrated its effectiveness;
- Riley Stoker (RS): One emissions test indicated that the emission limitation on subbituminous coal may be achievable, while two other tests indicate the emission limitation on bituminous coal cannot presently be met. With Riley's present burner and boiler design, the emission limitation on either coal may be difficult to achieve.

EPA has examined the impact of combustion modifications for $NO_x$ control on boiler tube corrosion; the Agency's assessment differs from the UARG position. Through an engineering contractor, EPA has experimentally measured corrosion rates by exposing corrosion coupons installed at the end of probes and inserted into "vulnerable" areas of the furnace both under baseline and low $NO_x$ firing conditions. The total exposure of the coupons for each test was 300 hours.

An assortment of boilers was examined, including B&W, CE, and FW designs. Based on the results of these studies and other design information, EPA believes that new units that would be designed to comply with the proposed $NO_x$ emission limits would not experience serious tube wastage for the following reasons:

- Coupon corrosion tests indicate that tube wastage is not significantly accelerated during low $NO_x$ operation of modern Combustion Engineering boilers. CE has stated that its modern units would be capable of achieving the proposed standards for both eastern bituminous and low rank western coals and lignite;
- Babcock and Wilcox has designed a new burner that will permit a furnace to be maintained in an oxidizing environment, thus minimizing the potential for furnace wall corrosion when high-sulfur bituminous coal is burned;
- Foster Wheeler and Riley Stoker are developing new burners that may

have the same advantage as the new Babcock and Wilcox burner. Also, Foster Wheeler introduces "boundary air" in its modern units to minimize reducing conditions near the boiler wall where tube wastage occurs;

- Foster Wheeler and Babcock and Wilcox have executed contracts to build units that will be required to comply with the state of New Mexico's $NO_x$ emission limit of 0.45 lbs per million Btu.

The application of specific control technologies by individual source operators will be strongly influenced by the percent reduction and emissions limitation requirements specified in EPA's final rulemaking. The results of ongoing modeling analyses and control technology testing, as well as comments from both the public and private sectors on the proposed rulemaking, will be important considerations in EPA's final determination. Ultimately the NSPS that are promulgated will need to be responsive to these inputs as well as to competing national environmental, energy, and economic objectives.

## Acknowledgment

This article is a condensation of a briefing paper prepared for the Department of Energy Assistant Secretary for Environment by Dr. Robert W. Dunlap, Dr. David V. Nakles, Barbara J. Goldsmith (ERT), and Roger Strelow (Leva, Hawes, Symington, Martin, and Oppenheimer) with the assistance of Karen M. Higgs (ERT) and Andrew D. Weissman (Leva, Hawes, Symington, Martin, and Openheimer).

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ES&T RESEARCH

# Sources and Fates of Aromatic Compounds in Urban Stormwater Runoff

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■ Petroleum-derived aromatic hydrocarbons and associated sulfur compounds in urban stormwater runoff and Delaware River sediment samples were characterized using a gas chromatograph equipped with a flame ionization/sulfur specific flame photometric detector system. Total petroleum hydrocarbon concentrations were determined gravimetrically in stormwater emanating from a northern Philadelphian storm sewer. Comparison of hydrocarbon and sulfur fingerprints of the aromatic fractions of environmental samples to reference oils indicated that crankcase oil was the most likely source of aromatics in stormwater runoff. A weathering study on used crankcase oil showed a loss of diaromatics accounting for their absence in the environmental samples. A method of transport by which land-based oil enters the aquatic environment and receiving water sediments was proposed. Dibenzothiophene was identified in the environmental samples by retention time and mass spectrometry. Concentrations of dibenzothiophene in stormwater runoff ranged from 44.2 to 62.3 ng/L.

The ever increasing dependence of today's society upon a technology based on petroleum fuels and products has led to widespread oil pollution of the environment. Until recently, the study of oil pollution focused on oil spills and recorded sources of pollution such as refinery and industrial effluents. Unrecorded sources of land-based oil have now been shown to contribute a significant amount of petroleum-derived hydrocarbons to the aquatic environment via stormwater runoff (*1, 2*). According to Brummage (*3*), disposal of used lubricating oils may be the most significant source of inland oil pollution. This is supported by an estimation that 1.1 billion gallons of automobile and industrial lubricants are released to the environment annually (*4*). Unrecorded sources of pollution such as stormwater would be expected to reflect a significant amount of these lubricants.

The nature and source of the petroleum components in stormwater may be examined by gas chromatography to give a characteristic hydrocarbon fingerprint. The use of a sulfur specific flame photometric detector in conjunction with a flame ionization detector gives additional information on the sulfur components which are usually "lost" on the hydrocarbon envelope. Although sulfur compounds represent, at the most, only 4% of a petroleum oil, Adlard et al. (*5*), Garza and Muth (*6*), and Warner (*7*) have shown that sulfur fingerprints can be a valuable aid in oil characterization and source correlation.

While petroleum studies have been primarily concerned with the aliphatic hydrocarbon fraction (*2*), the majority of the sulfur compounds occur in the less frequently studied aromatic fraction. According to Martin and Grant (*8*), the sulfur aromatics in petroleum oil are predominantly thiophenes. Warner (*7*) identified benzothiophene, dibenzothiophene, naphthobenzothiophene, and their alkyl derivatives in oils and marine samples.

The present study was directed toward the characterization, source, and probable fate of aromatic sulfur compounds in petroleum oils from stormwater runoff. Gas chromatographic fingerprints of the aromatic fractions from several environmental samples and standard oils were obtained using a dual flame ionization/flame photometric detector system. Emphasis was placed on the identification and quantitation of aromatic compounds in urban runoff emanating from a storm sewer in northern Philadelphia, discharging to the Delaware River.

### *Sampling and Experimental Methods*

The drainage basin sampled encompassed an urban area of 1520 acres. Land use data and a thorough description of sampling technique may be found elsewhere (*1*). Briefly, the storm events were sampled every 5 min for the duration of the storm. Samples were composited on a flow-proportionate basis and analyzed according to the scheme outlined in Figure 1.

The particulate and aqueous phases were separated by a Sharples Type T-1 continuous centrifuge at 15 000 rpm. The particulates, greater than 1 μm, were dried at 40 °C for 24 h. The soluble fraction was gravity fed to an activated carbon column (40 g, 32.0 × 2.5 cm bed) at a flow rate of 10 mL/min, through an all-glass system. Following adsorption, the carbon was dried at 40 °C for 24 h.

The soluble organics were extracted from the activated carbon by soxhlet extraction. The dried particulate fraction was also soxhlet extracted to remove adsorbed organics. Each fraction was successively extracted for 6 h with 250 mL of hexane, then benzene, and finally chloroform. This resulted in three extracts for the soluble and three for the particulate. All solvents were pesticide grade and all glassware was solvent rinsed and baked at 250 °C.

To examine the petroleum-derived aromatic hydrocarbons and aromatic sulfur compounds a silica gel separation scheme was employed (*9*). The particulate and soluble fractions were evaporated to dryness on 45 mL of silica gel (activated at 225 °C for 48 h) on a rotary evaporator at 45 °C. The silica gel was charged to a 67.5 × 20 cm i.d. Pyrex column with a fritted glass disk. The silica gel was first eluted with 80 mL of hexane to obtain the aliphatic hydrocarbons and then eluted with 80 mL of benzene to obtain the aromatic hydrocarbon and sulfur

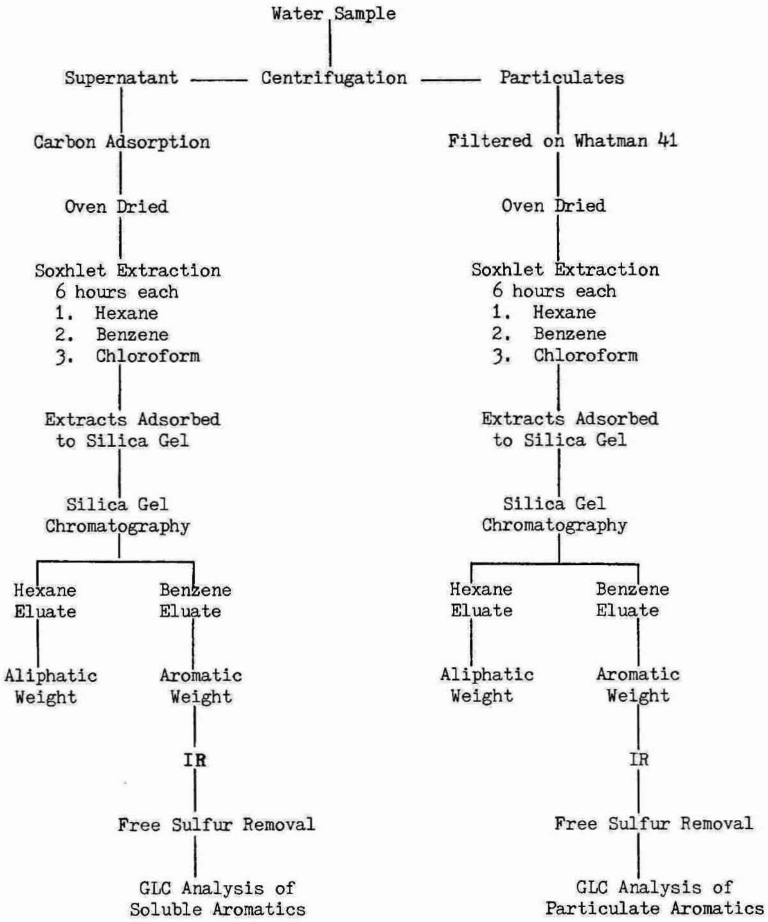

**Figure 1.** Analytical scheme

compounds. The eluates were evaporated to dryness under reduced pressure and their weight recorded. Concentrations of total petroleum-derived hydrocarbons in stormwater were determined based on the sum of the aliphatic and aromatic fractions in the soluble and particulate fractions.

Sediment samples from the Delaware River were randomly collected around the Marcus Hook area, south of Philadelphia, and composited. The samples were oven dried and ground with a mortar and pestle. Five hundred grams was soxhlet extracted with 1000 mL of chloroform for 72 h. Five hundred milliliters of the extract was evaporated to dryness on activated silica gel. The above elution was performed to obtain the aromatics.

Standard oil samples were furnished by the U.S. Coast Guard Research and Development Center, Groton, Conn. The used crankcase oil was obtained from a local garage. All oils were subjected to the above-mentioned separation scheme.

To study the effects of weathering on used crankcase oil, a Pyrex pan was coated with 100 mL of the oil and placed on the roof of the lab for 14 days in June. The pan was situated such that it received at least 10 h of sunlight a day. On the 14th day the oil residue was rinsed from the pan with methylene chloride and adsorbed to silica gel by rotary evaporation. The aromatic hydrocarbons and sulfur compounds were subsequently separated by elution.

Gas chromatographic analyses were performed on a Tracor 222 gas chromatograph equipped with a Tracor FID/FPD (sulfur mode) dual detector system. A dual pen recorder allowed for simultaneous response. A 6-ft, 4-mm i.d. glass column packed with 3% OV-17 on 80/100 mesh Supelcoport was programmed from 125 to 275 °C for fingerprint analyses.

The identification of benzothiophene, dibenzothiophene, and the triaromatics was based on GC retention time data and mass spectrometry, using a Finnigan 3200 GC/MS equipped with a Systems Industries 150 data system. Electron impact as well as chemical ionization spectra were obtained for confirmation. To quantitate dibenzothiophene in the stormwater samples, a standard curve of dibenzothiophene was run using 50 $\mu$g of dodecyl sulfide as an internal standard (Figure 2). All samples were quantitated with the same amount of internal standard. Prior to all injections, the aromatic fractions were resolubilized in methylene chloride and passed through a copper column to eliminate the possibility of free sulfur contamination (*10*).

## *Results and Discussion*

Concentrations of aromatic hydrocarbons in stormwater were determined for three different rain events and may be found in Table I. Gas chromatographic analyses of the soluble aromatics indicated that there was an absence of sulfur compounds in this phase. It may be noted that about 95% of the total aromatics was associated with the particulates, and

**Table I. Petroleum Hydrocarbons in Stormwater Samples**

| storm event date | discharge volume of storm, $10^6$ L | hydrocarbon type | associated hydrocarbons: particulates mg/L | particulates kg/storm | soluble mg/L | soluble kg/storm |
|---|---|---|---|---|---|---|
| 4/3/75 | 1.726 | aromatics | 1.10 | 1.89 | 0.06 | 0.11 |
| | | total petroleum hydrocarbons | 3.70 | 6.38 | 0.34 | 0.59 |
| 8/16/75 | 11.234 | aromatics | 1.65 | 18.54 | 0.07 | 0.78 |
| | | total petroleum hydrocarbons | 5.06 | 56.85 | 0.24 | 2.69 |
| 11/21/75 | 15.182 | aromatics | 0.99 | 15.03 | 0.04 | 0.61 |
| | | total petroleum hydrocarbons | 4.08 | 61.94 | 0.16 | 2.43 |

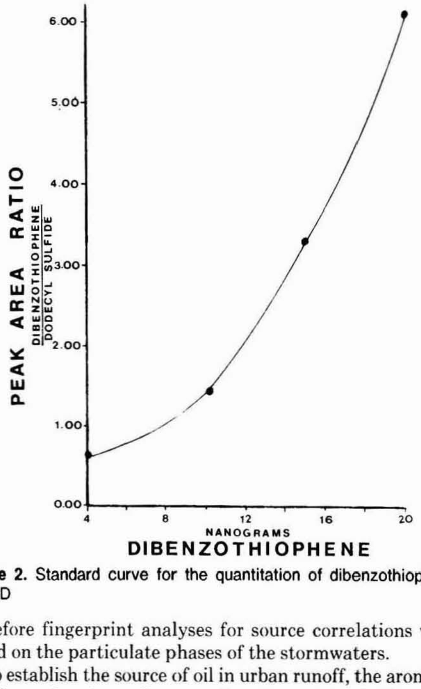

**Figure 2.** Standard curve for the quantitation of dibenzothiophene by FPD

therefore fingerprint analyses for source correlations were based on the particulate phases of the stormwaters.

To establish the source of oil in urban runoff, the aromatic fractions of various oils were also characterized. Since the source of oil in urban runoff was land-based, it may be assumed to be characterized by a refined oil. The heavier lubricating and residual fuel oils consist of high boiling compounds and are inherently resistant to extensive weathering, thus making them a prime suspect as a source of oil in urban runoff. Residual oils are primarily used for industrial heating purposes and are usually a blend of a gas–oil petroleum distillate and the heavy residual oil of a crude. The aromatic fractions of a number 6 fuel oil and a residual fuel oil were chromatographed and may be seen in Figures 3 and 4. In contrast, lubricating oils, such as hydraulic and crankcase oils, are distinct distillate cuts of a crude and are generally classified according to their different viscosities (*11*). Fingerprint chromatograms were obtained of the aromatic fractions of a used lube and crankcase oil and a hydraulic oil. The similarities and differences between the aromatics of the lube oils and the environmental samples may be noted in Figures 3 and 4.

The value of the sulfur profile is evident in these fingerprint comparisons. The FID fingerprints all show a large hydrocarbon envelope and the correlation is obscure. In contrast, the FPD sulfur profiles of the oils are quite different and a similarity between the used crankcase oil and the stormwater sample may be noted.

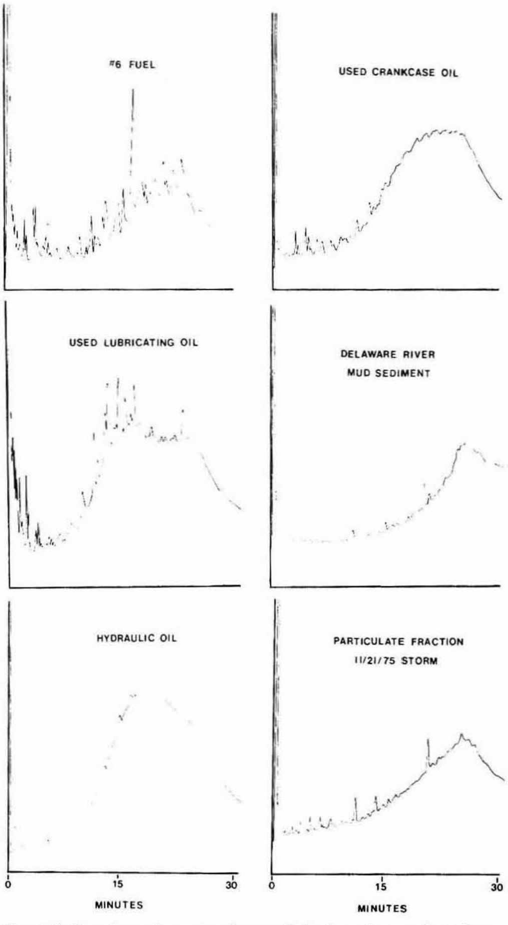

**Figure 3.** Gas chromatograms of aromatic hydrocarbons using a flame ionization detector

Therefore, while the high boiling, high molecular weight components of several petroleum products may have contributed to the oil pollution in urban runoff, used crankcase oil appeared to be the most likely contributor based on fingerprint correlation.

The comparison of chromatographic fingerprints is based on the similarity of origin and weathering effects. A closer look at the lower boiling diaromatic region revealed that a major

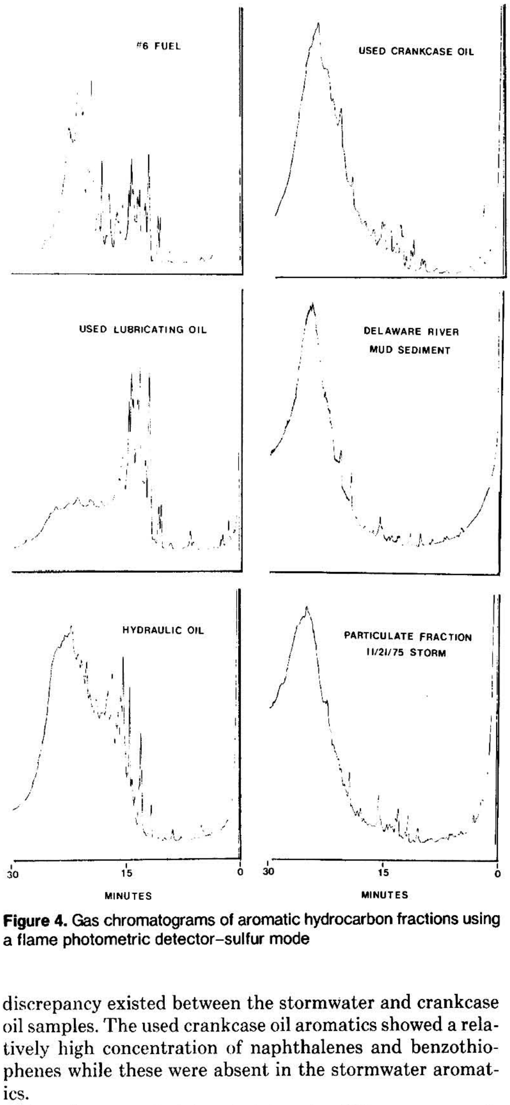

**Figure 4.** Gas chromatograms of aromatic hydrocarbon fractions using a flame photometric detector–sulfur mode

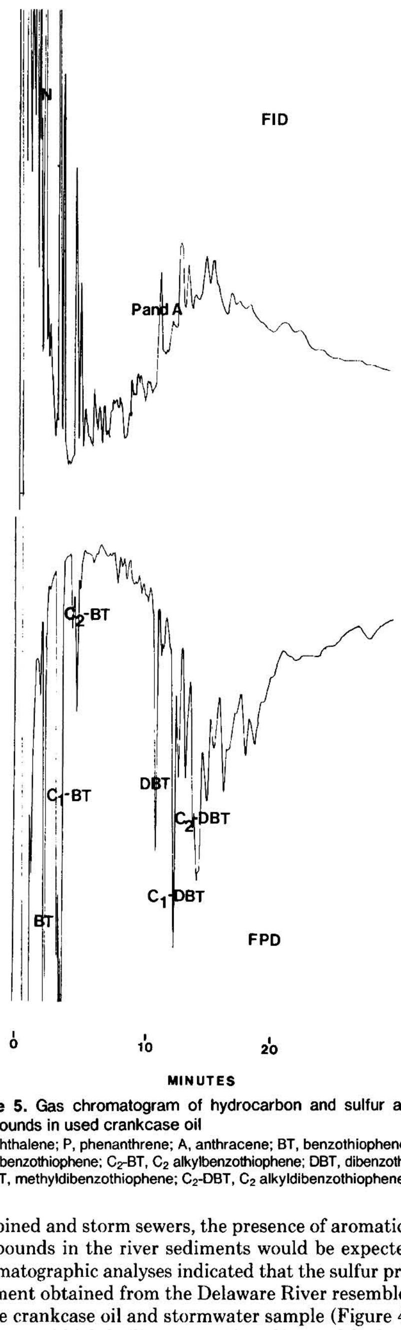

**Figure 5.** Gas chromatogram of hydrocarbon and sulfur aromatic compounds in used crankcase oil

N, naphthalene; P, phenanthrene; A, anthracene; BT, benzothiophene; $C_1$-BT, methylbenzothiophene; $C_2$-BT, $C_2$ alkylbenzothiophene; DBT, dibenzothiophene; $C_1$-DBT, methyldibenzothiophene; $C_2$-DBT, $C_2$ alkyldibenzothiophene

discrepancy existed between the stormwater and crankcase oil samples. The used crankcase oil aromatics showed a relatively high concentration of naphthalenes and benzothiophenes while these were absent in the stormwater aromatics.

A study was undertaken to determine if these compounds would be lost during natural weathering. After 14 days of weathering, the aromatic fraction of the used crankcase oil showed a reduction of peak height and in some cases a total loss of sulfur peaks in the diaromatic region. Natural weathering would account for the discrepancy noted.

The fate of aromatic sulfur compounds is suggested by their preferential association with the particulate matter in urban runoff. A general mechanism for the transport of petroleum-derived sulfur compounds may be proposed. Fuel oils and lubricating oils are released to the environment either by spills, direct disposal into storm sewers, or leakage of automobile crankcase oil onto roads. The oils become adsorbed to particulate matter and the lower boiling diaromatics are lost through natural weathering. The particulates are washed into sewers during a storm event. At this time the solids that have accumulated in the sewer are scoured from the collection system and to the receiving water. With a decrease in scouring velocity the heavier particulates undergo settling.

Since the Delaware River receives the discharges from many combined and storm sewers, the presence of aromatic sulfur compounds in the river sediments would be expected. Gas chromatographic analyses indicated that the sulfur profile of sediment obtained from the Delaware River resembled that of the crankcase oil and stormwater sample (Figure 4). The presence of high-boiling aromatic sulfur and hydrocarbon compounds in this sediment sample suggests that extensive degradation of these compounds does not occur in the sediments. Adlard et al. (5) also noted that in biologically weathered oil samples the normal paraffins were lost to a greater extent than the sulfur compounds. This was attributed to the selectivity of microorganisms. According to Warner (7), sulfur aromatics are also preferentially concentrated with respect to the associated hydrocarbons. It appears then that petroleum-derived aromatic sulfur compounds remain rela-

**Table II. Quantitation of Dibenzothiophene in Philadelphia Stormwater Runoff**

| date | discharge vol, $1 \times 10^6$ L | dibenzothiophene,[a] ng/L | loading, mg/storm |
|---|---|---|---|
| 4/3/75 | 1.726 | 44.2 | 76.3 |
| 8/16/75 | 11.234 | 46.1 | 517.9 |
| 11/21/75 | 15.182 | 62.3 | 945.8 |

[a] Concentrations adjusted for percent recovery of compound, 69.7%.

tively unchanged in the environment and probably undergo concentration in the sediments.

As previously noted, the lower boiling benzothiophenes (BT) and naphthalenes (N) were present in the used crankcase oil but absent in stormwater particulates and Delaware River sediment samples due to weathering. On the other hand, dibenzothiophene (DBT) and phenanthrene and/or anthracene were present in all samples (see Figure 5). Phenanthrene (P) and anthracene (A) could not be differentiated on the column used. These chromatograms were obtained by programming the column from 125 to 200 °C. The presence of DBT and naphthobenzothiophene in sediment samples has also been reported by Giger and Blumer (*12*) who tentatively identified them in samples taken from Buzzards Bay, Mass. The identification of the alkylbenzothiophenes (C-1 and C-2 BT) and dibenzothiophenes (C-1 DBT and C-2 DBT) was based in part on previous work by Warner (*7*), and also on mass spectral data.

The large unresolved sulfur envelopes noted in Figure 4 are thought to be composed primarily of four- and five-ring thiophenes as well as aromatic sulfides, thiols, and thiaindans according to Martin and Grant (*8*).

The concentrations of dibenzothiophene in stormwater samples may be found in Table II. An average of 69.9% of the dibenzothiophene was recovered by the analytical method and separation scheme. The concentrations were adjusted for percent recovery of the compound. While the concentrations ranged from 44.2 to 62.3 ng/L, the total loading of dibenzothiophene appeared to be exponentially dependent upon the total volume discharged.

Due to the polycyclic nature of dibenzothiophene, its possible carcinogenic and/or mutagenic effects are subject to question (*13*). The persistence of this compound as well as the higher molecular weight condensed thiophenes and other polynuclear aromatics suggests their concentration in the environment. While beyond the scope of this study, the eventual accumulation of polycyclic thiophenes and aromatics in the sediments may prove toxic to benthic communities.

### *Conclusions*

According to Giger and Blumer (*12*), the presence of polynuclear aromatics in sediments may be attributed to many sources. Runoff from the land appears to be a significant source of these aromatics. Adsorption of polynuclear aromatics to particulate matter and eventual settling of these particulates offer a method of transport of land-based oil to receiving water sediments.

Inland oils, as Brummage (*3*) suggests, would be characterized by used automobile and industrial lubricants which resist extensive weathering in the environment. Specifically, the source of aromatics in stormwater runoff may be attributed primarily to crankcase oil.

### *Acknowledgments*

Thanks are extended to the Surveillance and Analysis Division of the Environmental Protection Agency in Region II for the use of their mass spectrometers.

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# Design and Evaluation of a New Low-Pressure Impactor. 2

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■ The last two stages of the low-pressure impactor described in Part 1 of this paper have been calibrated using a laboratory-generated uranine aerosol. An electrostatic classifier was used to obtain a near-monodisperse aerosol and the deposited material was analyzed by fluorescence. For the final three stages, the particle diameters collected with a 50% efficiency were found to be 0.12, 0.075, and 0.05 $\mu$m. These cutoff diameters are the aerodynamic particle diameters at the reduced stage pressures; the relation to the particle Stokes diameter is discussed.

A low-pressure impactor has been developed which is capable of the size segregation of aerosols from 0.05 to 4.0 $\mu$m aerodynamic diameter. The design and previous laboratory and field evaluation of the impactor have been reported elsewhere (*1*). Presented here is the calibration of the 0.05- and 0.075-$\mu$m stages of the impactor using a laboratory-generated uranine aerosol.

The impactor consists of eight single jet stages, sampling at a mass flow of 1 L (NTP) per minute (L/min). Particles larger than 0.5 $\mu$m in aerodynamic diameter are collected at near atmospheric pressure using the first four stages of the Battelle (*2*) impactor (Delron No. DC15, Powell, Ohio). To this device four low-pressure stages have been added to size segregate the smaller aerosol. A critical orifice separating the low-pressure and atmospheric pressure stages determines the sample rate. The jet diameters and the stagnation pressures below the jet of each stage are listed in Table I.

In designing this impactor, it was desired to have an instrument which has both small cutoffs and which is sufficiently portable for field measurements. As the size of the pump limits the flow rate which may be obtained at these low pressures, the impactor was designed to be compatible with more sensitive analytical techniques. By using one jet per stage, the aerosol is confined to a small area which, for example, may be directly analyzed for aerosol nitrate or sulfur at the nanogram level (*3, 4*). For the low-pressure stages to collect small particles with the mass flow of 1 L/min (NTP) per jet, and also to attain sufficiently high jet Reynolds numbers to minimize cross-sensitivity between stages (*5*), it is necessary to use high jet velocities. The flow in the final three stages is compressible; the particle segregation results from the decrease in pressure rather than a decrease in jet diameter.

Of interest in the calibration of the impactor is the collection efficiency of each stage as a function of particle diameter. For a particular stage, the diameter of a particle which is collected with a 50% efficiency is referred to as the cutoff diameter, $d_{50}$. In Part 1 (*1*), the fourth, fifth, and sixth stages of the impactor were calibrated using monodisperse aerosols of polystyrene latex spheres. The latex particles on each stage were counted using an electron microscope. The collection efficiencies were calculated assuming that all of the aerosol was collected in the impactor.

It was not possible to calibrate the seventh and eighth impactor stages in this same manner. The number of particles passing through the impactor to the after-filter could not be determined. In addition, the smallest available latex sphere (0.088 $\mu$m diameter) is larger than the cutoff of the seventh stage. Proper calibration of these final two stages is especially important because the jet velocities are sonic. If the flow were incompressible, the cutoff diameters could be calculated from the value of the Stokes number corresponding to the cutoffs for the upper stages. For these sonic stages, the flow regime is sufficiently different that one cannot apply this theory. Experimental evaluation of the cutoffs is necessary.

## *Experimental*

The impactor was calibrated with a sodium fluorescein (uranine) aerosol. A near monodisperse aerosol was obtained using a Thermo Systems, Inc., Model 3071 Electrostatic Classifier (*6*). The samples were analyzed by fluorescence.

**Aerosol Generation.** A diagram of the aerosol generation and flow system is shown in Figure 1. The Thermo-Systems, Inc., Model 3075 constant output atomizer (*7*) contains a critical orifice to control the air flow at 3 L/min. Syringe pumps were used to feed a solution of 0.05% uranine in half-ethanol, half-water at a flow rate of 0.59 cm$^3$/min. The atomizer output was mixed with 11 L/min of dry air and allowed to equilibrate in a 25-L volume; then 3 L/min of the diluted aerosol was dried by three successive diffusion dryers with a combined length of 137 cm.

The dried polydisperse aerosol was introduced into the size classifier in which it acquired a bipolar Boltzmann charge distribution by exposure to an $^{85}$Kr source. The aerosol flow of 3 L/min was then introduced in an annular ring around a 20-L/min flow of particle-free sheath air. Positively charged aerosol is drawn by a cylindrically symmetric electric field across the sheath air flow toward the central collector rod. By varying the collector rod voltage, aerosol of a chosen electrical mobility is made to pass through a slit at the base of the rod. Singly charged particles should be of the desired size, but some larger doubly or triply charged particles will also be found.

In this study, two runs were made with larger aerosols of 0.22 and 0.39 $\mu$m Stokes diameter. To obtain these aerosols, the aerosol and sheath air flows in the Electrostatic Classifier were reduced to 1 and 8 L/min, respectively. Also, the concentration of the atomizer solution was increased to 0.5% uranine.

A photograph of the particles from a 0.064-$\mu$m aerosol is shown in Figure 2. Each of the calibration aerosols was photographed and sized by electron microscopy. The particles were collected on 500 mesh, carbon coated grids using a point-to-plane electrostatic precipitator (AIRES, Albuquerque, N.M.). The magnification of the micrographs is obtained by photographing a 54 864 lines/in. diffraction grating.

**Sample Collection.** The calibration aerosol was sampled both by the impactor and a total filter operated in parallel. For most of the runs, an after filter was used with the impactor. Thus, the total filter acted as a check on the mass balance for the system. The excess aerosol flow was vented through the electrometer portion of an Electrical Aerosol Analyzer (Thermosystems No. 3030), and the aerosol current was measured to monitor the output of the aerosol generation system. Details of the flow system can be seen in Figure 1. Note that the aerosol to be sampled by the impactor and total filter is first passed through an $^{85}$Kr charge neutralizer.

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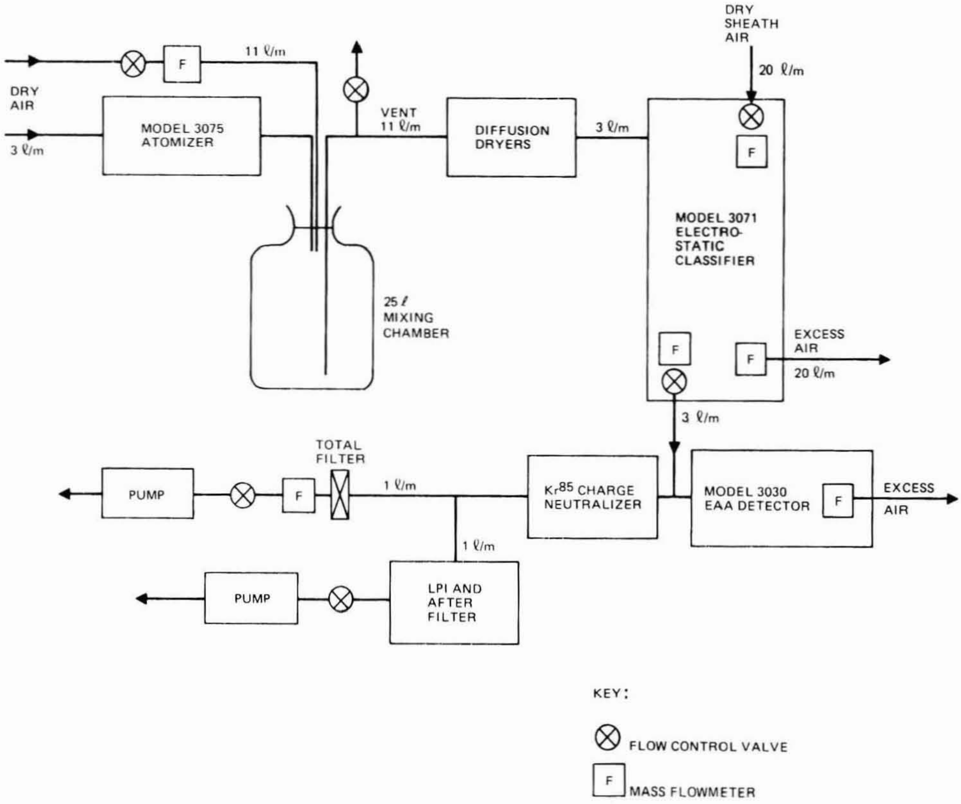

**Figure 1.** Aerosol generation and sampling system

**Table I. Low-Pressure Impactor Design and Operational Parameters**

| stage no. | $D_j$, cm | $P$,[a] mmHg | cutoff, µm |
|---|---|---|---|
| 1 | 0.249 | 744 | 4.0[b] |
| 2 | 0.140 | 743 | 2.0[b] |
| 3 | 0.099 | 740 | 1.0[b] |
| 4 | 0.064 | 720 | 0.50[b,c] |
| orifice | 0.036 | 150 | |
| 5 | 0.110 | 140 | 0.26[c] |
| 6 | 0.099 | 106 | 0.12[c,d] |
| 7 | 0.099 | 50 | 0.075[d] |
| 8 | 0.140 | 8 | 0.050[d] |

[a] Atmospheric pressure = 745 mmHg. [b] Calibration data from Delron Research Products (Powell, Ohio). [c] Polystyrene latex calibration of ref *1*. [d] This work.

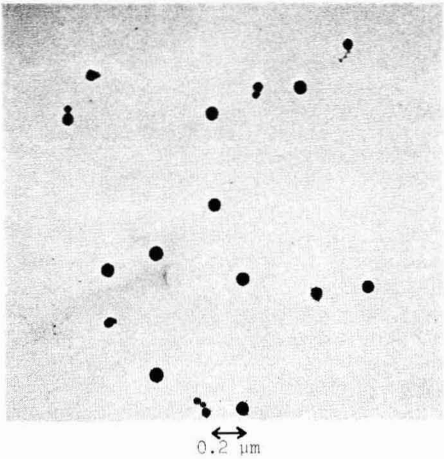

**Figure 2.** Uranine aerosol, 0.064 µm diameter

Although these small particles are expected to follow the air flow, the effect of splitting the aerosol stream between the impactor and the total filter was tested. For the 0.064- and 0.39-µm (microscopic diameter) aerosol (*5*), a filter was operated upstream of the impactor in parallel with the total filter. The air flow in both streams was 1 L/min. The ratio of the loadings for this impactor "prefilter" to the total filter was 0.99 ± 0.02.

The possibility of evaporation of the uranine at the reduced impactor pressures was also checked. Two filters were loaded with equal amounts of the uranine aerosol. One of these filters was then placed as an after-filter on the vacuum side of the impactor, and filtered room air drawn through the impactor. Two runs each with the filters subjected to the low pressures for 0.5 and 9.3 h both gave 3 ± 1% losses. The 9-h run is representative of the longest sampling times used in these experiments.

Earlier studies (*1*) demonstrated that it is essential to coat the collection surfaces to prevent particle bounce and reentrainment. Vaseline was found to prevent particle bounce and to be compatible with chemical analyses. Therefore, for this calibration study, Vaseline-coated collection surfaces were

**Table II. Uranine Aerosol Particle Diameters**

| microscopic diam.[a] | aerodynamic diameter[c] | | | | | |
|---|---|---|---|---|---|---|
| | nominal[b] | stage 8 | stage 7 | stage 6 | stage 5 | stages 1–4 |
| $0.39^{+0.10}_{-0.07}$ | 0.40 | 0.56 | 0.55 | 0.53 | 0.52 | 0.49 |
| $0.22^{+0.04}_{-0.03}$ | 0.28 | 0.32 | 0.31 | 0.31 | 0.30 | 0.28 |
| 0.085 ± 0.005 | 0.14 | 0.12 | 0.123 | 0.122 | 0.121 | 0.11 |
| 0.064 ± 0.004 | 0.10 | 0.093 | 0.093 | 0.092 | 0.091 | 0.086 |
| 0.057 ± 0.007 | 0.075 | 0.083 | 0.083 | 0.082 | 0.082 | 0.077 |
| 0.034 ± 0.003 | 0.050 | 0.050 | 0.049 | 0.049 | 0.049 | 0.047 |
| 0.0078 ± 0.0007 | 0.030 | 0.011 | 0.011 | 0.011 | 0.011 | 0.011 |

[a] Based on electron micrographs. [b] As given by classifier. [c] Based on uranine density and microscopically determined diameter (see text).

used throughout. In most of the calibration runs, the sample was collected on a stainless steel strip, 1 × 0.25 × 0.002 in., mounted in the center of a 1-in. diameter glass disk. These strips are the same as those used for aerosol sulfur analysis by the flash volatilization method (*3*). A Vaseline coating is applied to the center of the strip with a cotton swab. The impactor was also calibrated using 1-in. glass disks, for which the entire surface was coated with Vaseline.

**Chemical Analysis.** The uranine collected on each stage was measured by fluorescence. For the Vaseline-coated impactor samples, a double extraction was employed to dissolve both the grease and the uranine (*8*). The stainless steel strips and glass disks used in the impactor were ultrasonically extracted for 20 min with 3 mL of benzene. To the benzene solution, 4 mL of 0.1 N $NH_4OH$ was added, the test tube shaken to mix the two solvents, and then the ultrasonic extraction repeated for an additional 20 min. The benzene served to extract the Vaseline, while the uranine is soluble in the ammonium hydroxide solution. To maintain consistency in the procedure, the double extraction was also employed for the filter samples using 5 mL of benzene and 6 mL of 0.1 N $NH_4OH$ per filter. Before analysis, the extracts were centrifuged, impactor samples for 30 min and filter samples for 45 min. This served to separate the two immiscible solvents, and to remove suspended filter fragments. The aqueous layer was then analyzed with an Aminco Bowman spectrophotofluorometer, using excitation and emission wavelengths of 325 and 510 nm, respectively.

Several tests were made to check the analysis procedure. As uranine fluorescence is subject to quenching, it is important to determine that the difference in the collection substrate between the impactor and the filter not yield different responses to the same uranine loading. In the first of these tests, uranine standards of 142.2 ng/mL in 0.1 N $NH_4OH$ were mixed with benzene, sonicated, centrifuged, and analyzed, as described in the above extraction procedures. To mimic the filter analysis, 5 mL of benzene was mixed with 6 mL of the uranine standard in the same beakers used for the filter analyses. The stainless steel strip analysis was also mimicked in this same manner. Solution volumes were measured before analysis. The uranine recoveries, as compared with the original standard, are 93 ± 2% and 92 ± 1% for the filter and stainless steel strip type extractions, respectively. The tests were also run for clean filters and clean Vaseline-coated stainless steel strips. The specified extraction procedure was followed except that the uranine standard (142.2 ng/mL in 0.1 N $NH_4OH$) was substituted for the 0.1 N ammonium hydroxide in the aqueous extraction. Compared to the uranine standard, the recoveries for filter and strip systems are 90 ± 1 and 92 ± 1%, respectively. Errors represent the standard deviation of three measurements. The recoveries are corrected for the filter and strip blank values, measured to be 0.7 ± 0.5 ng/mL for both substrates. Although the benzene is observed to affect the uranine measurement somewhat, no significant quenching can be attributed to the filters or coated strips.

In another test, the extraction efficiency from Vaseline-coated strips spiked with uranine was checked. The uranine was applied to the strip using a microliter syringe, and the droplet allowed to dry before extraction. For five samples, the recovery is 90 ± 3%, which is within the error of the value obtained for the uranine standard–benzene system. Thus, the extraction is essentially complete.

## *Results and Discussion*

**Sizing of the Calibration Aerosol.** The diameters of the calibration aerosols are listed in the first column of Table II. For each aerosol, the average particle diameter is determined by microscopic sizing of 50 to 200 particles. The widths of the aerosol size distributions are taken from the mobility widths given by the size classifier manual. As a statistically small number of particles was actually sized, the width of the size distribution was not experimentally determined. However, for those particles which were sized, 70–90% of the mass is within the stated size range.

Considerable discrepancy is found between the measured diameters and the Stokes diameters calculated on the basis of the classifier settings. For example, particles, which according to the classifier should be 0.05 μm, were measured to be 0.034 μm in diameter. Yet 0.109-μm polystyrene latex particles were classified to be within 5% of their nominal size. This discrepancy may result in part because of the roughness of the surface of the uranine particles in comparison with the latex. The expression for the slip factor used to calculate electrical mobilities is based on data for smooth glass spheres and oil droplets. A second possibility is that some additional evaporation of the particles may occur as they are drawn into the dry sheath air of the classifier. However, particles collected immediately at the exit of the classifier, upstream of the impactor, are dry when examined microscopically. Experience with wet particles has shown that they are clearly visible as wet under the electron microscope. Should the particle dry while on the grid, a mark is seen around the central particle. No evidence of evaporation or wet particles was observed for these calibration aerosols. Thus, in this work, the aerosol diameters are taken from the microscopic measurements. The difference from the Stokes diameter given by the classifier is shown in Table II.

**Aerodynamic Diameter.** For the low-pressure impactor stages, the particle diameters are of the same order, or smaller than the mean free path. The aerodynamic diameter of the particles, $d_a$, is:

$$d_a = \left(\rho \frac{C_s}{C_a}\right)^{1/2} d_s \tag{1}$$

where $\rho$ = particle density, $d_s$ = Stokes diameter, and $C_s$ and $C_a$ are the slip corrections to the Stokes drag for particles of diameter $d_s$ and $d_a$, respectively. The slip factor is given by:

$$C = 1 + \frac{2\lambda}{d}\left[1.257 + 0.40 \exp(-0.55d/\lambda)\right]$$

where $d$ = particle diameter and $\lambda$ = mean free path. For particles much larger than the mean free path, $C = 1$, and $d_a = \sqrt{\rho d_s}$. In the limit of particles much smaller than $\lambda$, this expression reduces to the free molecular relation $d_a = \rho d_s$. In the transition regime, the aerodynamic diameter must be found by iteration of Equation 1. This iteration may be made to converge rapidly by noting that the exponential term varies slowly with particle diameter. Writing:

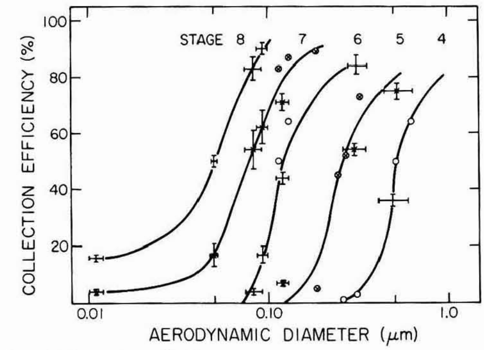

**Figure 3.** Impactor calibration curves

Uranine aerosol (this work): (+) stages 4, 6, and 8; (✱) stages 5 and 7. Polystyrene latex (ref *1*): (O) stages 4, 6, and 8: (⊗) stages 5 and 7

$$C = 1 + \frac{K\lambda}{d} \quad (2)$$

where

$$K = 2[1.257 + 0.40 \exp(-0.55d/\lambda)] \quad (3)$$

the aerodynamic diameter is:

$$d_a = 1/2[(K_a{}^2\lambda^2 + 4\rho d_s(d_s + K_s\lambda))^{1/2} - K_a\lambda] \quad (4)$$

$K_a$ and $K_s$ refer to Equation 3 evaluated for $d_a$ and $d_s$, respectively. Setting $K_a = K_s$ for the first iteration will give a value of $d_a$ accurate within at least 1% for $\rho = 1.5$, and within 4% for $\rho = 4$.

As the aerodynamic diameter is a function of both the mean free path and particle density, the value of $d_a$ for the uranine aerosols varies with impactor stage. The values of $d_a$ for each of the uranine calibration aerosols are given in Table II. The density of uranine is taken to be 1.46 g/cm$^3$, which is the average of values reported in the literature for both bulk uranine (*9, 11, 13*) and uranine aerosol (*10–12*). With the exception of Stein (*9*), the density of uranine aerosol (*10–12*) was not found to be significantly different from the density of the bulk material. As the particles are spherical, the Stokes diameter is assumed to be equal to the microscopically measured diameter.

**Stage Collection Efficiencies.** The measured collection efficiencies for the uranine aerosols are plotted in Figure 3, together with the polystyrene latex calibration points previously obtained (*1*). Except for the two largest sizes, several experimental runs were made for each uranine aerosol. Errors indicated in Figure 3 are the standard deviations of these measurements.

The collection efficiencies are based on the total aerosol loading, which is measured by both the impactor with after-filter, and by the total filter operated in parallel. A comparison of these two measurements is given in Table III. Good mass balances of 97–100% were obtained for uranine aerosol 0.057 μm and larger. However, for the 0.034- and 0.0078-μm aerosols, the amounts deposited on the collection stages and after-filter are, respectively, 82 ± 8 and 75 ± 7% of the total filter loadings. Diffusional losses are greater for the low pressures in the final impactor stages. The calculated wall losses for laminar diffusion in the free molecular regime are 7% for the 0.034-μm aerosol, and 35% for the 0.0078-μm aerosol. Most of these calculated losses occur between the eighth stage and the after-filter. Therefore, for these 0.034- and 0.0078-μm aerosols, the collection efficiences are based on the mass loading given by the total filter. For the larger aerosols for which the mass balance is quite good, the efficiencies are based on the impactor and after-filter measurements.

**Table III. Aerosol Size and Mass Balances**

| uranine particle diam. | (impactor + after-filter loading)/ total filter loading, % |
|---|---|
| 0.39 + 0.10<br>−0.07 | 102 ± 3 |
| 0.22 + 0.04<br>−0.03 | 97 ± 3 |
| 0.085 ± 0.005 | 99 ± 3 |
| 0.064 ± 0.004 | 97 ± 5 |
| 0.057 ± 0.007 | 98 ± 5 |
| 0.034 ± 0.003 | 82 ± 8 |
| 0.0078 ± 0.0007 | 75 ± 7 |

**Table IV. Collection Efficiencies with and without an After-Filter**

| stage no. | microscopic particle diam. | with after-filter | without after-filter |
|---|---|---|---|
| 8 | 0.034 | 50 ± 2 | 51 ± 1 |
| 8 | 0.0078 | 16 ± 1 | 17 ± 1 |
| 7 | 0.034 | 16 ± 3 | 20 ± 3 |
| 7 | 0.0078 | 5 ± 1 | 4 ± 2 |

Collection efficiencies were measured for two different impactor collection surfaces: 1-in. Vaseline-coated disks and Vaseline-coated 0.25 in. × 1 in. × 0.002 in. stainless steel strips. The strips were tested because they are used for the aerosol sulfur and nitrate analyses often employed with this impactor. For sample collection, the stainless steel strips are mounted on a 1-in. glass disk, in which a shallow groove had been sandblasted to hold the strip. In this manner, the jet-to-plate distance is unchanged. Only the strip is analyzed. Both of these collection surfaces were used for the 0.0078-, 0.034-, 0.057-, and 0.064-μm uranine particles. No significant difference is observed for any of the stages or particle sizes tested. The average ratio of the collection efficiencies measured with the strips, as compared with the disks for all of these runs, is 0.96 ± 0.08. It is concluded that little aerosol is deposited at the edge of the 1-in. diameter collection plate. The Vaseline coating and sample analysis can be confined to the center of the disk with no loss of accuracy.

For the final stage, the stagnation pressure below the jet depends on whether or not an after-filter is used. Using a 47-mm glass fiber (Gelman AE) filter raises this stagnation pressure from 8 to 18 mmHg absolute. The velocity of the jet is unchanged, for it will remain sonic unless the stagnation pressure below the jet exceeds approximately 22 mmHg. The other stages should not be affected so long as stage 8 remains sonic. For the 0.0078- and 0.034-μm aerosols, experiments were made with and without the after-filter to determine the effect upon the stage collection efficiencies. The results listed in Table IV show the average of two or three runs in each configuration. As can be seen from these data, no shift in the collection efficiencies occurs as a result of the pressure change below stage 8.

Since the results were about the same for the strips and disks, or runs with or without the after-filter, all of these data were averaged to prepare the efficiency curves of Figure 3. Reasonable agreement is found between this uranine calibration and the polystyrene latex calibration. The 50% efficiency cutoff for stage 6 is adjusted to 0.12 μm from the previously reported latex calibration of 0.11 μm. The cutoffs for stages 7 and 8 are 0.075 and 0.05 μm, respectively. The curves are reasonably steep as desired to minimize the cross-sensitivity between stages. For the final stage, the experimentally determined collection efficiency of particles smaller than the cutoff diameter does not approach zero as rapidly as for the

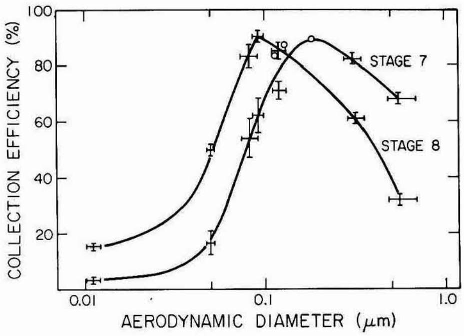

**Figure 4.** Collection efficiency curves: stages 7 and 8

### Table V. Stokes Cutoff Diameters

| ρ | stage 8 | stage 7 | stage 6 | stage 5 |
|---|---|---|---|---|
| 0.5 | 0.10 | 0.15 | 0.23 | 0.47 |
| 0.8 | 0.062 | 0.093 | 0.15 | 0.32 |
| 1.0 | 0.050 | 0.075 | 0.12 | 0.26 |
| 1.2 | 0.042 | 0.063 | 0.10 | 0.22 |
| 1.4 | 0.036 | 0.054 | 0.087 | 0.19 |
| 1.6 | 0.031 | 0.047 | 0.077 | 0.17 |
| 2.0 | 0.025 | 0.038 | 0.062 | 0.14 |
| 3.0 | 0.017 | 0.025 | 0.042 | 0.094 |
| 4.0 | 0.013 | 0.019 | 0.032 | 0.072 |
| 6.0 | 0.0084 | 0.013 | 0.021 | 0.048 |

other stages. This is in part attributed to the presence of a few larger particles in the text aerosol (*14*).

**Particle Rebound and Wall Losses.** Figure 4 shows the collection efficiency curves for the seventh and eighth impactor stages, including the collection efficiencies of the larger particles. As can be seen, the efficiency does not reach 100%, but actually decreases for the larger particles. These curves are similar to those of Rao and Whitby (*15*), who found that rebound of the larger particles limits their collection. For these high-velocity stages, it is not surprising that the larger particles bounce. Fortunately, the diameter for which the collection efficiency begins to decrease with increasing particle size is well above the cut point of the preceding stage. Thus, few large particles reach these stages. For example, even though the 0.39-μm (microscopic diameter) collection efficiency is only 32% for stage 8, the mass loading measured by the impactor alone (excluding the after-filter) is 96% of the total filter measurement. Similarly, for the 0.22-μm (microscopic diameter) aerosol, 99% of the aerosol is retained within the impactor. Thus, rebound of the larger particles from the lower (smaller cutoff) stages is not a problem in practice.

The wall losses for the particles 0.10 μm and smaller were measured by washing the inside impactor walls. The 0.1 N $NH_4OH$ wash solution was directly analyzed for uranine by fluorescence. A second wash checked that most of the aerosol had been removed. For these aerosols (0.10 μm and smaller), the losses were measured to be 5% of the total uranine sampled. The low-pressure stages accounted for 3%. Losses on stages 1–4 were 1%, and in the orifice itself, 0.05%. Wall losses were also measured for each of the 0.22- and 0.39-μm aerosol experiments. Here, attention was directed at the fifth stage, which immediately follows the flow-restricting orifice. As there is no plate below the orifice to dissipate the flow, particles in the jet could impact on the walls of the conical inlet to the stage 5 jet. For these two runs, the total losses were 4%, with 3% attributed to stage 5. These losses could perhaps be reduced by increasing the distance below the orifice to allow the jet to spread and the velocity to drop before reaching the walls.

**Physical Meaning of Low-Pressure Stage Cutoffs.** The low-pressure stages of the impactor size segregate the aerosol not according to the atmospheric pressure aerodynamic diameter, but according to the aerodynamic diameter at the reduced pressure. The cutoffs listed in Table I are the aerodynamic diameters at the pressure at which the impactor stage operates, as this is the quantity which characterizes the collection efficiencies.

For atmospheric behavior this low-pressure aerodynamic diameter is of little interest. To translate these sizes to a more meaningful value such as the Stokes diameter or the atmospheric pressure aerodynamic diameter, a value must be assumed for the density of the aerosol. For these small particles the actual (geometric) diameter is of interest since it determines the particle diffusion coefficient. For spherical particles, this particle diameter should equal the Stokes diameter, which is related to the aerodynamic diameter by Equation 4. In Table V the Stokes diameters corresponding to the stage cutoffs are listed as a function of particle density.

### *Summary*

The low-pressure impactor was calibrated using monodisperse uranine aerosols. Aerodynamic cutoff diameters at the reduced stage pressures were found to be 0.12, 0.075, and 0.050 μm for the sixth, seventh, and eighth stages, respectively. These are equal to the Stokes diameters for spherical particles of unit density at atmospheric pressure. For nonunit densities, the actual (geometric) diameters must be calculated from theory. Collection efficiencies did not change when a glass fiber after-filter was used. They were also not affected by the collection surfaces tested here, ¼-in. stainless steel strips, or 1 in. diameter glass disks. Wall losses were about 5%, probably resulting from the impaction of 0.26- to 0.5-μm particles on the inlet of the stage 5 jet, and diffusional losses of particles smaller than 0.04 μm.

### *Acknowledgments*

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# Evaluation of Boron Removal by Adsorption on Solids

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■ The adsorption method is moderately effective for the removal of low levels of boron from solution. At the initial boron concentration of 5 mg/L or less, Filtrasorb (activated carbon) is the adsorbent capable of achieving more than 90% removal. The pH of the suspension and initial concentration of boron are two critical factors in determining the removal efficiency. Boron can be removed by adsorption either as $H_3BO_3$ or as $B(OH)_4^-$. The adsorption of boron is not only due to the distribution of boron species but also to the type and/or number of active sites that may vary with changing pH, composition of solution matrix, and surface properties of the solid.

Boron is of special concern in irrigation water because of its beneficial and toxic effects in plants. On the other hand, it is an essential micronutrient for higher plants (*1*). A number of boron criteria in irrigation waters have been proposed. For instance, Wilcox (*2, 3*) has proposed the permissible limits of boron in irrigation water as 0.3–1.0 ppm for sensitive crops, 1.0–2.0 ppm for semitolerant crops, and 2.0–4.0 ppm for tolerant crops. With regard to citrus, Chapman (*4*) suggested boron concentrations of 0.5, 1.0, and 2.0 ppm for possible-, definite-, and serious-hazard classes for irrigation waters.

The concentration of boron has been reported to be in the ranges of 7 ppb to 0.2 ppm in tap water (*5, 6*), with a worldwide average of 13 ppb in fresh river waters (*7*), and about 5 mg/L in seawater (*8, 9*). A recent extensive survey of geothermal fluids found that the boron concentration varies widely (*10*).

Boron in aqueous solution is normally present as boric acid and borate ions. The dominant form of inorganic boron in natural aqueous systems is the undissociated boric acid. Boric acid is a very weak and exclusively monobasic acid which behaves in solution not as a proton donor but as an electron acceptor (Lewis acid), taking $OH^-$ (*11, 12*):

$$H_3BO_3 + H_2O \rightleftarrows B(OH)_4^- + H^+, K = 5.8 \times 10^{-10} \text{ at } 25\ ^\circ C$$

The ionization constant ($K$) of boric acid increases with increasing concentrations of strong electrolyte (*11, 13, 14*). It is mostly monobasic in dilute solution, but polymeric species may be present at concentrations above 0.1 M $H_3BO_3$ (*11*). Ingri (*15*) reported that when the concentration is less than 0.025 M total boron (0.1% $B_2O_3$ or 270 mg of B/L), most of the species present are essentially only $H_3BO_3$ and/or $B(OH)_4^-$. Polyanionic species such as $B_3O_3(OH)_4^-$, $B_5O_6(OH)_4^-$, $B_3O_3(OH)_5^{2-}$ and $B_4O_5(OH)_4^{2-}$ are formed in solutions between 0.025 and 0.6 M at a neutral to alkaline pH (approximately pH 6 to 11) (*15, 16*).

Despite its widespread use (*5*), little is known about the removal of boron from waters and wastewaters. So far, the use of ion exchange resins such as Amberlite XE-243 is the only method which is considered effective for the removal of boron (*5, 17, 18*). The lack of information on alternative boron treatment processes reflects the fact that boron has not been treated as a potential toxicant until recently. However, the adsorption of boron by clays, soils, and other minerals has been extensively studied by many investigators working in the field of geochemistry and soil science (*19–32*).

In the present study, specific efforts were made in studying adsorption of boron using various types of adsorbents such as activated carbon, activated bauxite, and activated alumina. Parameters examined include the boron concentration in the solution, pH, duration of treatment (contact time), salinity, and competition with or interference by other chemical species.

## *Experimental*

(A) **General Procedures for Adsorption Study.** Batch Adsorption Experiment. A continuously mixed batch technique was selected for the batch adsorption experiments. A prefixed amount of adsorbent (adsorbent dosage = 5 g/200 mL or 25 g/L) was weighed into a 250-mL linear polyethylene centrifuge bottle. Immediately after the addition of 200 mL of test solution, the bottle was shaken on a wrist-action shaker (Burrell Model-75) for a predetermined period of contact time at room temperature, 25 ± 2 °C. The solutions were first centrifuged at 18 000 rpm on a high-speed centrifuge (IEC Model B-20A) and then passed through a 0.45-$\mu$m Millipore filter (Type HA) if necessary. For the rate study, a vacuum syringe filtration technique was employed.

The pH of the solution and the concentrations of Al(III), Fe(III), Ca(II), and Mg(II) ions were measured prior to determination of boron. A control (without adsorbent) was used to evaluate error from adsorption on the container walls.

Background Solutions. Three different background solutions were used for the boron adsorption study: (1) deionized–distilled water (DDW); (2) clean seawater (SW) filtered through a 0.05-$\mu$m Millipore filter; and (3) simulated geothermal water (SGW) synthesized for the present study.

The deionized–distilled water was made by passing tap water through a mixed-bed ion exchange resin followed by distillation using a Corning water distillation apparatus (Mega-Pure, Model MP-3). The pH and conductivity of the deionized–distilled water were from pH 5.7 to 6.1 and 0.65–1.01 $\mu$mho, respectively, at 23 °C. The conductivity of solution was determined using a conductivity bridge (Barnstead, Model PM-70CB) and conductivity cell (Barnstead, Model B-10, cell constant = 1.0).

The chemical compositions of the simulated geothermal water and seawater are described in Table I. The conductivity of filtered seawater was 34.5 mmho at 23 °C. The salinity of the seawater, determined by a Goldberg T/C refractometer (American Optical Corp., Model 10419), was 33.0‰. The conductivity of the simulated geothermal water was 39.75 mmho at 23 °C. The salinity determined was 36.5‰.

Selection and Characteristics of Adsorbents. Selection of Adsorbents: Sigworth and Smith (*33*) reviewed activated carbon as a potential adsorbent for the removal of inorganic species from waters. Recent studies (*34–36*) showed that some inorganic species, such as mercury, cadmium, and chromium, could be successfully removed from water by activated carbon.

Boron is known to be adsorbed by soil material and minerals of aluminum, iron, and magnesium oxides and hydroxides (*19–22*). Therefore, three types of adsorbents were evaluated for the present boron adsorption study: activated carbon; activated bauxite; and activated alumina.

In the preliminary stage of the study, nine adsorbents listed below were examined by an adsorption rate test in deionized–distilled water background.

Activated carbons: Hydro Darco 3000 (ICI America; surface area = 600–650 m$^2$/g BET; mean particle diameter = 1.6 mm; raw material, lignite); Filtrasorb 300 (Calgon Corp.; surface

## Table I. Chemical Composition of Simulated Geothermal Water (SGW) and Seawater (SW) Used in This Study

| species | concn[a] SGW | concn[a] SW |
|---|---|---|
| Na | 14 000 | 12 000 |
| K | 1 050 | 390 |
| Ca | 0.6 | 434 |
| Mg | 0.02 | 1 262 |
| B | nd | 4.74 |
| Li | 135 | 0.2 |
| Si | 64 | 1.0 |
| Cl | 19 700 | 19 400 |
| F | nd | 1.32 |
| $HCO_3^-$ | 1 820 | 120 |
| $CO_3^{2-}$ | 18 | 12 |
| $SO_4^{2-}$ | 2 250 | 2 700 |
| TDS | 39 100 | 36 500 |
| pH | 8.2 | 7.7–8.0 |

[a] All are in milligrams per liter except for pH. nd, not detected.

area = 950–1050 $m^2/g$ BET; mean particle diameter = 1.5–1.7 mm; raw material, coal); Nuchar WV-1 (Westvaco, surface area = 1000 $m^2/g$ BET; mean particle diameter = 1.5–1.7 mm; raw material, pulp mill residue); and Norit (American Norit Co.; powder decolorizing; raw material, wood).

Activated aluminas: Aluminum oxide (E. Merck; neutral; activity grade I, for chromatography), ALCOA F-1 (Aluminum Company of America; surface area = 210 $m^2/g$; 28/48 mesh; granular), KA-201 (Kaiser Chemicals, surface area = 350 $m^2/g$; 8/14 mesh; granular).

Activated bauxites: PorOcel (Inglehard Minerals and Chemicals Corp.; 30/38 mesh) and Milwhite (The Milwhite Co., Inc.; 30/60 mesh; volatile matter 4.5–6.5%; domestic).

None of the adsorbents was subjected to additional pretreatment. After the investigation of adsorption rates, only four adsorbents (Hydro Darco 3000, Filtrasorb 300, ALCOA F-1, and Milwhite's activated bauxite) were selected for further investigations. It must be noted here that Hydro Darco, which was the least effective adsorbent for boron removal (see Figure 2), was selected only for the comparison with Filtrasorb.

General Characteristics of Adsorbents: All the adsorbents tested caused a rise in pH in solution. A considerable rise in pH occurs in the presence of the commercial grade activated aluminas; however, it is most probably an effect of caustic soda used in the manufacturing process. For instance, Kaiser's aluminas are produced by a modified Bayer process in which the bauxite mineral is digested with caustic soda at elevated temperature and pressure to dissolve the alumina from the bauxite.

Although the major component of activated bauxite is $Al_2O_3$, other oxides such as $Fe_2O_3$, $TiO_2$, and $SiO_2$ complexes (red mud) are present in appreciable amounts. Based on the manufacturer's information, for example, Milwhite's domestic bauxite contains 76.5% $Al_2O_3$, 4.0% $Fe_2O_3$, 3.5% $TiO_2$, 10.0% $SiO_2$, and volatile matter. Therefore, the physicochemical characteristics affecting adsorption of boron will differ from those of activated alumina.

Effect of pH on the Leaching of Boron from Adsorbents: The effect of $pH_{48}$ (pH of filtrate after 48 h of contact between the adsorbent and solution) on the leaching of boron from adsorbents has been investigated in deionized–distilled water background. Solution pH was controlled with HCl or NaOH.

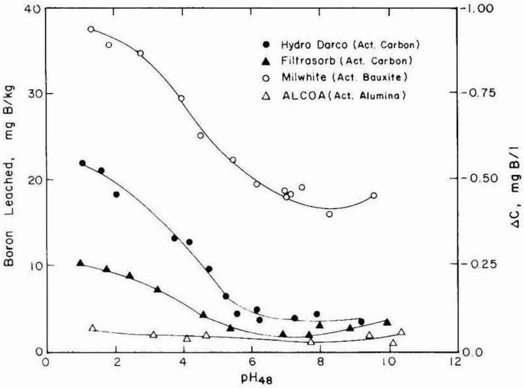

**Figure 1.** Amounts of boron leached from adsorbents as a function of pH

Background solution was deionized–distilled water (DDW); solid concentration = 25 g/L

(B) **Experimental Parameters and Methods.** Boric acid (reagent grade) was used as the source of boron throughout the study. Boron concentrations were determined by the improved curcumim method described in detail by Choi (*37*).

Rate of Adsorption. This set of experiments was used as a screening test for the selection of adsorbents. The adsorption rate test, on a solution containing 20 mg/L of boron in deionized–distilled water, was performed for 9 different adsorbents at room temperature. The adsorbent dosage was fixed at 25 g/L. Contact times were 1/30, 1/6, 1, 4, 12, 24, and 48 h. The suspension, immediately after shaking on a wrist-action shaker for a given contact time, was rapidly filtered through a 0.45-$\mu$m membrane filter. pH was not controlled for this set of experiments.

pH Effects. The effect of pH on boron removal was investigated using the four selected adsorbents (Hydro Draco, Filtrasorb, Milwhite, and ALCOA) in three different background solutions: deionized–distilled water (DDW); fourfold dilution of seawater (dil.(1:3)SW); and fourfold dilution of the simulated geothermal water (dil.(1:3)SGW) each containing 20 mg/L of boron. A 48-h contact time to reach approximate equilibrium was selected. To obtain well-distributed $pH_{48}$ values, different values of initial solution pH were produced by adding HCl or NaOH. However, when the desired $pH_{48}$ could not be obtained easily by the adjustment of the initial solution pH, the pH of the suspension was controlled within 4 h of initial mixing.

Salinity Effects. The effect of salinity on the removal of boron was investigated using seawater (salinity = 33.0‰) and the simulated geothermal water (salinity = 36.5‰). A series of solutions of different salinities was obtained by diluting the original seawater or simulated geothermal water with deionized–distilled water.

Concentration Effects. The effects of various initial boron concentrations ($C_0$ = 5, 10, 20, 40, 60, 100, and 200 mg/L of boron) on removal efficiency were investigated in the background solutions of deionized–distilled water, fourfold dilution of seawater, and fourfold dilution of simulated geothermal water.

Effects of Other Chemical Species. The effects of Ca(II), Mg(II), Si(IV), and $SO_4^{2-}$ on the removal of boron were investigated using 20 mg/L boron in deionized–distilled water containing each of the above species. The chemicals used were $CaCl_2 \cdot 2H_2O$ for Ca(II), $MgCl_2 \cdot 6H_2O$ for Mg(II), $Na_2SiO_3 \cdot 9H_2O$ for Si(IV), and $Na_2SO_4$ for $SO_4^{2-}$.

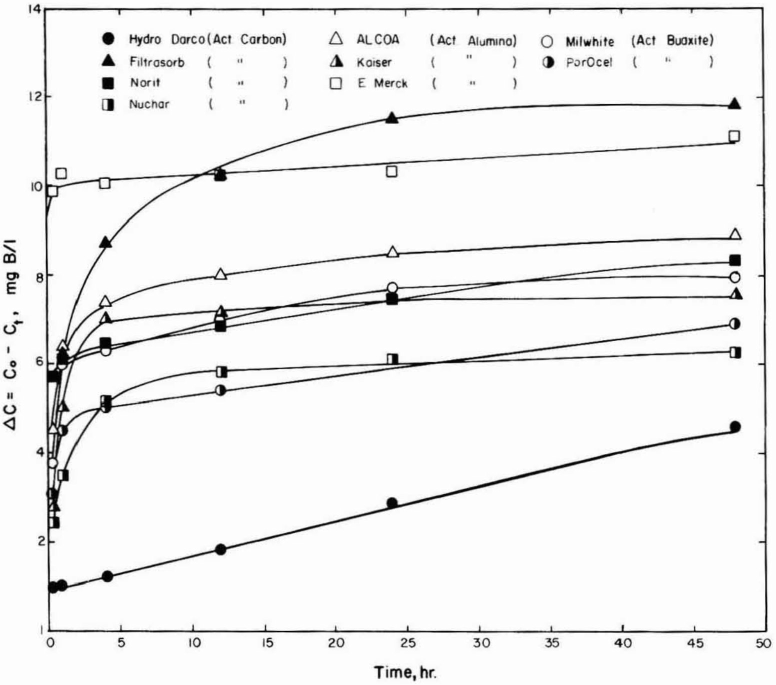

**Figure 2.** Rate of boron adsorption on various adsorbents
$C_0$ = 20 mg of B/L; background solution was deionized–distilled water; adsorbent dosage = 25 g/L

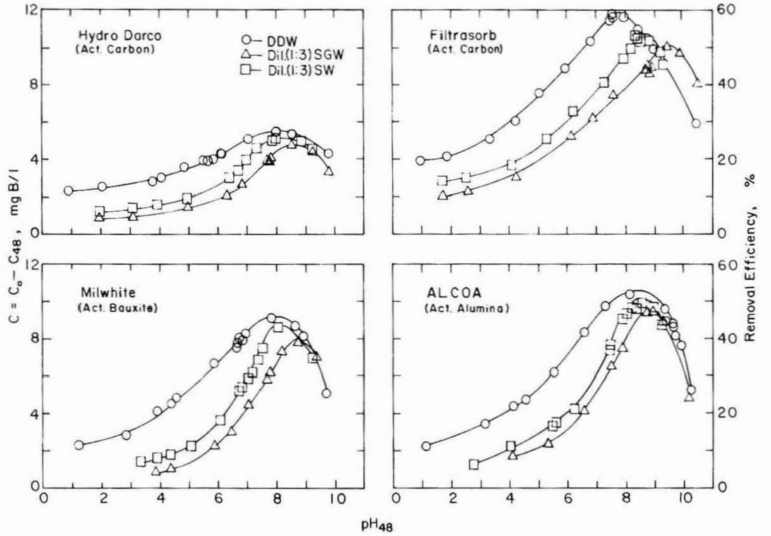

**Figure 3.** Effects of $pH_{48}$ on the removal efficiencies of boron in deionized–distilled water (DDW) and the fourfold dilutions of seawater (Dil.(1:3)-SW) and simulated geothermal water (Dil.(1:3)SGW) by various adsorbents
$C_0$ = 20 mg of B/L; adsorbent dosage = 25 g/L

## *Results and Discussion*

(A) **Effect of pH on the Leaching of Boron from Adsorbents.** The results obtained for boron leached from adsorbents are shown in Figure 1. It should be noted that negative values of $\Delta C$ ($\Delta C = C_0 - C_t$) in Figure 1 indicate leaching from the adsorbent while positive values of $\Delta C$ indicate removal from the solution. For all of the adsorbents, with the exception of activated alumina (ALCOA), the amount of boron leached increases with decreasing pH below 6. Within the pH range investigated, the amount of boron leached from every adsorbent remains approximately constant above pH 6. The least leaching for all the adsorbents occurs between pH 6 and 9. As shown in Figure 1, activated bauxite (Milwhite) produces the largest amounts of boron, followed by Hydro Darco (activated carbon).

(B) **Rate of Adsorption.** The results obtained for the rate of adsorption are shown in Figure 2. All the adsorbents except

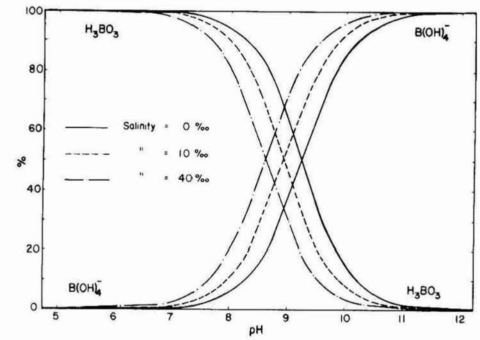

**Figure 4.** Distribution of $H_3BO_3$ and $B(OH)_4^-$ as a function of pH below the total boron concentration of 0.025 M as $H_3BO_3$ (270 mg of B/L) at three different salinities (*11, 12, 14*)

Hydro Darco generally show a high initial rate of boron adsorption diminishing markedly with time. Presumably, adsorption will continue beyond the 48-h contact time at a continuously diminishing rate. Although further adsorption is theoretically significant, it is not important for industrial and water treatment applications.

With considerations of performance, availability, and preference of commercial grade over analytical grade, the following adsorbents were selected for each group for further studies: Filtrasorb for activated carbons; Milwhite for activated bauxites; and ALCOA for activated aluminas. Hydro Darco was the least effective adsorbent among the adsorbents examined while Filtrasorb was the best. It is quite interesting to note that the opposite was true of fluoride removal (*37*). Thus, Hydro Darco was also selected for comparison with Filtrasorb.

(C) **pH Effects.** The effects of pH on the removal of boron in three different solution backgrounds are shown in Figure 3. In addition, the distribution of $H_3BO_3$ and $B(OH)_4^-$ as a function of pH (at three different salinities) below 0.025 M (i.e., 270 mg/L of boron) are plotted in Figure 4 for the purpose of comparison. The data plotted in Figure 4 have been calculated based on published and interpolated $pK_a$ values (9.23 at 0‰, 8.93 at 10‰, and 8.60 at 40‰) of boric acid (*11, 12, 14*). The data listed in Table II were obtained from Figure 3. The data indicate that the optimum pH for boron removal under the given experimental condition depends on both the background solution and the adsorbent. Regardless of adsorbent type, however, the optimum pH rose when the background solution changed from deionized–distilled water to the fourfold dilution of seawater or that of simulated geothermal water. The variation was not more than 0.7 pH unit for Hydro Darco, activated bauxite, and activated alumina. However, it varied as much as 1.8 pH units for Filtrasorb. The shift in

**Table II. Optimum $pH_{48}$ for the Maximum Removal of Boron**

| | Hydro Darco (act. C) | | Filtrasorb (act. C) | | Milwhite (act. bauxite) | | ALCOA (act. alumina) | |
|---|---|---|---|---|---|---|---|---|
| background solution | optimum $pH_{48}$ | max removal eff., % | optimum $pH_{48}$ | max removal eff., % | optimum $pH_{48}$ | max removal eff., % | optimum $pH_{48}$ | max removal eff., % |
| DDW[a] | 8.0 | 28 | 7.8 | 59 | 8.0 | 45 | 8.2 | 52 |
| dil.(1:3)SW[b] | 8.3 | 26 | 8.6 | 53 | 8.2 | 43 | 8.6 | 49 |
| dil.(1:3)SGW[c] | 8.6 | 24 | 9.6 | 50 | 8.6 | 39 | 8.9 | 47 |

[a] Deionized–distilled water. [b] Fourfold dilution of seawater. [c] Fourfold dilution of simulated geothermal water.

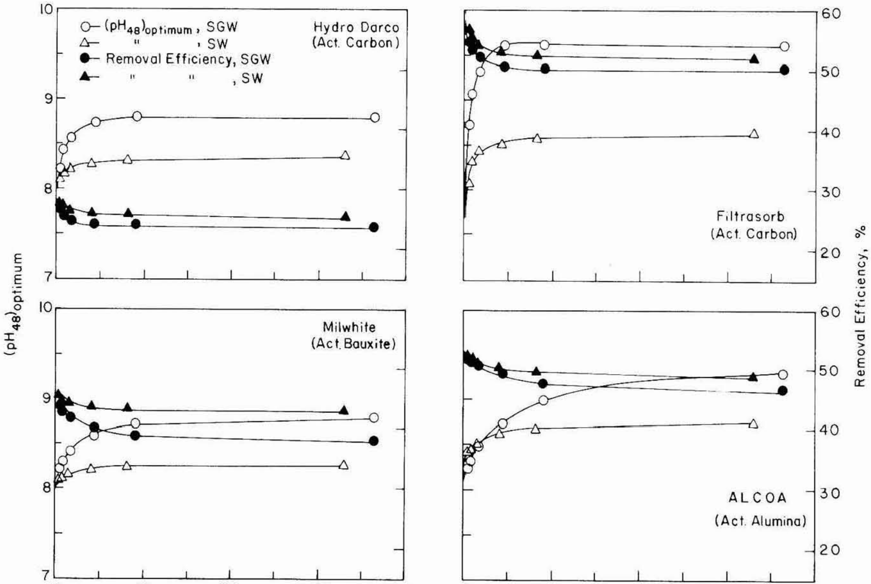

**Figure 5.** Effects of salinity on both removal efficiency of boron and optimum $pH_{48}$ for the removal of boron in the dilutions of seawater (SW) and simulated geothermal water (SGW) by various adsorbents
$C_0$ = 20 mg of B/L; adsorbent dosage = 25 g/L

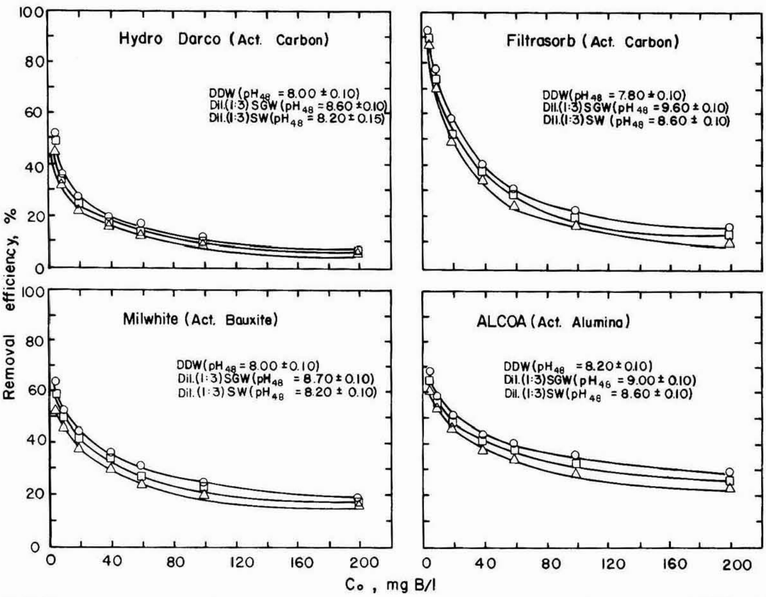

**Figure 6.** Effects of initial boron concentration ($C_0$) on the removal efficiency of boron in deionized–distilled water (DDW) and the fourfold dilutions of seawater (Dil.(1:3)SW) and simulated geothermal water (Dil.(1:3) SGW) (adsorbent dosage = 25 g/L)

optimum pH for the maximum retention of boron by different soil materials has been observed by Sims and Bingham (*21*) and Bingham et al. (*27*). Sims and Bingham (*20, 21*) reported that the maximum adsorption of boron on soil materials occurred at pH 8–9 for hydroxy iron forms and pH 7 for hydroxy aluminum forms, and suggested that the shift in optimum pH resulted from the type of surface hydroxy compounds of metals. However, no support for this hypothesis was found. Although the optimum pH depends on both the adsorbent and the background solution, the maximum removal of boron occurs when pH is 7.8 and 9.6. Regardless of the difference in suggested mechanisms, the pH range agrees well with the results of other studies (*5, 20, 27*). For example, the maximum removal of boron by ion exchange resin was reported to occur when pH was between 7.5 and 9.0 (*5*). The optimum pH for removal of boron by soil materials was found to range from pH 7 to 9 (*20, 27*).

Hingston et al. (*38*) reported that adsorption of undissociated acid is unlikely because of direct competition with water, which is the predominant species in solution. They ascribed the adsorption of undissociated molecules such as $H_3BO_3$ to proton dissociation at the surface of the adsorbent. The dissociated protons subsequently react with surface hydroxyl groups of neutral sites to form water which is then readily displaced by the anion. Thus, the maximum adsorption of the anion occurs most readily around the $pK_a$ value of acid.

It has been suggested that boron in aqueous solution can be removed not only as borate ion but also as boric acid (*19–21, 28–30*). This is supported by the present study results (note: compare the results in Figure 3 with the distribution of boron species shown in Figure 4). For example, as shown in Table II, Filtrasorb's optimum pH ranges for the removal of boron in deionized–distilled water and in the fourfold dilution of simulated geothermal water (salinity = 9.13‰) are pH 7.8 and pH 9.6, respectively. As shown in Figure 4, the fraction of borate ion at pH 7.8 (for salinity = 0‰) is negligible compared to that of boric acid, while those at pH 9.6 (for salinity = 10‰) are literally opposite.

Based on the results obtained in this study and the results reported by others (*27, 29, 39*), the adsorption of boron is not only due to the distribution of boron species, but also to the type and/or number of active sites that may vary with changing pH, composition of solution matrix, and surface properties of the solid.

(D) **Salinity Effects.** Effects of salinity on the removal efficiency and on the pH at which optimum removal occurs for a given salinity are shown in Figure 5. For all background solutions, the removal efficiency decreases sharply with increasing salinity up to about 8‰ for Hydro Darco, 5‰ for Filtrasorb, 8‰ for activated bauxite, and 10‰ for activated alumina. Above these salinities the removal efficiency is unchanged. It is interesting that the optimum pH changes with salinity. It increases sharply with increasing salinity to approximately the same values.

For all adsorbents, the magnitude of the salinity effect on both the removal efficiency and optimum pH is greater for simulated geothermal water than seawater. The decrease in the boron uptake with increasing salinity may be considered a result of competition with other chemical species or of blocking effects of other chemical species on active sites. No salinity effect could be observed above a certain value of salinity. Bingham and Page (*28*), from the study results of boron adsorption by soil, suggested that sites which adsorb boron are more or less specific, being essentially independent of other anions. However, it has been reported that monosilicic acid caused a reduction in boron uptake by iron and aluminum oxides (*39*). The reduction was attributed to either direct competition between monosilicic acid and boric acid for adsorption sites, or by changes in the oxide surface following Si adsorption (*39*). Results from a study on competition experiments (*29*) showed that there was possibly an effect due to the presence of $K_2SO_4$, but little or no effect was noted when boron adsorption was studied in the presence of $KH_2PO_4$. It is possible that boron as boric acid and/or borate ion competes with other chemical species for certain types of active sites while, for other types of active sites, boron is adsorbed preferentially. Therefore, the lack of salinity effects above a cer-

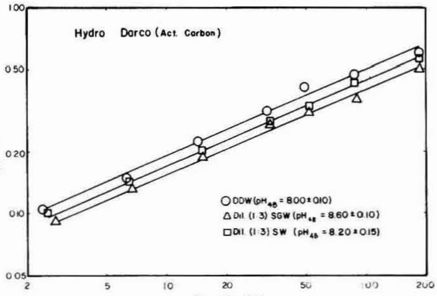

**Figure 7.** Freundlich isotherms for adsorption of boron in deionized–distilled water (DDW) and the fourfold dilutions of seawater (Dil.(1:3)SW) and simulated geothermal water (Dil.(1:3)SGW) on Hydro Darco (adsorbent dosage = 25 g/L)

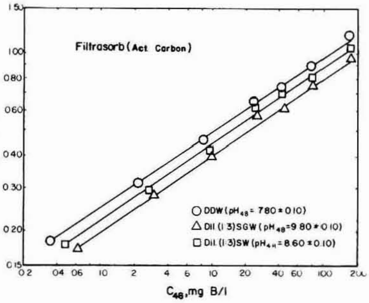

**Figure 8.** Freundlich isotherms for adsorption of boron in deionized–distilled water (DDW) and the fourfold dilutions of seawater (Dil.(1:3)SW) and simulated geothermal water (Dil.(1:3)SGW) on Filtrasorb (adsorbent dosage = 25 g/L)

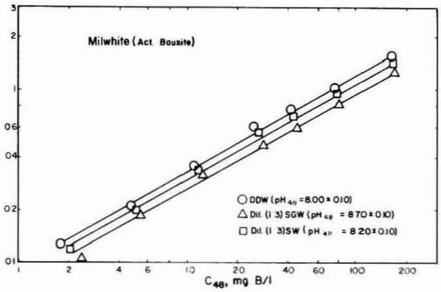

**Figure 9.** Freundlich isotherms for adsorption of boron in deionized–distilled water (DDW) and the fourfold dilutions of seawater (Dil.(1:3)SW) and simulated geothermal water (Dil.(1:3)SGW) on activated bauxite (adsorbent dosage = 25 g/L)

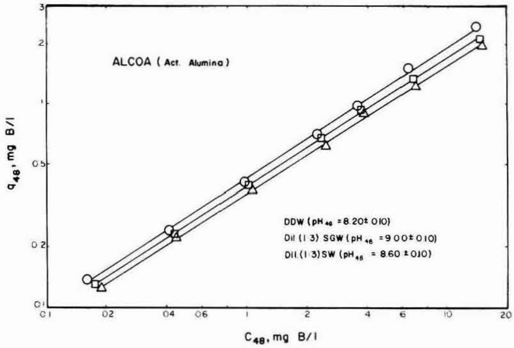

**Figure 10.** Freundlich isotherms for adsorption of boron in deionized distilled water (DDW) and the fourfold dilutions of seawater (Dil.(1:3)SW) and simulated geothermal water (Dil.(1:3)SGW) on activated alumina (adsorbent dosage = 25 g/L)

tain threshold is possibly attributable to the filling of nonspecific sites.

(E) **Concentration Effects.** The effects of initial boron concentration in three different background solutions are shown in Figure 6. Regardless of background solution and adsorbent, the removal efficiency (with an adsorbent dosage of 25 g/L) decreases relatively sharply with increasing initial concentration of boron to approximately 60 mg/L. Above this value, the removal efficiency decreases very slowly with initial concentration. The removal efficiency of boron by Filtrasorb was more strongly affected. For example, as shown in Figure 6, the efficiency at $C_0$ of 5 mg of B/L is about 90%, while at $C_0$ of 60 mg/L it is only about 30%. The concentration of boron is thus one of the critical factors in determining the efficiency of removal.

The maximum adsorption of boron by soils is about 19 mmol of B per 100 g of soil (about 2 mg of B/g of soil) (*29*). This value is comparable to those obtained with activated bauxite and activated alumina. Although the maximum adsorption value obtained for Filtrasorb is one-half that obtained for activated alumina, Filtrasorb is still very effective because of its superior removal efficiency for initial concentrations of less than 30 mg/L of boron.

Equilibrium adsorption isotherms (48 h) at optimum pH, with 5 g of adsorbent in 200 mL of solution, for boron from 5 to 200 mg/L are shown in Figures 7 to 10. All the results are fairly well represented by the Freundlich model for adsorption. The adsorption values plotted in these figures were calculated according to the Freundlich equation:

$$\log q_{48} = \log \frac{C_0 - C_{48}}{D} = \log K_F + (1/n) \log C_{48}$$

where $q_{48}$ = amount of boron adsorbed per unit weight of adsorbent (mg/g) at 48 h of contact time; $C_0$ = initial concentration of boron in the solution, i.e., at $t = 0$, mg/L; $C_{48}$ = concentration of boron in the solution at 48 h of contact time, mg/L; $D$ = adsorbent dosage, 25 g of adsorbent/L; and $n$ and $K_F$ are constants. The concentration and the amount of boron adsorbed by an adsorbent are always presented as mg/L and mg/g units, respectively. Boron concentrations and those of other chemical species present in waters are traditionally presented as mg/L unit or ppm. Thus, mass units are likely more convenient than mole units in the comparison of data.

(F) **Effects of Other Chemical Species.** The results obtained on the effects of other chemical species examined on boron removal are shown in Figures 11 to 14. As shown in Figure 11, there was an effect on the removal from the presence of Ca(II) ions. The increase in the concentration of Ca(II) to a certain value resulted in a decrease in the removal of boron. Little or no additional effect was found with further increase in the concentration of Ca(II) above the value. For example, the removal efficiency of boron by Filtrasorb decreased with increasing the concentration of Ca(II) up to 100 mg/L. No additional influence of Ca(II) with a further increase was found. It is interesting to note that, although there was an effect of Mg(II) ions on the removal of boron by Filtrasorb (Figure 12), little or no effect was noted with other adsorbents. Byrne and Kester (*13*) reported that the cations most likely to show significant ion pairing with boron in seawater are $Na^+$, $Mg^{2+}$, and $Ca^{2+}$ forming $NaB(OH)_4{}^0$, $MgB(OH)_4{}^+$, and

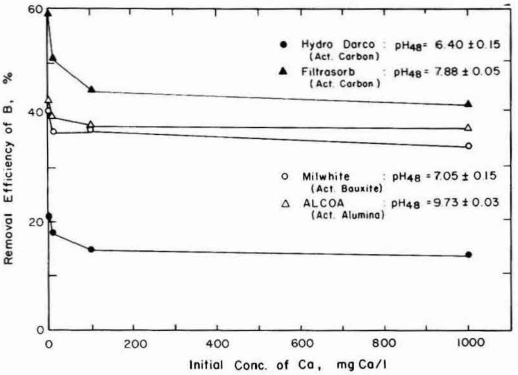

**Figure 11.** Effects of calcium concentration on the removal efficiency of boron in deionized–distilled water by various adsorbents
$C_0$ = 20 mg of B/L; adsorbent dosage = 25 g/L

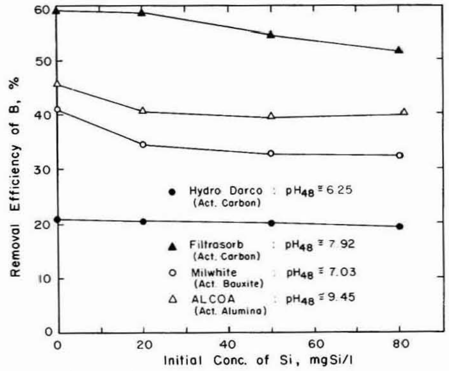

**Figure 13.** Effects of dissolved silica concentration on the removal efficiency of boron in deionized–distilled water by various adsorbents
$C_0$ = 20 mg of B/L; adsorbent dosage = 25 g/L

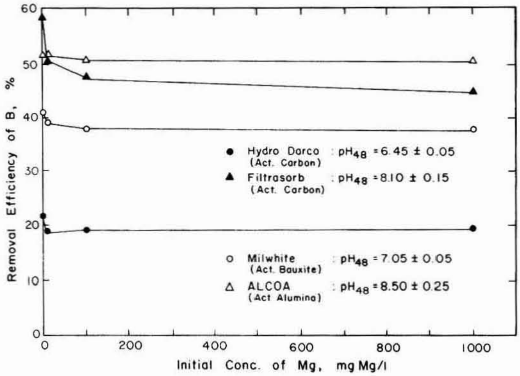

**Figure 12.** Effects of magnesium concentration on the removal efficiency of boron in deionized–distilled water by various adsorbents
$C_0$ = 20 mg of B/L; adsorbent dosage = 25 g/L

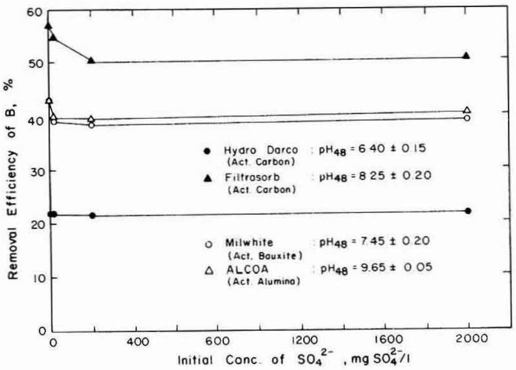

**Figure 14.** Effects of sulfate ion concentration on the removal efficiency of boron in deionized–distilled water by various adsorbents
$C_0$ = 20 mg of B/L; adsorbent dosage = 25 g/L

$CaB(OH)_4^+$, respectively. Thus, the results suggest a change in the solution chemistry or in the surface of the adsorbent following adsorption of Ca(II) or Mg(II) ions.

As shown in Figure 13, all the adsorbents except Hydro Darco showed effects of dissolved silica on boron removal. McPhail et al. (*39*) demonstrated that boron adsorption on hydrous oxides of aluminum and iron was decreased by adsorption of Si. They suggested that the reduced boron adsorption could be caused by either direct competition between monosilicic acid and boric acid for adsorption sites, or by changes in the oxide surface following adsorption. The competition for sites may occur because the maximum adsorption occurs in the same pH range as for boric acid ($pK_a = 9.2$) (*39–41*). Jepson et al. (*41*) reported that the isoelectric point of gibbsite falls with increasing silica adsorption to a limiting value of pH 3. Thus, boron adsorption may also be reduced by changes at the surface.

The effect of $SO_4^{2-}$ on the removal of boron is shown in Figure 14. All the adsorbents, except Hydro Darco, showed a relatively sharp initial decrease in the quantity of boron adsorbed. No progressive decrease was found with increase in the concentration of sulfate ions above 150 mg/L for Filtrasorb and about 200 mg/L for both activated bauxite and activated alumina. Bingham and Page (*28*) measured amounts of boron adsorbed by an amorphous soil from a solution of 50 mg/L of boron containing sulfate ions as $Na_2SO_4$ in varying concentrations up to 0.1 M (about 9600 mg/L of $SO_4^{2-}$). Adsorption was independent of the presence of sulfate ion. Schalscha et al. (*29*), however, suggested a possible effect on boron adsorption by volcanic ash soils from the presence of $K_2SO_4$.

For all chemical species examined, removal of boron decreased with increasing concentrations of the chemical species only to certain values, then remained unchanged. This may indicate at least two different types of sites; one is nonspecific while the other is boron specific. Filtrasorb may have more nonspecific sites than other adsorbents.

### *Summary*

All of the adsorbents examined, except Hydro Darco (activated carbon), are capable of removing boron from water to some extent. Among the adsorbents, Filtrasorb (activated carbon) is superior to others because of the greater removal efficiency at initial concentrations of boron below 30 mg/L, with an adsorbent dosage of 25 g/L.

The optimum pH for boron removal under experimental conditions depends on both the characteristics of the background solution and the type of adsorbent. The optimum pH shifts to more alkaline pH when the solution salinity increases. However, salinity effects on both optimum pH and on removal efficiency are found only up to a certain limit of salinity for a given adsorbent. At above this value no additional effect on the removal efficiency was seen. The salinity limits are approximately 5‰ for Filtrasorb, 8‰ for activated bauxite, and

10‰ for activated alumina.

Boron removal efficiency generally increases with decreasing initial concentration of boron in the solution. Filtrasorb shows a more pronounced initial concentration effect than the other adsorbents. Regardless of the characteristics of background solution, a boron removal efficiency of about 90% can be achieved with Filtrasorb (with an adsorbent dosage of 25 g/L) if the initial concentration of boron in the solution does not exceed 5 mg/L. The removal efficiencies of boron by activated bauxite and activated alumina (with an adsorbent dosage of 25 g/L) are less than 70% at the same initial concentration of boron.

Generally, the presence of chemical species such as calcium, magnesium, silica, and sulfate results in a reduction in boron removal efficiency. However, the effects increase only up to certain limits, and no additional effect was seen.

Although boron uptake depends on many factors, the pH of the suspension and initial concentration of boron are critical in determining the boron removal efficiency, especially for Filtrasorb.

The present results indicate that boron can be removed either as $H_3BO_3$ or as $B(OH)_4^-$. The numbers and types of available sites are different depending on the characteristics of the solution and solids. It is likely that some of the sites responsible for the removal of boron are activated in contact with solution. Depending on solution characteristics, e.g., salinity, the sites being activated on the surface of the adsorbent are, to some extent, either $H_3BO_3$ specific or $B(OH)_4^-$ specific. For instance, the sites on the surface of Filtrasorb in contact with deionized–distilled water have affinities for $H_3BO_3$, while those in contact with simulated geothermal water have high affinities for $B(OH)_4^-$.

### *Acknowledgments*

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# Emissions from Pressurized Fluidized-Bed Combustion Processes

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■ Results of the comprehensive analysis of emissions from a pressurized fluidized-bed combustion unit (the Exxon Miniplant) are described as an illustration of the methodology for comprehensive analysis. The results are discussed in the context of the overall environmental assessment of the process being conducted by the U.S. Environmental Protection Agency. The comprehensive analysis of the fluidized-bed combustion emissions and process streams involved approximately 740 measurements on about 90 samples, using more than 40 different inorganic, organic, and physical analytical methods. A brief discussion on the sampling methods and analytical techniques is also included.

Environmental data acquisition is one of the seven major steps (Figure 1) in conducting a complete environmental assessment of emerging energy technologies such as fluidized-bed combustion (FBC) of coal (*1*). The data are acquired primarily by comprehensive analysis of emissions. Precommercial-stage comprehensive analysis (CA) of emissions from FBC units provides an opportunity for detecting potential environmental problems early in the development of the process. The environmental assessment of the process based on the CA data should assist in the identification and/or development of the most cost-effective control technologies.

A phased approach in three levels is the currently accepted technique for sampling and analyzing emissions. The three levels of analysis are defined as follows:

- Level 1 analysis includes comprehensive screening of a wide variety of organic and inorganic components. Level 1 sampling and analysis are designed to rapidly identify the potential pollutants from a source, and to measure them with a target accuracy factor of ±3. It also identifies all process streams that may contain four types of pollutants: gaseous, particulates, liquids/slurry, and solids. In addition, level 1 strategy includes bioassay testing of several effluent streams to obtain a direct index or estimate of their toxicity potential.
- Level 2 analysis is based on level 1 results. More accurate, compound-specific analytical techniques are used to pinpoint problem pollutants and effluent streams. Level 1 data, together with bioassay data, will be used to identify the analytical needs of levels 2 and 3.
- Level 3 analysis (not yet defined completely) would include routine continuous monitoring of those pollutants identified as specific problems in level 2.

A set of 12 biological tests was used in level 1 testing. These tests and the samples on which they were used are given in Table I. They are designed to test the possible toxicity of a waste stream to mammalian, marine, freshwater, plant, and soil systems. This test protocol provides a fairly good representation of the various biological constituents of the environment that might be exposed to a waste stream. The bioassays are designed to be implemented quickly and inexpensively, in keeping with the screening nature of level 1 testing. Their output will permit a relative ranking of waste streams according to biological hazard, and, together with the chemical and physical data, will provide an overall hazard characterization of the waste streams.

The measurement techniques and results presented in this paper are based largely on level 1 analysis. The sampling matrix for level 1 (and some level 2 analysis of substances already known as problem pollutants) is shown in Table II. Data presented in this paper were obtained from the pressurized FBC facility at Exxon; sampling was conducted in accordance with Table II. This facility has a 0.32-m diameter reactor which was operated at 890 °C, 900 kPa, 1.2 m/s superficial velocity, 40% excess air, 75 kg/h coal feed, and 11.0 kg/h dolomite sorbent feed at a Ca/S molar ratio of 1.25 for the tests reported in this paper.

### *Experimental*

**Sampling Methods.** The comprehensive analysis program for the Exxon unit consisted of sampling seven of the nine streams shown in Figure 2. The nine streams are: (1) coal feed, (2) dolomite feed, (3) second stage cyclone discard, (4) bed reject material, (5) cyclone discard leachates, (6) bed reject material leachates, (7) undiluted stack gas, (8) diluted stack gas, and (9) dilution and combustion air. Sampling of the sorbent regenerator unit was not performed since this unit was not operated during the tests. Streams 5 and 6 were simulated in the laboratory since no leachate streams were actually present at the miniplant site.

Five tests were conducted at Exxon from March 28 to April 1, 1977; the Miniplant was operated continuously for about 80 h. Sampling was performed on an around-the-clock basis by two 7-man teams working 12-h shifts. During each test, lasting 5 h, the various FBC streams were sampled by the techniques given in Table II.

Grab samples of solids from the FBC process streams were taken periodically throughout each test. The individual samples were composited to obtain one sample per test. The gases (CO, $CO_2$, $O_2$, $SO_2$, etc.) in the undiluted flue gas at stream 7 were sampled continuously for analyses by Exxon on-line instrumentation. Integrated grab samples were also taken for $CO_2$, and $O_2$ analyses by Orsat. $SO_2$ and $NO_x$ were sampled by EPA methods 6 and 7, respectively, to provide backup data. The controlled condensation method was used to sample for $SO_3/H_2SO_4$, and special impinger trains were used for sampling $NH_3$, HCN, HCl, and HF.

Continuous sampling of the undiluted flue gas was performed for total hydrocarbon measurements. Grab samples in glass bulbs were taken several times during each test for gas chromatographic analysis of $C_1$–$C_6$ hydrocarbons and sulfur compounds.

The primary particulate sampling was performed in the flue gas stream which was reduced to near atmospheric pressure by dilution with air. The source assessment sampling system (SASS) was used to collect samples for chemical and physical analysis. In three tests, the stainless steel condenser module normally supplied with the SASS unit was replaced with a glass module of similar dimensions. The glass module modification was included in these tests since a preliminary sampling experiment indicated excessive corrosion of the stainless

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## Table I. Level 1 Bioassay Matrix

| sample type | health effects tests | | | ecology effects tests | | |
|---|---|---|---|---|---|---|
| water and liquids | microbial mutagenesis | rodent acute toxicity | cytotoxicity | algal bioassays | static bioassays | soil microcosm |
| solids | + | + | + | + | + | + |
| gases | | | | | | plant stress ethylene |
| particulates | + | | + | | | soil microcosm |
| sorbent | + | | + | | | |

## Table II. Sampling and Analyses to Be Performed in Comprehensive Analysis of FBC Units

| | | | system stream or material | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | stack | | | solid waste | | | | leachate from solid waste | |
| | | | particulates | | | | | | | | |
| species, pollutants | sample collection techniques[a] | analysis method[b] | mid $>3\ \mu m$ | fine $<3\ \mu m$ | gas | collection device discard | bed reject | coal feed | sorbent feed | collection device | bed |
| continuous gas measurements | | | | | | | | | | | |
| $CO_2$ | Cw | NDIR[c] | | | X | | | | | | |
| CO | Cw | IR or UV[c] | | | X | | | | | | |
| NO | Cw | CL[c] | | | X | | | | | | |
| $NO_2$ | Cw | CL[c] | | | X | | | | | | |
| $SO_2$ | Cw | NDIR[c] | | | X | | | | | | |
| $O_2$ | Cw | PM[c] | | | X | | | | | | |
| integrated gas measurements | | | | | | | | | | | |
| $CO_2$ | IG | FGC/TC | | | X | | | | | | |
| CO | IG | FGC/TC | | | X | | | | | | |
| $NO_x$ | IG + M7 | FGC/TC + M7 | | | X | | | | | | |
| $SO_2$ | IG + M6 | FGC/TC + M6 | | | X | | | | | | |
| $O_2$ | IG | FGC/TC | | | X | | | | | | |
| $N_2$ | IG | FGC/TC | | | X | | | | | | |
| $H_2O$ | IG | FGC/TC | | | X | | | | | | |
| $H_2S$ | IG | FGC/FPD | | | X | | | | | | |
| COS | IG | FGC/FPD | | | X | | | | | | |
| $CH_3SH$–$C_6H_{13}SH$ | IG | FGC/FPD | | | X | | | | | | |
| $C_1$–$C_6$ hydrocarbons | IG | FGC/FID | | | X | | | | | | |
| $C_1$–$C_{12}$ hydrocarbons | IG | FGC/FID | | | X | | | | | | |
| $C_1$–$C_6$ chlorocarbons | IG | FGC/EC | | | X | | | | | | |
| $NH_3$ | IG | FGC/TC | | | X | | | | | | |
| HCN | IG | FGC/TC | | | X | | | | | | |
| cyanogen | IG | FGC/TC | | | X | | | | | | |
| $SO_3/H_2SO_4$ | GT/St | ion chromatograph | | | X | | | | | | |
| HCl | St | titration | | | X | | | | | | |
| fluoride | St | SIE | | | X | | | | | | |
| integrated specimens for subsequent group anal. | | | | | | | | | | | |
| inorganic chemicals | | | | | | | | | | | |
| 71 elements (Li through U) | SASS/GS | SSMS | X | X | | X | X | X | X | X | X |
| proximate (fuels) | Gs | ASTM D3172-73 | | | | | | X | | | |
| ultimate | Gs | ASTM D3176-74 | X | X | | | | X | | | |
| sulfur forms (fuels) | Gs | ASTM D2492-68 | | | | | | X | | | |
| radionuclides (gross $\alpha$ & $\beta$) | SASS/Gs | LBPC | X | X | | X | X | X | X | | |
| organic chemicals | | | | | | | | | | | |
| organics by class | SASS/Gs | LC/IR (total sample and 8 fractions) | X | X | X | X | X | X | | | |
| organic compds | SASS/Gs | LC/LRMS (selected fractions) | X | X | X | X | X | X | | | |
| POM | SASS/Gs | GC/MS | X | X | X | X | X | X | | | |
| organic-reduced sulfur compounds | SASS/Gs | GC/FPD (8 fractions combined | X | X | X | X | X | X | | | |
| $C_7$–$C_{12}$ hydrocarbons | SASS/Gs | GC/FID | X | X | X | X | X | X | | | |
| organic mass | SASS/Gs | microbalance (8 fractions) | X | X | X | X | X | X | | | |
| integrated specimens for subsequent specific anal. | | | | | | | | | | | |
| volatile, toxic elements (Be, Cd, Hg, Pb, Se, Sb, Te) | SASS/Gs | AAS | X | X | X | X | X | X | X | X | X |
| As | SASS/Gs | colorimetric | X | X | X | X | X | X | X | X | X |
| $Cl^-$ | SASS/Gs | colorimetric | X | X | | | | | | X | X |
| $F^-$ | SASS/Gs | distillation/colorimetric | X | X | | X | X | | | X | X |

**Table II. continued**

| | | | system stream or material | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | stack | | | solid waste | | | | leachate from solid waste | |
| | | | particulates | | | | | | | | |
| species, pollutants | sample collection techniques[a] | analysis method[b] | mid >3 µm | fine <3 µm | gas | collection device discard | bed reject | coal feed | sorbent feed | collection device | bed |
| Na | Gs | AAS | | | | | | X | | | |
| Ca | Gs | AAS/titration | | | | | | X | X | | |
| Mg | Gs | AAS | | | | | | | X | | |
| $CO_3^{2-}$ | SASS/Gs | gas evolution | X | X | | X | X | X | X | | |
| $SO_4^{2-}$ | SASS/Gs | titration/ion chromatography | X | X | | X | X | X | X | X | X |
| $SO_3^{2-}$ | SASS/Gs | $SO_2$ evolution/ colorimetric | X | X | | X | X | X | X | X | X |
| $S^{2-}$ | SASS/Gs | $H_2S$ evolution/ titrations | X | X | | X | X | X | X | | |
| $NO_2^-$ | SASS/Gs | colorimetric | X | X | | X | X | X | X | X | X |
| $NO_3^-$ | SASS/Gs | colorimetric | X | X | | X | X | X | X | X | X |
| C (noncarbonate) | Gs | combustion | | | | X | X | X | X | | |
| heating valve | Gs | ASTM D 2015-66 | | | | | | X | | | |
| particle morphology | Gs | LM/SEM | | | | X | X | X | X | | |
| particle size | Gs | sieve ASTM D 410-38 | | | | X | X | X | X | | |
| particle mass | SASS/M5 | weight | x[d] | X | | | | | | | |
| biological assays | | | | | | | | | | | |
| health | | | | | | | | | | | |
| microbial mutagenesis | SASS/Gs | salmonella/ames | X | X | X | X | X | X | X | | X |
| cytotoxicity | SASS/Gs | human lung fibroblast (WI-38) | | | X | | | | | | X |
| cytotoxicity | SASS/Gs | rabbit alveolar macrophage (RMA) | X | X | | X | X | X | X | | |
| acute toxicity | SASS/Gs | in vivo rodent | | | | X | X | X | X | | X |
| ecological | | | | | | | | | | | |
| freshwater algal | SASS/Gs | algal bottle | | | | X | X | X | X | X | X |
| freshwater animal (daphnia) | SASS/Gs | static | | | | X | X | X | X | X | X |
| freshwater animal (fish) | SASS/Gs | static | | | | X | X | X | X | X | X |
| saltwater algal | SASS/Gs | unicellular marine algae | | | | X | X | X | X | X | X |
| saltwater animal (grass shrimp) | SASS/Gs | static | | | | X | X | X | X | X | X |
| saltwater animal (fish) | SASS/Gs | static | | | | X | X | X | X | X | X |
| terrestrial soil | SASS/Gs | soil microcosm | X | X | | X | X | X | X | X | X |
| terrestrial plant | SASS/Gs | stress ethylene | | | X | | | | | | |

[a] Cw, continuous withdrawal through nonreactive line with mechanical filtration; IG, integrated grab sample of gas in glass bulb; GR/St, Goksoyr-Ross coil/special sampling train; St, separate wet chemical train to collect gas (such as method 6); SASS, source assessment sampling system (train used for suspended particulates, organics, and volatile trace elements); Gs, grab multiple samples riffled to reduce to 100-g representative sample; M5, EPA method 5; M6, EPA method 6; M7, EPA method 7. [b] NDIR, nondispersive infrared; IR, infrared; UV, ultraviolet; CL, chemiluminescence; PM, paramagnetic; FGC/TC, field chromatograph/thermal conductivity detector; FGC/FPD, field chromatograph/flame photometric detector; FGC/FID, field chromatograph/flame ionization detector; FGC/EC, field chromatograph/electron capture detector; SIE, selective-ion electrode; SSMS, spark source mass spectroscopy; ASTM, American society for testing materials standard method; LBPC, low background gas proportional controller; LC, liquid chromatography; LRMS, low-resolution mass spectrometry; GC, gas chromatography; GC/MS, gas chromatography with mass spectrography; AAS, atomic absorption spectroscopy; LM/SEM, light microscopy/scanning electron microscope. [c] Or acceptable instrumentation already installed at FBC Unit. [d] Coarse (>10 µm) and filter (<1 µm) fractions included.

module during the sampling of the FBC emission. Two tests were performed using the stainless steel module.

Method 5 sampling was used to obtain compliance-related mass emission data.

The Balston filter sample of particulates from the undiluted flue gas stream was obtained to study changes in the particulate characteristics or composition that might be caused by the dilution of the flue gas stream. The dilution air was sampled with a Tenax trap to identify any organics that might contaminate the flue gas stream.

**Analytical Techniques.** Analyses were performed on samples from three of Exxon's sampling tests. Approximately 90 samples were analyzed, using more than 40 different techniques. (For details on analytical procedures used in comprehensive analysis, see ref 2.)

To assure sample integrity and representativeness, special preparation techniques were needed, e.g., compositing, pulverizing, and aliquoting. After suitable preparation, the samples underwent several inorganic and organic analyses. The inorganic analysis included determining 71 elements by SSMS, Hg by FAAS, Sb by AAS/GF, and As by colorimetric methods. The organic analyses comprised several level 2 as well as level 1 tests. Physical measurements of particles in all SASS and FBC stream solid samples were also taken. In addition, three methods were used to monitor the quality of the inorganic analysis data as follows: (1) the analysis of NBS standard reference materials (SRM); (2) dynamic spiking techniques; (3) comparison of results obtained by two different analytical methods, spark source mass spectroscopy (SSMS) and atomic absorption spectrometry (AAS).

In general, the sampling methods proved satisfactory, despite some technical problems. Most of the analytical techniques provided acceptable level 1 data. The quality control procedures resulted in several useful suggestions for improvements. Though quality control was applied primarily to inorganic analyses, a broader program to cover organic

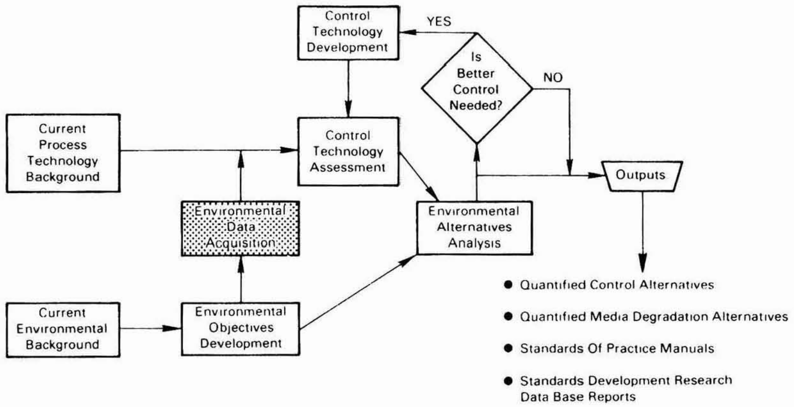

**Figure 1.** Simplified block diagram of environmental assessment steps

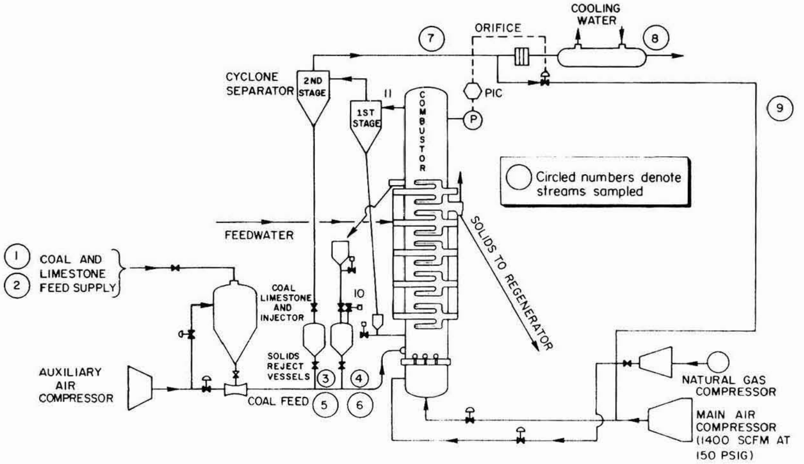

**Figure 2.** The fluidized-bed combustion miniplant at Exxon during comprehensive analysis tests

### Table III. Analysis of Flue Gas

| substances | concn, $\mu g/m^3$ (ppm) | air MATE, $\mu g/m^3$ | measured by |
|---|---|---|---|
| CO | 61 734 (53) | 55 000 | on-line instruments |
| $CO_2$ | $24 \times 10^6$ | $9 \times 10^6$ | |
| $O_2$ | 5.5% | none | |
| HC | 2 196 (3.3) | none | |
| $H_2SO_4$ mist + $SO_3$ | 2 079 (5) | 1 000 | wet chemistry |
| $SO_2$ | 74 813 (28) | 13 000 | |
| $NH_3$ | 501 (0.6) | 18 000 | |
| CN | 1.2 | 5 000 | |
| F | 10 120 (13) | | |
| Cl | 54 824 (33) | 3 000 | |
| $NO_x$ as $NO_2$ | 148 442 (70) | 9 000 | |
| As | <2 | 2 | atomic absorption |
| Be | <0.4 | 2 | |
| Cd | 0.1 | 8.2 | |
| Hg | 0.85 | 50 | |
| Pb | <1.2 | 150 | |
| Sb | <1.7 | 500 | |
| Se | <1.4 | 10.8 | |
| Te | <1.7 | 100 | |

**Table IV. Organic Compounds in Flue Gas**

| substances | concn, ng/m$^3$ | air MATE, ng/m$^3$ |
|---|---|---|
| anthracene/phenanthrene | 53 | 483 000 |
| methylanthracenes | 5 | 483 000 |
| fluoranthene | 26 | $90 \times 10^6$ |
| pyrene | 9 | $233 \times 10^6$ |
| methylpyrene/fluoranthene | 1.0 | no data |
| benzo[*c*]phenanthrene | 0.2 | $26.9 \times 10^6$ |
| chrysene/benz[*a*]anthracene | 3.8 | 44 800 |
| benzofluoranthenes | 1.0 | 897 000 |
| benz[*a*]pyrene | 0.5 | 20 |
| HC > $C_6$–$C_{12}$, µg/m$^3$ | 1740 | no data |
| HC > $C_{12}$, µg/m$^3$ | 58 | no data |

analyses and other subjects is under way.

*Comprehensive Analysis Results*

Before the results are discussed, some qualifications to the data presented below should be noted: (1) This is the first extensive analysis of emissions on a fluidized-bed unit. (2) Steady-state conditions may not have been achieved during the CA tests since the sulfur content of the coal varied. This resulted in drastic tapering of the $SO_2$ concentrations in the flue gas. (3) The regenerator was not operated during CA runs at the Miniplant. However, since the data collection process was well monitored and controlled, the data are considered reliable.

*Results and Evaluation*

**Comparisons to MATE Values.** To evaluate the significance of the measured concentration of substances in the effluent streams, the measured concentrations were compared to the MATE (minimum acute toxicity effluent) values (*3*). The procedures involved in developing MATE values can be found in ref *3*. MATE's are approximate concentrations of contaminants in air, water, or land effluents which may evoke *minimal* significant harmful responses to humans or the ecology, within 8 h. In general, types of data chosen to provide the basis for MATE's include threshold limit values (TLV), NIOSH recommendations, lethal dose concentrations, and other toxicity data, drinking water regulations, and water quality criteria. For a single substance, five specific MATE concentrations can be defined: two air and two water MATE's (each based on both health and ecology effects) and one land MATE (based on the lower water MATE).

MATE values indicate allowable concentrations of contaminant in effluent streams, and provide a point of reference for control technology goals. However, MATE's cannot be used as absolute indicators of minimum toxicity since they are still in the developmental stage.

**Emissions in Flue Gas.** Samples of the flue gas were collected at about 900 kPa pressure before air dilution, and analyzed. Table III shows flue gas composition measured with on-line instruments and wet chemistry tests.

The lowest concentrations of $SO_2$ and $NO_x$ in the flue gas are, respectively, 28 ppm (0.18 lb/$10^6$ Btu) and 70 ppm (0.09 lb/$10^6$ Btu). These are very low in comparison with existing new source performance standards for coal-fired steam generators: 1.2 lb/$10^6$ Btu for $SO_2$ and 0.7 lb/$10^6$ Btu for $NO_x$.

However, in comparison with the MATE's shown in Table III, both $SO_2$ and $NO_x$ have much higher concentration values than the MATE's allow. In fact, the $SO_2$ concentration in the flue gas is about 6 times the MATE value, and the $NO_x$ con-

**Table V. Inorganic Analysis of Particulate Emissions**

| substance | size range |  | land MATE | is land MATE exceeded at |  |
|---|---|---|---|---|---|
|  | 1–3 µm | 3–10 µm |  | obsd value | 1/100 obsd value |
|  | Volatile and Toxic Elements, µg/g$^a$ |  |  |  |  |
| As | 45 | 36 | 0.1 | yes | yes |
| Be | 15 | 11 | 0.03 | yes | yes |
| Cd | 2.1 | 1.3 | 0.004 | yes | yes |
| Hg | <0.02 | <0.02 | 0.02 | no | no |
| Pb | 44 | 43 | 0.1 | yes | yes |
| Sb | 4.0 | 2.3 | 0.4 | yes | no |
| Se | 27 | 22 | 0.05 | yes | yes |
| Te | <0.5 | <0.5 | 3.0 | no | no |
|  | Major Elements, µg/g |  |  |  |  |
| Al | 200 000 | 200 000 | 2.0 | yes | yes |
| Fe | 60 000 | 20 000 | 0.5 | yes | yes |
| Si | 200 000 | 200 000 | 300 | yes | yes |
| K | 3 000 | 1 500 | 1720 | yes | no |
| Ca | 30 000 | 30 000 | 32.4 | yes | yes |
| C (total carbon) | 12 000 | 11 000 |  |  |  |
|  | Anions, Wt % |  |  |  |  |
| $Cl^-$ | 0.011 | 0.007 |  |  |  |
| $F^-$ | 0.031 | 0.032 |  |  |  |
| $CO_3^{2-}$ | <0.2 | <0.2 |  |  |  |
| $SO_4^{2-}$ | 9.4 | 8.7 |  |  |  |
| $SO_3^{2-}$ | 0.001 | 0.004 |  |  |  |
| $S^{2-}$ | <0.03 | 0.03 |  |  |  |
| $NO_3^-$ | <0.001 | <0.001 |  |  |  |
| $NO_2^-$ | <0.001 | <0.001 |  |  |  |

[a] Atomic absorption spectroscopy method used except for As which was determined colorimetrically.

### Table VI. Inorganic Chemical Analysis of Bed Reject Material

| substance | obsd value | land MATE | obsvn exceeds MATE? |
|---|---|---|---|
| | Volatile and Toxic Elements, $\mu g/g$[a] | | |
| As | 21 | 0.1 | yes |
| Be | 2.7 | 0.03 | yes |
| Cd | 0.44 | 0.004 | yes |
| Hg | <0.02 | 0.02 | no |
| Pb | 8.0 | 0.1 | yes |
| Se | 0.8 | 0.05 | yes |
| Sb | 0.5 | 0.4 | yes |
| Te | <0.5 | 3.0 | no |
| | Major Elements, $\mu g/g$ | | |
| Al | 15 000 | 2.0 | yes |
| Fe | 10 000 | 0.5 | yes |
| Si | 15 000 | 300 | yes |
| K | 10 000 | 1720 | yes |
| Ca | 200 000 | 32.4 | yes |
| C (noncarbonate) | 1 600 | | |
| | Anions, Wt % | | |
| $Cl^-$ | 0.030 | | |
| $F^-$ | 0.003 | | |
| $CO_3^{2-}$ | 15.1 | | |
| $SO_4^{2-}$ | 27.7 | | |
| $SO_3^{2-}$ | 0.011 | | |
| $S^-$ | 0.005 | | |
| $NO_2^-$ | <0.001 | | |
| $NO_3^-$ | <0.001 | | |

[a] Atomic absorption spectroscopy method used, except for As which was determined colorimetrically.

### Table VII. Organic Chemical Analysis of Bed Reject Materials

| substances | land MATE | obsvn |
|---|---|---|
| Polycyclic Organic Materials, ng/g | | |
| anthracene/phenanthrene | 14 500 | <0.1 |
| others specifically sought | ND[a] | <0.1 |
| total | | |
| Hydrocarbon Content above C-6, $\mu g/g$ | | |
| hydrocarbon according to boiling point range | | |
| C-7 | ND | 20 |
| C-8 | ND | 22 |
| C-9 | ND | 12 |
| C-10 | ND | 4 |
| C-11 | ND | 5 |
| C-12 | ND | 3 |
| >C-12 | ND | 17 |
| Reduced Sulfur and Other Compds | | |
| reduced sulfur, $\mu g/g$ | ND | <0.2 |
| other compds detected | ND | none |

[a] ND, no data.

centration is 16 times. This fact does not necessarily mean that $SO_2$ and $NO_x$ are a problem; but it indicates that the MATE's are deliberately conservative and may need reevaluation and/or revision.

The concentrations of all the eight volatile toxic elements were well below the MATE's. Incidentally, arsenic concentration measured by spark source mass spectrography was higher than the MATE's, but the colorimetric analysis, classed as a level 2 technique, showed it to be less than the MATE value.

Concentrations of polycyclic organic matter in flue gas given in Table IV are lower than the air MATE's.

**Suspended Particulates in Flue Gas.** The particulate concentration in the flue gas, after passing through two conventional cyclones. but without going through fine particulate control equipment, was about 1.2 g/scf (1.9 lb/$10^6$ Btu) as compared to the EPA standard of 0.1 lb/$10^6$ Btu. However, if an appropriate third-stage particulate control device that removes over 96% of the particulates can be demonstrated, the EPA emissions standard would be met.

The physical properties of the collected dust from the flue gas may be of interest. The size distribution and morphology are: <1 $\mu$m, 9 wt %; 1–3 $\mu$m, 39 wt %; 3–10 $\mu$m, 21 wt %; >10 $\mu$m, 33 wt %; predominant shape, irregular; evident cleavage, none; structure, 3 phase; color, white, black, red. Thus, 46 wt % of the suspended particulates collected by the source assessment sampling system's cyclone (*4*) was less than 3 $\mu$m, and is in the respirable range. The $\alpha$ radioactivity averaged about 6 ± 3 pCi/g, and $\beta$ radioactivity, 30 ± 10 pCi/g.

Table V indicates that the toxic and volatile metal content in the particulates is of real significance. Since most of these particulates will be collected as solid wastes by any effective particulate collection system, the land MATE values apply. Of these metals, all but Te and Hg would exceed the land MATE even if the particulates were removed from the flue gas at a reasonable collection efficiency and were considered for land disposal (see Table V). The second "yes" in the MATE comparison column indicates that the particulates would still constitute a land disposal problem even when diluted by a factor of 100 by mixing with nontoxic materials (or some other technique) to reduce the toxic metal concentration. These conclusions are valid for elemental metals, but are not necessarily true for compounds of these metals.

**Emissions in Bed Solids.** Table VI shows the inorganic analysis of the bed reject solids. Several toxic metals exceed MATE values, although their compound form may be less toxic than implied by the comparison. The anion analysis indicates the degree of conversion from carbonate to sulfate within the bed. (For a complete trace metal composition of this material, see ref 2.) Whether the chemical form in which the metals are present is an unacceptable hazard for simple land disposal still needs to be determined. The concentration of polycyclic organic materials was found to be insignificant, as shown in Table VII. The organic constituents in the bed reject material pose no environmental problem for land disposal. Table VII also shows the content of hydrocarbons with more than six carbon atoms; these amounts appear to be fairly low.

**Leachates from Bed Reject Materials.** Leachates were generated in the laboratory using the spent bed materials (SBM). The 720-h shake method was employed. This method involved shaking 33 g of SBM with 100 mL of triple-distilled water in a reciprocating shaker for 72 h at 120 cpm. After 72 h, the liquid was decanted and saved. A fresh 100 mL of distilled water was again added to the same SBM sample. This process was repeated 10 times to get 720 h of shaking and 1000 mL of decanted leachates. By the same procedure, leachates were generated from the fly ash samples collected from the second cyclone. Both leachates were analyzed for inorganics, using level 1 techniques (SSMS) for elements. Some level 2 techniques (wet chemistry or atomic absorption spectroscopy) were employed to determine antimony, mercury, and arsenic. Leachates were also analyzed for anions ($SO_4^{2-}$, $SO_3^{2-}$, etc.)

**Table VIII. Inorganics in Leachates from Spent Bed Material (SBM) and Fly Ash (FA)**

| substance or parameter | concn, mg/L SBM | concn, mg/L FA | water MATE, mg/L | MATE exceeded? |
|---|---|---|---|---|
| Li | 6 | 20 | 0.38 | yes |
| Na | 10.4 | 52 | 800 | no |
| Mg | 9.6 | 6.4 | 87 | no |
| Al | 0.8 | 1.4 | 1.0 | yes |
| Ca | 460 | 1000 | 16.2 | yes |
| V | 0.1 | 0.1 | 0.15 | no |
| Fe | 0.2 | 0.2 | 0.25 | no |
| Ni | 0.03 | 0.03 | 0.01 | yes |
| Se | 0.07 | 0.07 | 0.025 | yes |
| Pb | 0.05 | 0.05 | 0.05 | no |
| As | 0.04 | 0.05 | 0.05 | no |
| $CN^-$ | <0.03 | <0.03 | 0.015 | undecided |
| $SO_4^{2-}$ | 1610 | 1950 | 250[a] | yes |
| pH | 12.2 | 9.0 | 5–9[a] | yes |

[a] Proposed U.S. EPA drinking water standards; no MATE value available.

**Table IX. Results of the Biological Testing of FBC Waste Streams**

| test | test parameter | waste streams: flue gas | suspended particulates | bed solids | bed solids leachate |
|---|---|---|---|---|---|
| Ames | +/− | | + | − | − |
| cytotoxicity RAM | $LD_{50}$ | | 596, 3000 | NT[a] | NT |
| rodent acute toxicity | $LD_{50}$ | | | NT | NT |
| aquatic | | | | | |
| freshwater | | | | | |
| algal | $EC_{50}$ | | | | 45% |
| daphnia | $LC_{50}$ | | | | 40.9% |
| fish | $LC_{50}$ | | | | 25.3% |
| saltwater | | | | | |
| algal | $EC_{50}$ | | | | NT |
| shrimp | $LC_{50}$ | | | | NT |
| fish | $LC_{50}$ | | | | NT |
| terrestrial soil microcosm | ranked in order of decreasing toxic. | | 2 | 3 | 1 |
| stress ethylene | % of increase over control | NT (0%) | | | |

[a] NT, no toxicity.

by standard wet chemistry. Organics were analyzed by level 1 techniques (liquid chromatography separation and infrared analysis). Significant results of inorganic analysis are presented in Table VIII in comparison with water MATE's (based on ecological effects). These results show that As, Ca, Ni, Pb, Li, Se, $SO_4^{2-}$, and Al are present in concentrations equal to or exceeding the MATE's. Hence, these substances should be analyzed by level 2 techniques in future leachate studies to accurately establish their concentrations and environmental effects. Also, the compound forms in which they are present should be investigated.

The results of organic analysis were not as conclusive as the results of inorganic analysis. Further work is needed to determine which specific organic compounds in leachates are present in harmful amounts.

**Leachate Analysis and the RCRA.** The importance of the above results to FBC waste disposal will be determined by comparing the leachate analyses with the requirements proposed under the Resource Conservation and Recovery Act (RCRA). Under Section 3001 of RCRA, waste will be defined as hazardous, if it is inflammable, corrosive, infectious, reactive, radioactive, or toxic. Of these criteria, corrosivity, reactivity, and toxicity are likely to be pertinent to FBC residue.

Based on draft RCRA guidelines, FBC waste will be considered corrosive if a saturated solution of the residue in water has a pH of less than 2 or greater than 12. The results in Table VIII showed the leachate from spent bed material to have a pH of 12.2 (corrosive). The pH of a saturated solution could be expected to be somewhat higher. However, the pH of the fly ash leachate was only 9.0. Therefore, if disposed together, the mixture of fly ash and spent bed materials may not be corrosive.

According to draft RCRA guidelines, FBC residue will be considered toxic if its leachate (to be generated by a "standard" method, not yet determined): (a) has a concentration of any substance greater than or equal to 10 times the drinking water standard; (b) has a concentration of any substance greater than or equal to 0.35 times the lowest oral mammalian $LD_{50}$ (mg/kg) for that substance, as listed in the NIOSH Registry of Toxic Effects of Chemical Substances; (c) has a concentration of any substance equal to 10 times the lowest 96-h $LC_{50}$ (mg/L) for the substance, as listed in the NIOSH Registry. In these studies, none of the primary drinking water standards is exceeded by a factor of 10 by either leachate. However, the results still must be measured against criteria b and c above.

If the MATE values for calcium are similar to the primary drinking water standards, calcium in leachates may well exceed the allowable standards by more than a factor of 10, thereby causing the FBC residues to be considered hazardous.

The importance of the designation "hazardous" lies in the somewhat stricter disposal requirements likely to be imposed, and the additional permits, testing, and record-keeping required by RCRA.

**Bioassay Results.** The biological test results for four FBC waste streams are given in Table IX. The health and ecological tests on each stream were performed according to the pilot level 1 bioassay program.

The flue gas stream was tested only with the stress ethylene test. At present, no other level 1 tests are suitable for testing gases. Results indicate the gas was nontoxic. Some caution is associated with this conclusion because the full quantity of gas required for the test was not available and the sample had to be stored for some time before testing. These are due to problems associated with methodology development.

Several tests were performed on the spent bed solids which showed very low or no toxicity in all tests, and would not likely constitute a biological hazard in its solid form. However, the leachate from the spent bed solids showed some toxicity in two of the tests. The results show that it was nontoxic to mammals (health tests) and marine organisms, but toxic to freshwater and soil organisms. This stream would likely require further study to determine its potential biological hazard.

Only the suspended particulates stream gave positive Ames test results. The particulates were mutagenic and thus may also be carcinogenic. This stream was also toxic to soil organisms.

Based on the biological tests alone, the relative ranking of the four waste streams, in order of decreasing toxicity, is: (1) spent bed solids leachate; (2) suspended particulates; (3) spent bed solids; (4) flue gas. It must be emphasized that the test results provide only relative data, and the actual hazard to humans and other organisms can be determined only through additional testing.

### *Summary and Conclusions on Comprehensive Analysis Results*

**On Source Emission Data.** The major conclusion is:

- Comprehensive analysis of emissions from emerging energy technologies yields useful results for completing the environmental assessment of the processes.

Other conclusions are:

- Pressurized coal-burning FBC units can meet existing new source performance standards for $SO_2$ and $NO_x$ emissions from coal-fired steam generators. Particulate emissions control needs demonstration.
- MATE's for $SO_2$, $NO_x$, CO, and possibly for other substances need reevaluation.
- Polycyclic organic matter (POM's) in flue gas or other effluents from FBC units do not appear to be health/ecological hazards. POM's are concentrated in fine particles ($<3$ μm) as opposed to coarse ($>3$ μm) particles in the suspended particulates.
- Though biological assay data are difficult to interpret at this stage, spent bed material leachate and suspended particulates do show a relatively higher toxicity than flue gas and bed solids. This trend corresponds with the greater than MATE's concentrations of many volatile and toxic trace elements (As, Ni, Pb, Li, etc.) in leachates from bed materials. These results, therefore, indicate the need for further study. The final interpretation of the bioassay results and their toxicity ratings is being considered by the U.S. EPA.
- The results of this study do not imply that fluidized-bed combustion of coal generates solid wastes of greater or lesser toxicity than other methods of coal combustion, since the solid wastes from other methods have not been subjected to such comprehensive analysis. Also, the above results need careful evaluation and further validation.

To obtain useful reliable data, steady-state operation and an adequate supply of uniform coal and sorbent for the duration of sampling must be assured.

### *Acknowledgments*

The studies described in this paper are part of the environmental assessment of the fluidized-bed combustion process which Battelle is conducting for the U.S. EPA, under the guidance of R. P. Hangebrauck and D. Bruce Henschel of the Agency's Industrial Environmental Research Laboratory, Research Triangle Park, N.C. The comprehensive analyses of emissions were conducted in cooperation with many individuals of Exxon. The authors sincerely appreciate the assistance and support of all these persons.

### *Nomenclature*

CA = comprehensive analysis

FBC = fluidized-bed combustion

SASS = source assessment sampling system

SSMS = spark source mass spectroscopy

AAS = atomic absorption spectrometry

AAS/GF = atomic absorption spectrometry/graphite furnace atomization

FAAS = flameless atomic absorption spectrometry

POM = polycyclic organic matter

NBS = National Bureau of Standards

SBM = spent bed materials

SRM = standard reference materials

MATE = minimal acute toxicity effluent

RCRA = Resource Conservation and Recovery Act

NIOSH = National Institute for Occupational Safety and Health

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# Free-Radical Oxidation of Organic Phosphonic Acid Salts in Water Using Hydrogen Peroxide, Oxygen, and Ultraviolet Light

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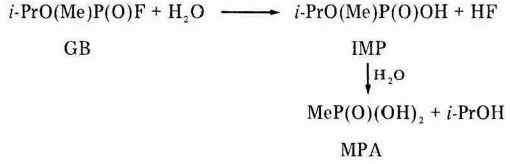
■ Photochemically initiated HO radical oxidations of 0.2–3.0 M isopropyl methylphosphonic acid (IPA) and methylphosphonic acid (MPA) (as sodium salts) have been carried out at 25 °C in water solution using 0.01–3.0 M hydrogen peroxide and oxygen to effect complete oxidations of both compounds to phosphoric acid, carbon dioxide, and water. No intermediate oxidation products were found from oxidation of MPA, whereas acetone, acetic acid, and methylphosphonic acid were found in the oxidation of IPA. From the relative proportions of these intermediates, the relative and absolute rate constants for reactions of HO radical with IPA and MPA were calculated. The experiments suggest that rapid and complete oxidation of alkyl phosphorus compounds to simple products may be possible but careful control of reaction variables is necessary to achieve efficient use of $H_2O_2$.

Oxidation with oxygen via free-radical intermediates is an attractive method for rapidly transforming trace amounts of organic compounds found in wastewater to carbon dioxide and water. Several reports have appeared on the use of oxygen, with hydrogen peroxide or ozone as sources of radicals, to remove acetate ion (*1*) or nitroaromatics (*2*). Although trace oxidations are rapid and fairly complete, information is lacking on the intermediates formed or the efficiency of the processes and there appears to be no useful data on oxidations at high concentrations of chemicals.

This paper describes the use of hydrogen peroxide, oxygen, and ultraviolet (UV) light to completely oxidize high concentrations of isopropyl methylphosphonate (IMP) and methylphosphonic acid (MPA). These phosphonic acid derivatives arise from hydrolysis of the nerve agent isopropyl methylphosphonofluoridate (GB):



$$\begin{tikzcd}[column sep=small] i\text{-PrO(Me)P(O)F} + H_2O \arrow[r] & i\text{-PrO(Me)P(O)OH} + HF \arrow[d, "H_2O"] \\ & \text{MeP(O)(OH)}_2 + i\text{-PrOH} \end{tikzcd}$$

GB IMP MPA

Neither IMP nor MPA is toxic; however, the possible re-formation of GB from IMP under some conditions has been reported (*3*). Although further conversion of IMP to MPA ensures against re-formation of GB, complete oxidation to carbon dioxide, water, and phosphoric acid greatly simplifies the problem of ultimate disposal.

The literature on oxidation of organic phosphorus(V) compounds is quite limited. Smirnov, Pristenskii, and Filinova (*4, 5*) report the oxidation of methylphosphonic acid with ozone and $Co(NO_3)_3$ to give a 40% yield of phosphoric acid in 9 h. Recently, Benschop and Halmann (*6*) described the UV irradiation of trimethyl phosphate and oxygen in water. Orthophosphoric acid, CO, and $CO_2$ were major products formed by stepwise oxidation of the methyl groups to give dimethylhydrogen and methyldihydrogen phosphoric acids as intermediates.

Since direct reaction of oxygen with most organic compounds is impractically slow at temperatures below 150–200 °C, some source of free radicals is usually needed to initiate the oxidation. Ozone or hydrogen peroxide is well suited for this purpose in water, particularly if used with UV light, which effects O–O bond cleavage to give O atoms or HO· radicals (*7*).

In this work we used hydrogen peroxide and UV light below 300 nm to provide the reactive HO· radicals needed to initiate the oxidative cleavage of these phosphoric acid derivatives. Oxygen was also present to convert carbon radicals to peroxy radicals. Because the HO· radical is extremely reactive toward most organic H-atom donors (*8, 9*), it should produce carbon radicals efficiently from MPA or IMP under conditions where other radicals, such as $RO_2\cdot$ or RO·, would be ineffective (*10*). Molecular oxygen should promote the stepwise degradation of IMP via MPA to carbon dioxide and phosphoric acid via $RO_2\cdot$ and RO· radicals and oxygenated intermediates. The following scheme indicates the probable major reactions involved in oxidation of MPA (in basic solution) (Equations 1–7b):

$$H_2O_2 \xrightarrow{h\nu} 2HO\cdot \tag{1}$$

$$HO\cdot + MePO_3Na_2 \rightarrow H_2O + \cdot CH_2PO_3Na_2 \tag{2}$$

$$R\cdot = CH_2PO_3Na_2$$

$$HO\cdot + H_2O_2 \rightarrow H_2O + HO_2\cdot \tag{3}$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \tag{4}$$

$$RO_2\cdot + HO_2\cdot \rightarrow RO_2H + O_2 \tag{5}$$

$$2RO_2\cdot \rightarrow R'CHO + R'CH_2OH + O_2 \tag{6}$$

$$R' = OP(ONa)_2$$

$$R'CHO + 2HO\cdot + 0.5O_2 \rightarrow CO_2 + (NaO)_2P(O)OH + H_2O \tag{7a}$$

$$R'CH_2OH + 2HO\cdot + O_2 \rightarrow CO_2 + (NaO)_2P(O)OH + 2H_2O \tag{7b}$$

The stoichiometry of the oxidation of MPA depends on whether oxygen or $H_2O_2$ or both are used.

$$MePO_3Na_2 + 2O_2 \rightarrow CO_2 + Na_2HPO_4 + H_2O \tag{8}$$

$$MePO_3Na_2 + 4H_2O_2 \rightarrow CO_2 + Na_2HPO_4 + 5H_2O \tag{9}$$

The oxidation of MPA requires four peroxide/MPA but only two $O_2$. The most efficient use of peroxide is to initiate Reaction 2 and other H-atom transfers from stable intermediates while minimizing Reactions 3 and 5.

The specific rate constant for H-atom transfer to HO· from MPA (Reaction 2) is probably similar to that for acetic acid or acetone, for which values of about $10^8$ $M^{-1}$ $s^{-1}$ have been measured (*9*). The principal competing reaction for HO· will be H-atom transfer from $H_2O_2$ itself (Reaction 3). This reaction has a rate constant of about $10^7$ $M^{-1}$ $s^{-1}$ (*9*). Thus, Reactions 2 and 3 are competitive at a 1:10 ratio of MPA to $H_2O_2$. At lower concentrations of MPA, Reaction 3 will compete and the efficiency of the oxidation process, as measured by the amount of MPA oxidized compared with the amount of peroxide consumed, will decrease. For comparison, the specific rate constants for the same process involving $RO_2\cdot$ or RO·

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**Table I. Oxidation of MPA Using $H_2O_2$ and UV Light**[a]

| expt no. | time, h | concns, M $[MPA]_0$ | $\lvert\Delta MPA\rvert$ | $[H_2O_2]_0$ | $\lvert\Delta H_2O_2\rvert$ | conversion of MPA, % | $\Delta H_2O_2/\Delta MPA$ |
|---|---|---|---|---|---|---|---|
| 2B | 2 | 0.17 | 0.17 | 1.73 | 1.58 | 100 | 9.3 |
| 2 | 2 | 0.67 | 0.38 | 3.5 | 1.6 | 56 | 4.2 |
| 3 | 2 | 0.40 | 0.11 | 2.1 | 1.1 | 28 | 10 |
| 4 | 1 | 1.67 | 0.41 | 1.7 | 0.9 | 24 | 2.2 |
| 5 | 1 | 1.82 | 0.15 | 0.95 | 0.95 | 8 | 6.3 |
| 6 | 1 | 1.96 | 0.25 | 0.20 | 0.20 | 13 | 0.8 |
| 8 | 1 | 1.25 | 0.19 | 3.9 | 2.0 | 15 | 10.5 |
| 7 | 1 | 1.00 | 0.36 | 5.2 | 2.9 | 25 | 8.1 |
| 1 | 2 | 1.00 | 0.57 | 5.2 | 3.9 | 57 | 6.8 |
| 11 | 2 | 1.00 | 0.44 | 2.6 | 1.67 | 56 | 3.8 |
| 13 | 1 | 1.00 | 0.81 | 2.6 | 1.64 | 61 | 2.7 |
| 14 | 2 | 1.00 | 0.59 | 2.6 | 2.6 | 59 | 4.4 |
| 20 | 12 | 0 |  | 3.0 | 0 |  | dark[c] |
| 21 | 12 | 1.00 |  | 3.0 | 0 | 0 | dark |
| 22 | 1 | 1.00 |  | 2.9 | 0.1 | 0 | Pyrex reaction tube |

[a] Mixtures flushed with pure $O_2$ and tightly capped before irradiation with a 450-W Hanovia mercury arc lamp, Model 78A10. [b] Initial pH was 8. Measured using $^1H$ NMR (see Experimental section). [c] Closed cabinet with no visible or UV light.

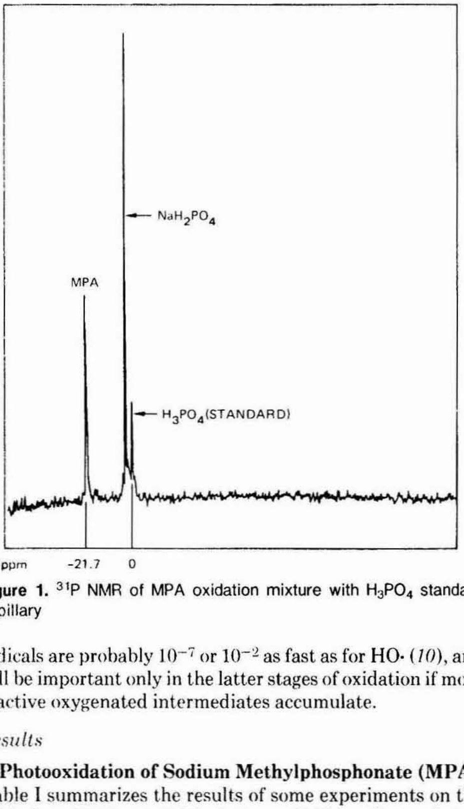

**Figure 1.** $^{31}P$ NMR of MPA oxidation mixture with $H_3PO_4$ standard capillary

radicals are probably $10^{-7}$ or $10^{-2}$ as fast as for HO· (*10*), and will be important only in the latter stages of oxidation if more reactive oxygenated intermediates accumulate.

*Results*

**Photooxidation of Sodium Methylphosphonate (MPA).** Table I summarizes the results of some experiments on the oxidation of 0.17 to 1.67 M solutions of MPA sodium salt (pH 8) with excess $H_2O_2$. With a large excess of $H_2O_2$ (experiment 2B), all the MPA was oxidized to carbon dioxide (and inorganic phosphorus) within 2 h; however, almost all the peroxide was also consumed. The last column of Table I measures the efficiency with which $H_2O_2$ is used to oxidize MPA. The ratio ($\Delta H_2O_2/\Delta MPA$) is not related to the conversion of MPA, only to the number of moles of peroxide needed to oxidize 1 mol of MPA. Higher values (low efficiency) were found when the *initial* ratio $[H_2O_2]/[MPA]$ was high, or when the irradiation time was short (1 h), or both (experiments 2B, 2, 3, 7, and 8). The lower ratios of $\Delta H_2O_2/\Delta MPA$ (high efficiency) were usually associated with lower initial ratios of peroxide to MPA (experiments 4, 6, and 11–14) as expected from the competition between Reactions 1–3. Experiment 6 shows that the process is very efficient (0.8) when a large excess of MPA is used.

Table I also shows results from control experiments with peroxide and with and without MPA (in the dark) or with peroxide in Pyrex tubes, which cut off UV light < 290 nm, all of which showed no reaction. A few experiments with 0.17 M MPA, 1.73 M $H_2O_2$, and air at pH 6–10 (in increments of 1 pH unit) not shown in Table I gave very similar results on irradiation for 2 h. Almost all the MPA was oxidized and 0.08–0.19 M $H_2O_2$ remained.

More detailed experiments were done on the products of oxidation from experiments 1, 2, and 7–14. Mixtures of 1 M MPA and 1–3 M peroxide with excess oxygen were irradiated for 1–2 h; 30–60% of the MPA was oxidized. Analysis of the reaction mixtures by $^1H$ NMR for MPA and intermediates showed only a diminution in the MPA doublet at 1.0 ppm (from $Me_4Si$). No evidence was found for formation of intermediate oxidized phosphorus acids, such as hydroxymethylphosphonic acid or formaldehyde. Experiment 2 (Table I) was also analyzed by $^{31}P$ NMR (Figure 1). At 56% conversion, only signals corresponding to $NaH_2PO_4$ and MPA were found and in the same ratio as found from the $^1H$ NMR spectrum for the same mixture.

The virtual absence of intermediates in the oxidation mixtures is also shown by an experiment summarized in Table II in which oxygen, 1 M MPA, and 2.6 M peroxide were sealed in a quartz tube and irradiated for 4 h. Peroxide was entirely consumed, and about 54% of MPA was oxidized. Gas analysis showed that 97% of the carbon from the reacted MPA was in the form of $CO_2$ and a trace amount of CO. In this reaction, about 4.8 peroxides were consumed for each MPA consumed, a fairly efficient process. Gas analysis also showed that additional oxygen was produced by the direct decomposition of peroxide.

**Photooxidation of Isopropyl Methylphosphonic Acid Sodium Salt.** Table III summarizes the results of three ex-

**Table II. Photooxidation of MPA with $H_2O_2$ (Millimoles)[a,b]**

| | initial | final | $\Delta$ |
|---|---|---|---|
| $O_2$ | 1.37 | 2.02 | 0.65 |
| MPA | 6.00 | 2.76 | −3.24 |
| $H_2O_2$ | 15.60 | 0 | −15.60 |
| CO | | 0.075 | 0.075 |
| $CO_2$ | | 3.032 | 3.032 |

balance on C = 96%[c]

[a] Solution volume 6 mL. [b] Sample sealed under oxygen and irradiated for 4 h with 450-W Hanovia mercury lamp. [c] $(CO_2 + CO)$/MPA.

**Table III. Photooxidation of IMP with $H_2O_2$ (Concentrations in Moles/Liter)**

| initial conditions[a] | expt 1 | expt 2 (mixture from 1 + $H_2O_2$) | expt 3 (mixture from 2 + $H_2O_2$) |
|---|---|---|---|
| liquid vol, mL | 3.80 | 2.09 | 0.64 |
| $O_2$, mmol | 2.11 | 0.66 | 0.51 |
| [IMP] | 1.00 | trace | 0 |
| [MPA] | 0 | 0.66 | 0.32 |
| $[H_2O_2]$ | 3.02 | 3.0 | 3.0 |
| [acetone] | 0 | 0.14 | 0 |
| [acetic acid] | 0 | 0.32 | 0.32 |
| **final conditions** | | | |
| $O_2$, mmol | 0.635 | 1.926 | 0.916 |
| $\Delta O_2$, mmol | −1.47 | +1.264 | 0.41 |
| [IMP] | 0.01 | 0 | 0 |
| [MPA] | 0.94 | 0.46 | 0.07 |
| $[H_2O_2]$ | 0 | 0 | 0 |
| [acetone] | 0.2 | 0.02 | 0 |
| [acetic acid] | 0.46 | 0.46 | 0.13 |
| $CO_2$, mmol | 3.35 | 0.52 | 0.36 |
| CO, mmol | 0.4 | 0.12 | 0 |
| C balance, % | 75 | 89 | 119 |

[a] Initial pH = 9. Solutions irradiated for 2 h.

periments with mixtures of IMP (as its sodium salt) and $H_2O_2$. The mixture was irradiated for 2 h, irradiation was stopped, and the reaction was analyzed for peroxide, IMP, MPA, and intermediate organic products. Irradiation was resumed with part of the same solution, to which was added more $H_2O_2$, so that the initial concentration of $H_2O_2$ was the same for each reaction. The process was repeated a third time. In experiment 1 (Table III), 1.0 M IMP was completely oxidized to acetic acid, acetone, $CO_2$, and MPA in 2 h with 3 M $H_2O_2$.

Experiment 2, with a portion of the reaction mixture from experiment 1 and more $H_2O_2$, shows that 0.66 M MPA partially oxidizes to $CO_2$, and 0.14 M acetone oxidizes almost entirely to $AcO^-$ but 0.32 M $AcO^-$ is largely resistant to oxidation. Only in experiment 3 with 0.32 M MPA and 0.32 M $AcO^-$ is most of the $AcO^-$ oxidized along with MPA.

The formation of both acetone and acetic acid in experiment 1 and oxidation of acetone to acetic acid in experiment 2 may indicate that these products are formed by two routes.

$$\begin{gathered}\mathrm{IMP + HO\cdot \rightarrow Me_2\dot{C}OPX + H_2O} \\ \mathrm{X = [(ONa)(O)(Me)]}\end{gathered} \tag{10}$$

$$\mathrm{Me_2\dot{C}OPX + O_2 \rightarrow Me_2C(-O_2\cdot)OPX} \tag{11}$$

$$\mathrm{Me_2C(-O_2\cdot)OPX + HO_2\cdot \rightarrow Me_2C(-O_2H)OPX + O_2} \tag{12}$$

$$\mathrm{Me_2(-O_2H)COPX + H_2O \rightarrow Me_2CO + H_2O_2 + HOPX} \tag{13}$$

$$\mathrm{Me_2C(-O_2H)OPX \xrightarrow{h\nu} MeC(-O\cdot)OPX + HO\cdot} \tag{14}$$

$$\mathrm{Me_2C(-O\cdot)OPX + IMP \rightarrow Me_2C(-OH)OPX + Me_2\dot{C}OPX} \tag{15}$$

$$\mathrm{Me_2C(-OH)OPX \rightarrow Me_2CO + HOPX} \tag{16}$$

$$\mathrm{Me_2CO + 1.5O_2 + 2HO\cdot \xrightarrow[\text{(several steps)}]{} MeC(O)OH + CO_2 + 2H_2O} \tag{17}$$

$$\mathrm{Me_2C(-O\cdot)OPX \rightarrow MeC(=O)OPX + Me\cdot} \tag{18}$$

$$\mathrm{MeC(=O)OPX + H_2O \rightarrow MeCO_2H + HOPX} \tag{19}$$

These results also indicate that most if not all $CO_2$ is formed by oxidation of acetic acid via several intermediates, possibly including acetoxy radical:

$$\mathrm{MeCOOH + HO\cdot \rightarrow MeCOO\cdot + H_2O} \tag{20}$$

$$\mathrm{MeCO_2\cdot \rightarrow Me\cdot + CO_2} \tag{21}$$

$$\mathrm{Me\cdot + 1.5O_2 + HO\cdot \rightarrow CO_2 + 2H_2O}\ \text{(several steps)} \tag{22}$$

Other plausible routes from acetic acid to $CO_2$ involving instead initial transfer of a methyl hydrogen can also be written.

**Reactivity of Phosphorus Acid Salts toward HO· Radicals.** The data in Table III can be used to estimate the rate constants for H-atom transfer from IMP and MPA to HO· based on the known rate constants for reactions of HO· with acetone and acetic acid (*8*, *9*), both of which are products from the oxidation of IMP. The ratio of rate constants for H-atom transfer from MPA ($k_2$) and acetate ($AcO^-$) ($k_1$) is derived from the relation:

$$d[AcO^-]/d[MPA] = k_1[AcO^-]/k_2[MPA] \tag{23}$$

which on integration becomes:

$$(k_1/k_2) = \ln([AcO^-]_0/[AcO^-])/\ln([MPA]_0/[MPA]) \tag{24}$$

When the data from experiment 3 (Table III) are substituted into Equation 24

$$(k_1/k_2) = \ln(0.32/0.13)/\ln(0.32/0.07) = 0.59$$

The value of $k_1$, for reaction of $AcO^-$ with HO·, is $7 \times 10^7\ M^{-1}\ s^{-1}$; therefore, $k_2 = 1.2 \times 10^8\ M^{-1}\ s^{-1}$. Experiment 1 also provides the basis for estimating the reactivity of IMP toward HO· using the reasonable assumption that the rates of oxidation of both IMP and MPA are controlled by simple consecutive first-order processes involving H-atom transfer to HO· radical:

$$\mathrm{IMP} \xrightarrow{k_4'} \mathrm{MPA} \tag{25}$$

$$\mathrm{MPA} \xrightarrow{k_2'} \mathrm{CO_2 + CO + H_3PO_4} \tag{26}$$

where $k_4' = k_4[HO]$ and $k_2' = k_2[HO]$. Under these conditions the concentration of MPA present at any time, $t$, is (*11*):

$$[MPA]_t = \frac{[IMP]_0 k_4'}{k_2' - k_4'}[e^{-k_4't} - e^{-k_2't}] \tag{27}$$

Equation 27 can be solved by trial and error for a value of $k_2'$ that satisfies the requirement that $[MPA]_t = 0.94$ M at $t = 120$ min and that $k_4' = 5 \times 10^{-4}\ s^{-1}$, as calculated from the data in experiment 1. A value of $k_2' = 1.1 \times 10^{-5}\ s^{-1}$ ($k_2'/k_4' = 0.027$) at $t = 120$ min gives [MPA] = 0.91 M. Since $k_2 \simeq 3.6 \times 10^8\ M^{-1}\ s^{-1}$, $k_4 = 1.3 \times 10^{10}\ M^{-1}\ s^{-1}$. This value agrees quite well with the value of $(2\text{–}4) \times 10^9\ M^{-1}\ s^{-1}$ for the rate constant for H-atom tranfer from isopropyl alcohol (*8*, *9*).

Knowledge of even approximate values of rate constants for HO· radical reactions with the organic reactants and products in this multistep process is of practical utility in planning for the most efficient use of expensive oxidant. For example, oxidation of IMP to MPA is rapid and efficient compared with further oxidation of MPA because the most reactive species is IMP and all the products, MPA, acetone, and acetic acid, are equally unreactive. These results show that $H_2O_2$ can be used with UV light and oxygen to oxidize large amounts of even very unreactive compounds rapidly at 25 °C in water.

## *Experimental*

**Materials.** Methylphosphonic acid was supplied by J. Epstein of Edgewood Arsenal and by R. Swidler of SRI, who had prepared it by acid hydrolysis of commercial dimethyl methylphosphonic acid. The 99+% pure acid was then recrystallized from acetonitrile. Sodium methylphosphonic acid was prepared either as a 2.0 M solution by neutralization or as the dry salt. Sodium isopropyl methylphosphonate was supplied by J. Epstein and used without further purification.

**Oxidation of MPA and MP.** Solutions of MPA and IMP sodium salts were made up in distilled water; 30% $H_2O_2$ was added in amounts needed to obtain the desired final concentrations of sodium salts and $H_2O_2$.

Photooxidations were carried out in 26 mm × 28 cm quartz tubes. Approximately 4 mL of the desired reaction mixture of MPA or IMP and $H_2O_2$ was added to each tube. The tube was flushed with oxygen for 3 min and stoppered with a serum cap, which was slashed to vent any pressure by the formation of oxygen and $CO_2$. Three tubes were clamped to the shaft of a stirring motor, which was mounted so that shaft and tubes rotated almost horizontally. The center of the shaft was 13 cm from the center of a Hanovia 450-W mercury arc lamp, Model 79A10, mounted horizontally and water cooled by a quartz condenser. The lamp was warmed up for 5 min before exposing the tubes, after which the tubes were rotated at approximately 60 rpm for the desired time while exposed to the light.

For gas analysis, quartz tubes fitted with break seals and filled on the vacuum line were used in the same way.

**Analysis of MPA and IMP Reaction Mixtures.** The aqueous reaction solutions containing MPA or IMP were analyzed directly by $^1H$ NMR using a Varian 100-MHz spectrometer. The large solvent peak ($H_2O$) did not interfere with peaks from MPA, IMP, acetic acid, or acetone, and no other peaks were found when solutions were scanned from 0 to 20 ppm. Solutions were made basic (pH 8) before analysis.

MPA was analyzed to ±5% precision using NMR by comparing the peak height of one of the doublet methyl peaks at 1.03 and 1.30 ppm from $Me_4Si$ with standard solutions of MPA. Analysis of IMP was more difficult and less accurate (±15% precision) because of the complex methyl multiplet. $^{31}P$ NMR spectra were taken on a Varian spectrometer operating at 40.5 MHz (Fourier transform) using 12 mm o.d. tubes.

Gas analyses on reaction mixtures were done using a vacuum line Toepler pump and furance system described in detail elsewhere (*12*).

## *Acknowledgment*

The referees made several comments that materially improved the clarity of this paper.

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# Acid Precipitation in the New York Metropolitan Area: Its Relationship to Meteorological Factors

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■ A study which examined the spatial, meteorological, and seasonal factors associated with precipitation pH in the New York Metropolitan Area has been completed. From 1975 through 1977, 72 events were studied. Among the eight sites in the study, there was some site-to-site variability. The mean pH was 4.28 and the lowest seasonal values occurred during the summertime. The storms were classified according to type for each event, and showers and thundershowers associated with cold fronts and air masses yielded the lowest pHs of 4.17 and 3.91, respectively. Closed low-pressure systems produced somewhat higher values. Air parcel trajectory analyses showed that these air mass and frontal storms were generally associated with winds from the west and southwest. These are the directions from which high emissions in the Northeast have their greatest impact on the New York Metropolitan Area.

The increasing acidity of precipitation in the northeastern United States has been documented by Likens (*1–4*), who reported a mean pH on the order of 4.0. The effects of this acidity have resulted in fish kills (*4–6*) and increased stress on vegetative systems (*7–9*). In certain types of soils, increased hydrogen ion concentrations have enhanced the leaching of heavy metals and calcium into surface and ground waters (*10*).

The acidity of precipitation is related to the presence of atmospheric pollutants, particularly sulfates and nitrates (*1*). Evidence has been presented which indicates that long-range transport of these pollutants, particularly sulfates, is a more important factor than locally generated pollutants in the northeastern U.S. (*1, 10, 11*).

The purposes of the study reported in this paper are twofold: to characterize the spatial and seasonal variations in precipitation pH in the most highly populated area of the northeastern U.S., the New York Metropolitan Area, and to examine the relationship between synoptic scale meteorological factors and precipitation pH. During 1975–1976, samples were obtained from 72 individual storms at 8 sites shown in Figure 1. The site-to-site relationships, seasonal variations, effects of storm type, and wind direction are discussed. In addition, the relationships between pH and the path of air parcel trajectories arriving in New York City during precipitation events are examined.

## *Experimental*

Prior to the onset of a precipitation event, clean plastic buckets were placed outdoors in locations which were 2–50 ft above the surface. In most cases, this was approximately 0–2 h before or after the event began. Once the event terminated, the rain samples were transferred to Nalgene or glass screw-capped bottles which had been thoroughly cleaned and rinsed with distilled water and then dried. The interval between this transfer varied considerably, from a few minutes to as much as 8 h if the precipitation ended during the night.

Snow was collected in the same manner, then covered with plastic wrap and allowed to melt in the bucket. The melted samples were then transferred to the Nalgene or glass bottles.

All samples were kept under refrigeration until they were analyzed the next day. Weekend samples were analyzed on Monday. The pH was determined with a Corning pH meter (Model 10) after the samples were allowed to reach room temperature. The instrument was standardized with certified buffer solutions of pH 4.0–7.0. In cases where the pH of the sample was less than 4.0, the instrument was restandardized with a buffer solution of pH 3.0.

## *Results*

**Site-to-Site Variations.** The mean pH values at each site are shown in Table I. The mean values were calculated using the average hydrogen ion concentrations and weighted according to the amount of precipitation per storm.

The distribution of the weighted hydrogen ion concentrations for individual sites was log normal. The standard deviations of the hydrogen ion concentration are expressed as pH values and they are shown in Table I. The standard deviation for the individual sites ranged between 0.20 and 0.37.

The mean pH for all sites was 4.28 with the mean pH for individual sites ranging from 4.25 to 4.64. In New Jersey and at adjacent sites in New York (Bronx and Manhattan), the variation of the means (4.25–4.34) was much smaller. To the east and northeast of the city, in Port Chester and Queens, the pH values were considerably higher.

The frequency distributions for all sites which reported data for more than 50% of the storms are shown in Figure 2. All sites show a predominant number of the observed pH values between 4.0 and 4.74 with the range 4.25–4.49 being the most common.

**Seasonal Variations.** A pronounced seasonal variation is observed in Figure 3. At all sites except Manhattan, the minimum pH occurred during July–September while the maximum occurred during October–December. For all sites, the mean increase from summer to autumn was 0.41 pH unit. In Manhattan, however, the minimum pH occurred in January–March and gradually increased throughout the year.

**Effects of Storm Types.** Precipitation events were classified into eight categories which are shown in Table II. Types 1 through 4 are typical frontal type low-pressure systems with a well-defined center (i.e., closed isobars). Types 1 and 2 are distinguished by the area over which the cyclogenesis occurred. Continental low systems, type 1, originated somewhere over Continental North America. A type 2 storm has a maritime origin, either over the Gulf of Mexico or the Atlantic Ocean. Types 3 and 4 are distinguished by the storm path relative to New York City. A low-pressure system which passes to the north or west of the city (type 3) keeps the New York area in the warm sector of the storm and is generally accompanied by southeasterly winds. In type 4 storms, the city is in the cold sector of the storm which most frequently produces northeasterly winds across the Metropolitan Area as the storm passes to the south or east of the city. Types 5 through 7 are described in Table II. Type 8 includes storms which could not be classified into any of the first seven categories.

It appears that continental storms have a slightly lower pH

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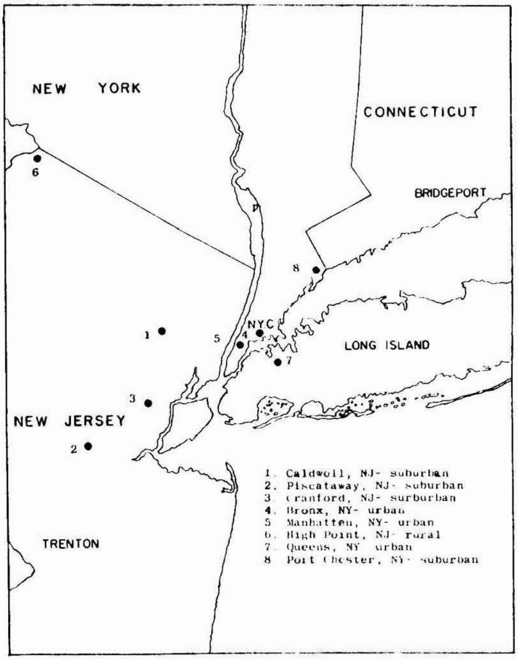

**Figure 1.** Sampling site locations for precipitation study

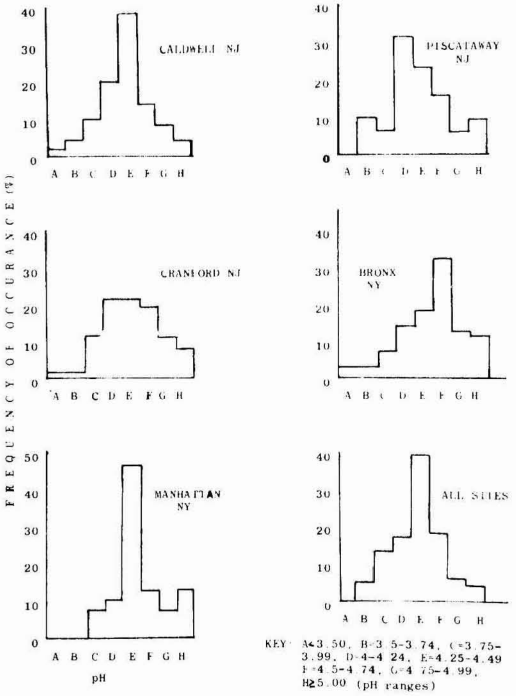

**Figure 2.** Distribution of pH values observed at each sampling site

than the maritime storms. The path of both types of storms, however, appeared to have no noticeable effect on the pH.

Lower pH values were observed during showers and thundershowers associated with cold fronts. The lowest pHs were observed during air mass type showers and thundershowers.

On August 9 and 10, 1976, the highest pH values recorded throughout the 2-year period were observed at most of the sites. This precipitation was the result of Hurricane Belle

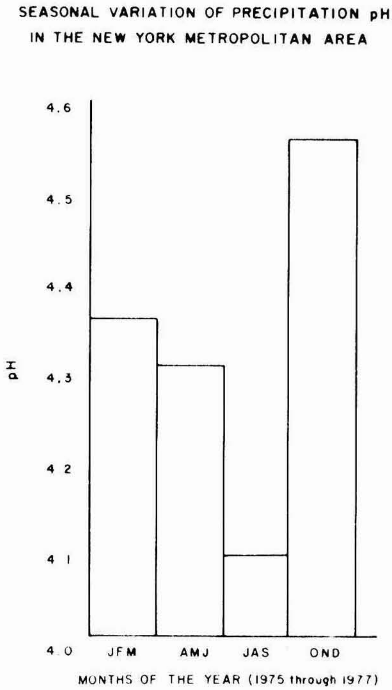

**Figure 3.** Seasonal variation of precipitation pH in the New York Metropolitan Area

### Table I. Mean pH Values in the New York Metropolitan Area (1975–1977)

| site | mean pH | SD | no. obsd | range |
|---|---|---|---|---|
| Caldwell, N.J. | 4.32 | 0.26 | 50 | 3.35–5.60 |
| Piscataway, N.J. | 4.25 | 0.36 | 64 | 3.57–5.50 |
| Cranford, N.J. | 4.34 | 0.34 | 48 | 3.44–5.95 |
| Bronx, N.Y. | 4.31 | 0.37 | 57 | 3.42–5.75 |
| Manhattan, N.Y. | 4.29 | 0.25 | 39 | 3.80–5.50 |
| High Point, N.J. | 4.25 | 0.30 | 25 | 3.74–4.90 |
| Queens, N.Y. | 4.63 | 0.35 | 20 | 3.98–5.28 |
| Port Chester, N.Y. | 4.60 | 0.19 | 21 | 4.00–5.10 |
| all sites | 4.28 | 0.32 | 72 | 3.50–5.16 |

### Table II. Storm Type Classification

| type | description of dominant storm system | no. obsd | mean pH |
|---|---|---|---|
| 1 | closed low-pressure system which formed over continental N. Amer. | 22 | 4.35 |
| 2 | closed low-pressure system which formed in Gulf of Mexico or over Atlantic Ocean | 21 | 4.43 |
| 3 | closed low which passed to W or N of N.Y.C. | 26 | 4.39 |
| 4 | closed low which passed to S or E of N.Y.C. | 17 | 4.39 |
| 5 | cold front in absence of closed low | 16 | 4.17 |
| 6 | air mass thunderstorm | 5 | 3.91 |
| 7 | Hurricane Belle | 1 | 5.16 |
| 8 | unclassified | 6 | 4.31 |

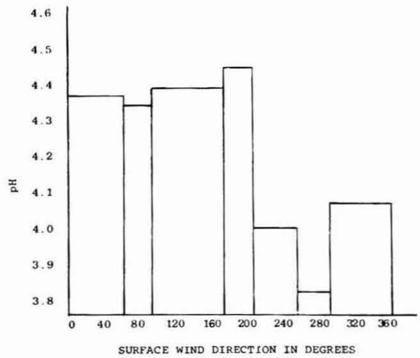

**Figure 4.** Mean pH values for all sites vs. wind direction

whose eye passed approximately 30 miles east of New York City.

**Effect of Surface Wind Direction.** The mean pH for all sites as a function of wind direction is shown in Figure 4. Wind direction was classified into seven categories which were selected on the basis of upwind sources. Before occurring in New York City, northeast winds traveled over New England, east winds over Long Island, southeast winds over the Atlantic Ocean, south winds over the Chesapeake and Delaware Bays, southwest over the Philadelphia–Camden area, west over central and northern Pennsylvania, and northwest over New York State.

The data indicate that the highest pHs occurred on northeast to south winds with the mean pH being 4.37. Lower pHs (mean 3.95) occurred on southwest to northwest winds. The lowest mean value, 3.82, occurred on westerly winds.

**Effects of Air Parcel Trajectory Path.** Using wind data from the National Weather Service's upper-air observation network, air parcel trajectories were calculated for the surface layer (here taken to be from 400 to 1400 m). The calculation procedures have been described elsewhere (*12*). Since trajectories which terminated in New York City were available every 6 h, the trajectory selected during any given storm was the one which best corresponded to the period of heaviest precipitation.

Trajectories for approximately 25% of the precipitation events were available and were plotted on a map of the northeastern U.S. The wind direction sector from which the air parcel approached the New York City area was analyzed and the results are summarized in Figure 5. Trajectories from southwest and west had the lowest pHs, while trajectories from the east and the north resulted in the highest pHs.

*Discussion*

Maximum pH values occur during the autumn months while the minimum values occur during the summer months. This should be expected if most of the acidity is due to sulfates. Two studies conducted in the northeastern U.S. have shown evidence of a summertime sulfate maxima and an autumn sulfate minima (*13, 14*). Under the influence of a high-pressure system, evidence has also been presented demonstrating the association of high atmospheric sulfate levels with the photochemical smog process (*15, 16*) which exhibits the same seasonal variation.

In addition to the higher summertime sulfate levels in the atmosphere, there is another factor which may contribute to the lower summertime pHs. The lowest pHs were associated with cold front and air mass type precipitation events. These occur much more frequently in the summer months. Of the 21 events of this type, 13 occurred during the summer months. In contrast, only one of the 43 types' 1 and 2 storms occurred during the summer.

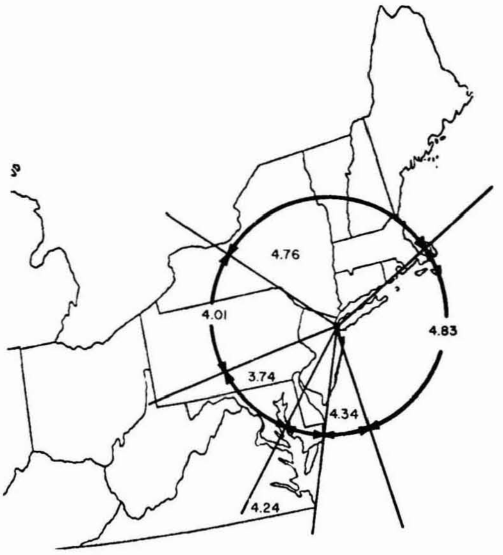

**Figure 5.** The variation in precipitation pH according to the sector from which an air parcel approached the New York Metropolitan Area.

It was also noted that lower pHs occurred on west or southwest winds. Of the ten events which occurred on southwest or west surface winds, six were associated with frontal or air mass type storms. In most cases examined by trajectory analysis, frontal or air mass type events were associated with southwest, west, or west northwest trajectories, while cyclonic events were associated with south or east trajectories.

Conditions which are most conducive for air mass type showers or thundershowers generally occur within the back side or return flow around a high-pressure system. This is also the part of the air mass which, in the summertime, experiences the highest concentrations of photochemically produced pollutants including sulfates (*15–18*). Precipitation associated with cold fronts generally occurs when the heavier cold air behind the front lifts the warmer less dense air preceding the front off the ground. This warmer air is generally the trailing edge of the backside of a high-pressure system. As a result, both the air mass and frontal type events occur generally in a polluted air mass.

All storms with southwesterly or westerly wind directions and/or trajectories produced lower pHs than those associated with other directions. This is probably due to accumulation of sulfur oxides, nitrogen oxides, and hydrocarbons from the high emission density areas which exist in the Midwest and Washington, D.C. to Boston, Mass. corridor (*12, 18*). Easterly trajectories are probably associated with high pHs for three reasons. The first is the influence of the maritime environment. Aerosolized sea salt would tend to neutralize the acidity. This was dramatically illustrated during Hurricane Belle which produced the highest observed pHs. The second is the fact that trajectories traveling over the ocean have less opportunity to travel over high pollutant emission density areas. In addition, these storms have lifetimes on the order of days, while the air mass and frontal types have lifetimes on the order of hours. Since the highest rates of pollutant scavenging occur at the onset of the precipitation, short-lived storms contain more acidic pollutants.

### Limitations

In the study, a number of procedures were used to minimize errors which could arise from sampling and storage. Sampling buckets were placed out as close to the onset of the precipitation event as possible. This reduced and in many cases eliminated the dry deposition of material into the collector. Similarly, the samples were removed from the bucket as soon as possible after the event terminated.

Stored samples were refrigerated to reduce any chemical or biological activity which might have altered the pH.

There was no apparent relationship between the pH and the length of time (up to 72 h) the samples were stored. Therefore, the authors think no significant changes occurred in the pH during storage.

After approximately a dozen events, samples were split and half were stored in Nalgene bottles and half in glass bottles. The mean difference between the two was less than ±0.01 pH unit.

Another source of error was the deposition of leaves, insects, and soot in the collector during the event. These samples were included in the analysis only if the difference between the pH of the contaminated sample and the mean pH of the samples collected at the other sites during the same event was less than 1.00 pH unit.

### Conclusions

The mean pH of precipitation falling on the New York Metropolitan Area during the 2-year study was 4.28. The lowest mean pH occurred during the summer months and this was 4.12.

Precipitation events associated with cold fronts and air mass type showers and thundershowers produced the lowest mean pHs of 4.17 and 3.91, respectively. Both storm types were generally associated with the back side of a polluted high-pressure system.

Well-defined low-pressure systems which affected the New York Metropolitan Area resulted in mean precipitation pHs of about 4.40. Since these storms are generally accompanied by easterly winds off the Atlantic Ocean, the air parcels have less opportunity to accumulate pollutants from high pollutant emission density areas than the air mass and frontal storms. The latter are generally associated with west or southwest winds which passed over polluted areas in the Midwest and Washington, D.C. to Boston, Mass. corridor. In addition, frontal and air mass type storms generally have a lifetime on the order of hours, while low-pressure systems exist for days. Since scavenging of pollutants by the precipitation would be more pronounced during the initial phase of the storm, the longer the lifetime of the event, the less polluted the ambient air.

### Acknowledgments

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# Toxicity of Copper to Cutthroat Trout (*Salmo clarki*) under Different Conditions of Alkalinity, pH, and Hardness

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■ Median lethal concentration (96-h $LC_{50}$) values for acute copper toxicity to 3–10-g cutthroat trout (*Salmo clarki*) have been determined for nine different combinations of alkalinity, hardness, and pH. Equilibrium calculations were performed on the copper $LC_{50}$ values; seven different soluble species of copper were considered: $Cu^{2+}$, $CuOH^+$, $Cu(OH)_2{}^0$, $Cu_2(OH)_2{}^{2+}$, $CuHCO_3{}^+$, $CuCO_3{}^0$, and $Cu(CO_3)_2{}^{2-}$. The acute toxicity of copper was inversely correlated with water hardness and alkalinity. At a given alkalinity, hardness determined the $LC_{50}$; at a given hardness, alkalinity determined the $LC_{50}$. At a given alkalinity and hardness, the concentrations of the copper species were determined by the pH of the water. Under the conditions tested, $Cu^{2+}$, $CuOH^+$, $Cu(OH)_2{}^0$, and $Cu_2(OH)_2{}^{2+}$ were toxic forms of copper to cutthroat trout; $CuHCO_3{}^+$, $CuCO_3{}^0$, and $Cu(CO_3)_2{}^{2-}$ were not toxic. Results of 11 96-h copper toxicity bioassays on 1- to 26-g rainbow trout (*Salmo gairdneri*) under uniform water chemistry conditions are also reported.

A variety of environmental factors influence the toxicity of copper to fishes (*1, 2*). Among these factors are pH, hardness, alkalinity, and inorganic and organic complexation. The work of several investigators (*3–9*) indicates that organically bound copper is nontoxic and copper toxicity decreases as the copper(II) ion is chelated. Consequently, the toxicity of copper to fishes is attributed to the inorganic forms of copper.

It is now recognized, as noted by Lloyd and Herbert (*10*), that copper is more toxic in soft water than it is in hard water. Alkalinity and hardness are usually directly related. Stiff (*11*) hypothesized that if copper(II) ion were the toxic form of copper and if the copper carbonate complex, noted by Scaife (*12*), were relatively nontoxic, then the difference in toxicity of copper between soft and hard water would be related to the difference in alkalinity, rather than the hardness, present in those waters. In support of this, Andrew (*13*) stated that bicarbonate alkalinity has a major role in limiting copper toxicity in natural waters. Alkalinity is directly related to pH (*14*); because a relationship can be established between alkalinity and the copper(II) ion activity, pH is also related to the copper(II) ion activity.

Although it is generally accepted that the copper(II) ion is toxic to fishes, it is not the only toxic form of copper. Shaw and Brown (*9*) concluded that $Cu^{2+}$ and $CuCO_3{}^0$ are the toxic forms of copper to rainbow trout (*Salmo gairdneri*). Pagenkopf et al. (*15*) reported that $Cu^{2+}$ is toxic and $CuOH^+$ may be toxic. Andrew (*13*) stated that toxicity is directly related to the ionic activity of the cupric ion and not to its inorganic complexes. However, in a more recent study (on *Daphnia magna*), Andrew et al. (*16*) state that copper toxicity is directly related to activities of $Cu^{2+}$, $CuOH^+$, and $Cu_2(OH)_2{}^{2+}$. Howarth and Sprague (*17*), in work on rainbow trout, also concluded that $Cu^{2+}$, $CuOH^+$, and $Cu_2(OH)_2{}^{2+}$ are toxic.

Stiff (*18*) applied an analytical scheme to differentiate the chemical states of copper into $Cu^{2+}$,$CuCO_3{}^0$, and Cu(organic). Mancy and Allen (*19*) developed a mathematic model to dedetermine the concentration of each species in the copper–carbonate system. Various computer programs (*20, 21*) are available for evaluation of the equilibrium relationships to predict the speciation of metals in aqueous systems.

This paper reports on a series of bioassays on the toxicity of copper to cutthroat trout (*Salmo clarki*) under different conditions of alkalinity, hardness, and pH; no copper toxicity studies have previously been reported for this species.

## *Experimental*

Nine acute copper toxicity flow-through bioassays on cutthroat trout were conducted at the Montana State University Fisheries Bioassay Laboratory, located at the Bozeman (Montana) Fish Cultural Development Center (FCDC), U.S. Fish and Wildlife Service. Test fish, obtained from FCDC, were a west slope strain reported to be free from any possible hybridization. The source of water for the bioassays was a natural groundwater spring located at FCDC. This water had a hardness of ~200 mg/L as $CaCO_3$, alkalinity of ~175 mg/L as $CaCO_3$, and no other appreciable constituents (Table I). To reduce the hardness and/or alkalinity this water was first passed through cation and/or anion exchange resin columns (Culligan Water Conditioning Co., CH-1 and CS-2), and then mixed with untreated spring water to achieve the desired hardness and alkalinity for each test. In tests in which either hardness or alkalinity were to be increased to levels over those of the mixtures, reagent grade calcium chloride or sodium bicarbonate was added with capillary flow meters or fluid metering pumps. Bioassays were conducted in nine different water combinations (Table II) in a 3 × 3 experimental design with three concentrations (high, medium, and low) each of alkalinity and hardness similar to the classification developed by the U.S. Geological Survey (*22*).

Reagent grade copper(II) chloride in demineralized water acidified with concentrated hydrochloric acid was used as the toxicant. The test solution was delivered by a proportional diluter (dilution factor = 0.75) having the basic design of Mount and Brungs (*23*) at a flow rate of 500 mL every 2–3 min to each of six copolymer plastic tanks: five test and one control. The water volume of each tank was 62 L.

Copper concentrations in test tanks were determined according to the cuprethol method (*24*) using 10-cm cells. Copper was measured on nonfiltered samples; however, a series of copper analyses was conducted on 0.45-$\mu$m filtered and nonfiltered samples of the test waters used in the bioassays. From these analyses appropriate factors (Table III) were obtained so that the concentrations of copper measured on nonfiltered samples could be converted to dissolved copper as defined by the 0.45-$\mu$m filter.

Total alkalinity was determined as in "Standard Methods for the Examination of Water and Wastewater" (*25*) with methyl purple as the indicator. Total hardness (EDTA), calcium (EDTA), nitrate nitrogen, and ammonia nitrogen were determined according to analytical procedures described in "Standard Methods" (*25*). Nitrite nitrogen was determined according to the U.S. EPA (*26*). Magnesium was calculated from total hardness and calcium hardness (*25*). Dissolved oxygen was measured using a Y.S.I. Model 54 meter, temperature with a calibrated mercury thermometer, and pH with a Beckman Phasar-I digital meter. Colorimetric measure-

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### Table I. Chemical Characteristics of the Untreated Dilution Water Used in Bioassays [a]

| | | | |
|---|---|---|---|
| alkalinity, as $CaCO_3$ | 176 | Ca | 53 |
| hardness, as $CaCO_3$ | 199 | Mg | 36 |
| pH | 8.0 | Na | 4.0 |
| temp, °C | 9.8 | K | 0.64 |
| | | Al | <1 |
| sp equiv conductance, µmho/cm, 25 °C | 328 | As, µg/L | 1.5 |
| total org C | 3.3 | Cd | <0.005 |
| turbidity, NTU | 1.7 | Cr | <0.005 |
| $NH_3$-N | 0.00 | Cu | 0.008 |
| $NO_2$-N | 0.00 | Fe | 0.03 |
| $NO_3$-N | 0.23 | Hg, µg/L | <0.05 |
| $Cl^-$ | 0.44 | Mn | 0.003 |
| $F^-$ | 0.4 | Ni | <0.005 |
| $PO_4{}^{3-}$ | <0.1 | Pb | <0.01 |
| $SO_4{}^{2-}$ | 10.0 | Se, µg/L | 0.8 |
| | | Zn | 0.01 |

[a] All values in milligrams/liter unless otherwise noted.

ments were made using a Varian Model 635 ultraviolet–visible spectrophotometer. Organic constituents were not detected when measuring nitrate nitrogen at 275 nm.

A chemical profile of the untreated dilution water is presented in Table I. For each 96-h bioassay, each tank was monitored on an average of 3 times for copper, 5 times for pH, alkalinity, and hardness, and 2 times for calcium, dissolved oxygen, temperature, ammonia nitrogen, nitrate nitrogen, and nitrite nitrogen. A summary of test tank water chemistry data is given in Table II.

Sixty fish were used for each test, 10 per tank. Fish were acclimated to the dilution water in the test tanks for 2–3 days before introduction of toxicant. Prior to the tests, fish were fed a commercial salmon ration three times daily, but were not fed during the acclimation or test periods. Fish were weighed collectively at the beginning of each test and were measured individually for total length as mortalities were observed or at the conclusion of each test. Fish mortalities, as evidenced by complete immobilization and lack of respiration, were recorded at 4-h intervals for the first 36 h and at 12-h intervals thereafter.

The median lethal concentration ($LC_{50}$) values and their 95% confidence intervals were calculated from the experimental data using a computer program developed for the trimmed Spearman–Karber method (27); toxicity curves were computer-generated using $LC_{50}$ and time values from each time of mortality observation.

Speciation of the $LC_{50}$ copper values was accomplished using the computer program COMICS (20). This program handles only homogeneous equilibria in solution and was considered adequate within the copper concentration and pH range of these bioassays. The copper species selected as being most important were $Cu^{2+}$, $CuOH^+$, $Cu(OH)_2{}^0$, $Cu_2(OH)_2{}^{2+}$, $CuHCO_3{}^+$, $CuCO_3{}^0$, and $Cu(CO_3)_2{}^{2-}$. The chemical equilibria considered in these calculations are presented in Table IV. The ionic strength calculated for the most concentrated test

### Table II. Water Chemistry Conditions for Acute Copper Bioassays on Cutthroat Trout

| | high alkalinity | | | medium alkalinity | | | low alkalinity | | |
|---|---|---|---|---|---|---|---|---|---|
| hardness/alkalinity [a] | H/H | M/H | L/H | H/M | M/M | L/M | H/L | M/L | L/L |
| test no. | 391 | 378 | 453 | 412 | 370 | 379 | 424 | 413 | 425 |
| total hardness, mg/L $CaCO_3$ | | | | | | | | | |
| av | 205 | 69.9 | 18.0 | 204 | 83 | 31.4 | 160 | 74.3 | 26.4 |
| (range) | (202–208) | (66.0–75.0) | (15.0–25.4) | (165–224) | (80–88) | (30.0–34.0) | (128–190) | (50.4–96.2) | (23.0–30.0) |
| total alkalinity, mg/L $CaCO_3$ | | | | | | | | | |
| av | 178 | 174 | 183 | 77.9 | 70 | 78.3 | 26.0 | 22.7 | 20.1 |
| (range) | (173–188) | (142–222) | (150–270) | (74.4–80.0) | (66–72) | (58.0–114) | (24.6–28.0) | (21.0–24.6) | (19.0–20.4) |
| pH | | | | | | | | | |
| av | 7.73 | 8.54 | 8.07 | 7.61 | 7.40 | 8.32 | 7.53 | 7.57 | 7.64 |
| (range) | (7.69–7.77) | (8.27–8.77) | (7.62–8.65) | (7.50–7.78) | (6.60–7.70) | (8.22–8.57) | (7.32–7.60) | (7.39–7.76) | (7.38–7.79) |
| total Ca, mg/L | | | | | | | | | |
| av | 49.8 | 18.4 | 4.8 | 64.7 | 20.4 | 7.9 | 57.5 | 24.7 | 6.0 |
| (range) | (48.1–50.5) | (17.0–20.1) | (4.1–5.6) | (51.7–72.6) | (19.6–22.5) | (7.2–8.9) | (45.1–67.0) | (17.2–32.5) | (5.6–6.5) |
| total Mg, mg/L | | | | | | | | | |
| av (calcd) | 19.6 | 5.8 | 1.5 | 10.3 | 7.8 | 2.7 | 4.0 | 3.1 | 2.8 |

[a] H = high, M = medium, L = low. Other parameters (averages and ranges over all bioassays): dissolved oxygen, 7.7 (6.7–8.9) mg/L; temperature, 13.7 (12.3–15.7) °C; ammonia nitrogen, 0.05 (0.00–0.17) mg/L; nitrate nitrogen, 0.05 (0.00–0.20) mg/L; nitrite nitrogen, all values 0.00 mg/L.

### Table III. Multiplication Factors for Conversion of Nonfiltered to 0.45-µm Filtered Copper Concentrations as Measured by the Cuprethol Method

| hardness/alkalinity [a] | H/H | M/H | L/H | H/M | M/M | L/M | H/L | M/L | L/L |
|---|---|---|---|---|---|---|---|---|---|
| hardness, mg/L $CaCO_3$ | 195 | 70 | 25 | 192 | 83 | 31 | 154 | 74 | 27 |
| alkalinity, mg/L $CaCO_3$ | 160 | 174 | 169 | 72 | 70 | 78 | 20 | 23 | 20 |
| pH | 7.0 | 8.5 | 8.5 | 7.0 | 7.4 | 8.3 | 6.8 | 7.6 | 7.0 |
| unfiltered Cu concns, mg/L | 0.34–1.28 | 0.11–0.40 | 0.01–0.08 | 0.12–0.23 | 0.04–0.28 | 0.02–0.16 | 0.04–0.16 | 0.03–0.11 | 0.01–0.03 |
| factor | 0.92 | 0.94 | 0.89 | 0.82 | 0.87 | 0.86 | 0.78 | 0.79 | 0.74 |

[a] H = high, M = medium, L = low.

## Table IV. Equilibria for Copper Test Water Solutions (*28*)

| reaction | log $K_{eq}$ [a] |
|---|---|
| $H^+ + OH^- \rightleftarrows H_2O$ | 14.0 |
| $H^+ + CO_3^{2-} \rightleftarrows HCO_3^-$ ($K_2$) | 10.33 |
| $2H^+ + CO_3^{2-} \rightleftarrows H_2CO_3$ ($K_1 + K_2$) | 16.68 |
| $Ca^{2+} + H_2O \rightleftarrows CaOH^+ + H^+$ | −12.7 |
| $Ca^{2+} + H^+ + CO_3^{2-} \rightleftarrows CaHCO_3^+$ ($1.0 + K_2$) | 11.33 |
| $Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_3^0$ | 3.15 |
| $Mg^{2+} + H_2O \rightleftarrows MgOH^+ + H^+$ | −11.42 |
| $Mg^{2+} + H^+ + CO_3^{2-} \rightleftarrows MgHCO_3^+$ ($0.95 + K_2$) | 11.28 |
| $Mg^{2+} + CO_3^{2-} \rightleftarrows MgCO_3^0$ | 2.88 |
| $Cu^{2+} + H_2O \rightleftarrows CuOH^+ + H^+$ | −7.7 |
| $Cu^{2+} + 2H_2O \rightleftarrows Cu(OH)_2^0 + 2H^+$ | −14.32 [b] |
| $2Cu^{2+} + 2H_2O \rightleftarrows Cu_2(OH)_2^{2+} + 2H^+$ | −10.3 |
| $Cu^{2+} + H^+ + CO_3^{2-} \rightleftarrows CuHCO_3^+$ | 12.3 [c] |
| $Cu^{2+} + CO_3^{2-} \rightleftarrows CuCO_3^0$ | 6.75 |
| $Cu^{2+} + 2CO_3^{2-} \rightleftarrows Cu(CO_3)_2^{2-}$ | 9.92 |

[a] Constants determined at 18–25 °C and corrected to zero ionic strength. [b] Constant from Vuceta and Morgan (*29*). [c] Constant from Childs (*30*).

## Table V. Acute Copper Toxicity to Cutthroat Trout under Different Conditions of Alkalinity and Hardness (10 Fish/Tank)

| test no. | fish size: wt, g | fish size: length, cm | alkalinity | hardness | 96-h $LC_{50}$ (95% C.I.), mg/L $Cu_{total}$ [a] |
|---|---|---|---|---|---|
| 391 | 4.2 | 7.4 | high | high | 0.367 (0.319–0.424) |
| 378 | 3.2 | 6.9 | high | medium | 0.186 (0.172–0.202) |
| 453 | 9.7 | 8.8 | high | low | 0.0368 (0.0350–0.0387) |
| 412 | 4.4 | 8.1 | medium | high | 0.232 |
| 370 | 2.7 | 6.8 | medium | medium | 0.162 (0.148–0.176) |
| 379 | 3.2 | 7.0 | medium | low | 0.0736 (0.0672–0.0805) |
| 424 | 5.2 | 8.5 | low | high | 0.0910 (0.0832–0.0996) |
| 413 | 4.4 | 7.7 | low | medium | 0.0444 (0.0403–0.0489) |
| 425 | 5.7 | 8.9 | low | low | 0.0157 |

[a] $Cu_{total}$ as measured by cuprethol on 0.45-μm filtrate.

## Table VI. Acute Copper Toxicity to Rainbow Trout of Different Sizes, under Uniform Water Chemistry Conditions [a]

| test no. | no. fish per tank | fish size: wt, g | fish size: length, cm | 96-h $LC_{50}$ (95% C.I.), mg/L $Cu_{total}$ [b] |
|---|---|---|---|---|
| 128 | 20 | 1 | | 0.169 (0.148–0.193) |
| 496 | 20 | | 4.9 | 0.0853 (0.0767–0.0950) |
| 403 | 10 | 2.1 | 6.0 | 0.0833 (0.0748–0.0928) |
| 503 | 20 | 2.5 | 6.1 | 0.103 (0.0961–0.111) |
| 169 | 20 | 2.6 | | 0.274 (0.222–0.337) |
| 136 | 20 | 4.3 | | 0.128 (0.101–0.162) |
| 141 | 20 | 9.4 | 9.2 | 0.221 (0.201–0.243) |
| 236 | 5 | 11.5 | 9.9 | 0.165 (0.137–0.198) |
| 233 | 5 | 18.7 | 11.8 | 0.197 (0.152–0.254) |
| 166 | 10 | 24.9 | 13.5 | 0.514 (0.434–0.610) |
| 160 | 10 | 25.6 | 13.4 | 0.243 (0.210–0.281) |

[a] Water chemistry data averaged over all tests (averages with ranges in parentheses): pH 7.84 (7.77–7.91); alkalinity, 174 (173–176) mg/L $CaCO_3$; hardness, 194 (192–196) mg/L $CaCO_3$; calcium, 55.1 (49.7–61.4) mg/L; magnesium (calculated), 13.7 mg/L; dissolved oxygen, 7.9 (5.6–9.6) mg/L; temperature, 12.8 (11.8–13.9) °C; ammonia nitrogen, 0.07 (0.00–0.27) mg/L; nitrate nitrogen, 0.12 (0.00–0.31) mg/L; nitrite nitrogen, all 0.00 mg/L. [b] $Cu_{total}$ as measured by cuprethol on 0.45-μm filtrate.

water was $5.38 \times 10^{-3}$ M. The equilibrium constant, log $K_2$, for the bicarbonate–carbonate system calculated with this correction is 10.20, as compared to the uncorrected value of 10.33. Considering the variability of equilibrium constants available in the literature, this difference was considered negligible and the equilibrium constants for the reactions presented in Table IV were used without correction. The other variables introduced into COMICS included pH and the molar concentrations of total inorganic carbon, calcium, and magnesium. Total inorganic carbon (moles/liter) was calculated from bicarbonate alkalinity and pH using the following equations:

$$[\text{inorganic C}] = \frac{[HCO_3^-]([H^+] + K_1)}{K_1}$$

$$[\text{inorganic C}] = \frac{[HCO_3^-]([H^+] + K_2)}{[H^+]}$$

### *Results and Discussion*

The 96-h $LC_{50}$ values and their 95% confidence interval (C.I.) end points for the bioassays are presented in Table V, and the toxicity curves for these bioassays are shown in Figure 1; $LC_{50}$ values for time periods other than 96 h can be estimated from these curves. The curves illustrate that the 96-h test period was sufficient to attain an asymptotic $LC_{50}$, also known as the incipient $LC_{50}$ (*31*).

Fish size data are also presented in Table V. Although the test fish were all obtained from the same pool, the tests were conducted over a 3-month period during which fish grew in size prior to testing. We have no data relating the susceptibility of cutthroat trout of different sizes to copper toxicity under uniform water chemistry conditions, but in 11 separate bioassays which were under uniform water chemistry conditions we have studied this relationship using 1- to 26-g rainbow trout as the test fish. These data are presented in Table VI. There was a small but significant effect on the susceptibility of the rainbow trout to copper toxicity based on fish size; the larger fish were slightly less susceptible than the smaller fish. The correlation coefficient for the relationship between fish weight and the observed $LC_{50}$ values was 0.68 ($P = 0.009$), and the equation of the regression line was $LC_{50} = (0.1266) \cdot (1.0374)^{\text{weight}}$. Howarth and Sprague (*17*) have recently reported that 10-g rainbow trout were 2.5 times more resistant to copper than 0.7-g trout. Considering the narrower range of fish weight (3–10 g) in our cutthroat trout bioassays (Table V), it was assumed that fish size in our experiments was not significantly related to susceptibility to copper toxicity.

The copper $LC_{50}$ values presented in Table V verify the long-standing observation that the toxicity of copper to fishes is inversely correlated with the hardness of water. Results of the COMICS equilibrium calculations using the copper 96-h $LC_{50}$ values (in molarity) are presented in Table VII, and percent distributions of the copper species are given in Table VIII. Hardness and alkalinity determined the magnitude of the copper $LC_{50}$ value. The estimated partial correlation between the copper $LC_{50}$ value and hardness, holding alkalinity fixed, is 0.882 (90% C.I. = 0.571–0.972); the estimated partial correlation between the copper $LC_{50}$ value and alkalinity, holding hardness fixed, is 0.756 (90% C.I. = 0.246–0.938). The effect of alkalinity on the $LC_{50}$ may be due in part to its effect on copper speciation, but cannot be explained entirely on this basis. Alkalinity and pH independently control the speciation of copper.

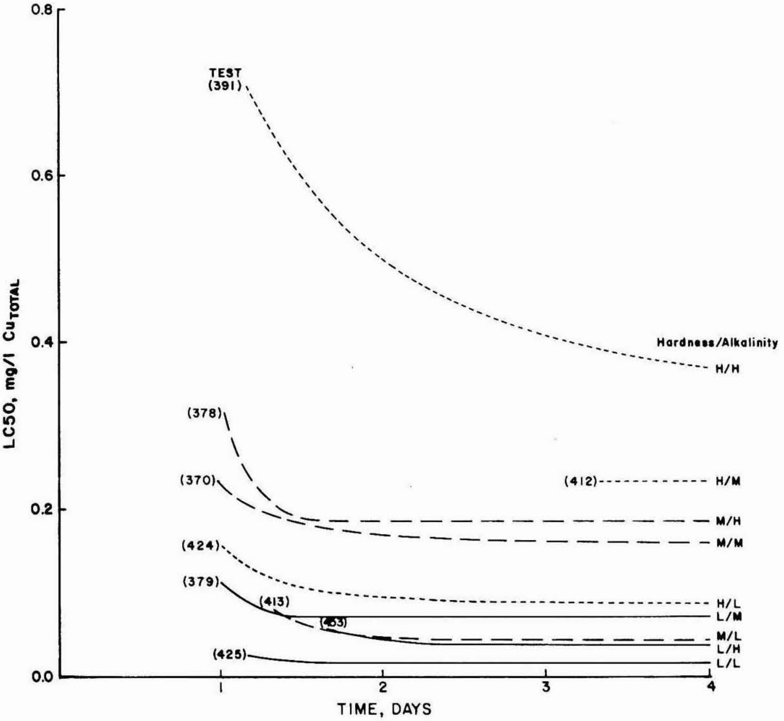

**Figure 1.** Toxicity curves for copper bioassays on cutthroat trout (H = high, M = medium, L = low)

## Table VII. Metal Speciation for Copper 96-h $LC_{50}$ Values for Cutthroat Trout (Concentrations in Moles/Liter)

| | hardness/alkalinity $^a$ and test no. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | H/H<br>391 | M/H<br>378 | L/H<br>453 | H/M<br>412 | M/M<br>370 | L/M<br>379 | H/L<br>424 | M/L<br>413 | L/L<br>425 |
| $Cu_T$ $^b$ (×$10^8$) | 578 | 293 | 57.9 | 365 | 255 | 116 | 143 | 69.9 | 24.7 |
| $Ca_T$ $^c$ (×$10^4$) | 12.4 | 4.59 | 1.20 | 16.1 | 5.09 | 1.97 | 14.3 | 6.16 | 1.50 |
| $Mg_T$ $^c$ (×$10^4$) | 8.07 | 2.39 | 0.617 | 4.24 | 3.21 | 1.11 | 1.65 | 1.28 | 1.15 |
| $HCO_3^-$ $^d$ (×$10^4$) | 35.6 | 34.8 | 36.6 | 15.6 | 14.0 | 15.7 | 5.20 | 4.54 | 4.02 |
| inorganic C (×$10^4$) | 37.1 | 35.4 | 37.3 | 16.4 | 15.2 | 15.9 | 5.54 | 4.81 | 4.23 |
| pH | 7.73 | 8.54 | 8.07 | 7.61 | 7.40 | 8.32 | 7.53 | 7.57 | 7.64 |
| $CO_3^{2-}$ (×$10^8$) | 871 | 5510 | 2000 | 289 | 162 | 1510 | 80.7 | 78.0 | 81.7 |
| $Ca^{2+}$ (×$10^8$) | 118 000 | 41 300 | 11 300 | 158 000 | 50 100 | 19 000 | 142 000 | 61 300 | 14 900 |
| $CaOH^+$ (×$10^8$) | 1.27 | 2.86 | 0.264 | 1.28 | 0.251 | 0.792 | 0.961 | 0.454 | 0.130 |
| $CaHCO_3^+$ (×$10^8$) | 4110 | 1400 | 409 | 2390 | 692 | 294 | 724 | 275 | 59.7 |
| $CaCO_3^0$ (×$10^8$) | 1460 | 3210 | 318 | 644 | 115 | 406 | 162 | 67.5 | 17.2 |
| $Mg^{2+}$ (×$10^8$) | 77 800 | 22 300 | 5890 | 41 700 | 31 700 | 10 800 | 16 400 | 12 700 | 11 500 |
| $MgOH^+$ (×$10^8$) | 15.9 | 29.4 | 2.63 | 6.46 | 3.02 | 8.59 | 2.11 | 1.80 | 1.90 |
| $MgHCO_3^+$ (×$10^8$) | 2400 | 675 | 191 | 563 | 390 | 149 | 74.5 | 51.0 | 40.9 |
| $MgCO_3^0$ (×$10^8$) | 514 | 931 | 89.1 | 91.4 | 39.0 | 124 | 10.0 | 7.54 | 7.10 |
| $Cu^{2+}$ (×$10^8$) | 8.78 | 0.319 | 0.313 | 13.9 | 18.5 | 0.385 | 12.1 | 5.47 | 1.58 |
| $CuOH^+$ (×$10^8$) | 9.41 | 2.21 | 0.733 | 11.3 | 9.26 | 1.61 | 8.21 | 4.05 | 1.38 |
| $Cu(OH)_2^0$ (×$10^8$) | 121 | 183 | 20.6 | 111 | 55.8 | 80.5 | 66.7 | 36.1 | 14.4 |
| $Cu_2(OH)_2^{2+}$ (×$10^8$) | 0.111 | 0.00612 | 0.000676 | 0.161 | 0.108 | 0.00324 | 0.0848 | 0.0207 | 0.00238 |
| $CuHCO_3^+$ (×$10^8$) | 2.84 | 0.101 | 0.106 | 1.97 | 2.38 | 0.0556 | 0.577 | 0.229 | 0.0590 |
| $CuCO_3^0$ (×$10^8$) | 430 | 98.8 | 35.1 | 226 | 169 | 32.8 | 55.1 | 24.0 | 7.26 |
| $Cu(CO_3)_2^{2-}$ (×$10^8$) | 5.54 | 8.06 | 1.03 | 0.964 | 0.404 | 0.733 | 0.0658 | 0.0277 | 0.00878 |

[a] H = high, M = medium, L = low. [b] $Cu_T = Cu_{total}$ as measured by cuprethol on 0.45-μm filtrate. [c] $Ca_T + Mg_T$ = hardness. [d] $HCO_3^-$ = alkalinity.

The most abundant forms of soluble copper over all the conditions tested were dissolved copper(II) carbonate, $CuCO_3^0$, and copper(II) hydroxide, $Cu(OH)_2^0$. The amount of copper(II) ion dramatically increased as the alkalinity and pH decreased, and a more subtle, but parallel, behavior was exhibited by $CuOH^+$ within the pH range tested. In contrast

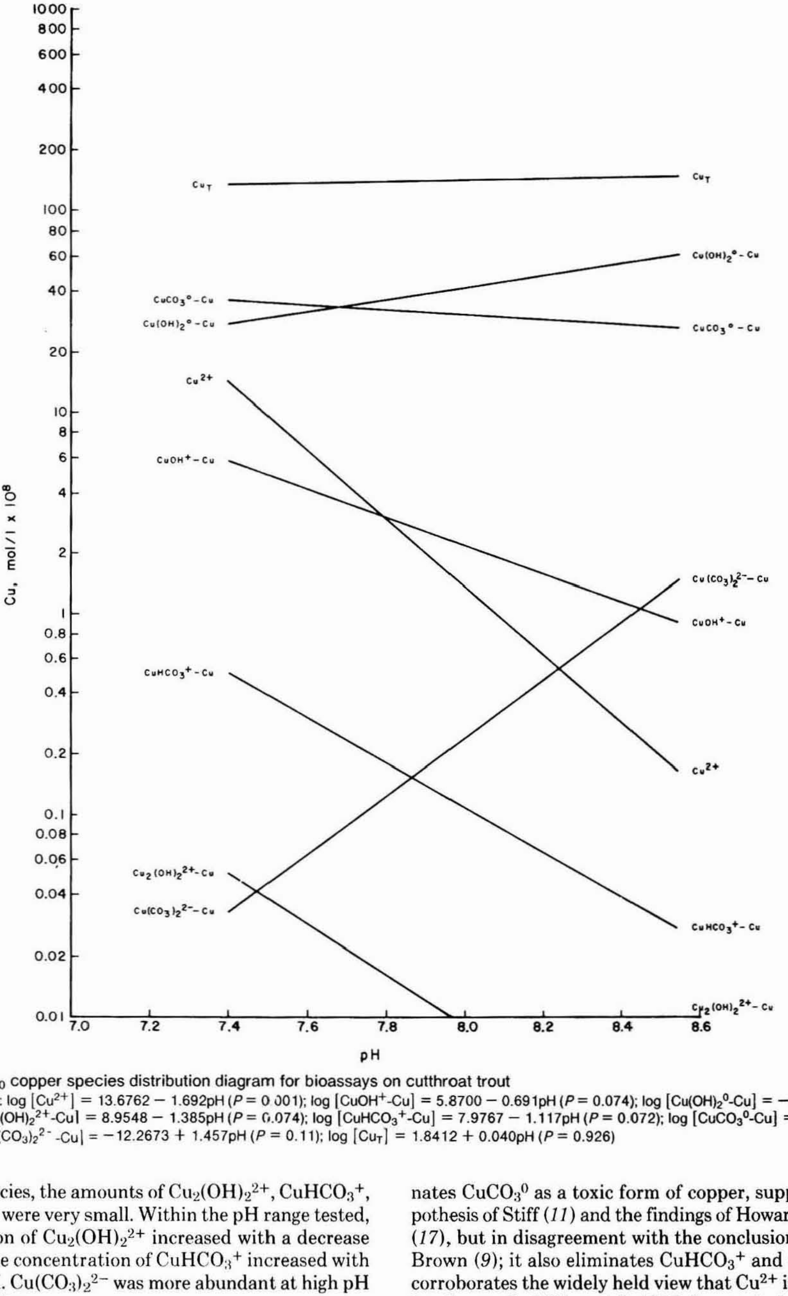

**Figure 2.** 96-h $LC_{50}$ copper species distribution diagram for bioassays on cutthroat trout

Regression equations: $\log [Cu^{2+}] = 13.6762 - 1.692pH$ ($P = 0.001$); $\log [CuOH^+\text{-}Cu] = 5.8700 - 0.691pH$ ($P = 0.074$); $\log [Cu(OH)_2{}^0\text{-}Cu] = -0.8204 + 0.307pH$ ($P = 0.384$); $\log [Cu_2(OH)_2{}^{2+}\text{-}Cu] = 8.9548 - 1.385pH$ ($P = 0.074$); $\log [CuHCO_3{}^+\text{-}Cu] = 7.9767 - 1.117pH$ ($P = 0.072$); $\log [CuCO_3{}^0\text{-}Cu] = 2.4379 - 0.118pH$ ($P = 0.830$); $\log [Cu(CO_3)_2{}^{2-}\text{-}Cu] = -12.2673 + 1.457pH$ ($P = 0.11$); $\log [Cu_T] = 1.8412 + 0.040pH$ ($P = 0.926$)

to these four species, the amounts of $Cu_2(OH)_2{}^{2+}$, $CuHCO_3{}^+$, and $Cu(CO_3)_2{}^{2-}$ were very small. Within the pH range tested, the concentration of $Cu_2(OH)_2{}^{2+}$ increased with a decrease in alkalinity. The concentration of $CuHCO_3{}^+$ increased with a decrease in pH. $Cu(CO_3)_2{}^{2-}$ was more abundant at high pH and high alkalinity.

Interpretation of the results of the experimental tests reported in this paper, along the above lines of reasoning which lead to prioritizing chemical species in order of relative toxicity, is constrained by the variation of pH among the tests conducted. However, pH was relatively constant in the three bioassays conducted at high hardness coupled with a high, medium, and low alkalinity (Table VIII: tests 391, 412, and 424). These data show that as the proportions of carbonate species decreased, the median lethal concentration of copper also decreased; as the proportions of $Cu^{2+}$ and the hydroxyl species increased, the $LC_{50}$ decreased. This behavior eliminates $CuCO_3{}^0$ as a toxic form of copper, supporting the hypothesis of Stiff (*11*) and the findings of Howarth and Sprague (*17*), but in disagreement with the conclusions of Shaw and Brown (*9*); it also eliminates $CuHCO_3{}^+$ and $Cu(CO_3)_2{}^{2-}$. It corroborates the widely held view that $Cu^{2+}$ is toxic and also implicates $CuOH^+$ and $Cu(OH)_2{}^0$ as toxic forms. The data indicate that $Cu_2(OH)_2{}^{2+}$ may also be toxic, as has recently been reported by Andrew et al. (*16*) and Howarth and Sprague (*17*); however, the concentration of $Cu_2(OH)_2{}^{2+}$ is two to four orders of magnitude smaller than $Cu^{2+}$, $CuOH^+$, and $Cu(OH)_2{}^0$, so its acute toxic effect may be negligible by comparison. The evidence from this study that $CuOH^+$ is toxic to fishes is in agreement with the conclusions of Pagenkopf et al. (*15*), Andrew et al. (*16*), and Howarth and Sprague (*17*). The present work further suggests that $Cu(OH)_2{}^0$ may also be toxic to fishes.

Examination of the data in Tables VII and VIII shows that

**Table VIII. Percent Distribution of Copper Species for 96-h $LC_{50}$ Values for Cutthroat Trout**

| | hardness/alkalinity [a] and test no. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | H/H | M/H | L/H | H/M | M/M | L/M | H/L | M/L | L/L |
| | 391 | 378 | 453 | 412 | 370 | 379 | 424 | 413 | 425 |
| $Cu_T$ [b] | 578 | 293 | 57.9 | 365 | 255 | 116 | 143 | 69.9 | 24.7 |
| alkalinity [c] | 178 | 174 | 183 | 77.9 | 70.0 | 78.3 | 26.0 | 22.7 | 20.1 |
| hardness [c] | 205 | 69.9 | 18.0 | 204 | 83.0 | 31.4 | 160 | 74.3 | 26.4 |
| pH | 7.73 | 8.54 | 8.07 | 7.61 | 7.40 | 8.32 | 7.53 | 7.57 | 7.64 |
| $Cu^{2+}$ | 1.5 | 0.1 | 0.5 | 3.8 | 7.2 | 0.3 | 8.5 | 7.8 | 6.4 |
| $CuOH^+$ | 1.6 | 0.8 | 1.3 | 3.1 | 3.6 | 1.4 | 5.7 | 5.8 | 5.6 |
| $Cu(OH)_2{}^0$ | 20.9 | 62.4 | 35.6 | 30.4 | 21.9 | 69.4 | 46.6 | 51.6 | 58.3 |
| $Cu_2(OH)_2{}^{2+}$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 |
| $CuHCO_3{}^+$ | 0.5 | 0.0 | 0.2 | 0.5 | 0.9 | 0.0 | 0.4 | 0.3 | 0.2 |
| $CuCO_3{}^0$ | 74.4 | 33.7 | 60.6 | 61.9 | 66.3 | 28.3 | 38.5 | 34.3 | 29.4 |
| $Cu(CO_3)_2{}^{2-}$ | 1.0 | 2.8 | 1.8 | 0.3 | 0.2 | 0.6 | 0.0 | 0.0 | 0.0 |

[a] H = high, M = medium, L = low. [b] $Cu_T$ = $Cu_{total}$ as measured by cuprethol on 0.45-μm filtrate; in moles/liter × $10^8$. [c] Alkalinity and hardness in milligrams/liter as $CaCO_3$.

(1) at constant alkalinity it is the pH that determines the relative distribution of $Cu^{2+}$, $CuOH^+$, and $Cu(OH)_2{}^0$; (2) at a constant pH, it is the alkalinity that determines the relative distribution of $Cu^{2+}$, $CuOH^+$, and $Cu(OH)_2{}^0$; (3) the highest concentrations of $Cu^{2+}$ and $CuOH^+$ occurred at the low pHs and low alkalinities; (4) the concentration of $Cu^{2+}$ is sensitive to changes in pH; (5) the percents of $Cu^{2+}$ and $CuOH^+$ are the same at pH 7.7; above pH 7.7 $CuOH^+$ is the predominant of those two species, whereas below pH 7.7 $Cu^{2+}$ predominates; and (6) the proportion of $Cu(OH)_2{}^0$ increases with increasing pH. To illustrate these observations in a more generalized manner, the data were used to construct the copper species distribution diagram shown in Figure 2. In this figure, the $LC_{50}$ concentrations for each test of the six copper species $CuOH^+$, $Cu(OH)_2{}^0$, $Cu_2(OH)_2{}^{2+}$, $CuHCO_3{}^+$, $CuCO_3{}^0$, and $Cu(CO_3)_2{}^{2-}$ are expressed as their concentrations of Cu; the sum total of these is the $LC_{50}$ as total dissolved copper.

In summary, hardness and alkalinity control the median lethal concentration of copper toxic to cutthroat trout. The most important copper species causing toxicity within the pH range tested are $Cu^{2+}$, $CuOH^+$, and $Cu(OH)_2{}^0$. The concentration of each of these species varies with pH and alkalinity. Lower pHs favor $Cu^{2+}$; higher pHs favor $CuOH^+$ and $Cu(OH)_2{}^0$. Lower alkalinities favor all three of these species.

It is concluded that the critical factors regarding copper toxicity to fishes are not so much which copper species are toxic, as are the controlling roles of hardness, alkalinity, and pH. To ensure the protection of aquatic life, it is recommended that consideration be given to establishing water quality criteria for copper not only on the measure of total copper, but also based on a stepwise scale dictated by the pH, hardness, and alkalinity of a given aquatic environment.

### *Note Added in Proof*

The constants used in these calculations were the best available in the literature. Recent unpublished data (W. G. Sunda, personal communication ,1978) raises some question concerning the formation constant for $Cu(OH)_2{}^0$. The calculations upon which the toxicity conclusions reported above are based have been redone using the alternate value for the formation constant for $Cu(OH)_2{}^0$. The effect of this is to reduce $Cu(OH)_2{}^0$ from a major to a minor species in the distribution of constituents, but the relative concentrations of all species, $Cu(OH)_2{}^0$ included, as a function of alkalinity, hardness, and pH, remain unchanged. Since the toxicity conclusions are based entirely upon trends in the concentrations of the various chemical species, these conclusions are valid regardless of which constant may ultimately prove to be correct. We wish to thank K. Emerson for assistance with recalculation of the data for comparison with our initial findings.

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# Chemical Speciation of Heavy Metals in Power Plant Ash Pond Leachate

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■ Soil attenuation of heavy metals from industrial leachates is dependent upon many factors. Data in this paper are based on field measurements from an active power plant fly ash disposal site and are organized via a thermodynamic approach which is facilitated by computer solutions to the equilibrium situation. Results for the site studied show that adsorption onto hydrous iron and manganese oxides is the major solubility control for cadmium, nickel, and zinc while precipitation of discrete phases controls for chromium, copper, and lead. The partitioning of heavy metals between solution and particulate phases is most affected by pH, p(FeOOH), p($MnO_x$), and p($SO_4^{2-}$).

The mobilization of undesirable materials into the environment through activities related to coal combustion has recently been given considerable attention (*1–4*). These materials include heavy metals, trace organic compounds (such as polynuclear aromatic hydrocarbons), large amounts of dissolved solids, and waste streams of extreme acidity or alkalinity. A pathway of some interest is leaching from fly ash and/or $SO_2$ scrubber sludge disposal sites. It has been shown that leachates from these areas can contain significant levels of heavy metals, sulfates, and total dissolved solids (*5*).

Once a leachate containing various substances enters the soil environment, it is desirable to know the types and extent of interaction which occur between leachate and soil particles, that is, the "natural attenuation capacity" of a specific soil component for a given leachate constituent. In the case of dissolved ions, these interactions will take the form of precipitation of a discrete solid phase or adsorption onto particle surfaces. Soluble complexes, if they are formed to an appreciable degree, will also affect these mechanisms.

In this study, data gathered from an active fly ash disposal pond will be presented and analyzed with the aid of a chemical equilibrium computer model so as to provide a realistic assessment of the subsurface reactions which various heavy metals have undergone since the initial construction of the facilities. Although the interactions among several soil and leachate components may be chemically rather complex, and are, of course, specific to the site studied, they are considered typical of the reactions which occur in a subsurface leaching zone. The site reported on here is viewed as representative of systems of generally wide environmental interest.

## *Site Description*

The site from which data were gathered is a 735-MW coal-fired power station located in a dunal area adjacent to Lake Michigan. There are two primary fly ash disposal ponds which are operated on an alternating basis, i.e., while one pond is being actively loaded the other is allowed to dry and the ash is removed and deposited elsewhere. A schematic diagram of the site is shown in Figure 1. Numbered circles refer to borings made as part of this study. This layout was constructed and put into operation in early 1974. Each pond has a capacity of approximately 62 000 $m^3$ (16.5 MG). Under normal operating conditions, the station produces between 310 and 360 metric tons/day (340–400 tons/day) of fly ash. This is sluiced to one of the ponds where it is allowed to settle. The normal hydraulic loading is 0.125 $m^3$/s (2.85 mgd). The supernatant is recycled with make-up water added to account for losses through evaporation and seepage. Calculations indicate a seepage rate of approximately 0.044 $m^3$/s (1 mgd).

The site is underlain by a well-drained dunal sand with an effective size of 0.18 mm and coefficient of uniformity of 1.5. The void ratio is approximately 0.5. The ponds are maintained at a constant head of 9.6 (31.5 ft) above the lake. The natural groundwater level is located 3 to 6 m (10–20 feet) beneath the ponds. The leachate zone drops quickly toward the lake but extends 150–200 m (500–650 ft) in the opposite direction. At this point (the approximate location of boring 13 for pond 1 in Figure 1) there is a confluence of pond leachate with natural groundwater and the flow returns toward the lake.

During the major portion of this study, only pond 1 was being actively loaded with ash; thus, much of the data pre-

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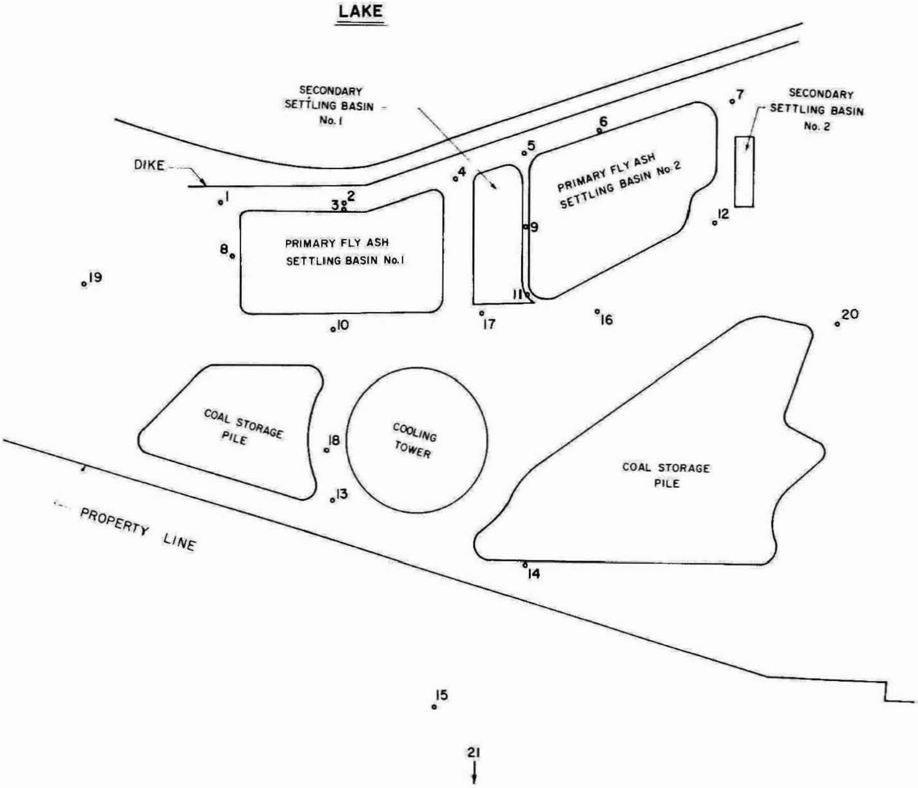

**Figure 1.** Layout of field study site; approximate scale, 4700:1

sented in this paper pertain to this area of the site. It should be noted that boring numbers 2, 3, 10, 18, 13, and 15 are located linearly along a flow path from pond 1, though boring 15 is located outside the leaching zone.

*Experimental Methods*

**Field.** A series of sampling wells was located at the positions of the borings in Figure 1 during the summer of 1976, about 2.5 years after initiation of disposal activities. Wells were located at depths of 1.5 to 2.5 m (5–8 ft) beneath the prevailing water table. Soil samples were taken at each 0.5-m interval although only samples at the groundwater interface were analyzed as part of this study. Samples for soluble metals were taken periodically.

**Laboratory.** Soil samples were analyzed for total heavy metals after a strong acid digestion by atomic absorption spectrophotometry (*6*). Other leachate constituents were determined by procedures outlined in "Standard Methods" (*7*). A more detailed account of both sampling and laboratory procedures can be found in previous references (*5, 8*).

**Computer Analysis.** Analysis of soil and leachate data was facilitated through application of the computer model REDEQL2 (*9*). It was assumed that equilibrium conditions are reasonable approximations for relatively slow moving groundwater systems over long time periods. The model is capable of thermodynamically speciating a chemical system given a set of input data. This includes complex formation, oxidation–reduction, precipitation–dissolution, and surface sorption reactions. The adsorption routine used was that of the solvent–ion interaction model which requires specification of specific chemical free energies of adsorption of a given sorbate–sorbent combination apart from coulombic or solvation effects (*10*). These were either determined in the laboratory, found in the literature, or estimated.

The general procedure for the application of the program was to input total concentrations of heavy metals and sorbing metal oxides plus the chemical composition of the leachate as determined analytically on soil fractions and well samples. In this manner, a present day assessment of the past contributions of various attenuation mechanisms at each boring could be made. The geometry of the borings around pond 1 provides a convenient distance parameter from which to determine the effects of changing soil and leachate properties.

*Results*

The power plant burned high sulfur coal mined in southern Illinois throughout the study period. This resulted in high sulfate concentrations in the fly ash pond leachate on the order of 500–1000 mg of $SO_4$/L. In contrast, alkalinities in the leaching zone were small, generally less than 10 mg/L as $CaCO_3$. A reversal of these concentration trends took place at the point of confluence of the leachate and the natural groundwater. Figure 2 gives a representative graphic presentation for heavy metal profiles. The peaks of many of the metals in Figure 2 occurred periodically and were shown to correlate with variations in ash loading to the pond. They represent chemical perturbations moving through the leaching zone (*5*).

An examination of the analyses from a typical volume of soil and water from the leaching zone (boring 18) reveals that less than 1% of the total for any metal exists in a soluble form, the rest being associated in some manner with the solid phase. These results are given in Table I. For a system such as this one in which soil accumulations of metals are a recent event,

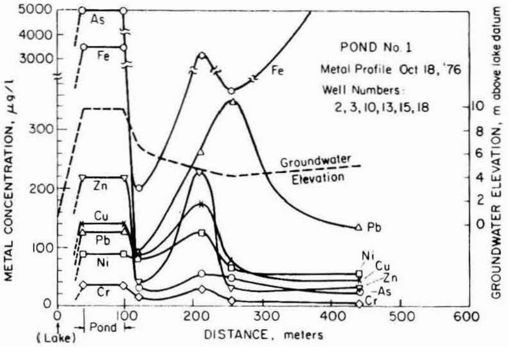

**Figure 2.** Trace metal profile vs. distance for Oct 18, 1976 (after Theis et al.; see ref *5*)

### Table I. Particulate and Soluble Metals in Soil–Water System at Michigan City [a]

| metal | particulate, μg/g | soluble, μg/g | % soluble [b] |
|---|---|---|---|
| As | 4.12 | 29 | 0.28 |
| Cd | 0.48 | 3.4 | 0.28 |
| Cr | 13.0 | 12.0 | 0.04 |
| Cu | 12.6 | 275 | 0.87 |
| Pb | 8.8 | 50 | 0.23 |
| Ni | 24.4 | 410 | 0.67 |
| Zn | 26.2 | 480 | 0.73 |

[a] Data for Oct 18, 1976 sampling date at well no. 18. Data for other wells and dates do not differ substantially. [b] Computed using an average void ratio of 0.5.

it is likely that they are present as a surface form which is chemically sensitive to even slight changes in solution chemistry. This could be expected to affect the partitioning of a metal between solution and solid phases.

In this study, the major sorbing sinks for heavy metals were assumed to be oxides of iron, manganese, and silica. The total amounts of iron and manganese found in the leaching field around pond 1 are given in Table II. In situ determinations of the oxide properties were not made; rather the representative values given in Table III for all three oxides were used. Combination of the information in Tables II and III yielded oxide data which were specific for the location of each boring in the leaching field. As indicated previously, adsorption data for each metal oxide combination apart from electrostatic and solvation effects ($\Delta G°_{chem}$) must be given. Values used in this study are given in Table IV.

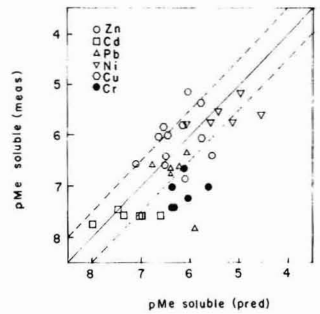

**Figure 3.** Total soluble metals measured in the field vs. total soluble predicted metals from calculation; data for Jan 4, 1977

### Table II. Total Iron and Manganese Values around Pond 1 (μg/g)

| boring | Fe | Mn |
|---|---|---|
| 2 | 2820 | 30.8 |
| 3 | 3360 | 41.1 |
| 10 | 1680 | 22.3 |
| 18 | 2470 | 36.2 |
| 13 | 2930 | 57.3 |
| 15 | 2690 | 52.1 |

### Table III. Oxide Properties Used in This Study [a]

| | ZPC | $\gamma_s$ [b] | $\epsilon$ [c] |
|---|---|---|---|
| α-FeOOH | 5.5 (*11*) | 85 (*11*) | 14 (*12*) |
| $MnO_x$ | 2.25 (*13*) | 280 (*14*) | 32 (*12*) |
| $SiO_2$ | 2.0 (*12*) | 0.013 (*11*) | 4.3 (*12*) |

[a] Numbers in italics in parentheses refer to references under Literature Cited. [b] Specific surface area, $m^2/g$. [c] Dielectric.

### Table IV. Specific Chemical Free Energies Used in This Study [a] (kcal/mol)

| | α-FeOOH | $MnO_x$ | $SiO_2$ |
|---|---|---|---|
| Cd | −6.0 (*15*) | −4.85 (*12*) | −6.54 (*13*) |
| Cr | −5.4 [b] | −4.85 (*12*) | −7.00 (*10*) |
| Cu | −5.4 [b] | −5.17 (*13*) | −7.98 (*12*) |
| Ni | −6.0 [b] | −4.25 (*13*) | −6.54 (*11*) |
| Pb | −5.4 [b] | −4.85 (*12*) | −6.50 (*12*) |
| Zn | −7.4 (*15*) | −4.85 (*13*) | −6.54 (13) |

[a] Italic numbers in parentheses refer to references under Literature Cited. [b] Estimated.

As a measure of the degree of correspondence between field and computer data, the total soluble measured metal concentrations were compared with those predicted. Results are given in Figure 3. Points falling within the dotted lines are within 0.5 log unit of the actual concentration. Points falling below the line indicate greater solubility predicted than measured. The modeling of chromium is seen to give results generally higher than measured. It is possible that the chemical free energy of adsorption for this metal onto iron oxide was underestimated, thus accounting for the discrepancy. It may, however, be due to a lack of agreement about the speciation of chromium. Modeling studies suggest that conditions favor the formation of appreciable amounts of soluble $Cr(OH)_4^-(aq)$. The formation of this species at the low concentrations of total Cr measured and neutral pH values is regarded as a slow reaction; thus, the equilibrium modeling of this metal may be limited by kinetic considerations. Most other points below the line of Figure 3 are predictions for boring 15 which was outside the leaching field. The soil chemistry characterization here is not considered as thorough as at other locations.

The computer-simulated speciation of specific metals as a function of distance is given in Figures 4a through 4d for chromium, copper, lead, and zinc, respectively. The results for cadmium and nickel were qualitatively similar to zinc. Leachate data for one sampling date were used; however, the speciation pattern changed very little for other sampling dates. For most metals free aquo and sulfato complexes are seen to dominate in the pond liquor. The hydroxo complex of chromium(III) is the major soluble form for this metal. When

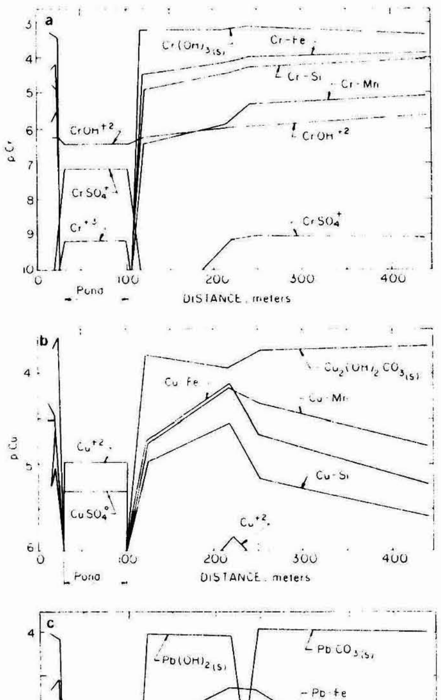

**Figure 4.** Metal speciation around pond no. 1 vs. distance: (a) chromium; (b) copper; (c) lead; (d) zinc

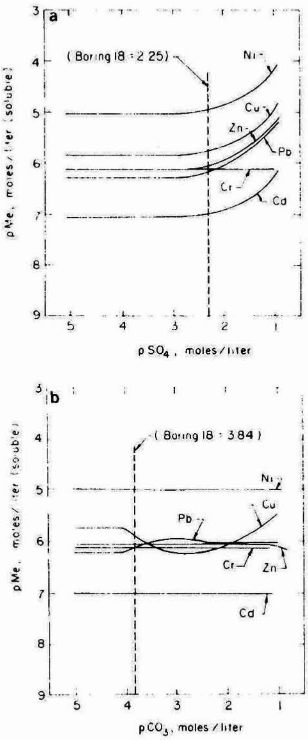

**Figure 5.** Predicted variation of total soluble metals with (a) sulfate and (b) carbonate as the determining parameter

the leachate stream enters the soil environment, several reactions occur. Zinc, cadmium, and nickel are attenuated predominantly by adsorption onto the iron oxide, manganese oxide playing a lesser role. In contrast, the solubilities of chromium, copper, and lead are controlled by discrete precipitates while adsorption is of diminished importance. Leachate conditions favor the formation of lead and chromium hydroxides in the immediate pond area. Copper precipitates as the basic carbonate, malachite, in spite of the low alkalinities. When inorganic carbon concentrations increase due to the presence of natural groundwater, the model predicts lead carbonate will form. In all cases, soluble metals are considerably lower than the solid phase concentrations in accord with the measurements given in Table I.

It is interesting to examine the effects which leachate and soil variables have on the soluble metals in solution. Figures 5a and 5b show predicted soluble metal concentration as a function of sulfate and carbonate in solution, respectively. Sulfate ion, $SO_4^{2-}$, forms weak complexes with all of the metals studied; however, since it is a common component of aqueous power plant waste streams, the effect of these complexes on attenuation in the soil should not be ignored. A typical sulfate concentration in the leaching field is indicated in Figure 5a. In this system it appears that sulfate has no appreciable solubilizing effect although concentrations only slightly higher, above approximately $10^{-2}$ M, could be expected to increase the proportion of the soluble metals. Thus, although the presence of high sulfate alone may be comparatively unobjectionable in these waters, the accompanying effect of heavy metal solubilization could be more serious. Chromium is relatively unaffected by sulfate due to the dominance of hydroxo complexes at this pH (7.0).

The effect of carbonate on the solubility of the metals in Figure 5b is less obvious. Chromium(III) does not form a stable carbonate and so is not affected. The carbonates of nickel and cadmium do not form under the conditions present, and zinc carbonate affects soluble zinc at total carbonate concentrations approaching $10^{-1}$ M. Carbonate interacts with both lead and copper by forming both soluble complexes and precipitates. Above $10^{-4}$ M total carbonate, copper precipitates as malachite while soluble lead actually increases due to the formation of a carbonate complex, $PbCO_3^0$. At higher carbonate levels, lead carbonate begins to precipitate while soluble copper increases as the negatively charged $Cu(CO_3)_2^{2-}$ complex forms.

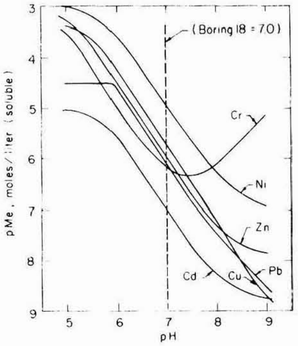

**Figure 6.** Sensitivity of predicted total soluble metals as pH varies

The effect of solution pH is shown in Figure 6. This variable brings about the most noticeable changes in soluble metals, affecting both the extent of adsorption and degree of precipitation. In general, higher pH results in greater adsorption while lower pH results in less adsorption and less precipitation. Chromium solubility increases at pH values above 7.5 due to the formation of soluble hydroxo complexes such as $Cr(OH)_4^-$, and, in fact, the line for chromium in Figure 6 represents a hydroxide solubility diagram. It should be noted for the other metals that the dominant attenuation mechanisms change as solution conditions change; thus, for example, lead sulfate exerts the major control on lead solubility at pH 5 while the stoichiometry of the copper precipitate changes from malachite to cupric hydroxide, $Cu(OH)_2$, at pH 9.

The changes in soluble metals as the quantities of soil components vary are shown in Figures 7a, b, and c for silica, manganese oxide, and iron oxide, respectively. Silica exerts only minor effects at very high surface areas per unit volume. In the model, this is due primarily to the low dielectric value of silica which brings about a correspondingly high oppositional energy of solvation for adsorption of the metal cations. The effects of both iron and manganese are more pronounced. Surface areas of manganese approaching $10^{-2}$ ha/L begin to exert an influence due to the large sorptive capacity of this oxide; however, the amounts measured in the field were generally insufficient to bring about this effect, so that manganese oxide adsorptive controls are secondary to adsorption into iron oxide. Figure 7c indicates that major effects due to iron become apparent at surface area concentrations higher than manganese. Field measurements suggest that this oxide is present in quantities sufficient to control cadmium, nickel, and zinc (Figure 4d). In comparing Figures 7b and 7c, the observation can be made that manganese oxide, if present in large enough quantities, is capable of becoming the dominant sink for all the metals studied, while iron oxide has only a minor influence over those metals which form discrete precipitates, that is, copper, chromium, and lead.

*Discussion*

The results imply some interesting possibilities with respect to heavy metal containment in ponded fly ash disposal sites. The removal of chromium, copper, and lead through a precipitation mechanism depends upon the solution chemistry of the leachate/soil system and so it could be expected to be operative for all times as long as conditions are favorable. Unless the metal oxides in the soil are replenished, however, it is to be expected that the adsorptive capacity of the system could eventually be exhausted, depending upon the quantities present initially, and those metals which are controlled through this mechanism (in this study, cadmium, nickel, and zinc) may migrate more freely.

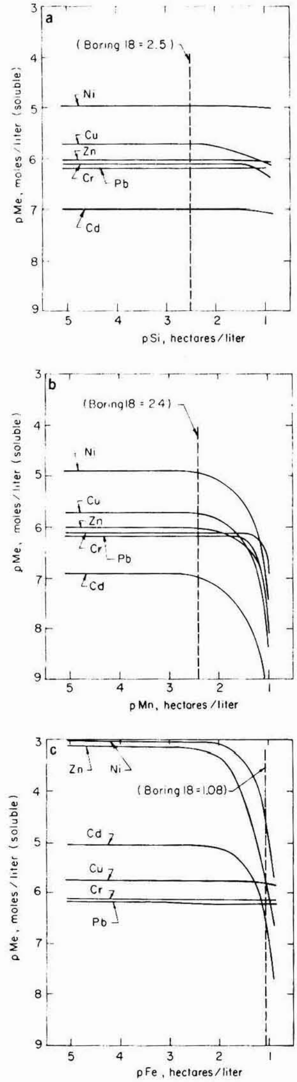

**Figure 7.** Sensitivity of predicted total soluble metals to changes in sorbing surface areas: (a) silica; (b) manganese oxide; (c) iron oxide

In either case, the partitioning of metals between the soluble and particulate phases is strongly influenced by solution pH and to a lesser extent by complex forming ligands such as sulfate and carbonate. This offers an explanation for the relatively wide variation in soluble metals shown in Figure 2 and previously related to chemical perturbations moving through the system.

The comparatively large sorptive capacity of maganese oxide is especially noteworthy and may warrant consideration as a control procedure for seepage type ponds such as the one studied. For this site, it is unclear whether the iron and manganese oxides found at various locations were present naturally or are being deposited from the fly ash. In the latter case, it is possible that certain fly ashes are capable of providing this ameliorating effect, a factor which should probably be taken into account when assessing various control procedures. The purposeful use of these oxides for heavy metal attenuation would depend upon maintaining an oxidizing soil environment. Our studies of ash disposal ponds have shown rather consistently that oxidizing conditions prevail in the active leaching zone.

In reviewing these results, it must be stressed that many of the trends indicated are derived from the anticipated thermodynamic behavior of the various components in the system. They are, however, based upon field measurements and are in general accord with observations made of heavy metal partitioning in the soil/water environment. It is felt that the information presented is a reasonable assessment of the attenuation mechanisms which are operative. This study suggests that the subsurface reactions between heavy metal leachate constituents and soil components are generally complex. Nevertheless, knowledge of these reactions is viewed as important in the overall evaluation of the pollution potential of a leachate/soil system.

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# An Approach to Estimating Probabilities of Transportation-Related Spills of Hazardous Materials

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■ An approach to estimating probabilities of transportation-related spills of hazardous materials is described. The approach involves, first, determining accident rates for appropriate modes of transportation and, second, determining the fraction of accidents that result in spills. Spill probabilities are then estimated from equations based on the Poisson distribution. Estimates of spill probabilities are presently limited by the nature of the statistics. However, the Materials Transportation Bureau (Department of Transportation) is now recording more details on accidents involving spills of hazardous materials, and, therefore, more precise and meaningful estimates of spills can be obtained as this data base develops. An example is presented on how the approach may be used to estimate spills associated with chemical plant operation. However, the approach may also be used in determining probabilities of spills for whole classes of chemicals, or within certain geographical areas. Such information could be used to design more appropriate hazardous materials spill prevention, countermeasure, and control plans.

Transportation-related spills of hazardous materials contribute to the overall environmental impact of chemical plant operations. Spills may occur during shipment of raw materials to the plant, shipment of products from the plant, or disposal of waste materials. Impacts of transportation-related spills may be more severe than spills which occur at the plant site because transportation-related spills often occur in noncontainment areas where the spilled material can escape into water bodies or affect terrestrial biota. Such spills can occur anywhere along the transportation route and thus impact environmentally sensitive areas or impose public safety problems if the spills occur in populated areas.

EG&G, Environmental Consultants recently completed a comprehensive assessment of the environmental effects of a new chemical plant which included an assessment of the probability of transportation-related spills. In approaching the problem of estimating spill probabilities, it was found that, with the exception of radioactive materials and water transport of oil, little published information on estimating spill probabilities existed. Therefore, the available statistics were reviewed and a simple approach to estimating transportation-related spills was developed. The objective of this paper is to outline the approach utilized and to give an example of its application. Limitations to the method are also discussed.

### *Estimation of Probabilities of Transportation-Related Spills*

In order to estimate the probabilities of transportation-related spills of hazardous materials, it is assumed that such spills are independent events that occur randomly with respect to the distance (or mileage) over which the material is transported. The probability of a spill occurring between the mileage distance $l$ and $l + \Delta l$ will be as follows:

$$\text{prob }\{\text{a spill occurs between } l \text{ and } l + \Delta l\} = \nu \Delta l \qquad (1)$$

where $\nu$ = the average number of spills per mile.

The number of spills, $n$, occurring over some distance $L$ is a discrete random variable, and, if Equation 1 is satisfied, then $n$ will be Poisson distributed with parameter $\nu L$:

$$P(n) = \frac{(\nu L)^n}{n!} e^{-\nu L} \qquad (2)$$

The Poisson distribution (Equation 2) is, in effect, a binomial distribution for a large number of independent events

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## Table I. Summary of Data Relating to Transport of Chemicals Associated with the Operation of a Hypothetical Chemical Plant

| transported chem | origin | destination | mode of transport. | capacity of transport. vehicle | length of transport. route, miles | frequency of shipment (annually) | miles transported (annually) |
|---|---|---|---|---|---|---|---|
| raw materials | | | | | | | |
| chlorine | Brunswick, Ga. | plant site | freight car (tank car) | 17 000 gal | 325 | 150 | 48 750 |
| caustic solution | Brunswick, Ga. | plant site | freight car (tank car) | 16 000 gal | 325 | 300 | 97 500 |
| methyl mercaptan | Houston, Tex. | plant site | freight car (tank car) | 20 000 gal | 700 | 160 | 112 000 |
| isobutyraldehyde | Pt. Lavaca, Tex. | plant site | freight car (tank car) | 20 000 gal | 600 | 200 | 120 000 |
| acetaldehyde | Bay City, Tex. | plant site | freight car (tank car) | 20 000 gal | 540 | 260 | 140 400 |
| muriatic acid | Moundsville, W.Va. | plant site | truck (tank truck) | 40 000 lb | 350 | 500 | 175 000 |
| final products | | | | | | | |
| product A (flammable liquid) | plant site | Axis, Ala. | freight car (tank car) | 20 000 gal | 300 | 80 | 24 000 |
| product B (corrosive) | plant site | La Porte, Tex. | truck (truck load) | 40 000 lb | 750 | 350 | 122 500 |
| waste materials | | | | | | | |
| hazardous waste (corrosive) | plant site | waste disposal site | truck (truck load) | 40 000 lb | 50 | 380 | 19 000 |

(transportation trips) that result in only a small number of occurrences in one of the two possible binomial classes (spill occurrence vs. no spill). It has been used by others to estimate spill probabilities related to transportation of radioactive materials (*1*) and oil (*2*). The Poisson distribution was used to determine the probability of one or more spills occurring in a given time interval, the most probable number of spills, and the number of spills bounding the interquartile range, i.e., the middle 50% of the probability curve.

If $L$ is taken as a random variable representing the number of miles between consecutive spills, and assuming that Equations 1 and 2 apply, then $L$ obeys an exponential distribution with the parameter $\nu$:

$$g(L) = \text{probability density function for } L = \nu e^{-\nu L} \quad (3)$$

Note that any or all of Equations 1, 2, and 3 may be taken as characterizing Poisson-type spill occurrences since it is possible to deduce any one of the relations starting with any other.

The mean spill rate is defined as the expected number of spills occurring over a distance interval of length unity, and is denoted by $\nu$. The expected distance between spills may be computed from Equation 3 to be:

$$E\{L\} = 1/\nu \quad (4)$$

The average number of years between spills (recurrence interval) is estimated from:

$$R = 1/\nu\delta \quad (5)$$

where $R$ = recurrence interval (years), $\nu$ = average number of spills per mile, and $\delta$ = average number of miles per year. Note that the reciprocal relation between mean spill rate and mean distance between spills is one of the implications of the Poisson assumption for spill occurrence, and may not hold true for other types of spill distributions.

Rail and highway transportation routes and frequencies were identified for the chemicals being considered. The distance of each transportation route was determined and multiplied by transportation frequency to obtain the number of miles that each chemical will be transported during a particular time interval (e.g., 1 year, 10 years, or operating life of chemical plant).

Historical accident rates for chemicals transported by rail were obtained from "Accident Bulletin—Summary and Analysis of Accidents on Railroads in the United States" (*3–5*) and "Yearbook of Railroad Facts" (*6*). Accident rates for highway transportation were determined from "Accidents of Large Motor Carriers of Property" (*7*). Records of highway accident rates were available from the Bureau of Motor Carrier Safety for only the period 1966 to 1970.

Historical transportation-related spill rates of hazardous materials were determined by multiplying the historical accident rate by $F_s$, the fraction of accidents resulting in spills. $F_s$ is dependent upon accident severity and integrity of the container in which the chemical is transported. Unfortunately, little historical information was available on spills of specific chemicals from railroad freight cars or trucks. Therefore, $F_s$ was estimated from spill records for general classes of chemicals having similar physical and chemical properties (data provided by Materials Transportation Bureau, U.S. Department of Transportation) and a model developed by the U.S. Nuclear Regulatory Commission for use with radioactive materials (*1*). $F_s$ as estimated by the former method refers only to spills causing more than $100 in property damage.

### *Application of the Method*

A hypothetical chemical plant is used to illustrate how the method of estimating spill probabilities might be applied. The plant receives shipments of six raw materials, produces and transports two products, and disposes of hazardous waste at a nearby waste disposal site (Table I). All materials are transported by either rail (freight car) or truck. The distances chemicals are transported annually range from 19 000 miles per year for hazardous waste to 175 000 miles per year in the case of muriatic acid, a raw material.

The average accident rate for freight cars operating in the United States during 1972 to 1974 was estimated to be $1.8 \times 10^{-6}$ accidents per freight car mile (Table II). The average accident rate for trucks was $2.5 \times 10^{-6}$ accidents per truck mile during 1966 to 1970 (Table III). Since the accident rate for trucks was relatively constant during 1966 to 1970, the average

**Table II. Accident Rates of Freight Cars Operating in the United States during 1972–1974**

| year | freight train accidents [a] | freight car accidents [b] | freight car miles [c] | accident rate, freight car accidents per freight car mile |
|---|---|---|---|---|
| 1972 | 4653 | 46 530 | $30.309 \times 10^9$ | $1.5 \times 10^{-6}$ |
| 1973 | 5792 | 57 920 | $31.248 \times 10^9$ | $1.8 \times 10^{-6}$ |
| 1974 | 6592 | 65 290 | $30.729 \times 10^9$ | $2.1 \times 10^{-6}$ |
| average | 5658 | 56 580 | $30.429 \times 10^9$ | $1.8 \times 10^{-6}$ |

[a] Number of freight train accidents was determined from data provided by the Federal Railroad Administration Office of Safety (*3–5*). Number of reported accidents involving collisions of two freight trains was doubled to reflect the fact that two trains were involved. [b] It was estimated (*8*) that an average of ten freight cars was involved in a train accident. Therefore, the number of freight car accidents was approximately 10 × number of freight train accidents. [c] Number of freight car miles was obtained from data provided by the Association of American Railroads (*6*).

**Table III. Accident Rates of Trucks Operating in the United States during 1966–1970**

| year | accident rate, [a] accidents per truck mile |
|---|---|
| 1966 | $2.4 \times 10^{-6}$ |
| 1967 | $2.4 \times 10^{-6}$ |
| 1968 | $2.5 \times 10^{-6}$ |
| 1969 | $2.4 \times 10^{-6}$ |
| 1970 | $2.7 \times 10^{-6}$ |
| average | $2.5 \times 10^{-6}$ |

[a] Accident rates were obtained from data provided by the Bureau of Motor Carrier Safety (*7*).

**Table V. Percentages of Accidents Involving Hazardous Materials Transported in the United States during 1966–1972, by Categories of Accident Severity [a]**

| category of accident severity [b] | % of accidents | |
|---|---|---|
| | freight car | truck |
| I | 50.00 | 55.00 |
| II | 30.00 | 36.00 |
| III | 18.00 | 7.00 |
| IV | 1.80 | 1.60 |
| V | 0.18 | 0.28 |
| VI | 0.013 | 0.11 |
| VII | 0.006 | 0.0085 |
| VIII | 0.001 | 0.0015 |
| total | 100.000 | 100.0000 |

[a] Data are taken from "Draft Environmental Statement on the Transportation of Radioactive Material by Air and Other Modes" (*1*). [b] Categories of accident severity are defined in terms of increasing crush and force and duration of fire (*1*).

accident rate for those years is likely to be representative of present and future rates.

Percentages of transportation-related accidents that resulted in spills causing more than \$100 in property damage in the United States during 1972 to 1976 are presented in Table IV for classes of chemicals exhibiting similar physical and chemical properties as the raw materials and final products. Since accidents resulting in spills are more likely to be reported than accidents in which no spills occur, percentages appearing in Table IV probably overestimate real spill frequencies.

In an evaluation of radioactive materials, the U.S. Nuclear Regulatory Commission (*1*) estimated spill probabilities for freight-car and truck transportation by categories of accident severity. Estimates of spill probabilities were based on two conceptual models. One model assumes that materials are transported in special containers placed in freight cars and trucks. Since these containers are more durable than containers used to transport nonradioactive materials, spill probabilities generated by this model probably underestimate the likelihood of spills of other, nonradioactive materials. The second model assumes that radioactive materials are shipped in containers of limited durability and, therefore, it is more suitable for estimating spill probabilities of other chemical materials. According to the second model, spills of hazardous materials are not expected in the first or lowest category of accident severity (Table V). Since this category represents 50% of all freight-car accidents and 55% of all truck accidents, probabilities of transportation-related spills of raw materials and final products transported by freight cars and trucks are, respectively, 0.50× and 0.45× probabilities of accidents. Spill probabilities generated by use of USNRC's second model correlate reasonably well with probabilities obtained by extrapolating spill percentages for general classes of chemicals to similar raw materials, final products, and hazardous wastes (Table IV).

Probabilities of transportation-related spills of chemicals associated with operation of the hypothetical plant are pre-

**Table IV. Percentages of Transportation-Related Accidents Resulting in Spills Causing More Than \$100 in Property Damage in the United States during 1972–1976, by Chemical Classes [a]**

| class of chem | mode of transport. | chem for which data apply | % accidents resulting in spills causing >\$100 prop. damage |
|---|---|---|---|
| flammable liquid | tank car | methyl mercaptan, isobutyraldehyde, acetaldehyde, product A | 52.0 |
| corrosive material | tank car | caustic solution | 51.0 |
| | tank truck | muriatic acid, product B, hazardous waste | 37.0 |
| nonflammable compressed gas | tank car | chlorine | 27.0 |

[a] Analysis is based on Hazardous Material Incident Reports filed with Material Transportation Bureau (computer printout of reports was obtained from the Materials Transportation Bureau, U.S. Department of Transportation). Only full tank cars and tank trucks were considered in the analysis.

**Table VI. Probabilities of Transportation-Related Spills Involving Chemicals Associated with the Operation of a Hypothetical Chemical Plant**

| | | spill probability | | | | |
|---|---|---|---|---|---|---|
| | | | life of plant (50 years) | | | |
| transported chem | mode of transport. | 1-year period, 1 or more spills | 1 or more spills | 5 or more spills | most probable no. of spills | no. of spills bounding interquartile range |
| raw materials | | | | | | |
| chlorine | freight car (tank car) | 0.023 | 0.694 | 0.007 | 1 | 0–2 |
| caustic solution | freight car (tank car) | 0.086 | 0.989 | 0.463 | 5 | 3–6 |
| methyl mercaptan | freight car (tank car) | 0.100 | 0.995 | 0.601 | 6 | 4–7 |
| isobutyraldehyde | freight car (tank car) | 0.106 | 0.996 | 0.660 | 6 | 4–7 |
| acetaldehyde | freight car (tank car) | 0.123 | 0.998 | 0.784 | 7 | 5–9 |
| muriatic acid | truck (tank truck) | 0.149 | 0.999 | 0.906 | 8 | 6–10 |
| final products | | | | | | |
| product A (flammable liquid) | freight car (tank car) | 0.022 | 0.675 | 0.006 | 1 | 0–2 |
| product B (corrosive) | truck (truck load) | 0.107 | 0.996 | 0.667 | 6 | 4–7 |
| waste materials | | | | | | |
| hazardous waste (corrosive) | truck (truck load) | 0.017 | 0.585 | <0.001 | 1 | 0–2 |
| all materials combined | | 0.540 | 0.999 | 0.999 | 39 | 35–44 |

sented in Table VI. To demonstrate how estimates are obtained, consider the case of the raw material chlorine. The parameter $\nu L$ for 1 year is 48 750 miles/year × (1.8 × $10^{-6}$ accident/mile) × (0.27 spill/accident) = 0.02369; $\nu L$ for 50 years is 50× the above, or 1.1846. So, in Table VI, the probability for one or more spills in 1 year is 1 − exp(0.02369) or 0.02341. For 50 years, it is 1 − exp(1.1846), or 0.6491. For 50 years, using Equation 2 and $\nu L$ = 1.1846, the probabilities of zero, one, two, three, and four spills are, respectively, 0.3059, 0.3623, 0.2146, 0.0847, and 0.0251. So the probability of five or more spills of chlorine is 1 − 0.9926, or 0.0074. It is seen from the above probability estimates that one is the most probable number of spills.

During a 1-year period, the probability of one or more transportation-related spills associated with operating the hypothetical plant ranges from 1.7% for hazardous waste to 14.9% in the case of the raw material muriatic acid. For all materials combined, there is a 54% chance that one or more spills will occur in a 1-year period. During the expected life of the plant (50 years), the probability of one or more spills is 58.5% for hazardous waste and increases to 99.9% for muriatic acid. The most probable number of spills of a raw material ranges from one for chlorine to eight for muriatic acid. For the final products A and B, the most probable number of spills is one and six, respectively, and, for hazardous waste, one spill is the most likely number. The interquartile range is used to indicate the number of spills that bound the middle 50% of the probability curve. For individual chemical materials, the range is zero to two spills for chlorine, product A, and hazardous waste. The range increases to six to ten spills for muriatic acid, and for all materials combined, the interquartile range is 35–44 spills.

The spill recurrence intervals for chemicals associated with the plant are presented in Table VII. To demonstrate how these were calculated again consider the case of chlorine. From Equation 5 the recurrence interval ($R$) for spills of chlorine is 1/0.02369 or 42.2 years. For raw materials, recurrence intervals range from 6.2 years for muriatic acid to 42.2 years for chlorine. Recurrence intervals for products A and B are 44.5 and 8 years, respectively. A recurrence interval of 56.9 years is obtained for hazardous wastes. When all materials are considered together, a spill is expected to occur once every 1.3 years.

**Table VII. Recurrence Intervals for Transportation-Related Spills Involving Chemicals Associated with Operation of a Hypothetical Plant**

| transported chem | mode of transport. | spill recurrence interval, years |
|---|---|---|
| raw materials | | |
| chlorine | freight car (tank car) | 42.2 |
| caustic solution | freight car (tank car) | 11.2 |
| methyl mercaptan | freight car (tank car) | 9.5 |
| isobutyraldehyde | freight car (tank car) | 8.9 |
| acetaldehyde | freight car (tank car) | 7.6 |
| muriatic acid | truck (tank truck) | 6.2 |
| final products | | |
| product A | freight car (tank car) | 44.5 |
| product B | truck (truck load) | 8.8 |
| waste materials | | |
| hazardous waste (corrosive) | truck (truck load) | 56.9 |
| all materials combined | | 1.3 |

*Discussion*

The approach outlined above provides a relatively simple method of arriving at estimates of spill probabilities. The essential features of the method include first determining accident rates for appropriate modes of transportation and, second, determining the fraction of accidents that results in spills. Spill probabilities are then estimated from equations based on the Poisson distribution.

Fractions of accidents that result in spills were estimated from data provided in Spill Incident Reports filed with the Materials Transportation Bureau. Reporting of spills of hazardous materials to the Bureau was initiated in 1972 and relatively few statistics have been obtained on spills of specific chemicals. For example, during 1974–1975, only 11 spills of chlorine were reported. The relatively small data base for individual chemicals reflects both the short duration over which these statistics have been recorded as well as the general lack of knowledge regarding reporting of spills during the first few years following initiation of the reporting requirement.

To circumvent the problem of too small a data base for individual chemicals, data for whole classes of chemicals having similar characteristics to the individual chemicals were used.

Prior to 1977, data recorded by the Materials Transportation Bureau on spills of hazardous materials did not include information on the volume of materials spilled. The magnitude of the spill could be judged only from the resulting costs. In the approach outlined in this paper, spills were considered "significant" when they resulted in damage and clean-up costs exceeding $100. This is a relatively low cost and using this figure as a criterion will overestimate the probabilities of spills that result in significant adverse environmental effects. The problem of judging the magnitude of a spill and its associated impacts from the cost of a spill will be alleviated in the future since the Materials Transportation Bureau has begun to record additional details, including spill volumes, on reported transportation-related spills. As this data base develops, more precise and meaningful estimates of spill probabilities can be obtained.

This paper provides an example of how the method may be employed to estimate probabilities of spills associated with the operation of an individual chemical plant. The method also could be applied to estimate probabilities of spills occurring in a particular region (e.g., state) or for a particular chemical (e.g., chlorine) transported throughout the country. Regional and chemical-specific information on the probabilities of transportation-related spills could be used to help design hazardous materials spill prevention, countermeasure, and control plans.

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**NOTES**

# On the Degradation of 2,3,7,8-Tetrachlorodibenzoparadioxin (TCDD) by Means of a New Class of Chloroiodides

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■ A new method for the decomposition of 2,3,7,8-tetrachlorodibenzoparadioxin (TCDD) and other substances containing ether bonds together with aromatic rings is described in this note. The reaction requires the use of chloroiodides obtained from different quaternary ammonium salt surfactants and does not need the presence of light. Experiments have been realized with pure TCDD and with samples from the contaminated area of Seveso, Italy. A possible mechanism for the observed reaction is discussed.

This work describes the cleavage of ethers by means of a new class of compounds in micellar solution. This group of substances shows interesting application in the field of pharmaceutical chemistry because of its antibacterial activity and at the same time is of interest because of its possible applications in the field of environmental sciences as inactivating and decontaminating agents of toxic substances containing one or more ether groups in their molecules.

Although more detailed and complete data will be given in a forthcoming paper, great interest in the results obtained in 2,3,7,8-tetrachlorodibenzoparadioxin (TCDD) (structure I) degradation experiments, together with an urgent need for decontamination techniques (*1–6*), prompted us to report on this subject.

Molecular degradation of TCDD has been realized by means of chloroiodides (*7–12*) obtained from quaternary

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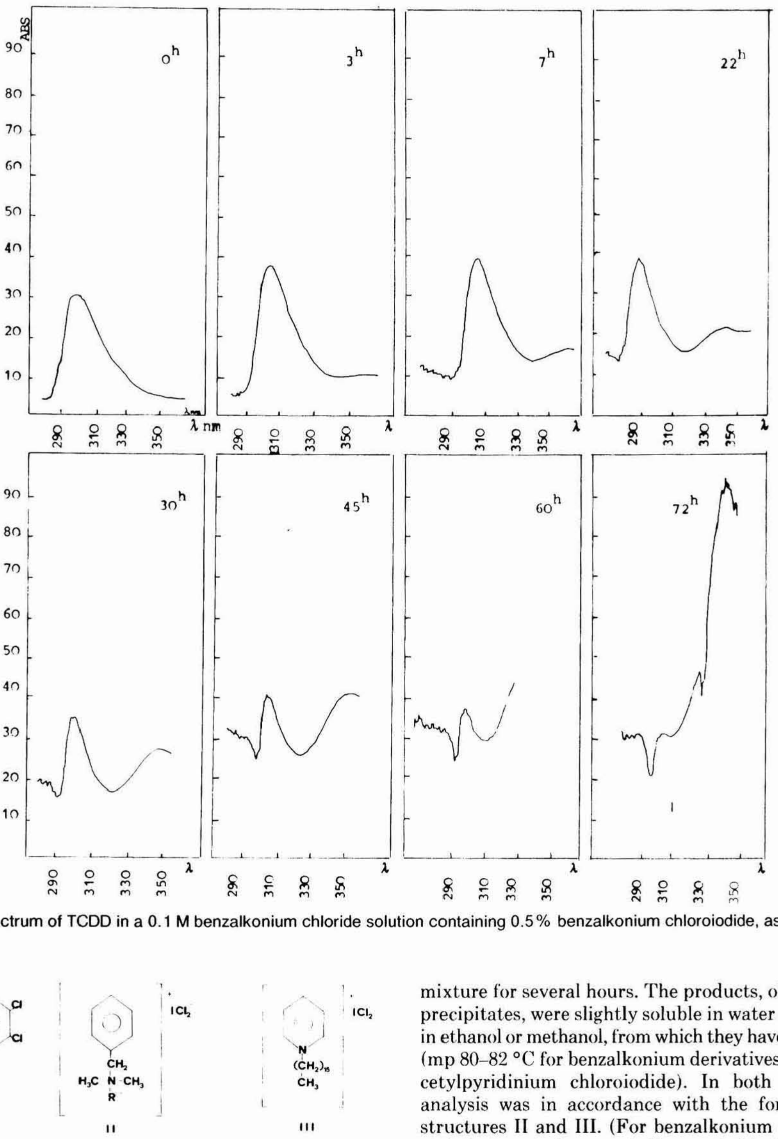
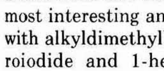


**Figure 1.** UV spectrum of TCDD in a 0.1 M benzalkonium chloride solution containing 0.5% benzalkonium chloroiodide, as a function of time



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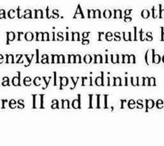
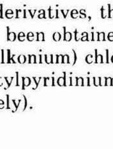


II

* R represents a mixture of the [illegible]



III

ammonium salt surfactants. Among other derivatives, the most interesting and promising results have been obtained with alkyldimethylbenzylammonium (benzalkonium) chloroiodide and 1-hexadecylpyridinium (cetylpyridinium) chloroiodide (structures II and III, respectively).

## *Experimental*

All surfactants and reagents were of analytical grade. TCDD was a pure sample supplied by Rochester University, Rochester, N.Y. UV measurements were carried out with a Perkin Elmer–Hitachi 200 spectrophotometer, using quartz cells having a path length of 10 mm. IR spectra were realized by means of a Perkin-Elmer 521 spectrophotometer.

Chloroiodides have been prepared by treating an aqueous solution of each surfactant, containing a slight excess of iodine, with gaseous chlorine which was bubbled through the reaction mixture for several hours. The products, obtained as yellow precipitates, were slightly soluble in water and more soluble in ethanol or methanol, from which they have been crystallized (mp 80–82 °C for benzalkonium derivatives and 72–74 °C for cetylpyridinium chloroiodide). In both cases elemental analysis was in accordance with the formulas shown in structures II and III. (For benzalkonium chloroiodide, the ratio between nitrogen, iodine, and chlorine has been considered.) The principal IR absorption peaks are at 700, 730, 765, 1400, 1500, 2840, 2910, 2940, 3020, and 3060 $\text{cm}^{-1}$ for benzalkonium derivatives and 730, 695, 785, 1480, 1495, 1640, 2880, 2945, and 3080 $\text{cm}^{-1}$ for cetylpyridinium derivatives.

The low solubilities in water of these new substances can be increased by the use of micellar solutions, and the same surfactants, used for the preparation of the chloroiodide derivatives, have been used for this purpose (i.e., benzalkonium chloride was the solubilizing agent for benzalkonium chloroiodide, while cetylpyridinium chloride micelles solubilized cetylpyridinium chloroiodide).

As far as TCDD cleavage is concerned, the following experimental conditions have been used: 10 mL of a benzene solution containing 10 μg/mL of TCDD was vacuum evaporated and the residue was treated with 10 mL of a 0.1 M cationic surfactant aqueous solution containing 50 mg of chloroiodide derivative. The test solutions were kept in a dark place at room temperature and checked periodically for UV

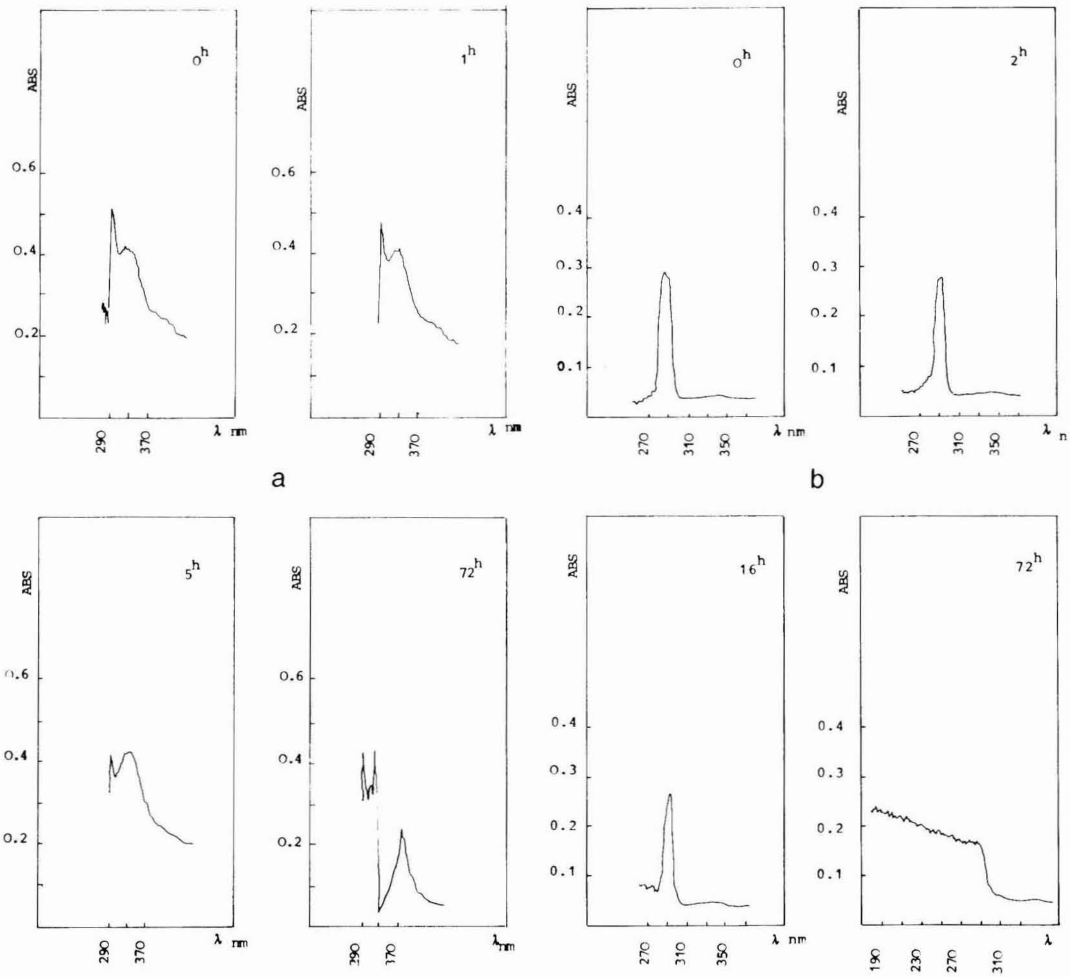


Figure 2. (a) UV spectrum of TCDD in a 0.1 M cetylpyridinium chloride solution containing 0.5% cetylpyridinium chloroiodide, at different times. (b) UV spectrum of xanthene in a 0.1 M benzalkonium chloride solution containing 0.5% benzalkonium chloroiodide, at different times

absorbance; appropriate blanks containing all reagents except TCDD were prepared as references. Results are reported in Figures 1 and 2a where it is possible to observe the variation of the spectrum as a function of time: the maximum related to TCDD decreases while decomposition products appear. Several substances are formed from the decomposition of TCDD, such as chlorophenols, phenols, and 2-phenoxychlorophenols, whose compositions have not yet been determined.

In order to verify, by means of another analytical method, TCDD decomposition by treatment with chloroiodides, a sample solution, prepared as described above, was diluted, after 24 h, with 50 mL of water and then extracted six times with 60-mL portions of methylene chloride. The organic phases were collected together and evaporated under reduced pressure; the residue was then tested for a quantitative determination of TCDD by means of the method proposed by Camoni's research team (*13*). An LKB 900S instrument was used for this purpose. When benzalkonium chloroiodide in benzalkonium micelles was used as reagent, it was found that 71% of TCDD was decomposed, and an even higher yield for such decomposition reaction (92%) was reached when cetylpyridinium chloroiodide in cetylpyridinium chloride was used. These data have been obtained by means of mass spectrometry measurements.

Experiments for TCDD degradation have also been attempted with soil samples from the contaminated area of Seveso, Italy. Two different effects must be considered in this case: the solubilizing properties of surfactant micelles toward TCDD, previously described (*14*), and the decomposition reaction related to the presence of chloroiodide. In order to verify the peculiar properties of tested chloroiodides, appropriate blanks have been prepared by treatment of the soil with a solution containing surfactant micelles without chloroiodides. Preliminary results, obtained with 100-g soil samples containing an average amount of 23 μg of TCDD, showed that 19.8 μg of TCDD was still present after treatment for 24 h with 100 mL of a 0.05 M benzalkonium chloride solution as solubilizing agent (*14*), while only 11.0 μg has been detected when 0.2% benzalkonium chloroiodide was added to the micellar solution. Therefore, although a lower yield has been obtained if compared with the experiments obtained with pure TCDD, as could be expected because of the presence of many other substances besides TCDD in soil samples, the loss of 38% of TCDD can be ascribed to the decomposition reaction catalyzed by benzalkonium chloroiodide.

It is interesting to point out that the same reaction has been realized using other substances containing ether groups and structural similarities to TCDD, such as xanthene and benzofuran. Results with xanthene are reported in Figure 2b where the disappearance of xanthene absorption maximum is evident. (The maximum related to the benzene ring due to decomposition of xanthene is hidden by the background and the absorption of benzalkonium chloride.)

## *Discussion*

We may conclude that the observed micellar catalysis can be applied in many cases in which the cleavage of an ether linkage is needed; furthermore, such a reaction can be realized without the direct use of hydrogen iodide in strongly acidic solutions, at room temperature, in aqueous media, and without irradiation (*14, 15*), which makes it more feasible for decontamination processes.

In our experimental conditions Π–Π interactions between the aromatic moiety of sufactants and benzene rings of tested ethers can be assumed; this is further supported by the fact that the use of surfactants without aromatic ring systems in their molecule leads to no appreciable decomposition of ethers. We may therefore presume that hydrogen iodide, which slowly solubilized within micelles from chloroiodides, finds TCDD nearby or other aromatic ether molecules arranged in an appropriate way so that the cleavage takes place in an easier and faster way related to such specific interaction. In fact, a worthwhile feature of this micellar interaction is an increase in iodide concentration and a parallel decrease of 1.5 pH unit values. $I^-$ concentration, which changed from $10^{-8}$ to $10^{-3}$ M, was checked by means of a potentiometric method using an Orion selective electrode. Therefore, the mechanism of the cleavage of ether bonds by means of chloroiodides can be assimilated to the well-known one which directly involves hydrogen iodide.

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# A Comparison of Time and Time–Weather Models for Predicting Parathion Disappearance under California Conditions

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■ Time and time–weather models for predicting parathion disappearance on California Valencia foliage were compared. The time-based first-order disappearance model explained 67% of the residue data variation for 7 dilute application experiments and 55% of the residue data variation for 7 low-volume experiments. The time–weather first-order disappearance model considerably improved predictive accuracy to 83% for both experimental series. Utilization of pesticide disappearance models which incorporate weather conditions is suggested for harvest-time and worker reentry regulations and for reducing dependence on environmental monitoring studies.

The health hazard posed by residues of organophosphorothionate parathion (*O,O*-diethyl *O*-*p*-nitrophenyl phosphorothionate) to agricultural field workers who enter treated fields has received wide attention (*1*). The major source of intoxicant appears to be the dislodgeable foliar residues sorbed to particulate matter, primarily dust, on the leaf surface. Field workers are currently protected from acute exposure to organophosphorus residues by regulations which deny reentry into treated fields or groves until a specific time interval after pesticide application has elapsed. However, these largely toxicologically based regulations have not been completely successful in the central valley of California (2) and this lack of success remains unexplained. Beyond more stringent regulations, three approaches to circumvent additional worker illnesses have been suggested. Worker reentry regulations determined by mathematical modeling based on the known toxicology and environmental behavior of organophosphorus insecticides have been suggested (*3–5*). A recent report stresses field monitoring with portable equipment for actual residue levels before worker reentry (*6*). A third approach utilizes the prediction of pesticide levels on leaf surfaces through the use of weather models of pesticide behavior (*7, 8*).

The purpose of this study was to determine if the disappearance of parathion from California orange foliage could be accurately described with a first-order model employing a weather-dependent rate coefficient.

## *Experimental*

Experimental design, application methodology, sampling, analytical methodology, and the residue data have been previously reported (*1*). The first-order weather decay model, statistics, heating-degree-day transformation, and computer programs have also been previously reported (*7, 8*).

## *Discussion*

The year-round empirical models illustrated in Figures 1 and 2 show that the use of a time–weather model of pesticide disappearance for California parathion data improved the $R^2$ values considerably. For both the dilute application (15.0 kL

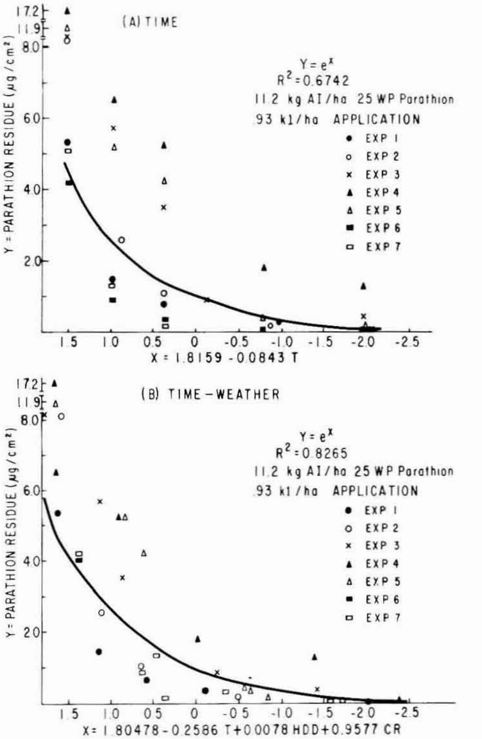

**Figure 1.** Parathion exponential decay models compared with data using (A) exponential of time alone (*T*) in days and (B) exponential of a linear sum of time (*T*) in days, heating-degree-days (HDD) in °C-days, and cumulative rainfall (CR) in inches (concentrated application)

**Table I. Matrix of Individual Correlations between Parathion Concentrated Application[a] and Cumulative Environmental Variables**

| parathion | heating degree days | cumulative time, days | cumulative rainfall, in. |
|---|---|---|---|
| 1.000 | −0.668[b] | −0.743[b] | 0.063 |
| | 1.000 | 0.985 | 0.456 |
| | | 1.000 | 0.434 |
| | | | 1.000 |

[a] 11.2 kg of active ingredient/ha in 0.93 kL/ha. [b] $P < 0.01$.

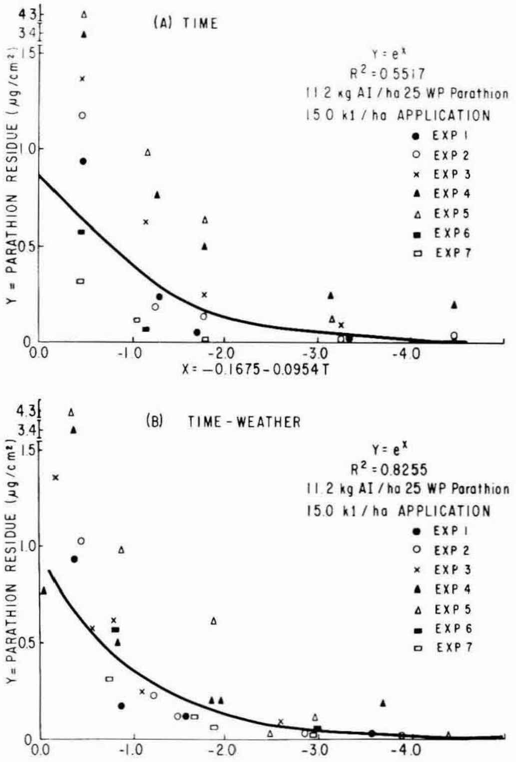

**Figure 2.** Parathion exponential decay models compared with data using (A) exponential of time alone (*T*) in days and (B) exponential of a linear sum of time (*T*) in days, heating-degree-days (HDD) in °C-days, and cumulative rainfall (CR) in inches (dilute application)

**Table II. Matrix of Individual Correlations between Parathion Dilute Application[a] and Cumulative Environmental Variables**

| parathion | heating degree days | cumulative time, days | cumulative rainfall, in. |
|---|---|---|---|
| 1.000 | −0.755[b] | −0.821[b] | −0.099 |
| | 1.000 | 0.985 | 0.456 |
| | | 1.00 | 0.434 |
| | | | 1.000 |

[a] 11.2 kg of active ingredient/ha in 15.0 kL/ha. [b] $P < 0.01$.

of diluent/ha) and the low-volume application (0.93 kL of diluent/ha), 83% of the variation observed was correlated with the time–weather data. For the 15.0 and 0.93 kL/ha applications, time alone explained only 67 and 55% of the residue data variation, respectively. These results are very similar to the previously described Florida citrus foliage ethion residue disappearance model where 94% of the variation was explained by the time–weather model and 57% by time alone (*7*), and the Florida citrus foliage models for parathion where 90% of the variation was explained by the time–weather model and 30% by time alone, and for carbophenothion, where 93% of the variation was explained by the time–weather model and 47% by time alone (*8*).

These data analyses for California parathion data illustrate several additional important considerations in using weather plus time to predict pesticide disappearance. Time was the most highly correlated individual variable (Tables I and II) with California data, whereas in Florida, rainfall, air temperature, and solar radiation were generally the most highly correlated variables. This supports the supposition of Nigg et al. (*9*) that time would probably be the most important environmental parameter in an empirical weather model under stable weather conditions. It was difficult to correlate California pesticide disappearance to cumulative rainfall due to the lack of any significant amount of rainfall. It should be noted, however, that individual correlations with rainfall were +0.063 and −0.099 (Tables I and II), suggesting no effect on pesticide disappearance. The sign of the coefficients is positive for both rainfall and heating-degree-days in the multiple correlation equations (Figures 1 and 2). This can lead to a predicted increase in pesticide residue under certain weather conditions. For the October 1974 data, with 2 in. of rainfall, an increase was in fact predicted, but a decrease occurred. A possible solution to this problem in modeling pesticide dis-

**Table III. Time Model Half-Lives of Parathion on California Orange Leaves**

| | 11.2 kg of active ingredient/ha | | | | | |
|---|---|---|---|---|---|---|
| | dilute application | | | concd application | | |
| expt | slope | $T_{1/2}$,[a] days | $R$ | slope | $T_{1/2}$, days | $R$ |
| 1 | −0.13 | 5.3 | −0.97 | −0.08 | 8.7 | −0.98 |
| 2 | −0.11 | 6.3 | −0.97 | −0.10 | 6.9 | −0.98 |
| 3 | −0.07 | 9.9 | −0.87 | −0.06 | 11.6 | −0.96 |
| 4 | −0.04 | 17.3 | −0.86 | −0.06 | 11.6 | −0.98 |
| 5 | −0.09 | 7.7 | −0.96 | −0.10 | 6.9 | −0.99 |
| 6 | −0.12 | 5.8 | −0.91 | −0.09 | 7.7 | −0.96 |
| 7 | −0.11 | 6.3 | −0.91 | −0.06 | 11.6 | −0.83 |
| $\bar{X}$ | −0.095 | 7.3 | | −0.078 | 8.9 | |

[a] $T_{1/2}$ = 0.693/slope.

appearance has been suggested (*9*). Theoretical pesticide disappearance models incorporating both chemical parameters and environmental parameters would also circumvent this inaccuracy.

The variation in half-lives of parathion on California orange leaves illustrates the possible inaccuracy of a time-based model (Table III). The current approach sets tolerances based on a monitoring study at harvest time. If the factors affecting pesticide disappearance change in a subsequent year, residue levels may be out of tolerance. This inaccuracy of the time model has been partially circumvented by Gunther et al. (*1*) with a split-time model which describes the initial rapid loss of pesticide as "disappearance" behavior and the slower subsequent residue loss as "persistence" behavior (*1*). This practice has not been accepted for the purpose of setting tolerances, and it is of little general predictive value for use in model development.

The time and time–weather estimates of organophosphate residue behavior presented here represent the combination of seven separate experiments. This approach seeks to accurately predict pesticide levels under any set of weather conditions. Although the weather transformation of the first-order rate equation was accurate for Florida experiments, these California data illustrate possible inaccuracies in applying this model. The California weather–time model suffers from a lack of variation in temperature and rainfall. Thus, another physical factor either separate from or confounded with temperature and rainfall may account for the variation in half-lives between experiments (Table III).

Both the time and time–weather models show some initial inaccuracy (note point spread in figures). This inaccuracy has been previously noted (*3*) and is probably due to vaporization, leaf penetration, runoff, and other short-term processes. Models of organophosphate disappearance from leaf surfaces may ultimately include explicit vaporization and hydrolysis models as well as weather variables.

Regardless of the predictive model used, its utilization should be simple to apply without higher mathematics and it should be field tested. Once field testing is completed, utilization of pesticide disappearance models should improve pest management decisions, harvest-time regulations, and worker safety reentry regulations and should reduce the current dependence on expensive and endless monitoring studies.

The data presented show that an empirical time–weather predictive model of California pesticide disappearance was about twice as accurate as time alone. Pesticide disappearance models which utilize the physical factors causing pesticide disappearance could be put into practice by requiring the accumulation of rainfall, average temperature, or a combination of rainfall and temperature data, and in some cases, time, before reentering pesticide-treated fields. The adoption of field-tested weather models of pesticide disappearance would be more reliable than the current regulations used in protecting field workers reentering pesticide-treated crops and would take into consideration variations in pesticide disappearance due to regional climatic differences.

### *Acknowledgments*

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SIR: Let me offer a few comments on the recent note by Lonneman, Seila, and Bufalini (*1*) concerning the importance of terpene emissions from vegetation in the generation of ambient ozone levels. Air samples were collected in two Florida orange groves at about noon in May 1976. While citrus trees have been shown to emit various monoterpenes ($C_{10}H_{16}$) at this time of year (*2–4*), GC analyses conducted 4–5 days after sample collection failed to detect any $C_{10}$ terpenes. The authors have thus concluded that "the amount of naturally emitted hydrocarbon is low" and that "these low levels cannot possibly contribute to the production of significant levels of ozone" in the area studied.

The data presented by these authors do not provide strong support for either of these two conclusions. When dealing with a photochemically generated pollutant such as ozone, ambient precursor concentrations do not provide a good index of either mass emissions or relative importance among precursor sources. This fact is easy to overlook, since most smog chamber studies have been batch reaction systems. In such systems, the amounts of reactants can be expressed on either a concentration or a mass basis. It is the mass of reactant injected into these systems which determines the initial concentration. The basic nature of photochemical ozone generation adds further insight. In the critical reaction process, organic compounds function as NO oxidizing agents through a *chain reaction* sequence of hydrocarbon oxidation and free-radical formation, while NO is involved in a *cyclic* oxidation–photodissociation sequence. Thus, the practice of describing batch reaction smog chamber studies in terms of initial reactant concentrations obscures the essential significance of hydrocarbon mass emissions.

Real world smog systems involve essentially continuous reactant injection. In such real atmospheres, low ambient concentrations of a precursor compound could indicate either well-diffused emissions from isolated, high concentration point sources; cumulatively high mass emissions from widespread but individually minor emission sources; or high reaction rates regardless of source concentration. Thus, the study described by Lonneman et al. must be evaluated in terms of two interrelated but distinct issues: whether a significant ambient $C_{10}$ terpene concentration should have been expected in the first place, and whether natural terpene compounds play a significant role in atmospheric photochemical reactions.

I have approached the issue of expected ambient terpene concentrations by using the following simple spherical volume, steady-state model derived by analogy to the traditional simple box model:

$$\text{canopy concn} = \frac{\text{terpene emission rate} \times \text{canopy diam}}{\text{canopy vol} \times \text{wind speed}}$$

In May 1977, Zimmerman (*2, 3*) measured a terpene emission rate for Florida orange trees of 3.1 $\mu g/(g{\cdot}h)$ on a foliage dry-weight basis. Since no data on tree size were reported by Lonneman et al., I have used data from some California citrus trees (*5*). A 29-year-old orange tree (4.72 m tall, with a trunk diameter of 27.2 cm) had a crown circumference of 15.7 m and a foliage biomass of about 450 kg (fresh weight). Data from three 10-year-old orange trees indicated that foliage dry weight averaged 50% of foliage fresh weight.

Figure 1 illustrates expected steady-state canopy terpene concentrations for this 29-year-old orange tree as a function of wind speed. Inherent model assumptions are a uniform laminar wind flow, free air movement through the canopy, "clean" air unaffected by upwind trees, and no chemical reactions. A terpene molecular weight of 136.24 and a temperature of 25 °C are also assumed. Figure 1 indicates that wind speeds over 2.7 m per s (5.2 miles per h) would produce a canopy terpene concentration of less than 1 ppb [11.34 ppbC (parts per billion of carbon)]. Lonneman et al. do not report any wind speed measurements. They do note that samples were taken outside the tree canopy (a few inches to 10 ft from the trees) at noon on a day when the mixing depth was greater than 2000 m. All of the key assumptions inherent in my simple model are violated by real world conditions. It seems most reasonable to me that the model overestimates the ambient terpene concentration expected in the collected air samples.

The authors note that ambient ozone levels at the time of sample collection were about 45 ppb. They also note that 50% pump losses of ozone were experienced. Tests with known terpene samples (5–25 ppbC) indicated no pump losses and excellent storage characteristics. Test conditions are not explained in much detail. It would have been quite informative if additional terpene storage tests had been conducted using an air plus 20–25 ppb$O_3$ mixture to simulate actual sample storage conditions.

As recognized by the authors, monoterpenes react rapidly with ozone under both light and dark conditions (*6–9*). Rate constants for terpene–ozone reactions have been reported in some studies (*8, 9*). Those presented in ref *9* were used by Lonneman et al. to estimate potential terpene storage losses from reaction with ozone. These rate constants were determined from flow system experiments having reaction times ranging from 4 s to 4.5 min. Reaction rates determined in both ref *8* and *9* were based on systems having terpene concentrations significantly in excess of ozone concentrations. This is certainly not the expected condition for the air samples analyzed by Lonneman et al. It is also noteworthy that, where determinations could be made by Grimsrud et al. (*9*), terpene to ozone loss ratios ranged from 0.47 to 1.5; loss ratios of 0.7 to 1.4 were reported for myrcene, limonene, and $\alpha$-pinene.

Thus, with an initial ozone concentration of 20 times the expected terpene concentration, I am not surprised by the failure of Lonneman et al. to detect any $C_{10}$ terpenes after 4–5 days of sample storage.

The significance of terpenes to photochemical smog reactions can best be judged by their contribution to the reactive organic emission inventory for an appropriate geographic area. Zimmerman (*2, 3*) has estimated that terpenes from natural vegetation account for 68% of the total reactive organic emissions in the St. Petersburg–Tampa area. While available emission inventory data for that area need significant refinement, this estimate clearly indicates that terpenes are a major hydrocarbon source in the area studied by Lonneman et al. Terpenes are highly reactive with ozone, as previously mentioned. These chain and cyclic olefins are also highly reactive in the typical photochemical system (*7–15*), being some of the most reactive compounds yet tested. It should also be noted that the ozone–terpene reaction can lead to free-radical formation, either directly or by photodissociation of resultant aldehydes and ketones (*16*). Thus, even the daytime scavenging of ozone by terpenes can lead to subsequent downwind ozone generation. All things considered, Zimmerman's terpene emission estimates seem easy to reconcile with low ambient terpene concentrations.

One final factor needs to be recognized in assessing the significance of terpenes to photochemical smog reactions. These reactions will not proceed unless NO or $NO_2$ sources are also present. While I have not fully investigated the lit-

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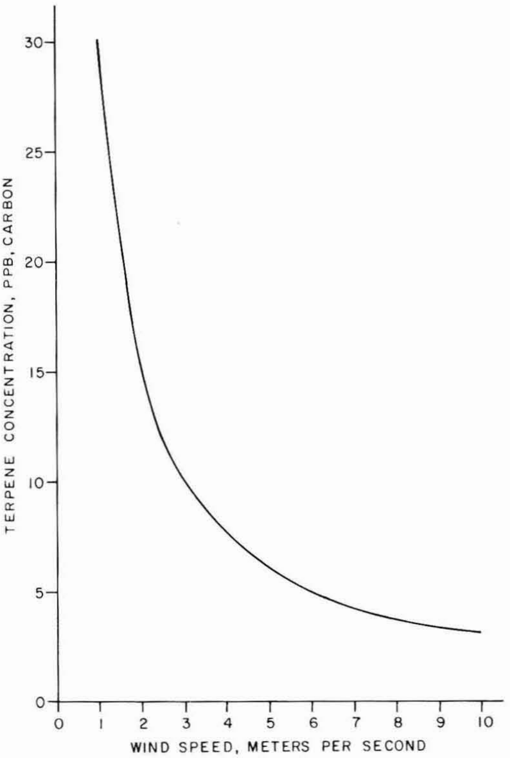

**Figure 1.** Effect of wind speed on expected canopy concentration of monoterpenes

erature on natural NO and $NO_2$ sources, I remain skeptical of their significance for two simple reasons. Natural background ozone levels, while subject to argument as to sources, are clearly low. There is also abundant evidence of visible injury to vegetation produced by relatively low ozone levels. Thus, I can only conclude that photochemical smog is clearly a product of modern technology. In this regard, the NO and $NO_2$ produced by combustion processes may be at least as important as hydrocarbon emissions from anthropogenic sources. I would also conclude that while terpene emissions can be a significant hydrocarbon source (and need to be recognized when formulating smog control strategies), this does not in any way mean they are "the cause" of observed smog levels.

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SIR: Lonneman et al. (*1*) recently presented data concerning the abundance of natural hydrocarbons in the Florida atmosphere and advanced the conclusion that natural sources are not significant. Our review of this paper indicates that because of limitations in their sampling, storage, and analytical systems, this conclusion is not justified and further work is required to determine the true abundance of natural emissions.

Contrary to the authors' reasoning as to why terpenes and other natural organic compounds were not detected in the field samples, our calculations indicate that because these compounds are not stable under the conditions imposed by the sampling and storage system, substantial concentrations could have existed in the ambient atmosphere. The samples which best indicate such storage loss are those taken in the orange grove, samples G-2 and G-3. Based on the authors' assumption that the emissions in the orange grove should include the volatile constituents of orange oil [composition >97% *d*-limonene, 1–3% myrcene, and a trace of $\alpha$-pinene (*2, 3*)] one would expect to find *d*-limonene and possibly myrcene in the samples. However, calculations of the *d*-limonene and myrcene storage loss in the Tedlar bags in the same manner as used by the authors for $\alpha$-pinene show that in the 5 h allotted for reaction with ozone, 98.7% of the *d*-limonene and 99.98% of the myrcene would have been destroyed. These calculations are based on ozonolysis rate constants of 0.016 and 0.031 $ppm^{-1}\ s^{-1}$ for *d*-limonene and myrcene, respectively (*4*).

Obviously, there is a very high probability that these important terpenes were completely destroyed by storage in the Tedlar bags and were never delivered to the GLC for analysis. Our calculations also show that the initial bag concentrations of these terpenes could have been as high as 77 ppbC (parts per billion of carbon) *d*-limonene and 90 ppbC myrcene. Considering that substantial losses of these terpenes would also be expected during sampling when ozone was also present, it is evident that very high ambient concentrations of these terpenes could have existed.

Another problem with the storage loss position taken by the authors is the fact that no data were presented for the terpene laboratory storage test. Based on the ozonolysis rate given, it is assumed that $\alpha$-pinene was used in this test. Ripperton, Jeffries, and White (*5*) have reported that $\alpha$-pinene reacts much faster with ozone than calculated by the first-order kinetics used by the authors. Ripperton and co-workers postu-

**Table I. Volatiles from Oranges. Reprinted with Permission from *Journal of Food Science* (29 (6), 790–5 (1964)); Copyright 1964 by Institute of Food Technologists**

| Peak no. | Substance | Peak no. | Substance |
|---|---|---|---|
| 1 | Methane [a] | 27 | Ethyl butanoate [b] |
| 2 | Methyl chloride [a] | 28B | Ethyl benzene [a] |
| 3 | Acetaldehyde [b] | 29 | p-Xylene and/or m-Xylene [a] |
| 4 | Ethanol [b]<br>Acetone [b] | 29A | 3-Hexen-1-ol [b] |
| 5 | Diethyl ether [c] | 29B | 2-Hexen-1-ol [e]<br>1-Hexanol [b] |
| 6 | Ethyl formate [d] | 30 | *o*-Xylene [a] |
| 7 | 2-Methylpentane [a] | 35 | Myrcene [b]<br>Ethyl hexanoate [e] |
| 7A | *n*-Butyraldehyde [e] | 38 | Limonene [b] |
| 8 | 3-Methylpentane [a]<br>Methyl ethyl ketone [e] | 40P | Methyl 3-hydroxy-hexanoate [e] |
| 9P | 1-Propanol [d] | 42 | *n*-Octanol [b]<br>*p*-Isopropenyltoluene [b] |
| 9 | *n*-Hexane [a] | 44 | Linalool [b] |
| 10 | Ethyl acetate [d] | 47 | Ethyl 3-hydroxy-hexanoate [e] |
| 11 | 2-Methyl-3-buten-2-ol [e] | 51 | Terpinen-4-ol [b] |
| 12 | Methyl cyclopentane [a] | 52 | Ethyl octanoate [d]<br>α-terpineol [b] |
| 13 | Benzene [a] | 53 | Decanal [b] |
| 14 | Ethyl sec-butyl ether [e] | 54 | Octyl acetate [d] |
| 15 | Cyclohexane [a] | 58 | Citronellol [d] |
| 23 | 1,1-Diethoxy ethane [d]<br>4-Methyl-2-pentanone [e] | 59 | Carvone [d] |
| 24 | 3-Methyl-1-butanol [b] | 60P | Citral [b] |
| 25 | Toluene [a] | 60 | Perillaldehyde [e] |
| 26 | *n*-Hexanal [b] | 68 | Biphenyl [f] |

[a] Source unknown, perhaps from solvent used to apply resin to the fruit.
[b] Previously reported as an orange volatile with identification by classical or spectral methods.
[c] Solvent used in present work.
[d] Previously suggested as an orange volatile or tentatively identified.
[e] Newly found orange volatile.
[f] Fungistat from packaging material.

lated that a product from the reaction between α-pinene and ozone was rereacting with α-pinene, as one of the steps which leads to aerosol formation. These investigators report that the ratio of α-pinene/$O_3$ reacting varies from 2 to 5.5 depending upon initial reactant concentrations. Since under the conditions of the field sample storage, the ozone concentration is probably greater than that of the α-pinene, an enhanced loss of α-pinene over that calculated would be expected. Furthermore, other trace atmospheric constituents such as $NO_x$, $SO_x$, $H_2O$, particulate matter, etc., may react with the α-pinene (and other terpenes) and adversely affect storage stability. Experiments to assess these possibilities are necessary before concluding that α-pinene and other terpenes are stable when stored in Tedlar bags for long periods.

A further concern with the storage system is the expected loss of oxygenated compounds arising from natural sources, to the walls of the Tedlar bags during storage. While Lonneman et al. show that Tedlar bags are strong sources for some of these compounds, viz. acetaldehyde and acetone, the bags would be expected to be strong sinks for others. Polasek and Bullin (*6*) have shown that carbon monoxide, stored in Tedlar bags, exhibits an average 42% loss in a 100-h period. This period of time is comparable to the 4 to 5 days that Lonneman et al. stored their samples in Tedlar bags prior to analysis. More reactive oxygenated compounds would be expected to show even greater storage loss. To further complicate matters, Denyszyn and co-workers (*7*) have indicated that Tedlar bags are sources of significant concentrations (1–2 ppmC) of FID responsive species in the $C_5$ to $C_{10}$ range. These authors have also shown that α-pinene and β-pinene, at the 10-ppbC level, stored in stainless steel containers, exhibit a 40% loss in 2 days and a 100% loss in 1 week. They considered stainless steel containers superior to Tedlar bags for storage of most $C_5$ to $C_{10}$ hydrocarbons. Table I (from ref. *8*) lists over 30 compounds which might be expected to be present in the orange grove ambient samples and which would be expected to exhibit significant loss in extended Tedlar bag storage. In addition to these compounds, oxygenated and other compounds formed by the atmospheric reactions of the directly emitted natural hydrocarbons would also be expected not to store well in Tedlar bags. Related to this is the question as to whether the GLC system used by the authors was calibrated to detect the higher molecular weight oxygenated compounds such as are shown in Table I. Since only $C_2$ and $C_3$ oxygenates are included in the analytical listings shown in the Lonneman paper, it is assumed that the analysis of these higher molecular weight compounds was not attempted.

In summary, our calculations and the work of others show that the results presented by Lonneman are consistent with use of a sampling and storage system in which large losses of natural emissions and their atmospheric reaction products would be expected. To determine the extent of these emissions requires a sampling/storage/analytical system which will handle not only the reactive hydrocarbons and oxygenates which are directly emitted from natural sources, but also the volatile atmospheric reaction products of these compounds as well. This is a complex and difficult problem which requires more sophisticated and advanced techniques than have yet been developed and applied by the authors. Until such techniques are developed and applied, the results presented by Lonneman et al. cannot be interpreted to indicate that natural emission sources are not significant.

In the meantime, the static/dynamic enclosure technique developed by Zimmerman (*9*) minimizes the sampling/storage loss problems associated with ambient sampling methods and appears to provide the most reliable emission data for trees, shrubs, and other natural sources.

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SIR: The correspondence of Sculley agrees in general with the conclusions made in our paper (*Environ. Sci. Technol.*, **12**, 459 (1978)). Although using a different approach, Sculley concludes that ambient concentrations of natural hydrocarbons are low and probably not the cause of high smog levels. We presume that when Sculley says "smog" he means ozone. The technique used by Sculley combined a simple diffusion model with natural hydrocarbon emission rate estimates (*2*) to predict ambient concentration of natural hydrocarbons. We have used similar techniques for a loblolly pine forest in North Carolina and have also concluded low downwind concentrations of $\alpha$-pinene (*3*).

There were specific comments in Sculley's correspondence that suggest a misunderstanding of our results and require additional comments. These comments include the long-term storage of bag samples that contain mixtures of $C_{10}$ terpenes and ozone, the reactivity of terpene hydrocarbons, i.e., the ability of $C_{10}$ terpenes to produce ozone, and the importance of the oxygenated products of terpene ozonolysis in the downwind formation of ozone.

The bag storage of terpene hydrocarbons in the presence of $O_3$ was discussed in detail in our paper (*1*). Loss of terpene by ozonolysis was compensated for by the application of a pseudo-first-order rate equation. It was also pointed out that bag surface deposition of ozone competes with terpene ozonolysis in these stored samples. Complete loss of stored ozone in these small 10–15 L Tedlar bags was estimated to occur in the order of 4–6 h. After this time, the terpene loss due to ozonolysis drops to zero. Later studies designed to simulate the collection of ambient air containing 50 ppb of $O_3$ indicated that a 4–6 h storage period was a gross overestimation. A more reasonable storage period for ozone would be about 1 h for these bags. Although not presented in the paper, past storage studies of air–hydrocarbon mixtures (including several of the $C_{10}$ terpenes) in Tedlar bags suggest excellent storage of these compounds for up to 30 days. Therefore, if the concentration of the $C_{10}$ terpene compounds in these Florida samples were just a few parts per billion of carbon (ppbC) we should have been able to observe them on our gas chromatographic system. Also, in concluding that the $C_{10}$ hydrocarbons should not be expected in the bags because of their reaction with ozone, Sculley has neglected the fact that the *cis*-2-olefins, the pentenes, and propylene were found in the samples. These olefins would also be expected to react if Sculley's argument is correct.

The issue of natural hydrocarbon reactivity suggested by Sculley as an important consideration in the formation of rural ozone requires further comment. True, the $C_{10}$ terpenes are among the most reactive hydrocarbons tested in smog chamber studies (*4, 5*); however, it is not correct to relate hydrocarbon reactivity to ozone production. In recent studies performed in our laboratory (*6*), maximum ozone formation per hydrocarbon compound reacted was investigated for several natural hydrocarbons. Propylene was also investigated. Some of the results from these studies are given in Table I. In the table it is shown that at lower $HC/NO_x$ ratios the amounts of ozone produced per carbon reacted are quite similar for all the hydrocarbon compounds tested. However, at high $HC/NO_x$ ratios, typical to those found in rural areas, the natural olefinic hydrocarbons become less efficient producers of ozone. This is primarily due to ozonolysis reactions and aerosol formation. If butane or any other paraffin were studied, the results would show that these compounds are the most efficient producers of ozone on a carbon parts per million basis.

**Table I. Ozone Production Efficiency Relative to Carbon Consumption as a Function of $HC/NO_x$ Ratio**

| | ppb$O_3$ produced/ppbC consumed | | |
|---|---|---|---|
| $HC/NO_x$ | propylene | isoprene | $\alpha$-pinene |
| 4 | 0.50 | 0.50 | 0.30 |
| 5 | 0.42 | 0.40 | 0.21 |
| 10 | 0.27 | 0.22 | 0.10 |
| 15 | 0.21 | 0.15 | 0.07 |
| 20 | 0.18 | 0.12 | 0.05 |
| 50 | 0.10 | 0.05 | 0.02 |
| 100 | 0.06 | 0.03 | 0.01 |

The issue that natural hydrocarbons produce gaseous aldehydes that serve as downwind sources of free radicals is not substantiated by past laboratory studies (*7*). In these studies it was found that less than 15% of the $C_{10}$ terpenes formed gas-phase oxygenates; the remainder is apparently converted to aerosols. Since natural hydrocarbons react quickly with ozone and hydroxyl radicals to produce oxygenates that quickly form aerosols, it seems reasonable that the best attempt to determine the ambient burden of natural hydrocarbon would be to measure both gas-phase concentration of the $C_{10}$ hydrocarbon and the organic fraction of the collected aerosols. In past studies (*8*), however, the organic portions of collected aerosols were typically low, no more than 10% of the total mass, i.e., 10% of 100 $\mu g/m^3$ (TSP) or approximately 10 $\mu g/m^3$. If we assume that this entire fraction is comprised of oxygenate terpenes, we still observe that ambient levels of natural hydrocarbon are just a few parts per billion. Of course, we would have to take deposition velocities of the aerosols into consideration if we are to arrive at a better estimate of natural hydrocarbon emissions rates; however, particulates being photochemically produced would be in the small size range (fraction of a micron) and therefore have a low deposition velocity.

Zimmerman has reported (*2*) that natural hydrocarbons account for 68% of the total hydrocarbon emissions in the Tampa Bay area of Florida. If this indeed is correct, we would expect similar composition in the ambient air, i.e., 68% of the TNMHC to be of natural origin, particularly in the rural areas where our samples were collected. These samples, however, show a predomination of anthropogenic emissions. Efforts to account for natural hydrocarbon loss due to ozonolysis and hydroxyl radical reactions (*3*) do not significantly change this dominance of anthropogenic emissions. In order to explain the discrepancy between Zimmerman's estimate of natural hydrocarbon abundance and observed ambient air sample composition, we propose two possibilities: Zimmerman's natural hydrocarbon emission rates are too high or anthropogenic emission source strengths in the Tampa Bay area are underestimated. We believe that a combination of both is the more likely explanation.

Lastly, it is important to comment on the role of smog chamber results to predict ambient air photochemistry. It is correct to state that smog chamber results cannot be directly related to the real world conditions; however, the importance of smog chamber studies is in the determination of the photochemical mechanism taking place in the ambient atmosphere. This is done by investigating the reactants and products of simple hydrocarbon–nitrogen oxide systems. From these results, a photochemical reaction mechanism or model is developed and validated. More complicated parameters such as intermittent hydrocarbon and $NO_x$ injection, atmospheric dilution, sunlight, and temperature variations can later be added to the model to more simulate the real world. At present, no model is perfect and updating of the photochemical mechanism is a seemingly constant operation. However, without the use of smog chambers and their contribution to the development of ambient air models, our knowledge of the photochemistry of hydrocarbon–nitrogen oxide mixtures would be minimal.

### Table II. Storage Studies of Selected $C_{10}$ Olefinic Hydrocarbon–Air Mixtures in 2 Mil Tedlar Bags

| compd | concn, ppbC<br>init | final (30 days) | % decrease |
|---|---|---|---|
| α-pinene | 98.9 | 95.4 | 3 |
| β-pinene | 92.3 | 84.1 | 9 |
| myrcene | 65.1 | 63.8 | 2 |
| Δ-carene | 82.8 | 79.8 | 4 |
| *d*-limonene | 64.8 | 64.7 | 1 |

Many of the comments made in reference to Sculley's note are also applicable to the correspondence of Ludlum and Bailey (L&B). There are, however, some additional specific comments that we would like to direct to the note of L&B.

In response to the first point, we will agree that this is indeed a possibility, i.e., that the rate constants for $O_3$ with myrcene and $O_3$ with *d*-limonene are much greater than the rate constant used in our calculations for isoprene, and, therefore, much more natural hydrocarbon had reacted. However, the calculations made by us and also employed by L&B are no longer applicable when the rate constant between the natural hydrocarbon and $O_3$ is very large. Our calculations show that all of the $O_3$ will be consumed by the natural hydrocarbons. Therefore, if 30 ppb of $O_3$ were present this could obviously react with 30 ppb of reactive hydrocarbon assuming 1:1 stoichiometry. Since myrcene and *d*-limonene are $C_{10}$ hydrocarbons, the amount of *d*-limonene or myrcene reacted will be 300 ppbC. When both are present at the same time, i.e., in the same container, then 197 ppbC of myrcene and 103 ppbC of *d*-limonene are expected to react with 30 ppb of $O_3$. This assumes that there is no degradation of $O_3$ to the walls.

We indicated in our paper that the Tedlar bag surfaces compete with the terpene hydrocarbons for ozone reaction. We had calculated the $O_3$ lifetime of 5 h in our original work (*1*). This calculation was based on ozone stability studies in large $O_3$-treated Tedlar bags (approximately 150 L). We have reinvestigated the collection of ambient air samples that contain ozone into the smaller 10–15 L untreated Tedlar sample bags. We found that most (about 80%) of the ambient ozone is destroyed during the filling process, probably due to the turbulent mixing of the sample air and the more frequent contact of ozone with the bag surface. After the filling process, the remaining ozone is essentially gone after a 30–60-min period. The short lifetime of the remaining ozone in the smaller bags is probably due to the large surface to volume ratio. Therefore, the calculations made in our paper (*1*) overestimated the amount of $C_{10}$ olefin loss expected in the sample bags. This will also affect the calculations given earlier. We would expect less hydrocarbon to have reacted since the $O_3$ will also degrade to the walls.

The nonstoichiometry of terpene/$O_3$ reactions is another interesting issue. Ripperton et al. (*4*) did indeed find that the α-pinene/$O_3$ ratio varied between 1.9 and 3.4. However, the duplication of the experiments was poor. Also, not all natural hydrocarbons react in the same manner. Arnts and Gay (*6*) have recently shown that the isoprene–ozone reaction is stoichiometric when excess isoprene is present; however, when excess ozone is present the reaction is less stoichiometric with more ozone than isoprene consumed. The apparent explanation for this lack of stoichiometry is that the diolefin will continue to consume ozone as long as there is a double bond available for reaction. Therefore, two ozone molecules will be consumed for every isoprene. We expect the same results for the terpenes with more than one double bond, such as myrcene, *d*-limonene, α-terpinene, ocimene, and β-phellandrene.

When stoichiometry is considered in calculations given earlier, 197 ppbC of myrcene and 103 ppbC of *d*-limonene need to be corrected for the number of double bonds present. Since myrcene is a triolefin and limonene a diolefin, one should expect 65 ppbC of myrcene and 51.5 ppbC of limonene to react with the 30 ppb of $O_3$.

The limit of sensitivity of 1 ppbC for the hydrocarbons was given as a gross approximation in our original work. This was largely done since it simplified the calculations. However, as can be seen in the data presented, our limit of detection for the hydrocarbons is in fact closer to 0.2 ppbC for the heavier compounds and 0.1 ppbC for the lighter molecular weight hydrocarbons. Since the total amount olefin (ignoring ethylene) observed in samples is 5.3 ppbC for G-2 and 5.2 ppbC for G-3, then the reactivity factor, i.e., the rate constant × concentration, will be approximately $10^{-3}$ ppm$^{-1}$ s$^{-1}$ ($5.2 \times 10^{-3}$ ppm) or $5.2 \times 10^{-6}$ s$^{-1}$. If the limit of sensitivity of 0.2 ppbC is used for *d*-limonene, then a reactivity factor of ($1.6 \times 10^{-2}$)($0.2 \times 10^{-3}$) or $3.2 \times 10^{-6}$ s$^{-1}$ is obtained for the *d*-limonene. Since *d*-limonene was not observed in any of our samples, and we did observe other olefins, we must conclude that little if any *d*-limonene was present in the original samples. A similar argument could be made with myrcene. However, as L&B suggest, this hydrocarbon constitutes only 1–3% of orange oil and therefore cannot be considered as a very important natural hydrocarbon in the atmosphere.

There is no experimental evidence to suggest that $SO_x$ and $NO_x$ will react at significant rates with natural hydrocarbons to make these reactions important. Also, since both $NO_x$ and $SO_x$ compounds are in the low ppb level it is highly unlikely that their reactions with the natural hydrocarbons would be very significant at all. No reaction is expected with $H_2O$. To our knowledge, particulate matter does not react at a significant rate with olefins. When one considers even a moderately loaded atmosphere of 150 μg/M$^3$, the gaseous equivalent of this particulate loading is in the low ppb level. Unless the reaction of natural hydrocarbons with particulate is extremely fast, the reaction cannot possibly be important.

On the issue of stability of the natural hydrocarbons in Tedlar bags, we stated in our paper (*1*) that storage studies showed excellent stability of the $C_{10}$ terpenes down to 5–25 ppbC. These studies were done for 5–10 days only. In Table II are shown some longer term storage studies done in Tedlar bags for 30 days. Obviously, our results do not agree with those referenced by L&B (*9*). In our studies the natural hydrocarbons showed excellent stability.

In retrospect, hydrocarbon emissions near citrus type vegetation may be unimportant. In our original work (*1*) we considered citrus vegetation the most important source of natural hydrocarbons in the Tampa Bay area; consequently, grab samples were collected within inches of orange trees. However, in ensuing studies by Zimmerman (*10*), emissions from citrus type vegetation contributed only 3% of the total natural hydrocarbon emission burden. Zimmerman (*10*) reported that deciduous or broad leaf type vegetation constituted the largest percentage of natural hydrocarbon source burden, with isoprene being the single most important hydrocarbon. In our samples, isoprene was the only natural hydrocarbon observed. This compound, however, contributed only 1–4% of the total nonmethane hydrocarbon concentration.

In summary, our calculations and our past work done in this area show that the conclusions put forth in our paper are correct. The results showed that natural hydrocarbon emissions are not as important as anthropogenic sources of hydrocarbons in the formation of ambient ozone.

#### *Literature Cited*

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*Technol.*, **12,** 459–63 (1978).
(2) Zimmerman, P., "Procedure for Conducting Hydrocarbon Emission Inventories of Biogenic Sources and Some Results of Recent Investigation", presented at EPA Emissions Inventory/Factor Workshop, Raleigh, N.C., Sept 1977.
(3) Bufalini, J. J., Lonneman, W. A., "Ozone Formation from Rural Hydrocarbons", presented at the 1978 Coordinating Research Council Air Pollution Research Symposium, New Orleans, La., May 1978.
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(5) Pitts, J. N., Winer, A. M., Darnall, K. R., Lloyd, A. C., Doyle, G. J., in "International Conference on Photochemical Oxidant Pollution and Its Control, Proceedings", B. Dimitriades, Ed., Vol. II, pp 687–704, EPA 600/3-77-001b, 1977.
(6) Arnts, R. R., Gay, B. W., "Photochemistry of Naturally Emitted Hydrocarbons Isoprene, *p*-Cymene, and Selected Monoterpenes", to be published as an EPA report, 1978.
(7) Gay, B. W., Arnts, R. R., "International Conference on Photochemical Oxidant Pollution and Its Control, Proceedings", B. Dimitriades, Ed., Vol. II, pp 745–51.
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(9) Denyszyn, R. B., Hardison, D. L., Harden, J. M., McGaughey, J. F., Sykes, A. L., "Evaluation of Various Hydrocarbon Sampling Devices," presented at NBS Symposium on Trace Organic Analysis, Gaithersburg, Md., April 10–13, 1978.
(10) Zimmerman, P. R., "Bimonthly Progress Report, No. VIII, Determination of Emission Rates of Hydrocarbons from Indigenous Species of Vegetation in the Tampa/St. Petersburg, Florida, Area", EPA Contract No. 68-01-4432, Aug 26, 1977.

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## Correction

In the article, "Chemical Modeling of Trace Metals in Fresh Waters: Role of Complexation and Adsorption" [*Environ. Sci. Technol.*, **12,** 1302–9 (1978)], by Jasenka Vuceta* and James J. Morgan, the following corrections should be made. Figure 3 on page 1303 should be interchanged with Figure 5 on page 1304. The existing captions for both figures should remain where originally printed. Figure 4 on page 1304 should be interchanged with Figure 6 on page 1304. The existing captions for both figures should remain where originally printed. On page 1305, the second line of the title to Table III should read $3 \times 10^{-5}$ ha/L $Fe(OH)_3(s)$, instead of $(OH)_3(s)$ as printed.

# ES&T INDUSTRY TRENDS

**FMC Corp.** has an order for more than $1 million to furnish 52 Straightline sludge collectors to the Los Angeles County Joint Water Pollution Control Plant at Carson, CA.

**Ecodyne's Graver Water Division** (Canada) has a contract in excess of $1.3 million from Enterprise Nationale Sonatrach (Algeria) to supply 4 condensate treatment systems.

**Davy Powergas Inc.** (Lakeland, FL) will provide Davy/Wellman-Lord $SO_2$ recovery systems for Units 3 and 4 of Public Service of New Mexico's plants at Farmington, NM. Combined capacity is 1100 MW.

**Dames & Moore** (Los Angeles, CA) will prepare an environmental impact statement for mine and processing facilities being designed for Thiess Bros. Pty., Ltd., and Shell Co. of Australia, Ltd., in South Wales, Australia.

**Peabody Welles** (Roscoe, IL) has a $3 million order for a 7-mgd water treatment plant for the Western Farmers Electric Cooperative. This is the company's largest single contract ever.

**SAI Technology Co.** (San Diego, CA) is now offering a technique of measuring trace element concentrations by Neutron Activation Analysis, on a contractual basis.

**Gilbert/Commonwealth** will develop and test, for the Dept. of Energy (DOE), a computer-based model for conversion of biomass materials into fuel. Available technologies and cost analyses will be emphasized.

**United McGill Corp.** (Columbus, OH) has a $7.6 million contract to design, engineer, manufacture, and install 8 large electrostatic precipitators for National-Southwire Aluminum Co., at Hawesville, KY.

**Koppers Co., Inc.** has provided a specially developed roofing material to help protect a solar energy system installed at the nation's first solar-heated city hall at Cerritos, CA.

**Randolph & Associates, Inc.** was certified by Illinois to provide bacteriological testing of drinking water, and has moved to larger quarters in the Peoria, IL area.

**Air Pollution Technology, Inc.** (San Diego, CA) has an EPA contract to develop an electrostatically augmented A.P.T. Dry Scrubber. Potential applications are fluidized-bed combustion and coal gasification.

**Catalytic, Inc.,** and **The Kuljian Corp.,** both of Philadelphia, Pa., will provide consulting and construction management services for a combination water desalting and power plant in Saudi Arabia.

**Envirotech/BSP** will supply two multiple-hearth furnaces for a new sludge-handling facility at Ossining, NY, which will incinerate 2800 lb/h, and reduce fuel consumption, as well as dewater sludge.

The **Electric Power Research Institute** (EPRI, Palo Alto, CA) and the **British Gas Corp.** will test utilization of eastern U.S. caking coals in a large-scale test plant, in order to improve efficiency.

**Springborn Laboratories, Inc.** (Enfield, CT) will expand its regulatory service activities by establishing an Occupational and Environmental Health and Safety Department.

**Computer Genetics Corp.** (Wakefield, MA) is marketing a commercial Lidar service for atmospheric, water, and oceanic measurement. The system can give detailed three-dimensional measurements.

**Envirotech/Chemico Air Pollution Control** has received an order for the first centralized, mobile coke-pushing emission control system from U.S. Steel Corp.

**Research-Cottrell, Inc.** will supply an electrostatic precipitator to collect fine particles from the catalytic cracker at Mobil Oil Co., at Paulsboro, N.J.

**Met-Pro Corp.'s Systems Division** will supply 2 iron removal filters to Sydnor Hydrodynamics (Richmond, VA) for use in improving drinking water at the Woodberry Forest School, Madison County, VA.

**Infilco Degremont Inc.** will provide equipment to treat water at the Public Service Co. of Colorado's new Pawnee power station (5500 gpm). The water will be for cooling, boiler makeup, and general supply.

**Parkson Corp.** (Fort Lauderdale, FL) will supply 3 Lamella™ Gravity Settler/Thickeners for the 25-mgd potable water plant at Bridgeport, CT. The system cuts space needs by 90%, and allows for an alum sludge concentration of over 10% to be produced.

**Sumitomo Chemical Co., Ltd.** (Osaka, Japan) has established a storage facility for Sumithion, a low-toxicity insecticide, at Rotterdam, Holland.

Promotional events for air and water pollution control products are assisted by the **U.S. Dept. of Commerce,** and listed in an Overseas Export Promotion Calendar. For more information, contact William Jordan, telephone (202) 377-2722.

**Montgomery Industries International** (Jacksonville, FL) is marketing a new, high-output model of its tire shredder to make tires acceptable for landfilling.

**Natural Energy Corp.** (Washington, DC) plans to acquire Gulf Thermal Corp. (Bradenton, FL), a manufacturer of solar components for heating and cooling systems.

**Calgon Corp.** has a contract to supply 23 activated carbon adsorption units to control hydrogen sulfide odors at San Francisco's Southeast Water Pollution Control Plant. About 70 000 lb of Type IVP granular activated carbon will be used.

**Jacobs Engineering Group** (Pasadena, CA) says that its Jacobs-Del Solar Systems subsidiary will construct a solar energy system to supply steam and hot water for the Home Laundry Co., in Pasadena, with DOE support. Value is $455 000.

**Catalytic, Inc.** has established a new consulting service to aid industry in complying economically with Prevention of Significant Deterioration (PSD) under the Clean Air Act Amendments of 1977.

# PRODUCTS

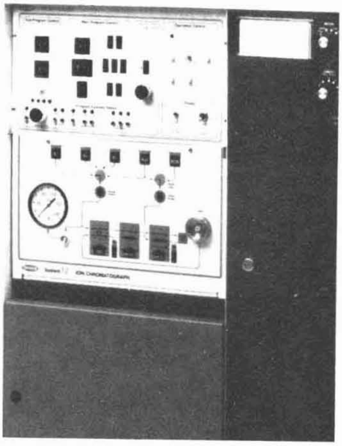
**Retractable stack monitor**
This smoke emissions stack monitor slides into the stack for opacity readings and can then be removed to the "zero" pipe position. The unit is clamped to the existing stack pipe. Robert H. Wager **125**

**Water treatment control system**
By continuously monitoring and adjusting pH and conductivity, the system automatically controls the quality of open recirculating cooling water systems; corrosion of components, scale formation and microbial fouling are minimized. Uniloc **129**

**Digester gas analyzer**
The instrument is a specific gravity comparator designed to provide a practical and continuous indication of anaerobic sludge digester performance. The unit continuously monitors the $CO_2$ content of the digester gas, which is an accurate index of the digester reaction. Permutit Company **103**

**Aerosol sampler**
This high-flow electrostatic aerosol sampler collects microorganisms, viable aerosols and inert particles at flow rates ranging from 300–1200 Lpm or 2500–15 000 Lpm, depending on the model. Environmental Research **104**

**Stack gas monitor**
The unit utilizes the company's second-derivative adsorption spectroscopy measurement technique. This second-generation instrument offers improved accuracy and reliability, and greater selection of measurement ranges. Adjustments are more accessible. Lear Siegler **105**



**Automatic ions in solution analyzer**
The system can be used in air pollution—ambient aerosols, rainwater and $SO_2$ in air; water pollution—inorganic and organic anion profiles; and soil analysis—soil extracts, for example. Dionex Corp. **106**

**Plasma spectrometer**
This automated instrument can be programmed to determine any number of elements at any desired wavelength. Background correction and the portion of the plasma to be observed can also be selected. The program plus calibration values can be stored on magnetic-tape cassette. Instrumentation Laboratory **108**

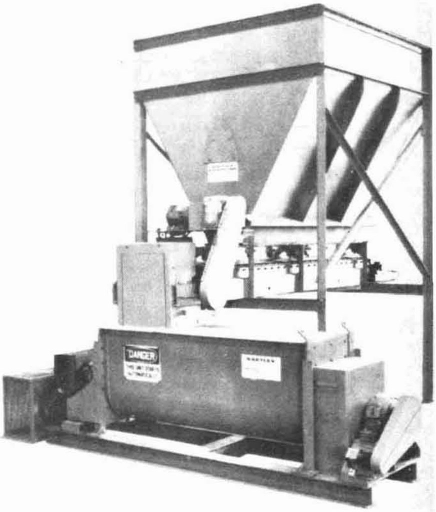
**Sonic flowmeter**
The newest feature is "dynamic zeroing," which permits adjustment of the zero setting under actual flowing conditions, and at any flow rate over the operating range of the meter. MAPCO **109**

**Corrosion inhibitor**
The nonpolluting product is especially designed for use in solar energy systems. Used in collector tanks and piping, the corrosion inhibitor can minimize scaling and corrosion in these systems. Wright Chemical **130**

**Signal averager**
The unit determines the arithmetic mean of analog input signals. The calculated averages are displayed and recorded. Averaging periods can be selected from a range of 1–99 minutes. Scientific Engineering Systems **131**

**Carbonizing plant**
This horizontal, continuous unit produces "top-grade" charcoal from forest products and agricultural waste. Linked to a furnace which burns its gas by-products, pollution can be eliminated. The charcoal produced has a carbon content of 80%, equal to metallurgical coke. Aldred Process Plant Ltd. **111**

**Cooling towers**
Towers are available in 65 standard sizes from 10–4800 nominal tons (25–19 500 gpm). They are of the compact single-fan side design with a variety of width and length combinations to permit varying configurations that fit into available space at the desired capacity. Baltimore Aircoil **112**



**Dust conditioning system**
The system, designed for manual, semi-automatic or fully automatic operation, is able to condition from 3–150 tph of dust. Hartley Controls **113**

**Precipitator cleaning system**
This automatic, self-cleaning system is adaptable to the company's electrostatic precipitators, and was developed for use in the forging industry. The system is basically a closed-loop recirculating oil bath that keeps the contaminants in the fluid state and periodically floods them off the collecting elements. United Air Specialists **114**

# ES&T LITERATURE

**Data acquisition.** Catalog lists new line of environmental data acquisition and buoy systems for *in situ* use. Many marine/oceanographic uses. Naico, Inc. **151**

**Water pipe.** Brochure TRX-38 describes advantages of the company's PVC water pipe which can sustain pressures of up to 100 psi. Easy to handle. Johns-Manville **152**

**Toxic gas sampling.** Data Sheet 08-02-02 describes the Samplair™ Pump for toxic gases and vapors. Can test atmospheres in accordance with OSHA procedures. Mine Safety Appliances Co. **153**

**Pumps.** Pumping guide lists many corrosion-resistant pumps for acids, alkalies, dyes, and many other chemicals and pharmaceuticals. Some 117 pumps are listed. Liquiflo Equipment Co. **154**

**Noise control courses.** Nine seminars for 1979 are listed in brochure on noise detection and control. Hands-on training is featured. B&K Instruments, Inc. **155**

**Lab safety.** Publications available on laboratory safety are listed in one brochure. Books and audiovisuals discuss safety and safe disposal of chemicals. Lab Safety Supply Co. **156**

**Chromatography.** Catalog lists complete line of products for chromatography and mass spectrometry, including many needed accessories. Scientific Glass Engineering–SGE, Inc. **157**

**Air monitoring.** Literature contains articles about MAP III, and the EPA Air Quality Measurements Laboratory, which the company built for EPA. Environmental Measurements, Inc. **158**

**Air velocity.** Bulletin H-100 covers air velocity measurement equipment which can assist engineers in air pollution control, ventilating, air conditioning, and other applications. Dwyer Instruments, Inc. **159**

**Dust control.** "Dust Control News" is a 4-page newsletter containing case histories of solutions to dust control problems, technical articles, and products/systems descriptions. Johnson-March Corp. **160**

**Smoke removal.** Bulletin 120 describes Hydro-Filter® and its applications to smoke removal, particulate collection, absorption, and odor/fume control. Environeering, Inc. **161**

**Chemical feed.** Bulletin 477 tells about a complete line of standard chemical feed systems and diaphragm pumps, as well as relief valves and by-pass feeders. Neptune Chemical Pump Co. **162**

**Fuel saving.** Bulletin P-81 explains how to save fuel through air/oxygen control, in boilers of 10 000–300 000 lb/h of steam. Fuel and dollar savings are charted. Thermox Instruments, Inc. **163**

**Pressure filters.** Brochure No. 3.139 describes the Uni-Pac pressure filter, which clarifies water by removing many kinds of suspended matter. Crane Co. **164**

**CO indicator.** Data Sheet 08-00-02 describes a carbon monoxide (CO) indicator that features a digital readout meter. Ranges 0–500 ppm. Mine Safety Appliances Co. **165**

**Safety items.** Catalog lists more than 4500 items for industrial safety. Industrial Safety & Security Co. **166**

**Grease removal.** Brochure describes a grease and skimmings concentrator which removes these materials, plus machine oil and biological scum from wastewater. Tate-Reynolds Co., Inc. **167**

**Water analysis.** Pub. 5952-5789 explains how a new gas chromatography accessory aids automated water analysis for compliance with water quality regulations. Contaminants to ppb ranges can be detected. Hewlett-Packard **168**

**Wastewater treatment.** For oil refineries and petrochemical plants, Bulletin 315-221 tells how to remove oil and suspended solids. BOD is cut by more than 95%, at costs as low as 17¢/gal. Envirex **169**

**Conductivity controllers.** Information is available, concerning conductivity controllers with ranges from near zero to 150 000 μmhos. Can control deionization, reverse osmosis, and many other processes. Presto-Tek Corp. **170**

**Titration calibration.** Literature describes the CSI-1700 Gas Phase Titration Calibration for NO/NO$_2$, SO$_2$, and ozone supply in precise amounts for instrument calibration, laboratory/field. Columbia Scientific Industries Corp. **171**

**Pollutant diffusion.** Company's air tracer studies, which define transport/diffusion of air pollutants from single or multiple sources, are described in a brochure. Metronics, Inc. **172**

**"Clear the air."** Glide/Pack Bulletin B-1300-18 tells how one can put together combinations of filters to solve many tough air quality situations. Farr Co. **173**

**Solar law.** Information about a new publication, *Solar Law Reporter*, is available. Solar Energy Research Institute, 1536 Cole Boulevard, Golden, CO 80401 (write direct).

**Mercury from soil.** Volatilization of mercury from soil EPA-600/3-78-054. EPA, Environmental Monitoring and Support Laboratory, Las Vegas, NV 89114 (write direct).

**Sewage sludge.** How to cope with it. CED-78-152. Comptroller General of the United States, Washington, DC 20548 (write direct).

**Polynuclear aromatics.** Polynuclear aromatics in the aquatic environment. Publication No. 4297. American Petroleum Institute, 2101 L St., N.W., Washington, DC 20037 (write direct).

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# ES&T BOOKS

**Solar Energy Directory 1978–79.** 215 pages. Centerline Co., Department 149, 401 South 36th Street, Phoenix, AZ 85034. 1978. $12.50.

This directory has over 1400 national and international listings. These listings cover architects, associations, education, wind, research, marketing, and other related topics. The idea is to try to bring suppliers and potential users of solar energy together.

**Sulfur in the Environment. Part II: Ecological Impacts.** Jerome O. Nriagu, Ed. xii + 482 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1978. $24.25, hard cover.

This volume consists of a number of contributed papers covering topics such as material damages done by atmospheric sulfur compounds. $SO_2$ effects on plants, chemistry pollutant sulfur in natural waters, the aquatic ecosystem and sulfur, soil, and acid mine drainage problems are also among the numerous subjects discussed.

**The Use of High-Purity Oxygen in the Activated Sludge Process, Vols. I and II.** J. R. McWhirter, Ed. Vol. I, 276 pages; Vol. II, 274 pages. CRC Press, Inc., 2255 Palm Beach Lakes Rd., West Palm Beach, FL 33409. 1978. Each volume, $53.95, hard cover.

Oxygen-activated sludge is one wastewater treatment technique evoking strong interest. These volumes discuss the field, and cover systems design, clarifiers, oxygenation itself, sludge production, digestion, and nitrification. Also dealt with are UNOX systems, ozone applications, safety, supply, and cryogenics.

**The Complete Greenhouse Book.** Peter Clegg and Derry Watkins. 280 pages. Garden Way Publishing, Charlotte, VT 05445. 1978. $8.95, paper.

Greenhouses can range anywhere between coldframes and sophisticated structures heated wholly or partly by solar energy. This book covers many of these structures, and explains the process of actually growing plants in them.

**Occupational Health and Safety Regulation.** Marshall Lee Miller, Ed. v + 154 pages. Government Institutes, Inc., 4733 Bethesda Ave., Washington, DC 20014. 1978. $18, paper.

This work constitutes the Proceedings of the First Annual Occupational Health and Safety Symposium, held at Washington, DC, last April. It is aimed at businessmen and industrial officials, both familiar with, and new to matters concerning occupational health/safety. Also, government people and others concerned should find it useful. It covers OSHA hazard citations; recordkeeping requirements; civil/criminal liabilities; what an inspector looks for; and many other pertinent topics.

**Environmental Chemistry and Cycling Processes: Proceedings of a Symposium.** D. C. Adriano, I. Lehr Brisbin, Eds. xxxii + 911 pages. National Technical Information Service, U.S. Dept. of Commerce, Springfield, VA 22161. 1978. $15, paper.

There are 61 papers covering design, sampling, and modeling; analytical techniques; soils and sediments; plant and animal uptake; and terrestrial and aquatic ecosystems. Designing experiments, analysis of data, and results of specific studies are among topics covered. Order CONF-760429.

**Advances in Pesticide Science.** H. Geissbühler et al., Eds. 3 vols., 844 pages. Pergamon Press, Fairview Park, Elmsford, NY 10523. 1979. $150 for the set.

The set consists of 110 invited contributions, and grows out of the Fourth International Congress of Pesticide Chemistry. It covers pesticide synthesis, chemical structure, biological activity, pest biochemistry, pesticide modes of action, and formulation chemistry. Pesticide residues and degradation are also considered.

**Proceedings—Water Treatment Waste Disposal.** American Water Works Association, 6666 West Quincy, Denver, CO 80235. 1978. $8.50.

These proceedings contain eight separate papers on the subject.

**Mutagenesis.** W. Gary Flamm, Myron A. Mehlman, Eds. xii + 401 pages. Halsted Press, 605 Third Ave., New York, NY 10016. 1978. $24.50, hard cover.

There are guidelines for determining maximum permissible levels of chemical mutagens, according to this book. Also discussed are needs for mutagenesis testing in mammals, detecting gene mutations, Ames testing, the role of nutrition, natural and synthetic mutagens, and many other related topics. The book is Vol. 5 in the series, "Advances in Modern Toxicology."

**Essentials of Toxicology.** 3rd ed. Ted A. Loomis, Ed. ix + 245 pages. Lea & Febiger, 600 Washington Square, Philadelphia, PA 19106. 1978. $12.50, hard cover.

As in previous editions, factors involved in the production of harmful effects on cells, or even whole animals, are described. However, a new section in this edition covers kinetics of toxicity induction, then exposure to small quantities of a given chemical over a long period of time. New toxicity tests and examples, carcinogenicity, and statistical methods are discussed.

**EARTHCARE: Global Protection of Natural Areas.** Edmund A. Schofield, Ed. xxi + 838 pages. Westview Press, 5500 Central Ave., Boulder, CO 80301. 1978. $30; hard cover.

What are the prospects of preserving or restoring Earth's natural systems? That is a broad question, but then, this book covers many subjects pertinent to this question. Among topics discussed are environmental impact analysis, national parks, wildlife in different habitats, deserts, polar regions, and similar matters. The book grows out of the Sierra Club's Fourteenth Biennial Wilderness Conference.

**Activated Carbon Manufacture and Regeneration.** Albert Yehaskel. xi + 329 pages. Noyes Data Corp., Mill Rd., at Grand Ave., Park Ridge, NJ 07656. 1978. $42, hard cover.

Activated carbon will be coming into much wider use, if certain proposed EPA regulations take effect, as expected. This work sets forth the latest art in active carbon's preparation from many sources. Oxidative and chemical methods of regeneration are covered, as are purification methods; granular and formed carbon, and process of recovery of various chemical constituents. Most recent patent data are presented.

# ES&T MEETINGS

**February 19–20** Washington, D.C.
**Toxic Substances: Decisions and Values.** Technical Information project

Topic of discussion will be decision-making. *Write:* Thomas Conry, Project Manager, Technical Information Project, 1346 Connecticut Ave., N.W., Suite 207, Washington, D.C. 20036

**February 27–28** Atlanta, Ga.
**Symposium on Control Technology in the Plastics and Resins Industry.** National Institute of Occupational Safety and Health (NIOSH)

*Write:* S. T. Fino, Enviro Control, Inc., 11300 Rockville Pike, Rockville, Md. 20852

**February 27–March 2** San Diego, Calif.
**Second National Conference on Hazardous Materials Management.** U.S. EPA, California State Department of Health Services, California Chemical Waste Processors Association

*Write:* O. James Pardau, Executive Director, P.O. Box 214878, Sacramento, Calif. 95821

**March 5–6** Washington, D.C.
**Cogeneration: For Large Users.** The Energy Bureau

*Write:* Robert W. Nash, Executive Director, The Energy Bureau Inc., 101 Park Ave., New York, N.Y. 10017

**March 9–10** New York, N.Y.
**New York Einstein Centennial Celebration.** The New York Academy of Sciences

*Write:* Einstein Committee, The New York Academy of Sciences, 2 East 63rd St., New York, N.Y. 10021

**March 11–13** Washington, D.C.
**7th Annual Meeting of the National Ocean Industries Association.** National Ocean Industries Association (NOIA)

The meeting will discuss ocean resource development. *Write:* NOIA, Suite 410, 1100 17th St., N.W., Washington, D.C. 20036

**March 11–14** Atlanta, Ga.
**Fuel Cycle '79.** Atomic Industrial Forum, Inc.

*Write:* Conference Office, Atomic Industrial Forum, Inc., 7101 Wisconsin Ave., N.W., Washington, D.C. 20014

**March 11–16** Easton, Md.
**Hydropower: A National Energy Resource.** The Engineering Foundation

*Write:* The Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

**March 12–13** Washington, D.C.
**Managing Solid Wastes: New Regulations, New Challenges.** The Energy Bureau, Inc.

*Write:* Robert W. Nash, Executive Director, The Energy Bureau, Inc., 101 Park Ave., New York, N.Y. 10017

**March 14–15** Washington, D.C.
**The National Council on Radiation Protection and Measurements (NCRP) 1979 Annual Meeting.** National Council on Radiation Protection and Measurements

*Write:* W. R. Ney, Executive Director, NCRP, 7910 Woodmont Ave., Suite 1016, Washington, D.C. 20014

**March 18–24** Washington, D.C.
**1979 American Society of Photogrammetry/American Congress on Surveying and Mapping Annual Meeting and Exhibit.** American Society of Photogrammetry and the American Congress on Surveying and Mapping

*Write:* Rosalie Breckenridge, Chairman, Registration Committee, 2047 Golf Course Drive, Reston, Va. 22091

**March 19–21** Miami Beach, Fla.
**8th National Conference and Exhibition on Municipal Sludge Management—Impact of Industrial Sources of Toxics on POTW Sludge.** Information Transfer Inc., and the Hazardous Materials Control Research Institute

*Write:* Beverly Walcoff, Sludge Management Conference, c/o Information Transfer Inc., Suite 202, 1160 Rockville Pike, Rockville, Md. 20852

**March 19–22** Los Angeles, Calif.
**The 6th Conference on the Prevention, Behavior, Control, and Cleanup of Oil Pollution.** The American Petroleum Institute, U.S. EPA, and the U.S. Coast Guard

*Write:* Conference headquarters, 1629 K St., N.W., Washington, D.C. 20006

**March 21–22** Washington, D.C.
**7th Annual APCA Government Affairs Seminar.** Air Pollution Control Association (APCA)

*Write:* Public Relations Department, APCA, P.O. Box 2861, Pittsburgh, Pa. 15230

**March 26–28** Orlando, Fla.
**5th Annual Research Symposium—Municipal Solid Waste: Land Disposal and Resource Recovery.** U.S. EPA, Florida Technological University

*Write:* Division of Continuing Education, Florida Technological University, P.O. Box 25000, Orlando, Fla. 32816

**March 29–30** New Orleans, La.
**10th Annual Symposium of the New Orleans Chromatography-Analytical Discussion Group of the Louisiana Section of the American Chemical Society.** New Orleans Chromatography Discussion Group

*Write:* Tom W. Pewitt, Shell Oil Co., P.O. Box 10, Norco, La. 70079

## Courses

**February 19–23** Madison, Wis.
**Administering EPA Construction Grants Contracts, Course No. 468.** The University of Wisconsin–Extension

Fee: $400. *Write:* The University of Wisconsin–Extension, Dept. of Engineering & Applied Science, 432 N. Lake Street, Madison, Wis. 53706

**February 19–March 2** Cincinnati, Ohio
**Analysis of Organic Compounds in Water.** The Finnigan Institute

Fee: $1500. *Write:* The Finnigan Institute, Atkinson Square Building 5, 11750 Chesterdale Road, Cincinnati, Ohio 45246

**February 20** Minneapolis, Minn.
**Permits Under the Clean Air Act.** Trinity Consultants

Fee: $150. *Write:* Trinity Consultants, P.O. Box 31481, Dallas, Tex. 75231

**Feburary 21** Chestnut Hill, Mass.
**Practical Lake Management.** Weston Observatory–Boston College

Fee: $40. *Write:* Lake Symposium III, c/o Carr Research Laboratory, Inc., 384 Washington St., Wellesley, Mass. 02181

*(continued on page 247)*

# CLASSIFIED SECTION ■ POSITIONS OPEN

## FACULTY POSITIONS
### ENVIRONMENTAL MICROBIOLOGY AND AIR QUALITY ENGINEERING

The School of Civil Engineering at Georgia Institute of Technology is seeking tenure track faculty members in environmental microbiology and in air quality and pollution control within the Environmental Engineering program. These two positions involve teaching at the undergraduate and graduate levels and leading the research thrust in the respective areas. A doctorate in environmental science or engineering with a microbiology specialty is required for the microbiology position; a doctorate in engineering is required for the air quality position. Rank and salary are commensurate with qualifications. A detailed resumé and names of three references should be submitted to **Dr. J. E. Fitzgerald, Director, School of Civil Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332.** An equal opportunity/affirmative action employer.

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## ELECTROSTATIC PRECIPITATOR SCIENTISTS, ENGINEERS

DENVER RESEARCH INSTITUTE requires Ph.D. or M.S. in Physics, Electrical, or Mechanical Engineering in expanding R&D programs sponsored by several government agencies and industrial organizations. Activities include theoretical studies of electrostatic fields and High Voltage Supply control; charging, collection, and adhesion phenomena; design, fabrication, and installation of bench-scale through pilot-scale precipitators; ESP consultation and analysis. Two years experience in one or more of these topics and two more years in related R&D engineering are desirable. Four to six years experience in closely-related activities at a high technical level will be considered. Send resume and salary history to:

**Mrs. Phyllis Riggs**
**DRI/Electronics**
**University of Denver**
**P.O. Box 10127, Denver, Colorado 80210**

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## EXECUTIVE DIRECTOR—STATE OF FLORIDA FLORIDA INSTITUTE OF PHOSPHATE RESEARCH

**Bartow, Florida (Temporary Address: 903 W. Tennessee St., Tallahassee, Florida)**

The Board of Directors invites applications for the position of Executive Director of the Institute. Qualifications are PhD/ScD or equivalent experience (phosphate preferred) in sciences related to mining, mineral processing, geology or environment; at least five years proven competence in research and administration; demonstrated skill in effective communication; ability to plan, allocate resources and provide for evaluation of programs. Salary is negotiable.

The application will require a vita and names of three references. Please forward all applications to Personnel Officer, Florida Board of Regents, Room 226, Collins Building, Tallahassee, Florida, 32304. Application deadline is March 15, 1979. For further information contact **C. W. Hendry, Jr., Chairman, Board of Directors, Florida Institute of Phosphate Research, 903 W. Tennessee St., Tallahassee, Florida 32304.**

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## SENIOR ENVIRONMENTAL ADVISOR

Pennzoil Company is seeking an individual with technical as well as good interpersonal skills to work in its corporate Environmental Safety and Health Department.

**The individual will advise operating and executive level management on the control of air, water and solid waste pollution. Job will include 50% travel to company's domestic facilities.**

**Candidate must have a BS in basic Engineering, and preferably, an MS in Environmental Control, with 5 years consulting experience in air, water, and solid waste pollution control. Familiarity with EPA regulations as well as prior experience in dealing with governmental agencies is necessary for this job.**

**Pennzoil Company offers a wide range of benefits, a good salary and a stimulating professional working environment. If you are interested in this position, please send your resume in confidence to:**

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**P.O. Box 2967**
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## AIR QUALITY SCIENTIST

GEOMET, Inc., an Environmental Sciences consulting firm in Gaithersburg, Maryland, has position available for individual with academic or professional experience in meteorology, dispersion modeling, air quality atmospheric chemistry, and/or related sciences.

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Masters degree required—PhD preferred—in relevant physical science.

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Principals only, please send resume, including compensation history, to:

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**Dr. Demetrios Moschandreas—Director of Environmental Sciences**
**GEOMET, Inc.**
**15 Firstfield Road, Gaithersburg, Maryland 20760**

# CLASSIFIED SECTION ■ POSITIONS OPEN

## ENVIRONMENTAL SCIENTISTS *AND BIOLOGISTS*

The Research Institute of the University of Petroleum & Minerals, Dhahran, Saudi Arabia, has immediate openings for the following positions:

1. *WATER QUALITY SCIENTIST:*
   Responsibilities include experience in new analytical technique and thorough background in water chemistry studies, statistical data interpretation and report preparation. Should be able to apply and employ a wide variety of instrumentations used in water pollution. Qualifications should include an M.S. or equivalent in Environmental Chemistry or related field. At least four years of related experience is necessary.
2. *AIR QUALITY SCIENTIST:*
   Applicants should have a minimum of a Master Degree in Environmental Science or related field with experience in air quality investigation including the application of a wide variety of instrumentations used in air pollution. Must have the ability to interpret data, prepare and report findings in good writing skills. At least four years of related experience is necessary.
3. *RESEARCH BIOLOGIST:*
   Responsibilities include experience in marine biology and fisheries. Applicant must hold a university degree in this specialty with a thorough background in the chemistry of water and air in addition to his field. Duties will include field sampling, bioassay capabilities, laboratory analyses, data handling and report writing. Experience in this field is a great factor in selecting applicant. M.S. degree or equivalent is preferred.

Minimum regular contract for two years, renewable. Competitive salaries and allowances, all earned income without Saudi taxes. Free air conditioned and furnished housing, free transportation to and from Dhahran annually. Attractive educational assistance grants for school-age children. Local transportation allowance in cash each month. Ten and a half month duty each year with 45 days vacation paid.

Apply with complete resume on academic and professional background, list of references and with copies of degrees/testimonials, including personal data such as home and office address, telephone numbers, family status (spouse's name, names of children, ages and sex) to:

**The Research Institute, University of Petroleum & Minerals**
**c/o Saudi Arabian Educational Mission**
**2223 West Loop South, Suite 400, Houston, Texas 77027**

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## MARKETING SPECIALISTS

**A large water and wastewater treatment equipment manufacturer requires two Product Engineers to prepare and present proposals, review cost and price data, and support a national direct field sales organization on equipment applications. An Engineering degree and excellent written and oral communication skills are required. Both competitive and user experience will be considered. Competitive salaries and benefits.**

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Pacific Environmental Services, Inc. is now expanding. PES provides services to industry and government to solve problems related to energy and the environment. Our nationwide consulting firm is seeking innovative and aggressive engineers and scientists who are interested in technical and management challenges. Positions are available at our Los Angeles, Chicago, and Durham, North Carolina offices.

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Consumers Power Company one of the largest investor owned utilities in the U.S., currently has an opening for an experienced Meteorologist. The individual will analyse and evaluate meteorological data, as well as perform the atmospheric diffusion modeling and dose calculation analysis that are required by NRC regulation for Nuclear Power Plant.

The individual should have a degree in meteorology with at least 2 years experience and interest in computer programming and data processing; thorough knowledge of NRC regulations; strong verbal and written communications skills; and ability to work independently.

Please send a complete resume and salary requirements to:

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A leading contract research organization needs junior or mid-level professionals for the following positions:

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Requires background in environmental health, public health, information or computer sciences. A *combined* background in biological and information sciences is highly desirable. Initial assignment will involve development of an interagency data system.

**Environmental Biologist**

Requires a background in environmental biology and chemistry, with experience in quality assurance activities. Initial assignment will be to assist an interagency group on standardization of environmental monitoring and bioassay programs.

Both positions require bachelor's degree with some graduate work and a minimum of two years experience, preferably in a consulting environment.

Please submit resume, including compensation history, to:

**Dr. Niren L. Nagda—Manager, Exposure and Health Effects Assessment**
**GEOMET, Inc.**
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**February 21–22** Minneapolis, Minn.
**Fundamentals of Dispersion Modeling.** Trinity Consultants

Fee: $320. *Write:* Trinity Consultants, P.O. Box 31481, Dallas, Tex. 75231

**February 22–23** Atlanta, Ga.
**Plant Energy Conservation.** The Association of Energy Engineers

Fee: $305 (members): $360 (nonmembers). *Write:* The Association of Energy Engineers. Attention: AEE Energy Seminars, 464 Armour Circle, N.E., Atlanta, Ga. 30324

**February 26–28** East Brunswick, N.J.
**Cooling Water.** The Center for Professional Advancement

Fee: $450. *Write:* Mary Sobin, Dept. NR, The Center for Professional Advancement, P.O. Box H, East Brunswick, N.J. 08816

**February 26–March 1** Cincinnati, Ohio
**Sampling and Evaluating Airborne Asbestos Dust, Course No. 582.** National Institute for Occupational Safety and Health

Fee: $200. *Write:* Donna Welage, Training Registrar. NIOSH, Div. of Training and Manpower Development, 4676 Columbia Parkway, Cincinnati, Ohio 45226

**February 26–March 2** Chicago, Ill.
**Applied Combustion Technology.** The Center for Professional Advancement

Fee: $685. *Write:* Mary Sobin, Dept. NR. The Center for Professional Advancement, P.O. Box H, East Brunswick, N.J. 08816

**March 1–2** Madison, Wis.
**Solid Waste Collection Systems.** University of Wisconsin-Extension

Fee: $130. *Write:* University of Wisconsin-Extension, 432 N. Lake St., Madison, Wis. 53706

**March 5–8** St. Louis, Mo.
**Sanitary Chemistry and Microbiology for Practicing Engineers.** The University of Missouri-Rolla

Fee: $325. *Write:* Ju-Chang Huang. Professor of Civil Engineering, University of Missouri-Rolla, Rolla, Mo. 65401

**March 6–8** Pittsburgh, Pa.
**Industrial Hygiene Training Course and Workshops.** Industrial Health Foundation, Inc.

Fee: $185 (members); $245 (nonmembers). *Write:* George Reilly, Industrial Health Foundation, 5231 Centre Ave., Pittsburgh, Pa. 15232

*(continued on page 248)*

**March 7–9** Atlanta, Ga.
**Solar Energy.** New York University

Fee: $610. *Write:* Registrar, 14th Floor, N.Y.U. Conference Center, 360 Lexington Ave., New York, N.Y. 10017

**March 7–9** Washington, D.C.
**Air Pollution Control Equipment—Operation and Maintenance.** George Washington University

Fee: $415. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

**March 8–9** Philadelphia, Pa.
**Industrial Safety.** Drexel University

Fee: $350. *Write:* Office of Continuing Professional Education, Drexel University, 32nd and Chestnut Streets, Philadelphia, Pa. 19104

**March 12–13** Washington, D.C.
**Environmental Regulation and Legislation.** New York University

Fee: $560. *Write:* Registrar, 14th Floor, N.Y.U. Conference Center, 360 Lexington Ave., New York, N.Y. 10017

**March 14–15** Cleveland, Ohio
**The National Conference on Energy Auditing and Conservation.** Association for Media-based Continuing Education for Engineers, Association of Energy Engineers, Case Institute of Technology

Fee: $225. *Write:* Yacov Y. Haimes, Conference Chairman, Case Institute of Technology, Cleveland, Ohio 44106

**March 19–20** San Antonio, Tex.
**Solar Energy Storage Options.** U.S. Department of Energy

Fee: $40. *Write:* Trinity University Continuing Education, Storage Workshop, 715 Stadium Drive, Box 79, San Antonio, Tex. 78284

**March 20–21** San Francisco, Calif.
**Energy Management in Buildings.** New York University's School of Continuing Education

Fee: $560. *Write:* Heidi E. Kaplan, Dept. 20 NR, New York University School of Continuing Education, 360 Lexington Ave., New York, N.Y. 10017

**March 21–22** Minneapolis, Minn.
**Reverse Osmosis/Ultrafiltration for Waste Water Treatment or Resource Recovery.** Osmonics, Inc.

Fee: $300. *Write:* Patricia A. Letson, Osmonics, Inc., 15404 Industrial Road, Hopkins, Minn. 55343

(*continued on page 250*)

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MEETINGS *(continued)*

**March 22–23** Madison, Wis.
**Power Plant Ash—$SO_2$ Management III.** University of Wisconsin-Extension

Fee: $130. *Write:* University of Wisconsin-Extension, 432 N. Lake St., Madison, Wis. 53706

**March 26–27** Washington, D.C.
**Hazardous Industrial Materials.** George Washington University

Fee: $325. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

**March 26–28** San Francisco, Calif.
**Occupational Dermatology Symposium.** National Institute of Occupational Safety and Health (NIOSH), and the University of California

Fee: $200. *Write:* Extended Programs in Medical Education, University of California Hospital, San Francisco, Calif. 94143

**March 26–30** Boston, Mass.
**Evaluation and Control of Occupational Hazards: Basic Skills.** Harvard University

Fee: $500. *Write:* Short Course Coordinator, Dept. of Environmental Health Sciences, Harvard School of Public Health, 665 Huntington Ave., Boston, Mass. 02115

## Call for Papers

**March 1 deadline**
**2nd Annual Meeting of the International Society of Petroleum Industry Biologists.** Society of Petroleum Industry Biologists

Conference will be held November 12–14, 1979 at Arlington, Va. *Write:* Geraldine V. Cox, American Petroleum Institute (API), 2101 L St., N.W., Washington, D.C. 20037

**March 20 deadline**
**The 2nd Symposium on the Transfer and Utilization of Particulate Control Technology.** Industrial Environmental Research Laboratory, U.S. EPA

Meeting will be held on July 23–27, 1979 at Denver, Colo. *Write:* Fred P. Venditti, Program Chairman, Denver Research Institute, University of Denver, P.O. Box 10127, Denver, Colo. 80208

**March 31 deadline**
**6th International Conference on Liquefied Natural Gas.** International Gas Union, and the Institute of Gas Technology.

Conference will be held April 6–11, 1980 in Kyoto, Japan. *Write:* David Roe, Secretary, Programme Committee, British Gas Corp., 59 Bryanston St., London, W1A 2AZ England

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- ☐ G. Pulp/Paper/Wood
- ☐ H. Soaps/Cleaners
- ☐ I. Paint/Coating/Ink
- ☐ J. Agrichemicals
- ☐ K. Stone/Glass/Cement
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